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Supplementary Materials for

Heterobiaryl synthesis by contractive C–C coupling via P(V) intermediates

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Published 16 November 2018, *Science* **362**, 799 (2018)
DOI: 10.1126/science.aas8961

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1. General Information

Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded at ambient temperature on a Varian 400 MR spectrometer (400 MHz), an Agilent Inova 400 (400 MHz) spectrometer, an Agilent Inova 500 (500 MHz) spectrometer, or a Bruker AV-111 400 (400 MHz) spectrometer. Chemical shifts (δ) are reported in ppm and quoted to the nearest 0.01 ppm relative to the residual protons in $CDCl_3$ (7.26 ppm), CD_3OD (3.31 ppm) or $(CD_3)_2SO$ (2.05 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 a Varian 400 MR spectrometer (100 MHz), an Agilent Inova 400 (100 MHz) spectrometer, an Agilent Inova 500 spectrometer (125 MHz) or a Bruker AV-111 400 (100 MHz) spectrometer. Chemical shift (δ) was measured in ppm and quoted to the nearest 0.01 ppm relative to the residual solvent peaks in $CDCl_3$ (77.00 ppm), $(CD_3)_2SO$ (39.51 ppm), CD_3OD (49.00 ppm) or CD_3CN (1.32 ppm).

Low-resolution mass spectra (LRMS) were measured on an Agilent 6310 Quadrupole Mass Spectrometer. High-resolution mass spectra (HRMS) were measured on an Agilent 6220 TOF LC/MS ("OTOF") interfaced to an Agilent 1200 HPLC with multi-mode (combined ESI and APCI) and Direct Analysis in Real Time (DART) sources. (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}).

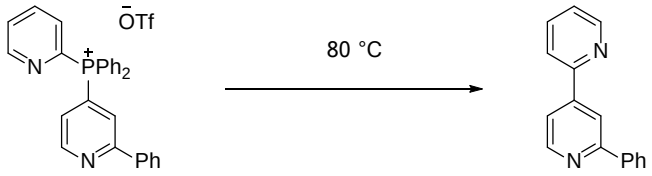
Analytical thin layer chromatography (TLC) was performed using pre-coated Silicycle glass backed silica gel plates (Silicagel 60 F254). Flash column chromatography was undertaken on Silicycle silica gel Siliaflash P60 40-63 um (230-400 mesh) under a positive pressure of air unless otherwise stated. Visualization was achieved using ultraviolet light (254 nm) and chemical staining with ceric ammonium molybdate or basic potassium permanganate solutions as appropriate.

Tetrahydrofuran (THF), toluene, hexane, diethyl ether and dichloromethane were dried and distilled using standard methods (*44*). 1,2-Dichloroethane (DCE), 1,4-dioxane, chloroform, chlorobenzene and acetone were purchased anhydrous from Sigma Aldrich chemical company. All reagents were purchased at the highest commercial quality and used without further purification. Reactions were carried out under an atmosphere of nitrogen unless otherwise stated. All reactions were monitored by TLC, ^{1}H NMR spectra taken from reaction samples, and liquid chromatography mass spectrometry (LCMS) using an Agilent 6310 Quadrupole Mass Spectrometer for MS analysis. Melting points (mp) were recorded using a Büchi B-450 melting point apparatus and are reported uncorrected.

Tf_2O (99%) was purchased from Oakwood Chemical and used without further purification but was routinely stored in a –20 ºC fridge. DBU was distilled before use. (2,2,2)-Trifluoroethanol (TFE) was purchased from Oakwood Chemicals and used without further purification. 200 proof ethanol was purchased from PHARMCO-AAPER and used without further purification. HCl (4.0 M in dioxanes) and trifluoromethanesulfonic acid (98%) were purchased from Sigma Aldrich chemical company and used without further purification but were routinely stored in a –20 ºC fridge.

2. Optimization Studies

Table S1: Optimization of Ligand Coupling Reaction

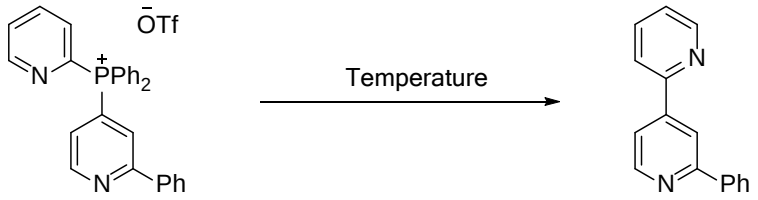


Entry	Solvent	Concentration	Equiv. HCl	Additive	% Yield*
1†	MeOH	0.125	-	-	0
2	MeOH	0.2	2	-	76
3	IPA	0.2	2	-	57
4	*t*-BuOH	0.2	2	-	51
5	TFE	0.2	2	-	59
6	HFIPA	0.2	2	-	68
7	Acetone	0.1	-	H_2O(10 equiv)	44
8	EtOAc	0.1	-	H_2O(10 equiv)	55
9	MeOH	0.2	0.5	-	48
10	MeOH	0.2	1	-	62
11	EtOH	0.2	2	-	70
12	EtOH	0.4	2	-	80
13†	EtOH	0.4	2	-	78
14†	EtOH	1.0	2	-	80
15	TFE	0.4	-	-	0
16	HFIPA	0.4	-	-	0
17	NEt_3	0.2	-	-	0
18	Pyridine	0.4	-	-	0
19	$CHCl_3$	0.2	2	*n*-propylthiol	14

				(10 equiv)	
20	$CHCl_3$	0.2	-	*n*-propylthiol (10 equiv)	0
21	$CHCl_3$	0.2	2	phenol (10 equiv)	13
22	$CHCl_3$	0.2	-	phenol (10 equiv)	0
23	$CHCl_3$	0.4	2	-	ND‡
24	THF	0.4	2	-	ND‡
25	EtOAc	0.4	2	-	ND‡
26	EtOH	0.4	-	-	0

* ^{1}H NMR yields shown using 1,3,5-trimethoxybenzene as an internal standard.
† Reactions were carried out on a 0.25 mmol scale instead of 0.1 mmol
‡ Products were not detected by LCMS

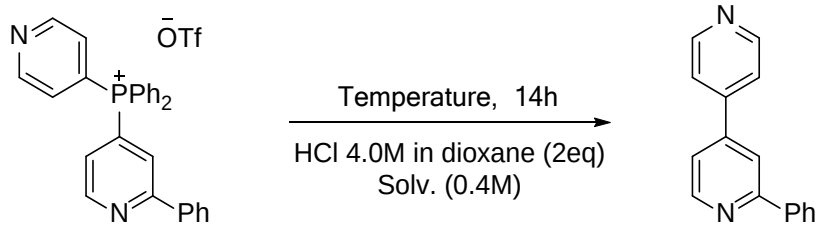
Table S2: Temperature Optimization of Ligand Coupling Reaction: 2,4' Coupling System



Entry	Solvent	Concentration	Equiv. HCl	Temperature	% Yield*
1	MeOH	0.2	2	40	12
2	MeOH	0.2	2	60	44
3	MeOH	0.2	2	70	60
4	MeOH	0.2	2	80	72
5	MeOH	0.4	2	80	83
6	EtOH	0.4	2	70	66
7	EtOH	0.4	2	80	78
8	EtOH	0.4	2	90	76

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

Table S3: Temperature Optimization of Ligand Coupling Reaction: 4,4' Coupling System



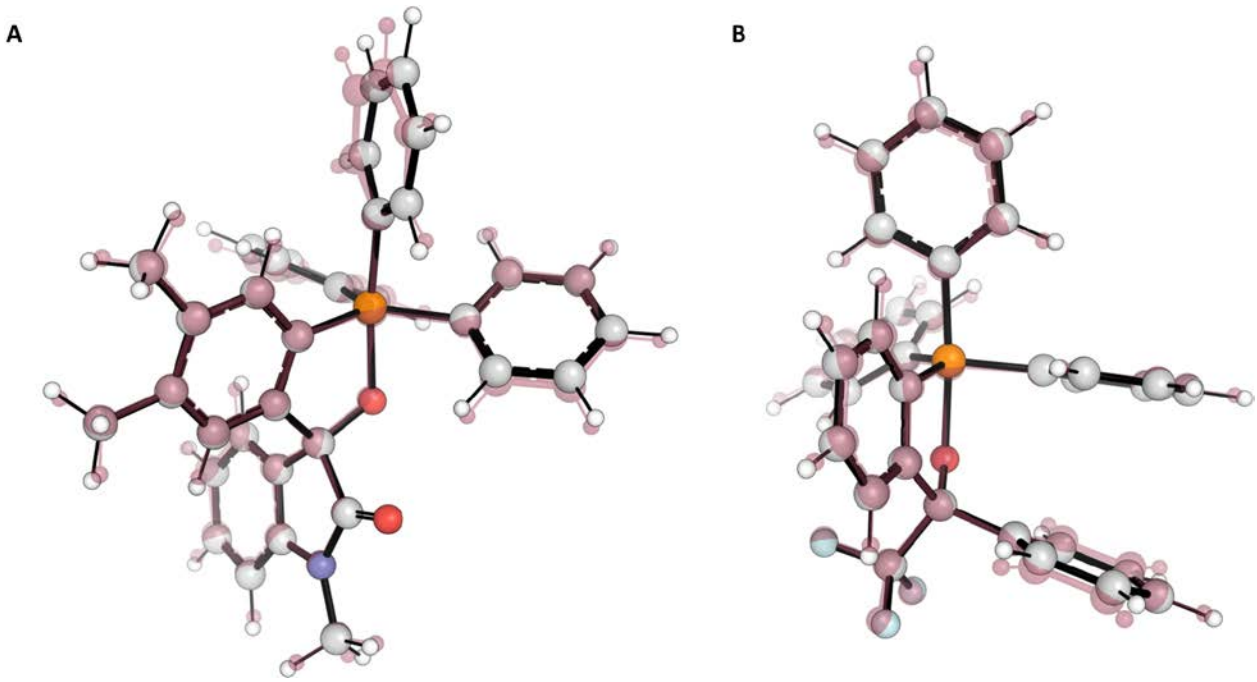
3a **4a**

Entry	Solvent	Temperature	% Yield*
1	MeOH	40	12
2	MeOH	60	75
3	EtOH	80	89 (88)
4	EtOH†	80	93

* ^{1}H NMR yields shown using triphenylmethane as an internal standard.
†Reaction ran for 18 hours with 2eq TfOH instead of 2eq HCl 4.0M in dioxane for 14 hours. Isolated yield shown in parentheses.

3. Computational Methods

The range-separated dispersion-corrected ωB97X-D density functional (*45, 46*) was used with the 6-31+G(d) (*47-51*) basis set to optimize the geometries of all stationary points. This functional captures weak, non-covalent interactions, such as the attractive London dispersion component of van der Waals interactions, which influences structures and energetics (*45, 52*). We evaluated the ability of our chosen level of theory in describing the structures of pentacoordinate P(V) species by comparison against alkoxyphosphoranes which have been characterized by X-ray crystallography (**Figure S1**). Considering that we used solvent (SMD = ethanol) in the calculations, which is of different polarity to the bulk crystal, and allowing for the possibility of crystal packing effects in the X-ray structures, the level of agreement between theory and experiment is high: P-C bond distances differ by less than 0.5%, P-O distances by less than 5%, and all angles and dihedrals are also well reproduced. It is worth mentioning that P-O bonds are highly polarized as observed in our NBO calculations (*vide infra*) and, therefore, the solvation of these molecules in the two environments (crystal packing and EtOH) probably has a relevant impact on the lengths of these bonds.



Bond	Bond length (Å)		Variation (%)
	Crystal	ωB97X-D	
P-O	1.819	1.909	4.9
P-C_{ax}	1.921	1.912	-0.4
P-C_{eq1}	1.845	1.847	0.1
P-C_{eq2}	1.828	1.829	< 0.1
P-C_{eq3}	1.840	1.841	< 0.1

Bond	Bond length (Å)		Variation (%)
	Crystal	ωB97X-D	
P-O	1.855	1.931	4.1
P-C_{ax}	1.910	1.906	-0.2
P-C_{eq1}	1.837	1.843	0.3
P-C_{eq2}	1.819	1.829	0.5
P-C_{eq3}	1.833	1.841	0.4

Figure S1. Top: Overlay of X-ray structures of 1',5,6-trimethyl-1,1,1-triphenyl-1H-spiro[2,1-benzoxaphosphole-3,3'-indol]-2'(1'H)-one (CCDC identifier: COSZOB) (*53*) (A) and 1,1,1,3-tetraphenyl-3-(trifluoromethyl)-1,3-dihydro-2,1-benzoxaphosphole (CCDC identifier: COTGUP) (*53*) (B), represented in dark red, with ωB97X-D/6-31+G(d)(SMD) optimized geometries, represented with standard colors. Bottom: Tabulation of P-C/P-O bond lengths determined experimentally and computationally.

In steps **Int-III**, **[Int-III·H]$^+$** and **[Int-III·2H]$^{2+}$**, a manual conformational search was performed. In this process, P substituents were placed in different axial and equatorial positions, and the different aromatic groups along with the methoxy group were rotated systematically and incrementally. During the conformational search, we found 7, 11 and 9 different structures for **Int-III**, **[Int-III·H]$^+$** and **[Int-III·2H]$^{2+}$**, respectively, from all the conformations studied (see section *Absolute Energy Values* for more information). For each isomer we obtained the subsequent reaction coordinate (**TS-I**, **Int-IV**, etc).

Vibrational frequency calculations were carried out to confirm that stationary points were either minima or first-order saddle points on the potential energy surface, and to obtain thermal corrections to Gibbs free energies at 353.15 K (80 ˚C). Additionally, intrinsic reaction coordinate (IRC) calculations (*54*) were performed to verify that the intermediates (**Int**) of the different

pathways connected to their corresponding transition structure (**TS**). Quasi-harmonic (QHA) corrections were applied to the computed vibrational entropies using a frequency cut-off value of 100.0 cm^{-1}, adopting the model proposed by Grimme (*55*). This was automated by the *GoodVibes* program (*56*).

Solvent effects were considered in all calculations (i.e. optimizations and single-point energy calculations) using the integral equation formalism variant of the polarizable continuum model (IEF-PCM) (*57-62*) with the SMD solvation model (solvent=ethanol) (*62*). Density functional theory (DFT) calculations were carried out in *Gaussian 16* (*63*), with an "ultrafine" pruned (99,590) grid for numerical integration of the exchange-correlation functional and its derivatives. Atomic charges and Wiberg bond orders (*64*) were computed using natural population analysis (NPA) with *NBO 6.0* (*65*), interfaced to Gaussian 16. Molecular graphics were generated using *PyMol* (*66*); Our display settings have been made openly accessible (*67*). Energy scatter plots were created using *GraphPad Prism* (*68*). Electron localization function (ELF) analysis (*69*) of **[TS-I·2H]$^{2+}$-PyH^{+},OMe,ax-a** (see the *Animation of Reaction Coordinate: Movie S1*) was carried out using *Multiwfn* (*70*) for points along the intrinsic reaction coordinate.

Electronic energies were refined by single point energy calculations on the optimized geometries. We used both DFT and correlated wavefunction theory: ωB97X-D/def2-QZVPP (*71, 72*) and DLPNO-CCSD(T) (*73-77*) /cc-pV(DT)Z (*78-82*) calculations, both with the inclusion of SMD solvation. Quasi-harmonic thermal corrections obtained at ωB97X-D/6-31+G(d) level of theory were applied to these single point energies.

Domain-based local pair-natural orbital coupled cluster with perturbative triple excitations (DLPNO-CCSD(T)) calculations were performed with *ORCA 4.0*. (*81, 82*) Using a normal truncation threshold ("normalPNO") DLPNO-CCSD(T) energies achieve an accuracy of 1 kcal mol^{-1} or better compared to CCSD(T) (*83*), which is widely regarded as a "gold standard" in computational chemistry (*84*). Extrapolation to the basis set limit was performed using cc-pVDZ and cc-pVTZ energies, treating the convergence of SCF and correlation energies separately:

(a) The convergence of the HF energy to the basis set limit is calculated as:

$$E_{SCF}^{(X)} = E_{SCF}^{(\infty)} + Ae^{(-\alpha\sqrt{X})} \quad (1)$$

where E_{SCF}^{X} is the SCF energy calculated with the basis set having highest angular momentum X, E_{SCF}^{∞} is the basis set limit SCF energy, α = 4.42 (empirically optimized for cc-pV(DT)Z), and A is a parameter to be determined.

(b) The correlation energy is assumed to converge as:

$$E_{corr}^{(\infty)} = \frac{X^{\beta}E_{corr}^{(X)} - Y^{\beta}E_{corr}^{(Y)}}{X^{\beta} - Y^{\beta}} \quad (2)$$

where $E_{corr}^{(\infty)}$ is the correlation energy calculated with the basis sets having successive highest angular momentums X and Y (in our case 3 and 2), and β = 2.46 (empirically optimized for cc-pV(DT)Z) (*85*).

4. Reaction Mechanism: Computational Analysis

4a. Nomenclature

We carried out configurational/conformational analysis for all minima and saddle points, systematically generating trigonal bipyramidal structures with substituents in different axial and equatorial positions (**Figure S2**). To enumerate these different structures, we refer to the two substituents in axial positions. For example, pentacoordinate P(V) species with one PyH^+ and one OMe group in axial positions, are referred to **(PyH^+,OMe,ax)**. For each configuration we also obtained multiple conformations with respect to rotation about the methoxy group, catalogued by different letters at the end of each name (*i.e.* a, b, c, etc). Discussion in the main text and energy profiles in the supporting information refer to the most stable rotameric conformation found for each P(V) configuration.

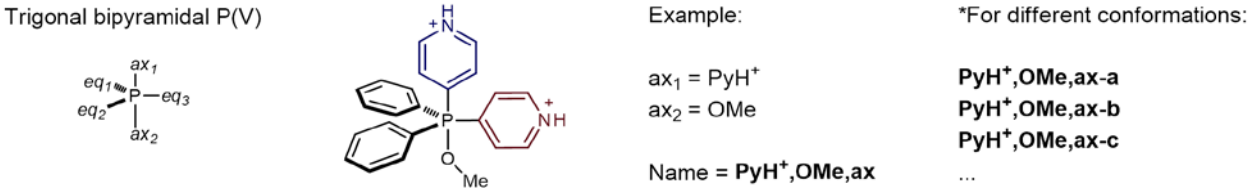


Figure S2. Descriptors used in the enumeration of compounds based on the configuration at phosphorus and the rotameric conformation of the methoxy group.

Furthermore, structures were differentiated based on protonation state (**Figure S3**).

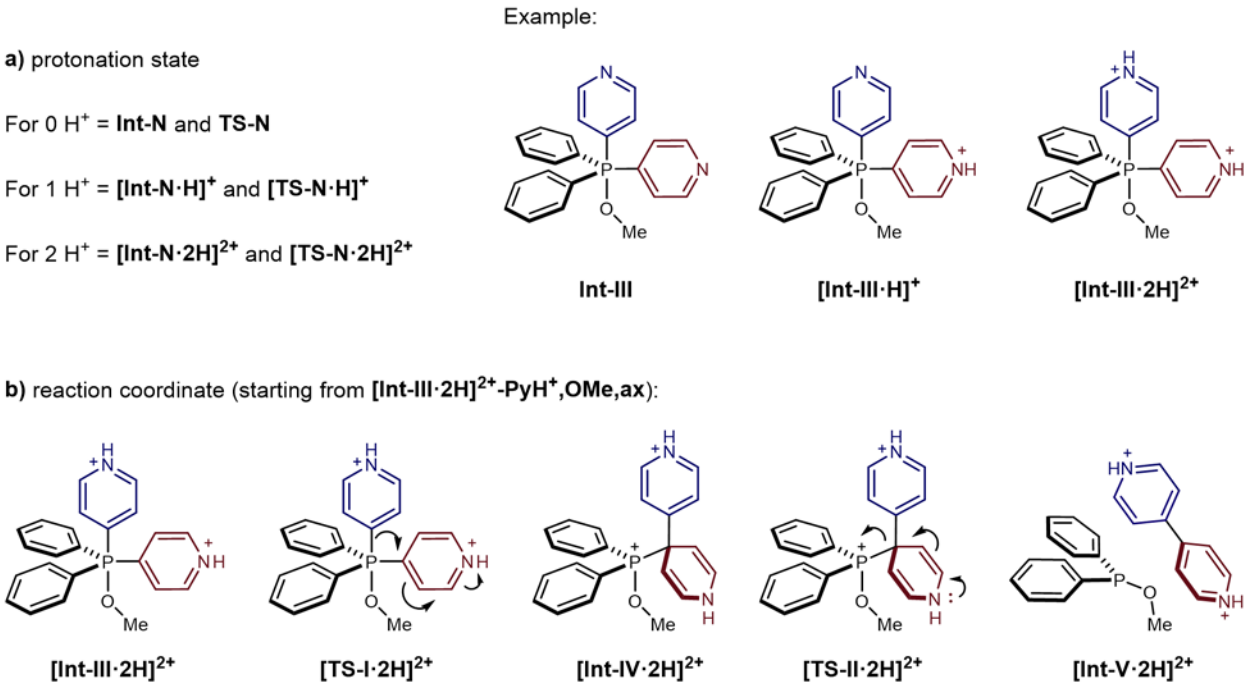


Figure S3. Nomenclature based on the number of H^+ equivalents added and reaction step.

Additionally, the phosphine and biaryl products formed in the ligand coupling step are referred to using the following scheme (**Figure S4**).

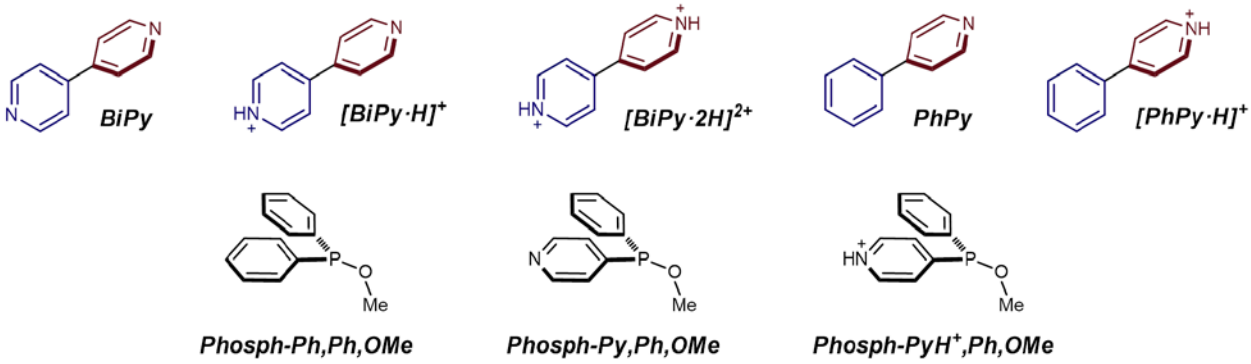


Figure S4. List of final phosphines and products.

4b. Configurational Energetics are Controlled by *Apicophilicity*

More electronegative substituents prefer to occupy axial (apical) positions in trigonal bipyramidal species in the absence of steric constraints (*86*). This preference known as apicophilicity dictates the relative stabilities of the stereoisomers for each of the pentacoordinate P(V) species. As shown in **Figure S5**, the axial preference follows the expected order in line with electron-withdrawing ability OMe > PyH^+ > Py > Ph. The relative stabilities are consistent across DFT and WFT calculations.

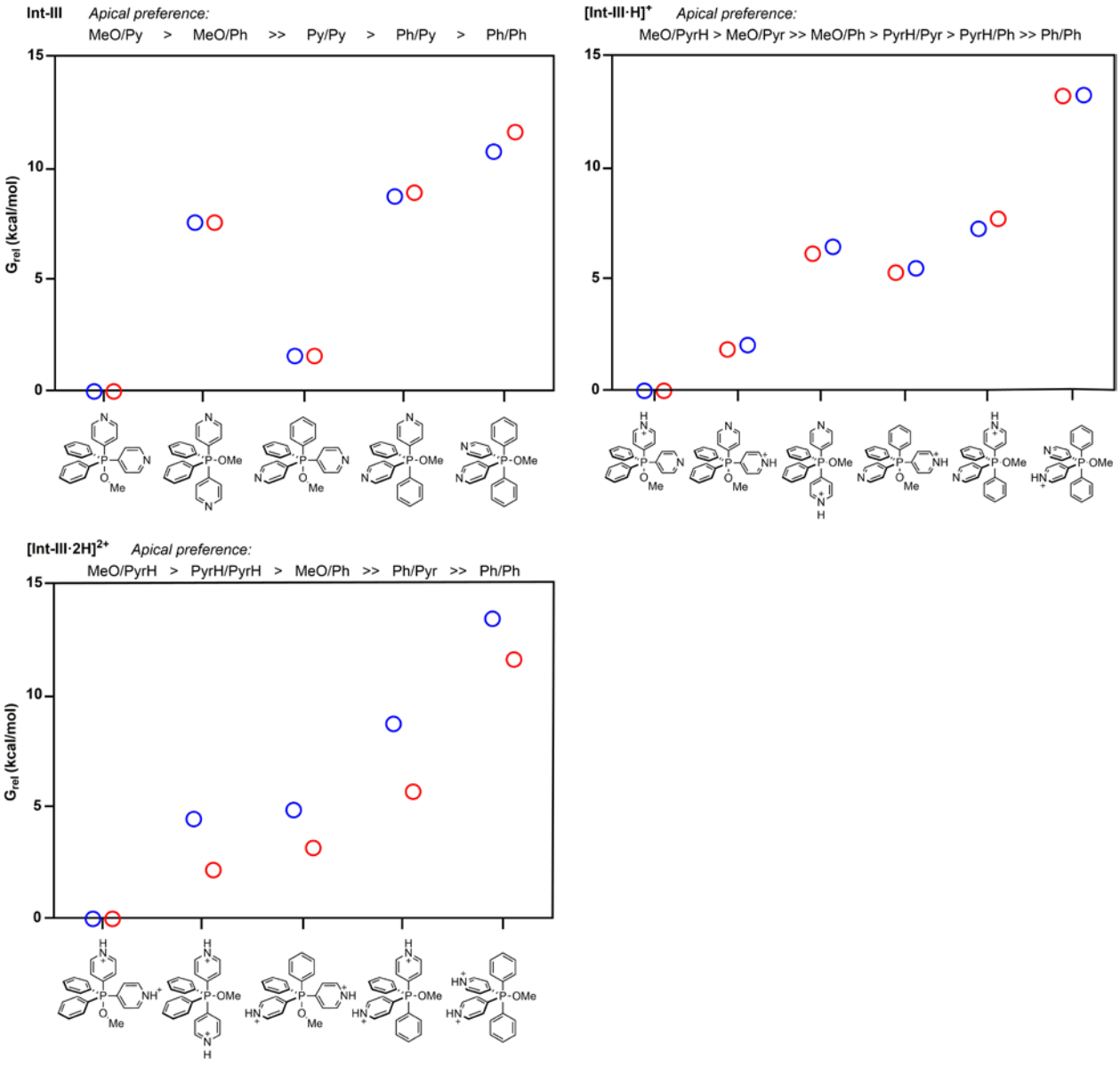


Figure S5. Relative stability of the different isomers of **Int-III**, **[Int-III·H]**$^+$ and **[Int-III·2H]**$^{2+}$. Blue = ωB97X-D/def2-QZVPP; red = DLPNO-CCSD(T)/cc-pV(DT)Z.

4c. Why Pyridine-Pyridine Coupling is Favored

The simplest example of ligand coupling from pentavalent phosphorus is that of PH_5. Orbital symmetry dictates that the coupling of equatorial and apical substituents is forbidden: the hydrogenic 1s orbitals of these substituents are of different phase in the highest occupied molecular orbital (HOMO) in PH_5 (**Figure S6**). There is no reaction coordinate for which a continuous evolution of orbitals leads to a ground-state configuration of both PH_3 and H_2. In contrast, a similar analysis of orbital phase suggests that coupling of two equatorial substituents is symmetry-allowed. Indeed, this transformation is possible and has an activation barrier of >35 kcal/mol (ωB97X-D). Axial-axial coupling is symmetry-allowed, although does not occur in a single step. After a Berry-pseudorotation the formerly-axial substituents are then equatorial and able to undergo equatorial-equatorial coupling.

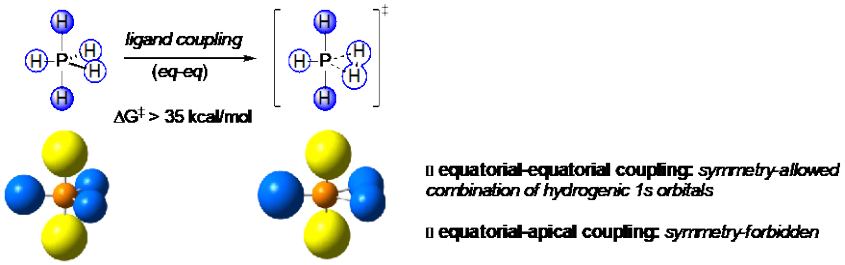


Figure S6. Ligand coupling in PH_5 is symmetry-controlled. Computed HOMOs in the reactant and TS show equatorial-equatorial coupling is symmetry-allowed, whereas equatorial-apical coupling is symmetry-forbidden.

Computed ligand coupling transition states from phosphorane **Int-III** establish that this transformation proceeds via apical-equatorial coupling. How is this possible when such a pathway is symmetry-forbidden for the PH_5 prototype? The answer lies in the fact that the new σ-bond results from the participation of one of the ligand's π/π* system, allowing symmetry-allowed overlap to occur (**Figure S7**). In the TS, a $\sigma_{C\text{-}P}$ bond interacts with the adjacent $\pi^*_{C\text{-}C}$, in a nucleophilic aromatic substitution (*S*$_N$*Ar*)-like process (See the *Animation of Frontier Molecular Orbital for C-C Bond Forming Event*: Movie S2). The involvement of nucleophilic $\sigma_{C\text{-}P}$ and electrophilic $\pi^*_{C\text{-}C}$ MOs is evident in the computed HOMO in the TS. The HOMO of the phosphorane intermediate is dominated by the $\sigma_{C\text{-}P}$ bond.

This process is fundamentally distinct from ligand-coupling in PH_5, where both $\sigma_{P\text{-}H}$ bonds are broken as the $\sigma_{H\text{-}H}$ bond is formed. This mechanistic interpretation is consistent with a computed reaction coordinate, for which a stable Meisenheimer adduct is obtained from the ligand-coupling TS (the final loss of phosphinite is, however, computed to occur rather easily and irreversibly to liberate the bipyridyl product). Furthermore, the distinct involvement of the two pyridyl groups along the reaction coordinate can be seen through comparing the aromaticity at the center of each ring, as evaluated by the nuclear independent chemical shift (NICS) values in **Figure S7**. The nucleophilic (apical) pyridyl ligand shows negligible change in ring aromaticity along the reaction coordinate since the p-system undergoes no changes in bonding. In contrast, aromaticity of the electrophilic (equatorial) pyridyl ligand is completely lost along the reaction coordinate as dearomatization occurs due to C-C bond formation.

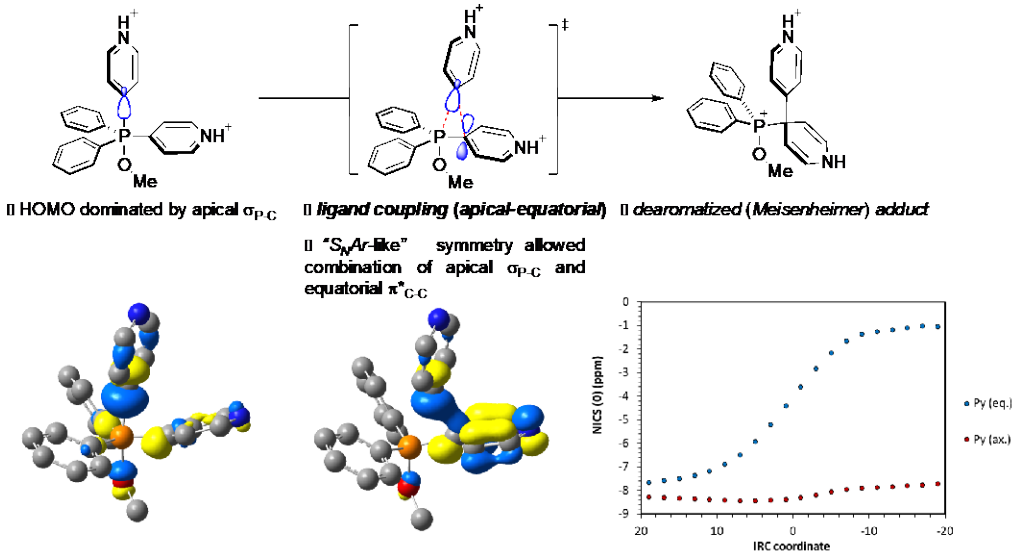


Figure S7. Orbital control in ligand coupling from **[Int-III·2H]**$^{2+}$. Equatorial-apical coupling is symmetry-allowed due to the involvement of the pyridyl π/π* system.

Additionally, the competing TS that lead to RO-Py couplings were calculated. ROPy is a potential byproduct of this reaction that was previously observed when using different reaction conditions (*31*). Under the reaction conditions used in this study, using 2 equivalents of HCl to protonate the two pyridine groups of the initial phosphonium salt, our calculations suggest that Py-Py couplings are the favored type of coupling (**Figure S8**). Also, we determined experimentally that RO-Py couplings do not take place under basic conditions when using EtOH as the solvent (**Figure S24**).

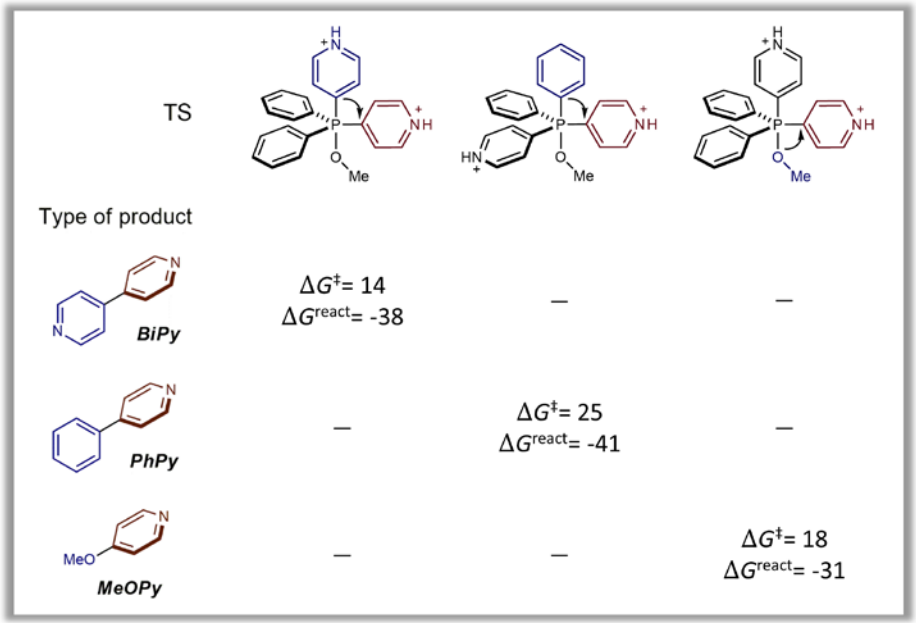
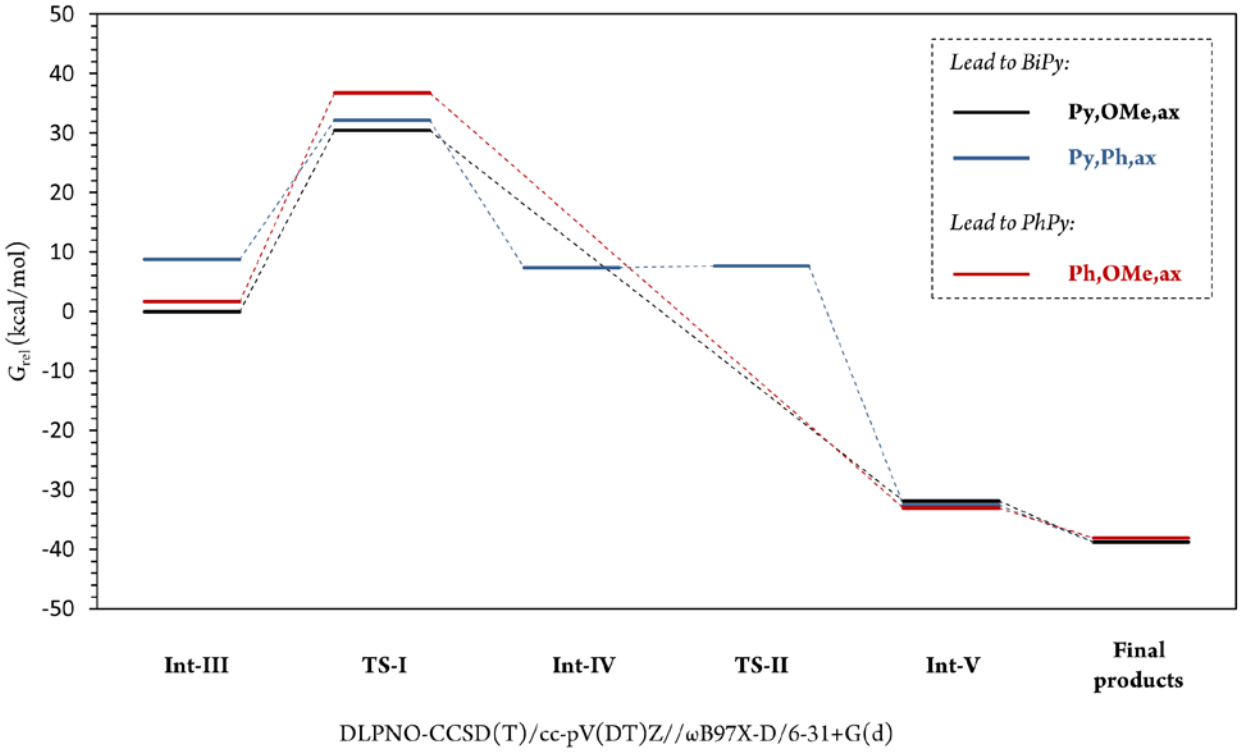
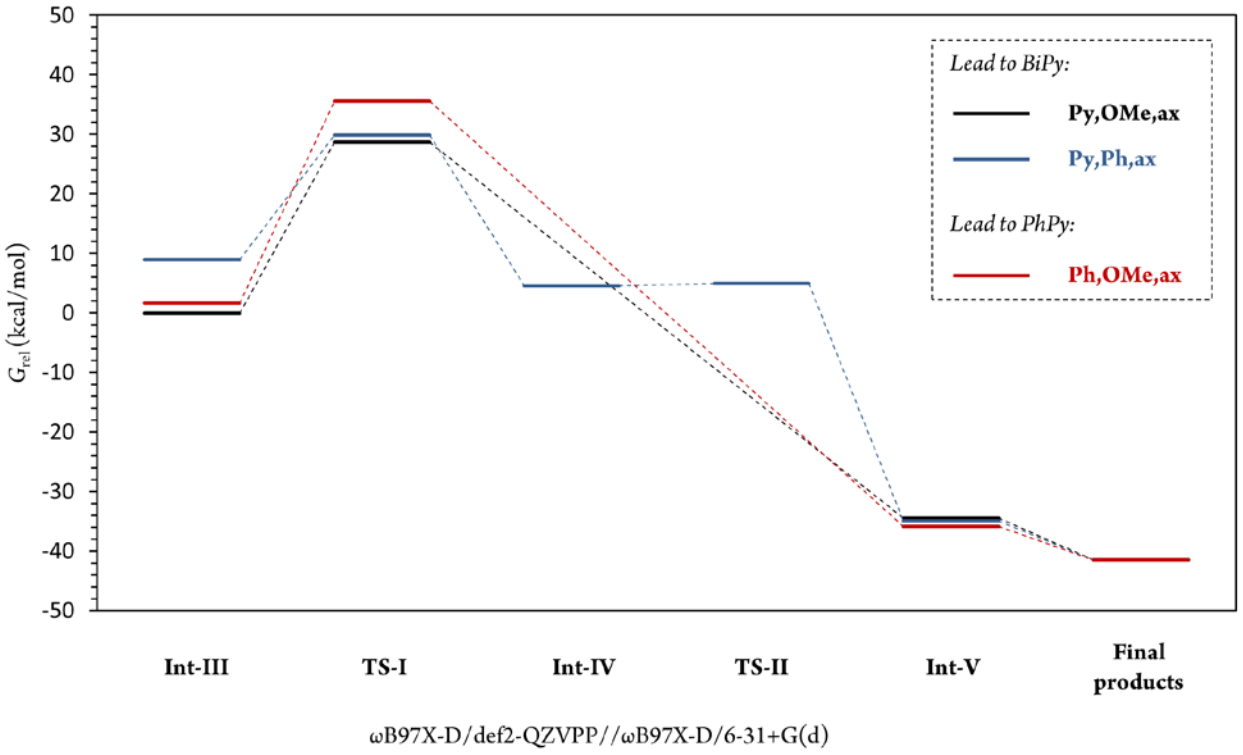


Figure S8. [TS-I·2H]$^{2+}$ activation barriers ($\Delta G^{‡}$) and change of G of the reaction (ΔG^{react}) for different types of couplings (SMD-DLPNO-CCSD(T)/cc-pV(DT)Z//ωB97X-D/6-31+G(d), kcal/mol).

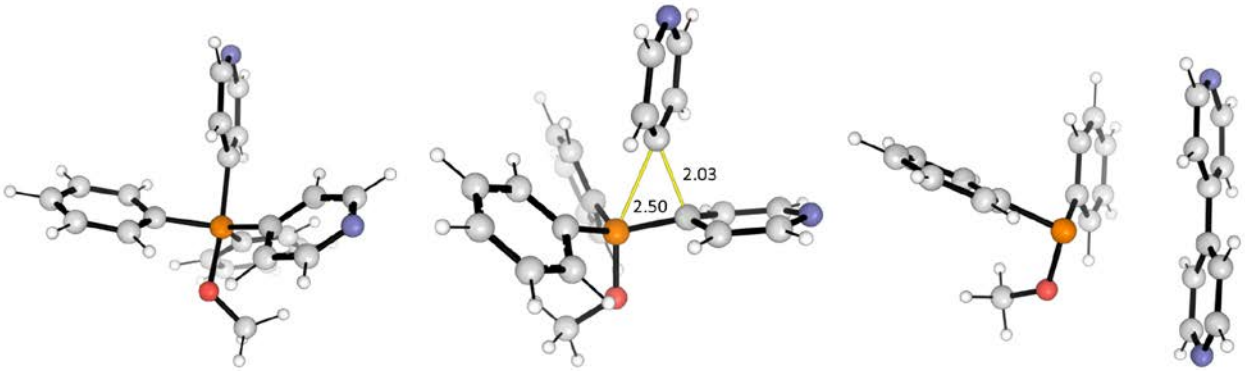
4d. Computed Reaction Mechanism from **Int-III**

Gibbs free energies along the reaction coordinate calculated with the ωB97X-D/def2-QZVPP and DLPNO-CCSD(T)/cc-pV(DT)Z methods show very similar profiles in all the pathways from **Int-III**, **[Int-III·H]$^{+}$** and **[Int-III·2H]$^{2+}$** (**Figures S9-11**). The ordering of different configurations is consistent across calculations using DFT and WFT. The reaction profiles correlate well from one method to another, showing energy variations within 3 kcal/mol across the majority of reaction steps, and the same trend upon protonation is found for both methods.





ωB97X-D/def2-QZVPP//ωB97X-D/6-31+G(d)



[Int-III]-Py,OMe,ax-b [TS-I]-Py,OMe,ax-a [Int-V]-Py,OMe,ax-b

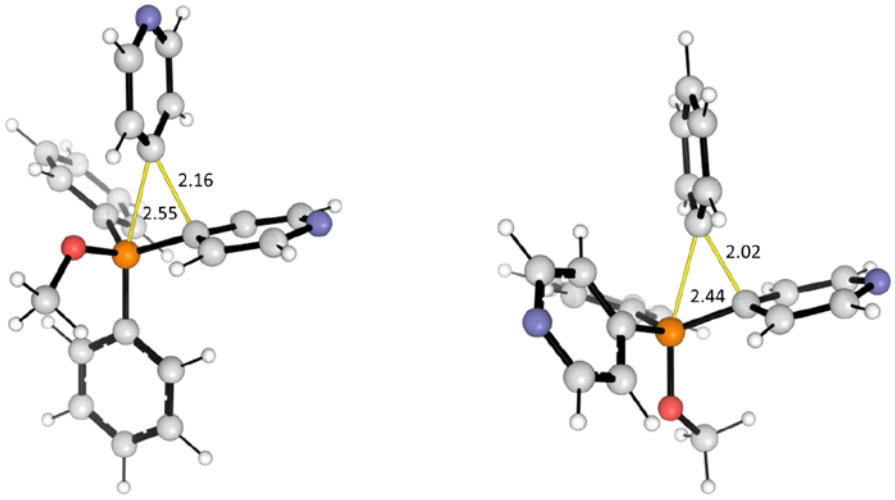
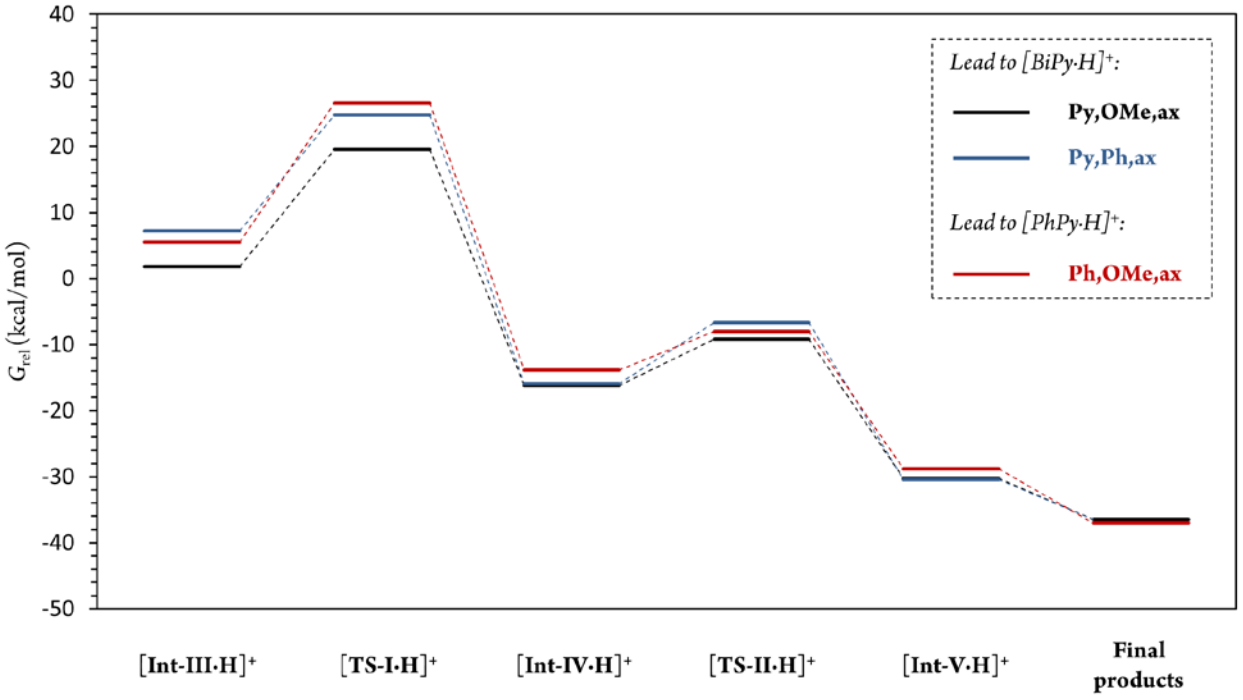


Figure S9. Reaction coordinate for the most favorable pathways of **Int-III**. Top: DLPNO-CCSD(T); Bottom: ωB97X-D. Below: most favorable structures along the reaction pathway (**Py,OMe,ax**) and other competing **TS-I** steps.

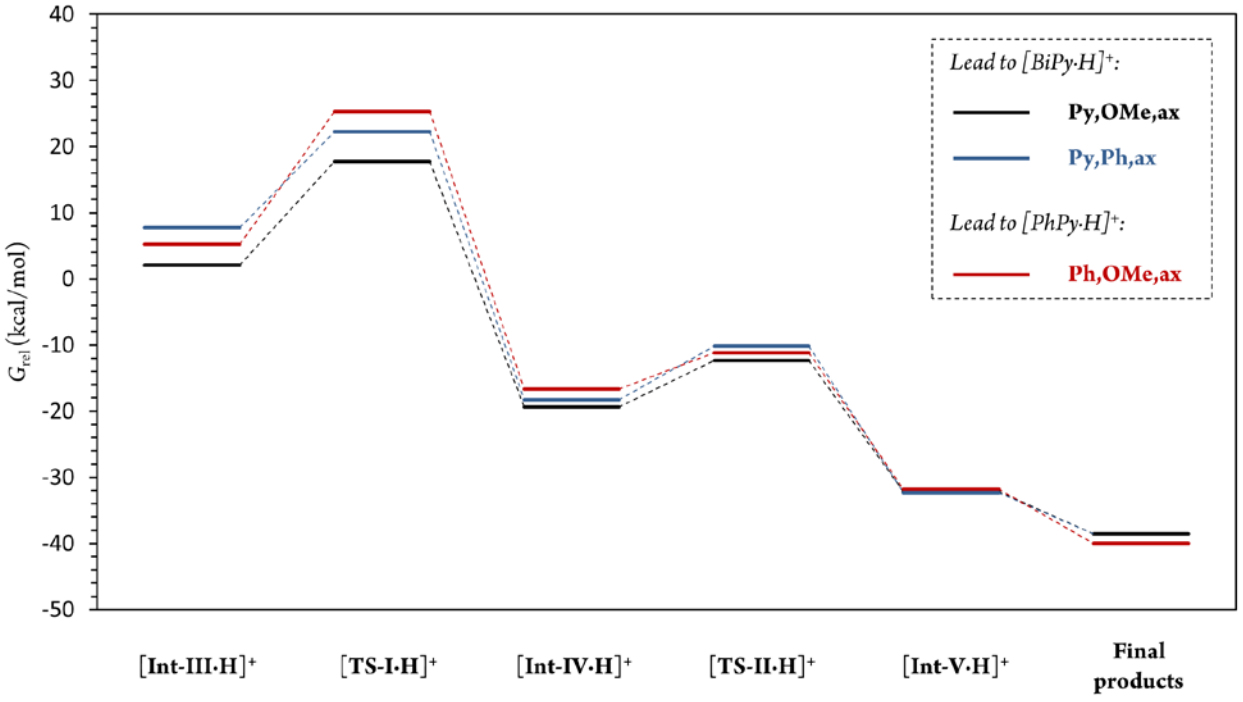
Table S4. Important bond lengths from the **[Int-III]-Py,OMe,ax** pathway.

Reaction Step	Distances (Å)				
	P-O (OMe ax)	P-C (Py ax.)	P-C (Py eq.)	P-C (Ph eq. 1)	P-C (Ph eq. 2)
[Int-III]-Py,OMe,ax-b	1.79	1.96	1.87	1.85	1.84
[TS-I]-Py,OMe,ax-a	1.63	2.50	1.77	1.81	1.82
[Int-V]-Py,OMe,ax-b	1.67	-	-	1.84	1.84

4e. Computed Reaction Mechanism from **[Int-III·H]$^+$**



DLPNO-CCSD(T)/cc-pV(DT)Z//ωB97X-D/6-31+G(d)



ωB97X-D/def2-QZVPP//ωB97X-D/6-31+G(d)

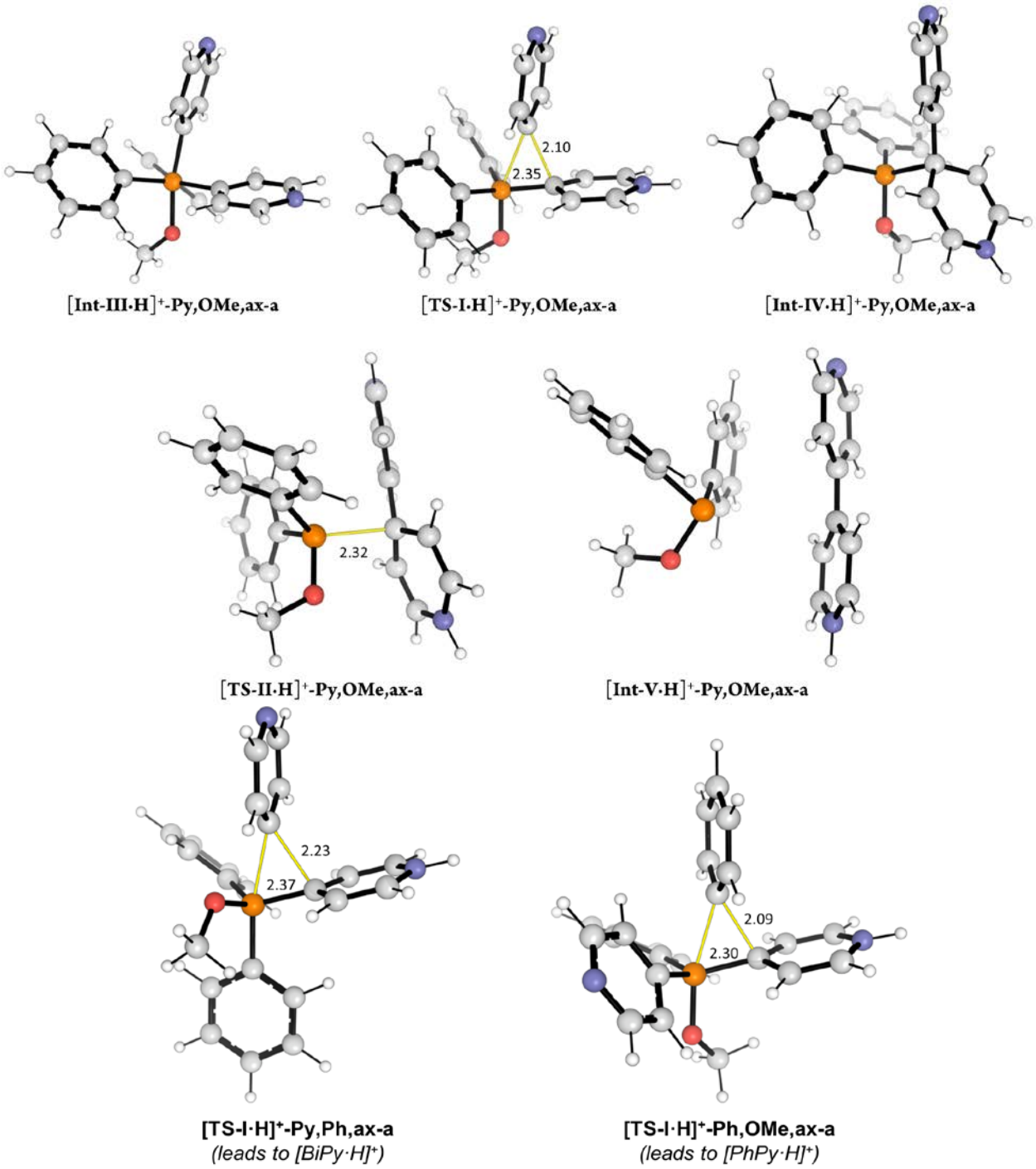
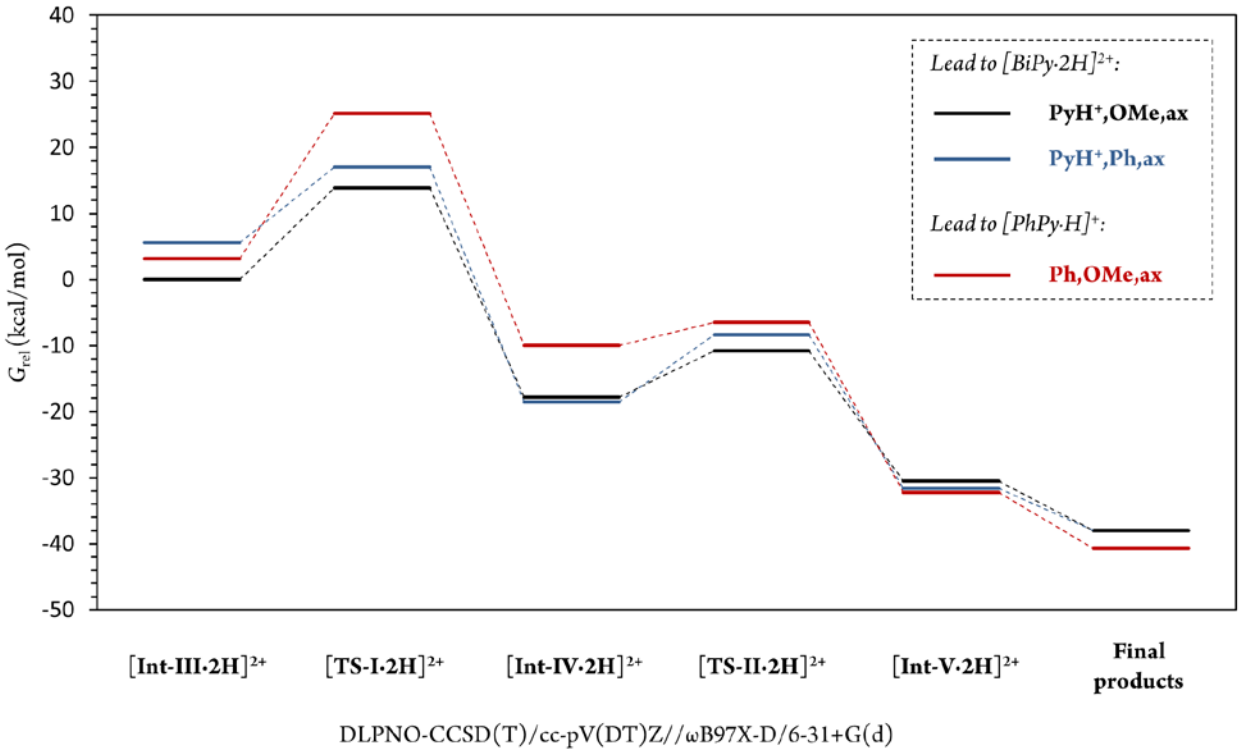


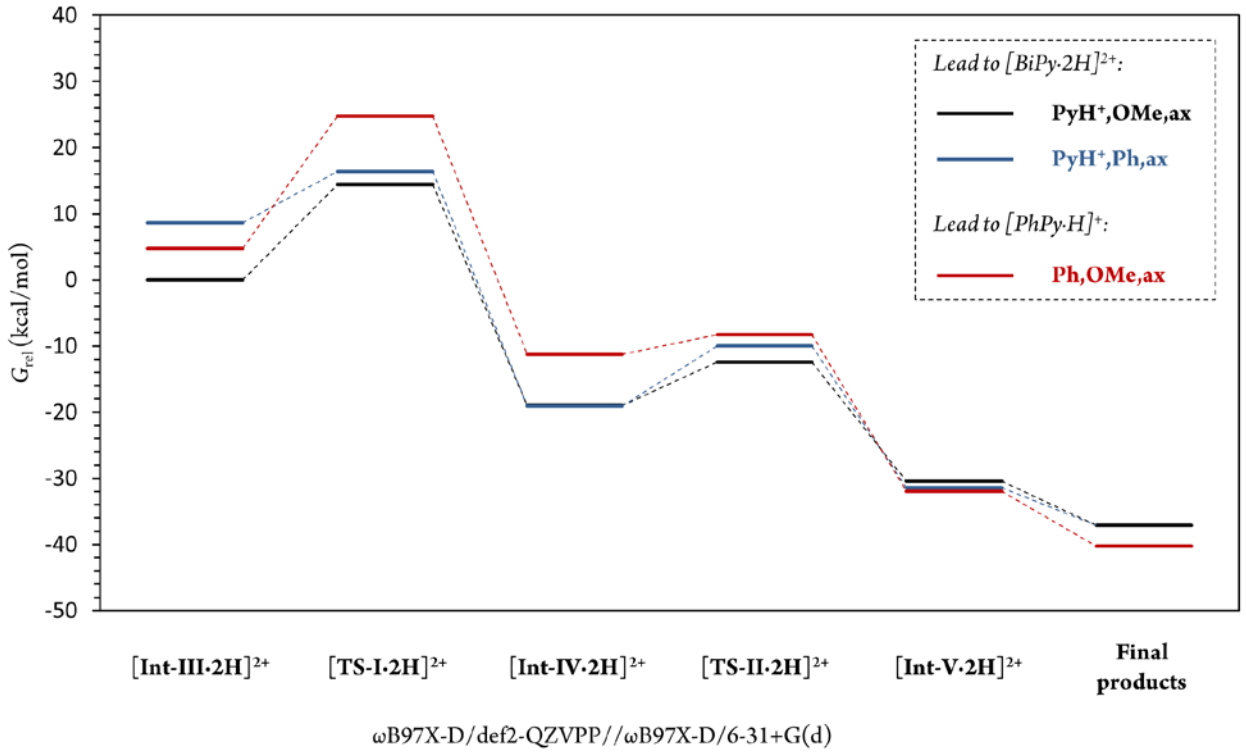
Figure S10. Reaction coordinate for the most favorable pathways of **[Int-III·H]**$^+$. Top: DLPNO-CCSD(T); Bottom: ωB97X-D. Below: most favorable structures along the reaction pathway (**Py,OMe,ax**) and other competing **[TS-I·H]**$^+$ steps.

Table S5. Important bond lengths from the **[Int-III·H]$^+$-Py,OMe,ax** pathway.

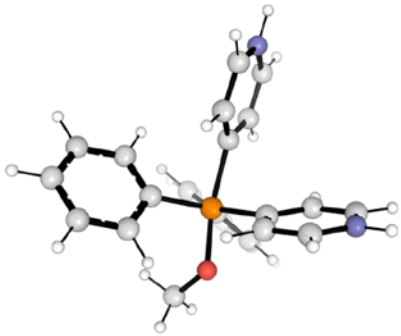
Reaction Step	Distances (Å)				
	P-O (OMe ax)	P-C (Py ax.)	P-C (Py eq.)	P-C (Ph eq. 1)	P-C (Ph eq. 2)
[Int-III·H]$^+$-Py,OMe,ax-a	1.77	1.95	1.87	1.85	1.84
[TS-I·H]$^+$-Py,OMe,ax-a	1.65	2.35	1.76	1.82	1.82
[Int-IV·H]$^+$-Py,OMe,ax-a	1.60	-	1.90	1.80	1.80
[TS-II·H]$^+$-Py,OMe,ax-a	1.62	-	2.32	1.81	1.81
[Int-V·H]$^+$-Py,OMe,ax-a	1.67	-	-	1.84	1.84

4f. Computed Reaction Mechanism from **[Int-III·2H]$^{2+}$**

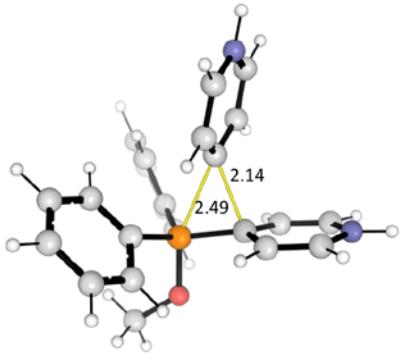




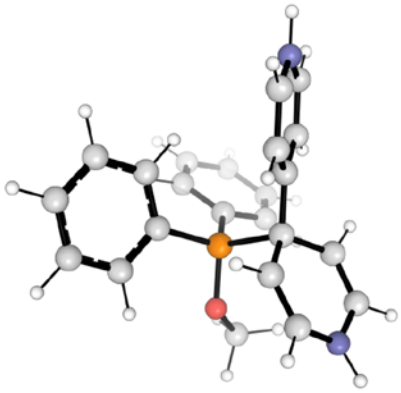
ωB97X-D/def2-QZVPP//ωB97X-D/6-31+G(d)



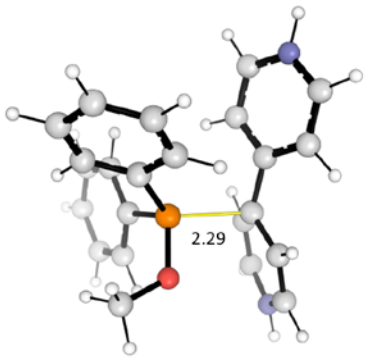
[Int-III·2H]²⁺-PyH⁺,OMe,ax-a



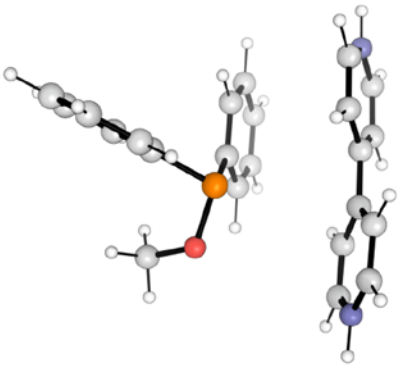
[TS-I·2H]²⁺-PyH⁺,OMe,ax-b



[Int-IV·2H]²⁺-PyH⁺,OMe,ax-a



[TS-II·2H]²⁺-PyH⁺,OMe,ax-a



[Int-V·2H]²⁺-PyH⁺,OMe,ax-a

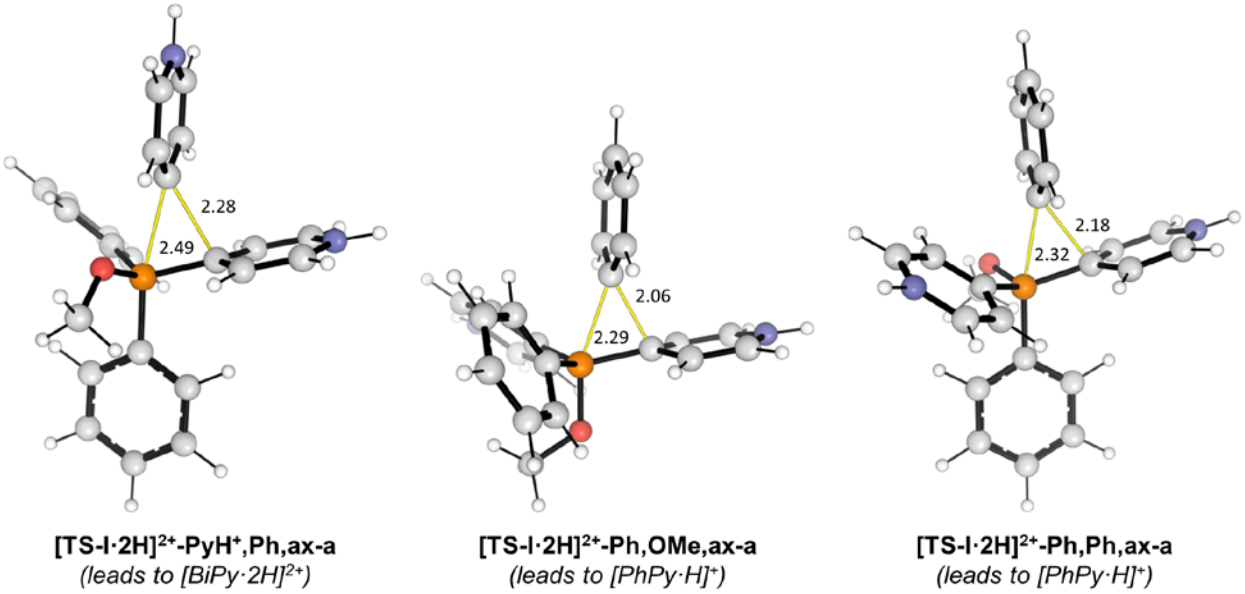


Figure S11. Reaction coordinate for the most favorable pathways of **[Int-III·2H]$^{2+}$**. Top: DLPNO-CCSD(T); Bottom: ωB97X-D. Below: most favorable structures along the reaction pathway (**PyH$^+$,OMe,ax**) and other competing **[TS-I·2H]$^{2+}$** steps.

Table S6. Important bond lengths from the **[Int-III·2H]$^{2+}$-PyH$^+$,OMe,ax** pathway.

Reaction Step	Distances (Å)				
	P-O (OMe ax)	P-C (Py ax.)	P-C (Py eq.)	P-C (Ph eq. 1)	P-C (Ph eq. 2)
[Int-III·2H]$^{2+}$-PyH$^+$,OMe,ax-a	1.73	1.99	1.86	1.85	1.84
[TS-I·2H]$^{2+}$-PyH$^+$,OMe,ax-b	1.63	2.49	1.78	1.81	1.81
[Int-IV·2H]$^{2+}$-PyH$^+$,OMe,ax-a	1.59	-	1.91	1.80	1.80
[TS-II·2H]$^{2+}$-PyH$^+$,OMe,ax-a	1.62	-	2.29	1.81	1.80
[Int-V·2H]$^{2+}$-PyH$^+$,OMe,ax-a	1.66	-	-	1.84	1.84

4g. Solvation Model Validation of SMD Using COSMO-RS

[Int-III·H]$^{+}$ and **[Int-III·2H]$^{2+}$** pathways involved mono- and di-protonated species, which involves a high G of solvation (see **Table S7**). This might cause problems when using SMD, since it is known that errors in calculated solvation G using SMD for ions are greater than for neutral molecules (*62*). In order to discard large systematic errors coming from G of solvation, we calculated the different most stable pathways for **Int-III**, **[Int-III·H]$^{+}$** and **[Int-III·2H]$^{2+}$** with COSMO-RS (*87-91*), which calculates G of solvation differently to SMD.

We adapted the standard procedure that COSMO-RS follows to calculate solvation G, since this procedure involves ground state optimization of molecules and does not allow for inclusion of transition states. In the standard protocol, first the program optimizes ground state structures in the gas and solution phase using Turbomole with BP/TZVP (COSMO), followed by single-point energy calculations in the two phases using Turbomole with BP/TZVPD (COSMO) and a fine grid marching tetrahedron cavity (FINE). We adapted this protocol to be able to model transition states. For this, we directly optimized geometries of ground and transition states with ωB97X-D/6-31+G(d) in gas and solution phase using Gaussian 16, and then we employed these optimized geometries as the input files for the final single-point calculations in gas and solution phase performed with COSMO-RS (BP/TZVPD (FINE, COSMO)) at 80 °C. EtOH was used as the solvent for the solvation G calculations, using also geometries optimized with ωB97X-D/6-31+G(d) as the ground and transition states studied.

In order to generate the reaction G profiles with the calculated COSMO-RS solvation G, first the G of the structures in gas phase was calculated as explained in the computational methods, including QHA entropy and single-point energy corrections using DLPNO-CCSD(T)/cc-pV(DT)Z//ωB97X-D/6-31+G(d) and ωB97X-D/def2-QZVPP//ωB97X-D/6-31+G(d) at 80 °C. Then the solvation G values calculated with COSMO-RS were added to the G values in gas phase to obtain the final G in solution **(Tables S7-8)**. In all the cases studied, similar G profiles were observed using the initial SMD and the generated COSMO-RS results (**Figure S12-13**), which suggests that there are not any major systematic errors coming from the calculation of G of solvation.

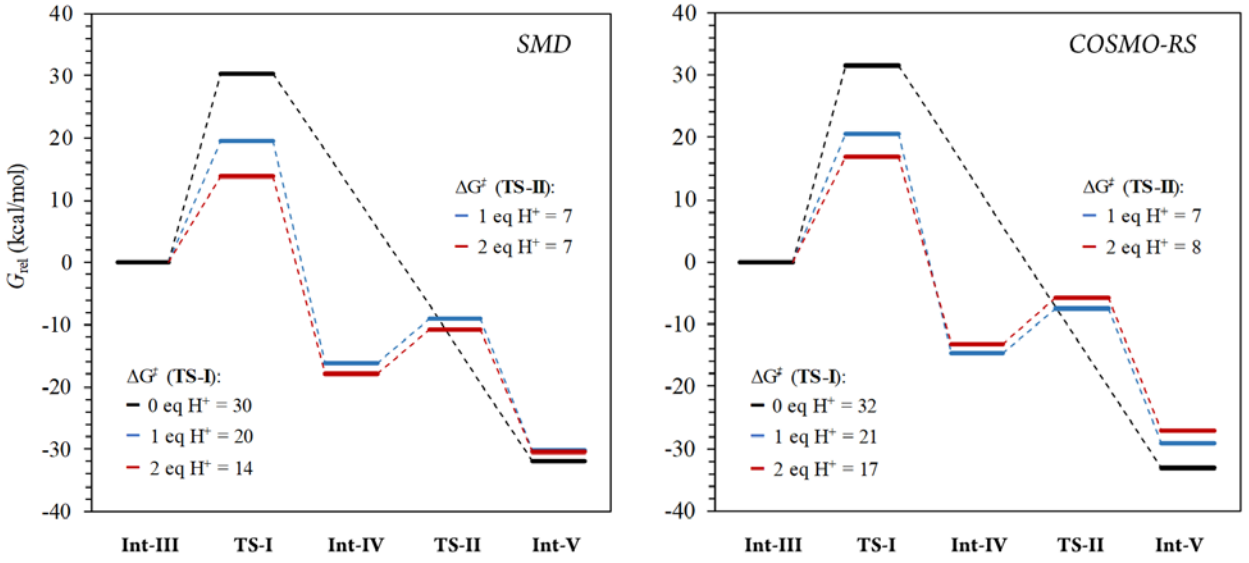
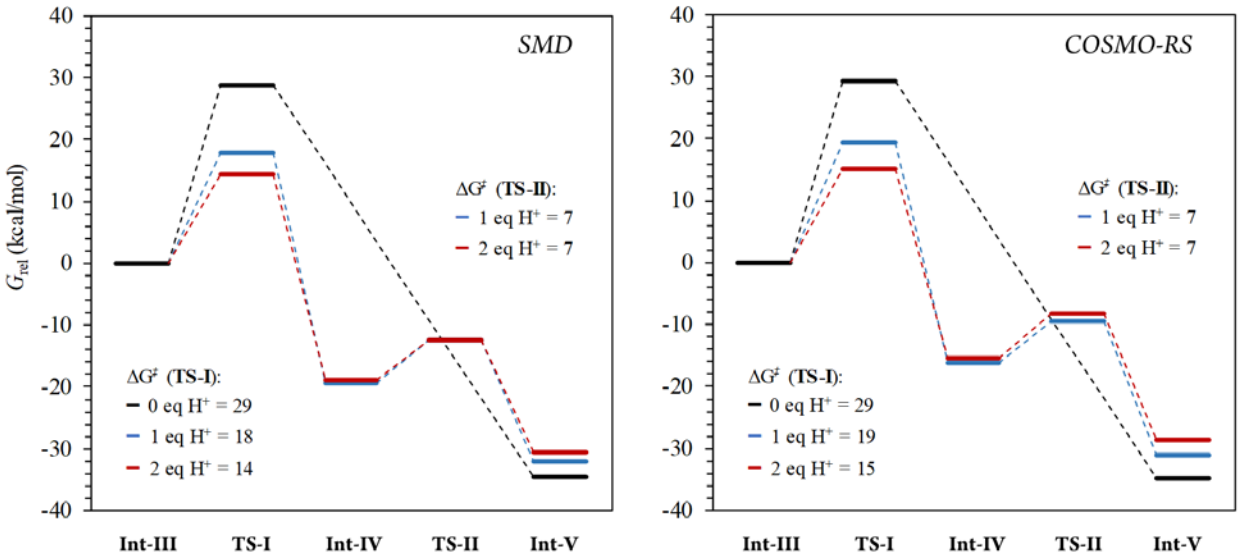


Figure S12. G profiles of the most stable reaction pathways of **Int-III**, **[Int-III·H]$^{+}$** and **[Int-III·2H]$^{2+}$** calculated with DLPNO-CCSD(T)/cc-pV(DT)Z//ωB97X-D/6-31+G(d).



ωB97X-D/def2-QZVPP//ωB97X-D/6-31+G(d)

Figure S13. G profiles of the most stable reaction pathways of **Int-III**, **[Int-III·H]$^{+}$** and **[Int-III·2H]$^{2+}$** calculated with ωB97X-D/def2-QZVPP//ωB97X-D/6-31+G(d).

Table S7. Thermochemical data including absolute energies, zero-point energies (ZPE), T·S, G of solvation (G_{solv}) and G of the most stable reaction pathways of **Int-III**, **[Int-III·H]$^{+}$** and **[Int-III·2H]$^{2+}$** using gas phase optimizations (G_{GP}) with DLPNO-CCSD(T)/cc-pV(DT)Z//ωB97X-D/6-31+G(d) and COSMO-RS.

System	E (kcal/mol)	ZPE (kcal/mol)	T·S (kcal/mol)	G_{GP} (kcal/mol)	G_{solv} (kcal/mol)	G_{GP} + G_{solv} (kcal/mol)	G_{rel} (kcal/mol)
[Int-III]-Py,OMe,ax-b	-886841.41	244.83	60.08	-886635.89	-18.66	-886654.55	0.00
[TS-I]-Py,OMe,ax-a	-886801.45	243.67	59.85	-886597.04	-25.95	-886622.99	31.56
[Int-V]-Py,OMe,ax-a	-886872.71	244.61	62.51	-886669.28	-18.36	-886687.64	-33.09
[Int-III·H]$^{+}$-PyH^{+},OMe,ax-b	-887087.27	254.00	60.36	-886872.74	-56.20	-886928.95	0.00
[TS-I·H]$^{+}$-Py,OMe,ax-a	-887071.33	252.97	60.44	-886858.10	-50.32	-886908.42	20.53
[Int-IV·H]$^{+}$-Py,OMe,ax-b	-887111.52	253.88	60.59	-886897.20	-46.39	-886943.59	-14.64
[TS-II·H]$^{+}$-Py,OMe,ax-a	-887101.03	253.17	60.65	-886887.68	-48.74	-886936.43	-7.48
[Int-V·H]$^{+}$-Py,OMe,ax-a	-887113.40	253.71	62.05	-886900.41	-57.69	-886958.11	-29.16
[Int-III·2H]$^{2+}$-PyH^{+},OMe,ax-a	-887271.38	263.08	60.43	-887047.79	-151.01	-887198.80	0.00
[TS-I·2H]$^{2+}$-PyH^{+},OMe,ax-b	-887261.62	261.82	60.58	-887039.46	-142.47	-887181.93	16.86
[Int-IV·2H]$^{2+}$-PyH^{+},OMe,ax-b	-887293.14	262.61	60.96	-887070.31	-141.73	-887212.04	-13.24
[TS-II·2H]$^{2+}$-PyH^{+},OMe,ax-a	-887282.83	261.92	61.27	-887061.21	-143.26	-887204.46	-5.67
[Int-V·2H]$^{2+}$-PyH^{+},OMe,ax-a	-887291.94	262.56	62.07	-887070.06	-155.75	-887225.81	-27.01

Table S8. Thermochemical data including absolute energies, zero-point energies (ZPE), T·S, G of solvation (G_{solv}) and G of the most stable reaction pathways of **Int-III**, **[Int-III·H]$^{+}$** and **[Int-III·2H]$^{2+}$** using gas phase optimizations (G_{GP}) with ωB97X-D/def2-QZVPP//ωB97X-D/6-31+G(d) and COSMO-RS.

System	E (kcal/mol)	ZPE (kcal/mol)	T·S (kcal/mol)	G_{GP} (kcal/mol)	G_{solv} (kcal/mol)	$G_{GP} + G_{solv}$ (kcal/mol)	G_{rel} (kcal/mol)
[Int-III]-Py,OMe,ax-b	-888055.66	244.83	60.08	-887850.14	-18.66	-887868.80	0.00
[TS-I]-Py,OMe,ax-a	-888017.97	243.67	59.85	-887813.55	-25.95	-887839.50	29.30
[Int-V]-Py,OMe,ax-a	-888088.64	244.61	62.51	-887885.20	-18.36	-887903.57	-34.77
[Int-III·H]$^{+}$-PyH^{+},OMe,ax-b	-888305.57	254.00	60.36	-888091.05	-56.20	-888147.25	0.00
[TS-I·H]$^{+}$-Py,OMe,ax-a	-888290.81	252.97	60.44	-888077.58	-50.32	-888127.91	19.34
[Int-IV·H]$^{+}$-Py,OMe,ax-b	-888331.30	253.88	60.59	-888116.98	-46.39	-888163.37	-16.12
[TS-II·H]$^{+}$-Py,OMe,ax-a	-888321.42	253.17	60.65	-888108.08	-48.74	-888156.82	-9.57
[Int-V·H]$^{+}$-Py,OMe,ax-a	-888333.53	253.71	62.05	-888120.53	-57.69	-888178.23	-30.98
[Int-III·2H]$^{2+}$-PyH^{+},OMe,ax-a	-888493.54	263.08	60.43	-888269.95	-151.01	-888420.96	0.00
[TS-I·2H]$^{2+}$-PyH^{+},OMe,ax-b	-888485.41	261.82	60.58	-888263.25	-142.47	-888405.72	15.24
[Int-IV·2H]$^{2+}$-PyH^{+},OMe,ax-b	-888517.59	262.61	60.96	-888294.77	-141.73	-888436.50	-15.54
[TS-II·2H]$^{2+}$-PyH^{+},OMe,ax-a	-888507.45	261.92	61.27	-888285.83	-143.26	-888429.09	-8.13
[Int-V·2H]$^{2+}$-PyH^{+},OMe,ax-a	-888515.76	262.56	62.07	-888293.88	-155.75	-888449.63	-28.68

4h. NBO Analysis

We carried out an IRC analysis starting from **[TS-I·2H]$^{2+}$-PyH^{+},OMe,ax-b** (conformations **a** and **b** lead to similar results) containing 40 points, in which point 0 represents the **TS-I** and points 20 and -20 represent the end points obtained towards the **Int-III** and **Int-IV** steps, respectively (**Figure S14**). We then calculated Wiberg bond orders of the various P-C/P-O bonds and electron populations of the two lone electron pairs of the oxygen atom (LP_{Ox}) from an NBO analysis every two IRC points (**Tables S9-10**).

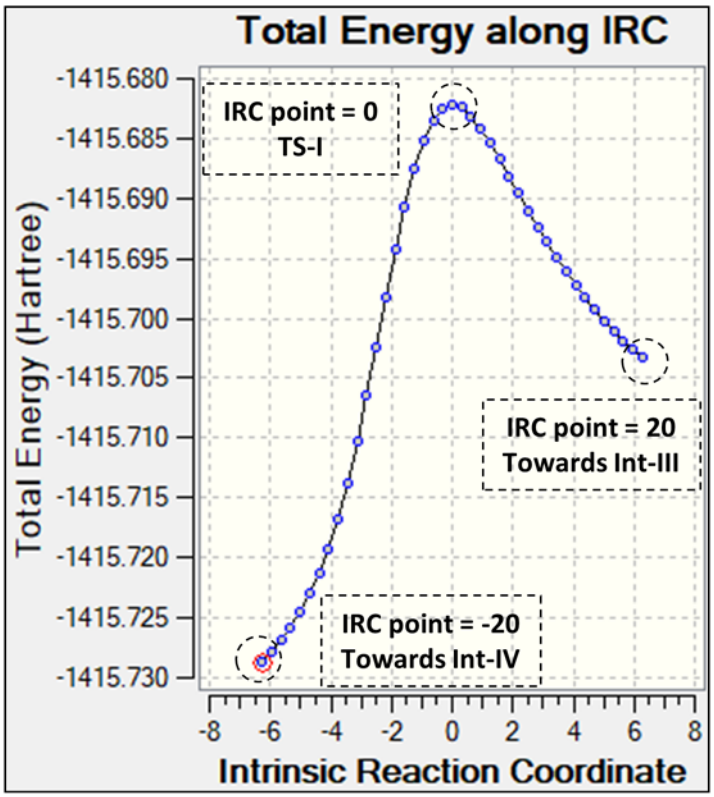


Figure S14. Enumeration of the points comprising the IRC analysis.

Table S9. Wiberg bond orders of different bonds involved in the **TS-I** step along the IRC analysis.

IRC step number	Wiberg Bond Orders		
	C-C bond formation	P-C bond (axial)	P-C bond (equatorial)
19	0.0634	0.5838	0.8132
17	0.0665	0.5644	0.8165
15	0.0705	0.5411	0.8199
13	0.0762	0.5140	0.8233
11	0.0846	0.4827	0.8273
9	0.0977	0.4465	0.8319
7	0.1186	0.4048	0.8375
5	0.1538	0.3556	0.8446

3	0.2105	0.2992	0.8528
1	0.2951	0.2379	0.8609
-1	0.4062	0.1773	0.8658
-3	0.5304	0.1256	0.8658
-5	0.6504	0.0862	0.8609
-7	0.7528	0.0585	0.8523
-9	0.8315	0.0403	0.8416
-11	0.8864	0.0290	0.8300
-13	0.9188	0.0221	0.8196
-15	0.9351	0.0182	0.8121
-17	0.9440	0.0160	0.8073
-19	0.9489	0.0143	0.8048

Table S10. LP_{Ox} along the IRC analysis.

IRC step number	Electron population	
	Lone electron pair 1	Lone electron pair 2
19	1.9506	1.9111
17	1.9508	1.9112
15	1.9509	1.9111
13	1.9509	1.9108
11	1.9507	1.9102
9	1.9503	1.9092
7	1.9497	1.9078
5	1.9491	1.9061
3	1.9483	1.9042
1	1.9476	1.9025
-1	1.9469	1.9011
-3	1.9463	1.9002
-5	1.9456	1.8993
-7	1.9447	1.8984
-9	1.9439	1.8974
-11	1.9431	1.8963
-13	1.9425	1.8957
-15	1.9421	1.8957
-17	1.9416	1.8961
-19	1.9411	1.8968

5. Potential Energy Surface (PES) Relaxed Scans

All the scans were performed using ωB97X-D/6-31+G(d) in gas phase and freezing the coordinates of the P and O atoms involved in the forming P-O bond. Distances at which the two atoms were frozen increased progressively by 0.1 Å starting from 1.71 Å, which is approximately the typical distance for P-O bonds observed in the different systems.

In agreement with the previous experimental results, when using an alkoxy salt, the RO^- attack to the initial phosphonium salt is barrierless and exergonic and, therefore, this should not be the rate-limiting step (RLS) of the process (**Figure S15**, left). Instead, the RLS in this case should be the RO^- attack to the Py group (**TS-I**, **Figure S9**). Contrarily, the addition of ROH to the initial phosphonium salt shows a high activation energy in the computational energy scans, which suggests that this is the RLS and agrees with the experimental kinetic studies **(Figure S15**, right). Similar results were obtained using other degrees of protonation (1 and 2 eq H^+).

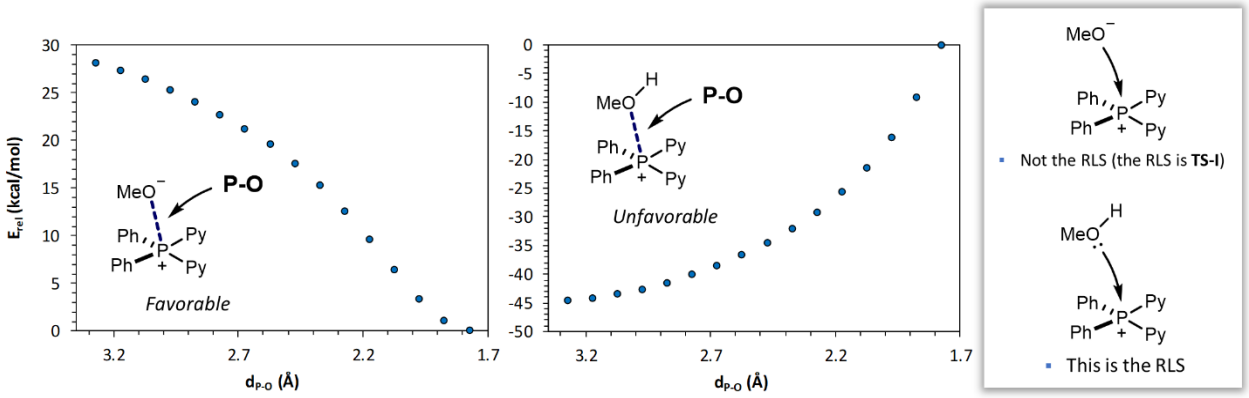


Figure S15. Relaxed PES scans of the addition of MeO^- (left) and MeOH (right) to PPh_2Py_2 (ωB97X-D/6-31+G(d)).

Additionally, PES relaxed scans were carried out to determine whether **Int-IV** could introduce an additional molecule of alcohol before P-C cleavage. As seen in **Figure S16**, the addition of an additional molecule of alcohol to form a P(V)-intermediate before product release shows a high activation barrier, which suggests that this is a slow reaction. Therefore, we ruled out this possibility since the competing P-C cleavage (**[TS-II·2H]$^{2+}$**) has a low activation barrier of 7 kcal/mol.

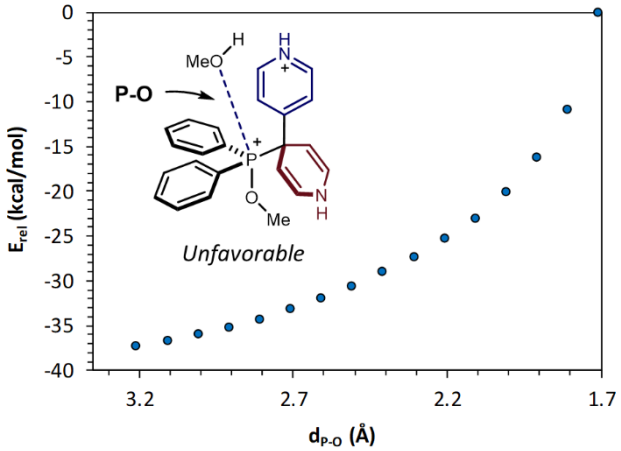


Figure S16. PES relaxed scan along the coordinate corresponding to the addition of MeOH to **[Int-IV·2H]$^{2+}$**. Similar results were obtained using different conformations of **[Int-IV·2H]$^{2+}$**.

6. Captions to Movies S1-2

Animation of Reaction Coordinate (computational analysis) Movie S1:

ELF analysis of [TS-I·2H]$^{2+}$-PyH^{+},OMe,ax-a. Electron localization function (ELF) analysis of transition state **[TS-I·2H]$^{2+}$-PyH^{+},OMe,ax-a** along its intrinsic reaction coordinate (IRC), showing only the ELF part corresponding to Py-Py bond formation. This video shows a typical axial Py·H^{+} attack to an equatorial Py·H^{+} in reaction step **TS-I**. See supporting computational details for the methods employed, the video was created using PyMol (using a contour level of 0.88), Adobe Photoshop and Windows Movie Maker.

Animation of Frontier Molecular Orbital for C-C Bond Forming Event (computational analysis) Movie S2:

Orbital analysis of [TS-I·2H]$^{2+}$-PyH^{+},OMe,ax-a. Changes in the HOMO involved in transition state **[TS-I·2H]$^{2+}$-PyH^{+},OMe,ax-a** along its intrinsic reaction coordinate (IRC). This video shows a typical axial Py·H^{+} attack to an equatorial Py·H^{+} in reaction step **TS-I**. See supporting computational details for the methods employed, the video was created using Multiwfn (using an isovalue of 0.08) and Windows Movie Maker.

7. ^{1}H NMR and ^{31}P NMR Salt Protonation Study

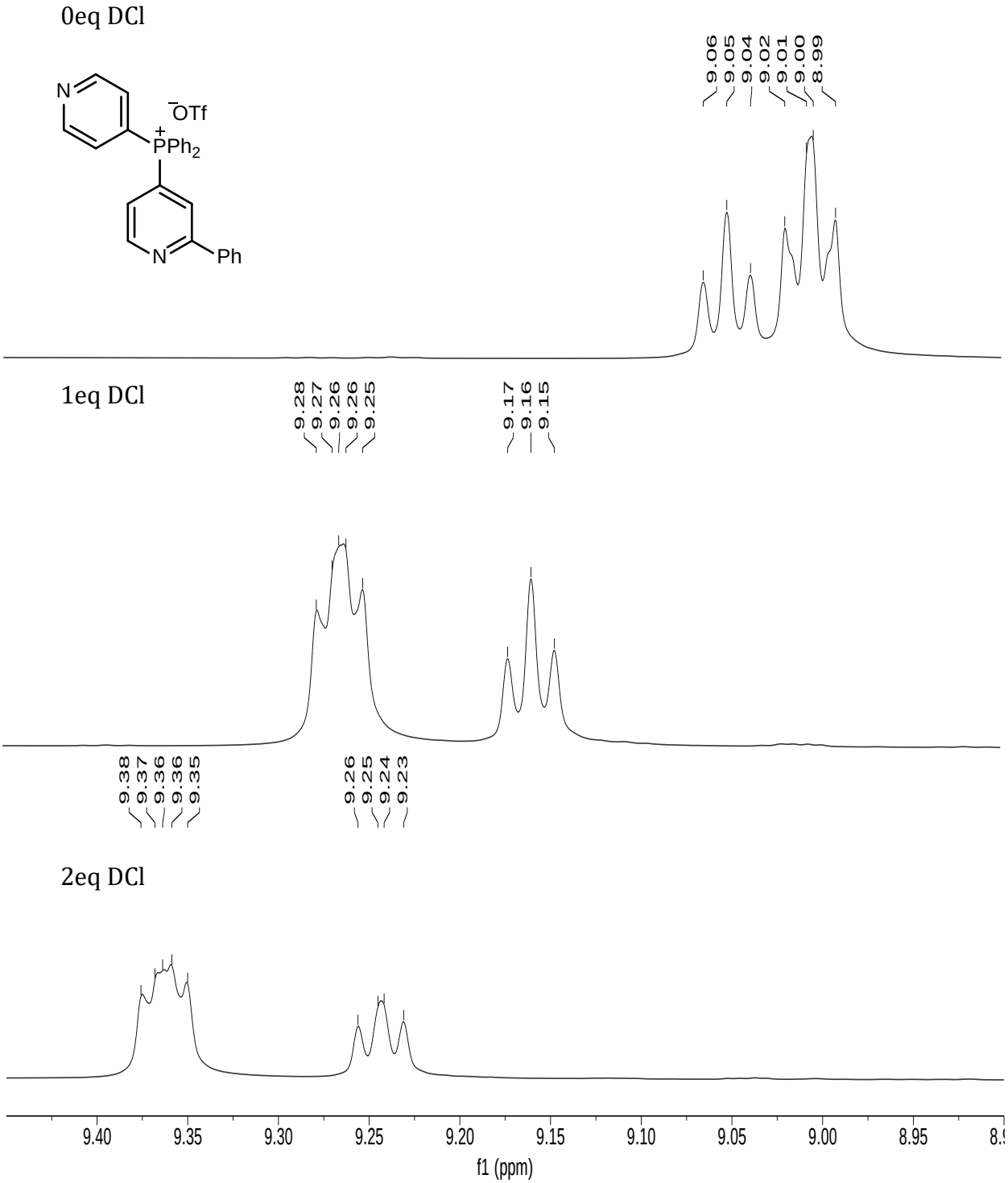


Figure S17. ^{1}H NMR study to determine protonation state of phosphonium salt (**3a**) upon addition of one and two equivalents of DCl at room temperature. DCl was generated *in situ* via reaction of CD_3OD with acyl chloride. ^{1}H NMR ran in CD_3OD and the residual solvent peak was calibrated to 3.31 ppm.

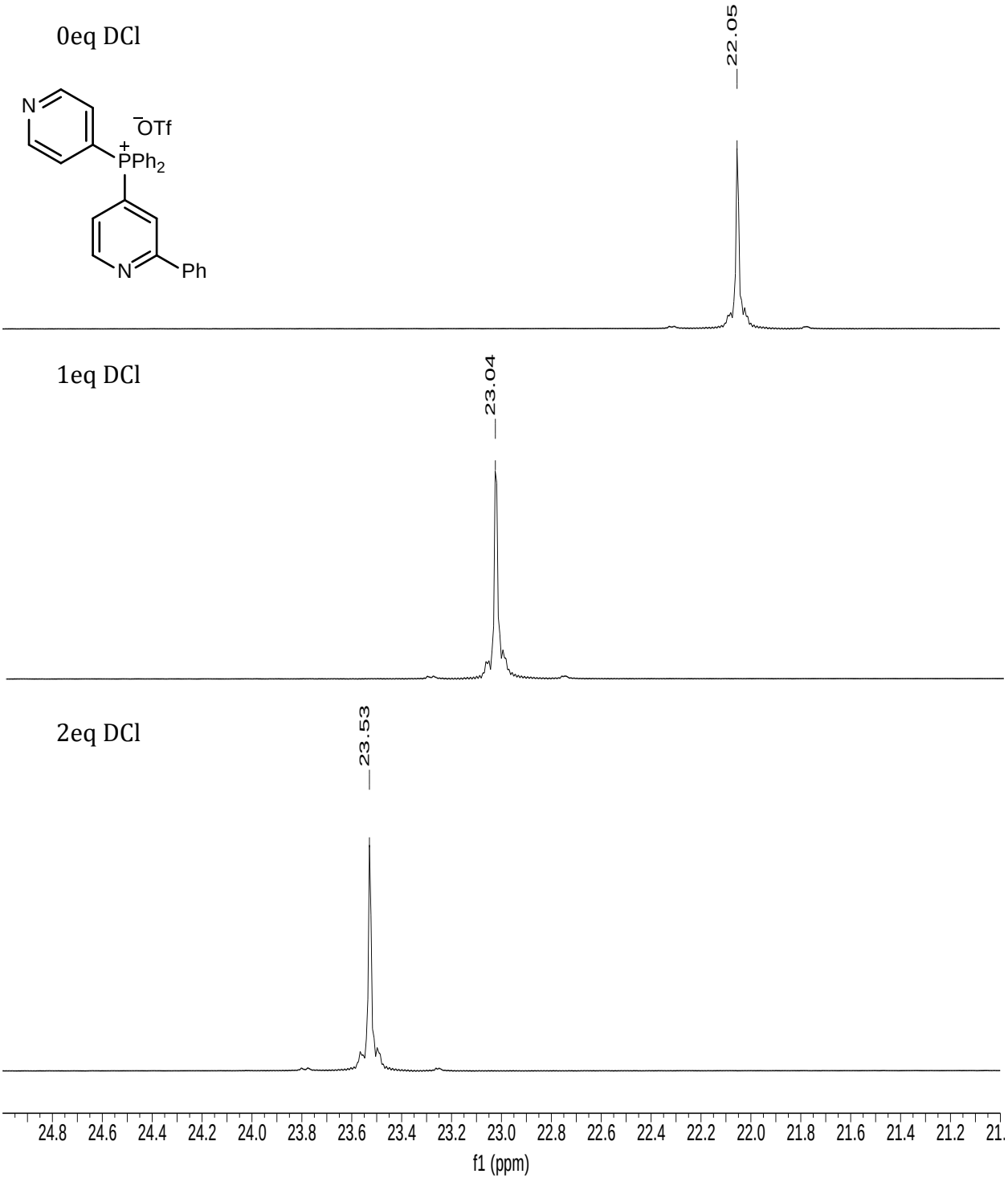
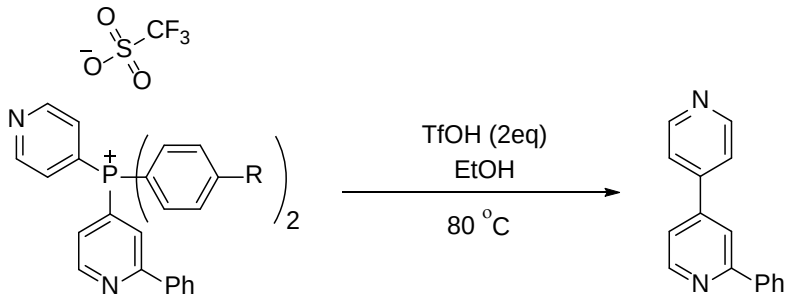


Figure S18. ^{31}P NMR study to determine protonation state of phosphonium salt (**3a**) upon addition of one and two equivalents of DCl at room temperature. DCl was generated *in situ* via reaction of CD_3OD with acyl chloride.

8. Aryl Group Substitution Study: Reaction Kinetics

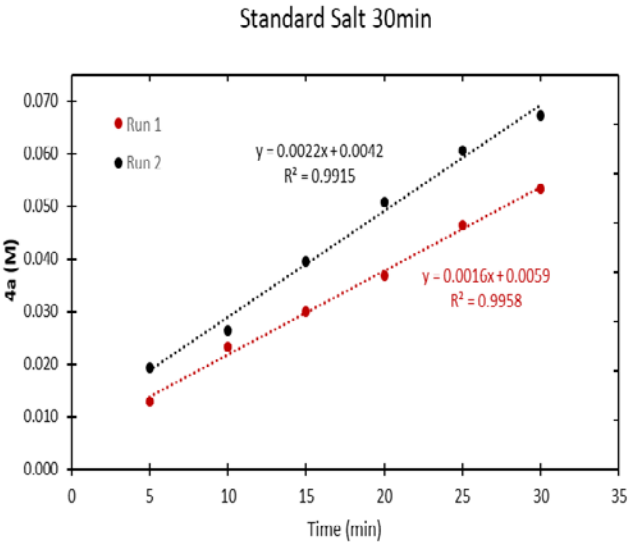


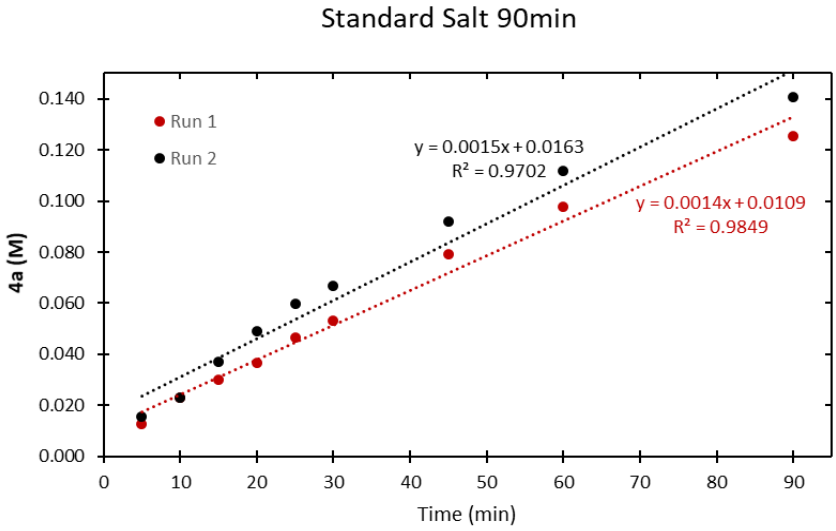
R= H (**3a**), OMe (**3a'**), Me (**3a''**), or Cl (**3a'''**)

Standard Conditions: Kinetic Profile

Standard Salt

Time	Run 1	Run 2	**Average:**
5	0.013	0.016	0.014
10	0.023	0.023	0.023
15	0.030	0.037	0.034
20	0.037	0.049	0.043
25	0.046	0.060	0.053
30	0.053	0.067	0.060
45	0.079	0.092	0.086
60	0.098	0.112	0.105
90	0.126	0.141	0.133
120	0.145	0.168	0.156
180	0.183	0.199	0.191
240	0.204	0.221	0.212
300	0.234	0.245	0.240
360	0.255	0.263	0.259
540	0.285	0.299	0.292
Final Yield:	88.8	89.3	
Average Rate:	**0.0019**		





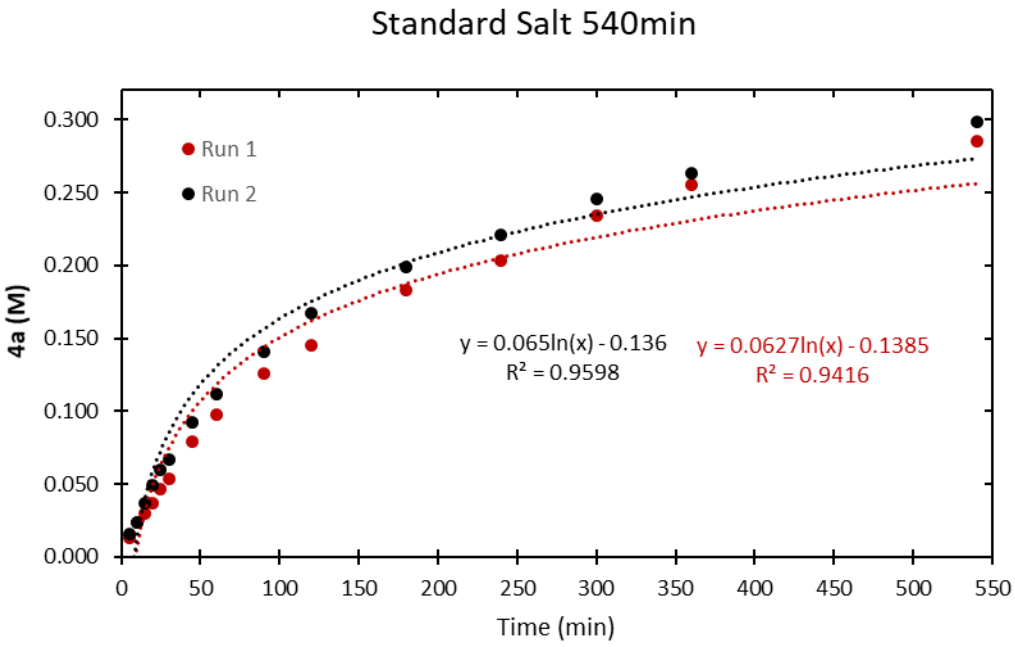


Figure S19. Concentration profile of **4a** over time with TfOH on phosphonium salt **3a**. Yields were determined at the given timepoints using ^{1}H NMR in CD_3OD with triphenylmethane as the internal standard. Procedure for data collection is detailed below.

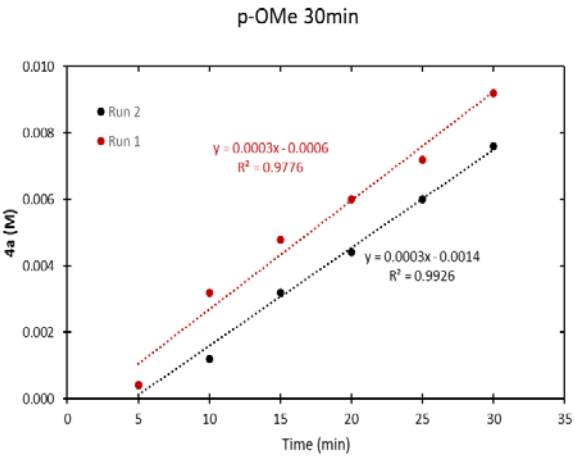
The standard reaction was monitored for 9 hours in duplicate and the average was used for comparison of initial rates with phosphonium salt derivatives **3a'** to **3a'''** (**Figure S23**). The linear range for the standard reaction (reaction time of 30 minutes; 15% yield) was chosen for analysis of the initial rate. Each reaction performed for the kinetic analysis was carried to completion to validate method of monitoring product formation instead of starting material consumption; each reaction regardless of phosphonium salt derivative gave a 85-93% yield.

Procedure for Aryl Group Substitution Study:

An oven dried 8 mL vial with a septa cap was charged with the phosphonium salt (Characterization of phosphonium salts shown in Preparation of Heteroaryl Phosphonium Salt section (**3a** to **3a'''**)) (0.5 mmol), triphenylmethane (122 mg, 0.5 mmol), and EtOH (1.25 mL). The vial was subjected to three rapid cycles of vacuum / nitrogen backfill and TfOH (132 μL, 1.0 mmol) was added via a syringe. The septa cap was quickly replaced with an unpierced one and the reaction vial placed in an oil bath preheated to 80 ºC. At each timepoint, 75 μL of the reaction mixture was sampled via a syringe and charged to a vial. The vial was then concentrated *in vacuo*. The resulting residue was then dissolved in CD_3OD and ^{1}H NMR spectrum was obtained on the sample. The reaction was allowed to progress until the phosphonium salt was fully consumed and the final yield for the reaction was obtained via ^{1}H NMR in CD_3OD(18-48 hours). Each reaction profile was performed in duplicate and the average of the two runs used for initial rate analysis (**Figure S23**). This procedure is identical to the protocol for the standard reaction rate investigation.

Data:

	p-OMe		
Time	Run 1	Run 2	**Average**
5	4.0E-04	4.0E-04	4.0E-04
10	3.2E-03	1.2E-03	2.2E-03
15	4.8E-03	3.2E-03	4.0E-03
20	6.0E-03	4.4E-03	5.2E-03
25	7.2E-03	6.0E-03	6.6E-03
30	9.2E-03	7.6E-03	8.4E-03
45	1.5E-02	1.3E-02	1.4E-02
60	2.1E-02	1.7E-02	1.9E-02
90	3.3E-02	2.6E-02	3.0E-02
Final Yield:	92.0	84.9	
Average Rate:	**0.0003**		



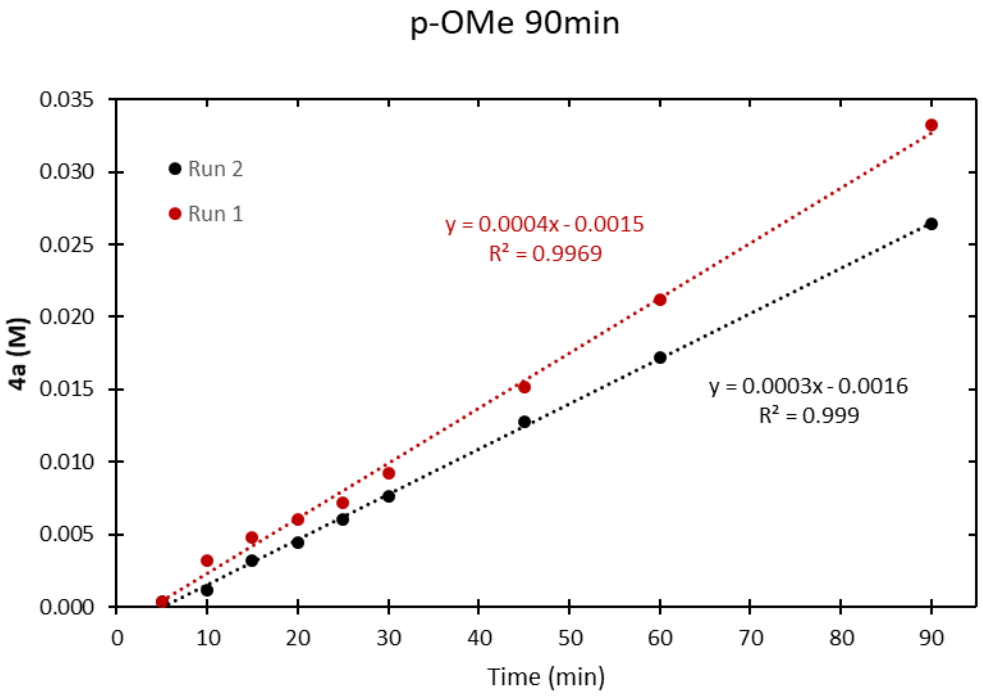
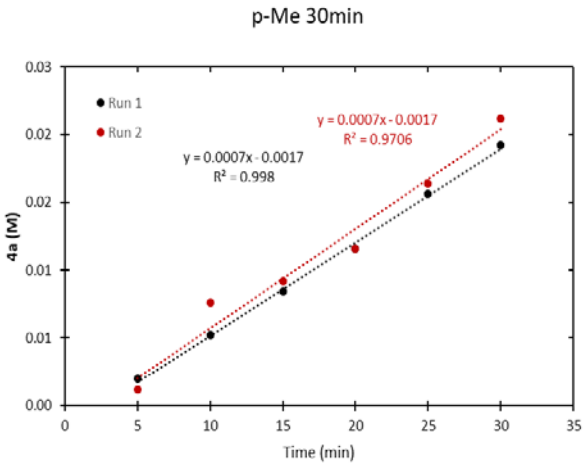


Figure S20: Standard reaction conditions run with TfOH with phosphonium salt **3a′** to obtain the initial reaction rate. Study was ran in duplicate. Yields were determined at the given timepoints using ^{1}H NMR in CD_3OD with triphenylmethane as the internal standard.

	p-Me		
Time	Run 1	Run 2	**Average**
5	0.002	0.001	0.002
10	0.005	0.008	0.006
15	0.008	0.009	0.009
20	0.012	0.012	0.012
25	0.016	0.016	0.016
30	0.019	0.021	0.020
45	0.030	0.033	0.032
60	0.040	0.041	0.041
90	0.059	0.061	0.060
Final Yield:	93.4	94	
Average Rate:	**0.0007**		



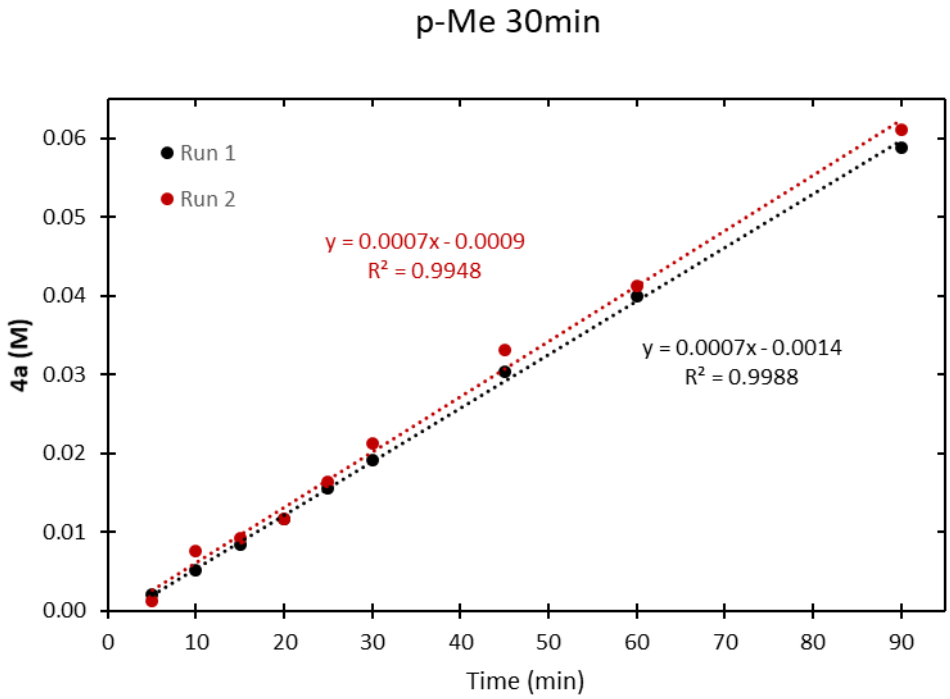
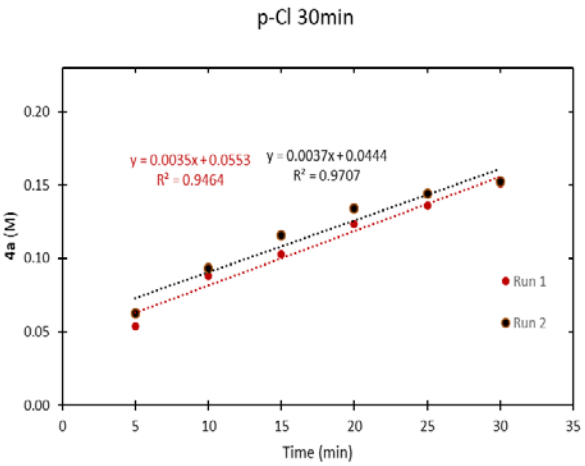


Figure S21: Standard reaction conditions run with TfOH with phosphonium salt **3a″** to obtain the initial reaction rate. Study was ran in duplicate. Yields were determined at the given timepoints using ^{1}H NMR in CD_3OD with triphenylmethane as the internal standard.

	p-Cl		
Time	Run 1	Run 2	**Average**
5	0.054	0.063	0.058
10	0.088	0.094	0.091
15	0.103	0.116	0.109
20	0.124	0.134	0.129
25	0.136	0.144	0.140
30	0.151	0.152	0.152
45	0.169	0.174	0.171
60	0.186	0.191	0.188
90	0.209	0.213	0.211
Final Yield:	89.5	89.2	
Average Rate:	**0.0036**		



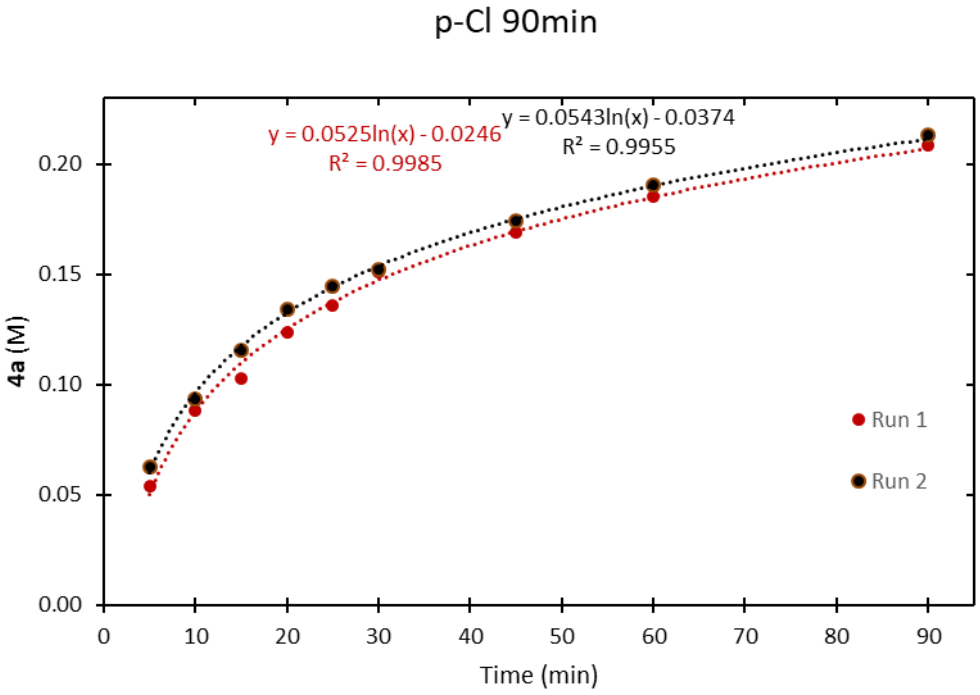
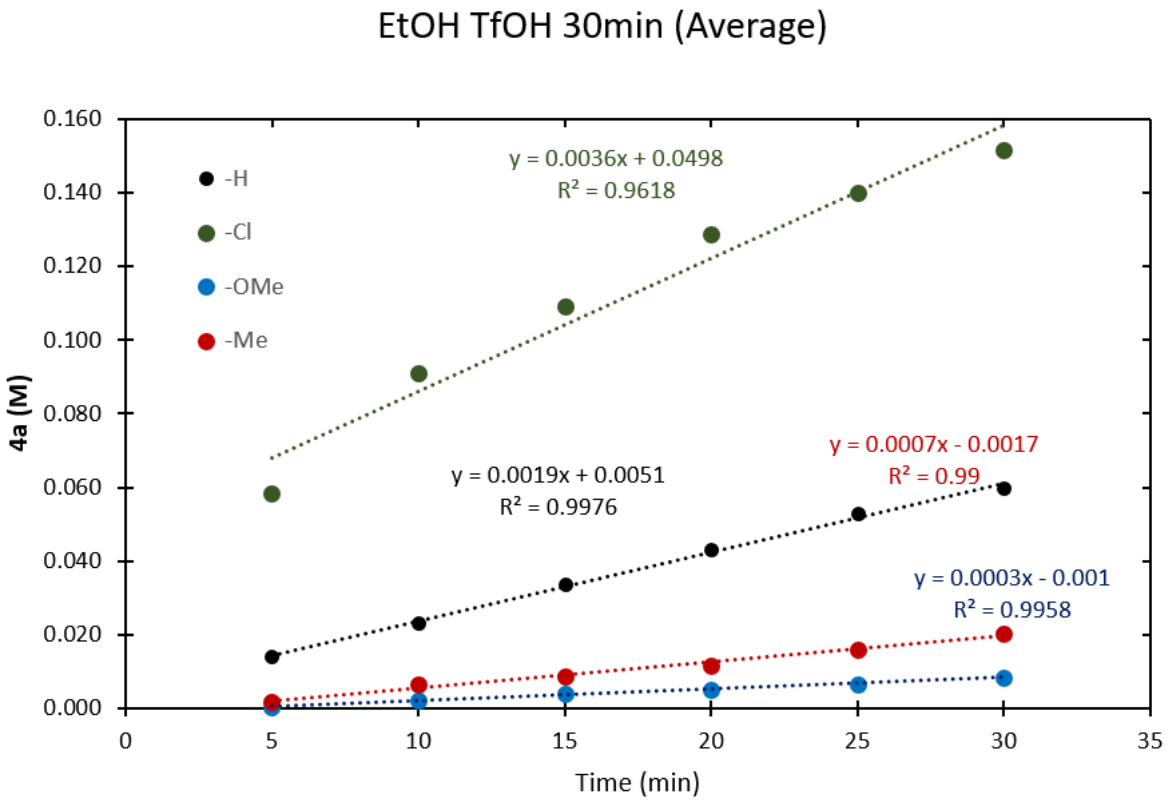


Figure S22: Standard reaction conditions run with TfOH with phosphonium salt **3a‴** to obtain the initial reaction rate. Study was ran in duplicate. Yields were determined at the given timepoints using ^{1}H NMR in CD_3OD with triphenylmethane as the internal standard.

Conc. of 4a (Average of 2 Runs)

Time (min)	-Cl	-H	-Me	-OMe
5	0.058	0.014	0.002	4.00E-04
10	0.091	0.023	0.006	2.20E-03
15	0.109	0.034	0.009	4.00E-03
20	0.129	0.043	0.012	5.20E-03
25	0.140	0.053	0.016	6.60E-03
30	0.152	0.060	0.020	8.40E-03
45	0.171	0.086	0.032	1.40E-02
60	0.188	0.105	0.041	1.92E-02
90	0.211	0.133	0.060	2.98E-02



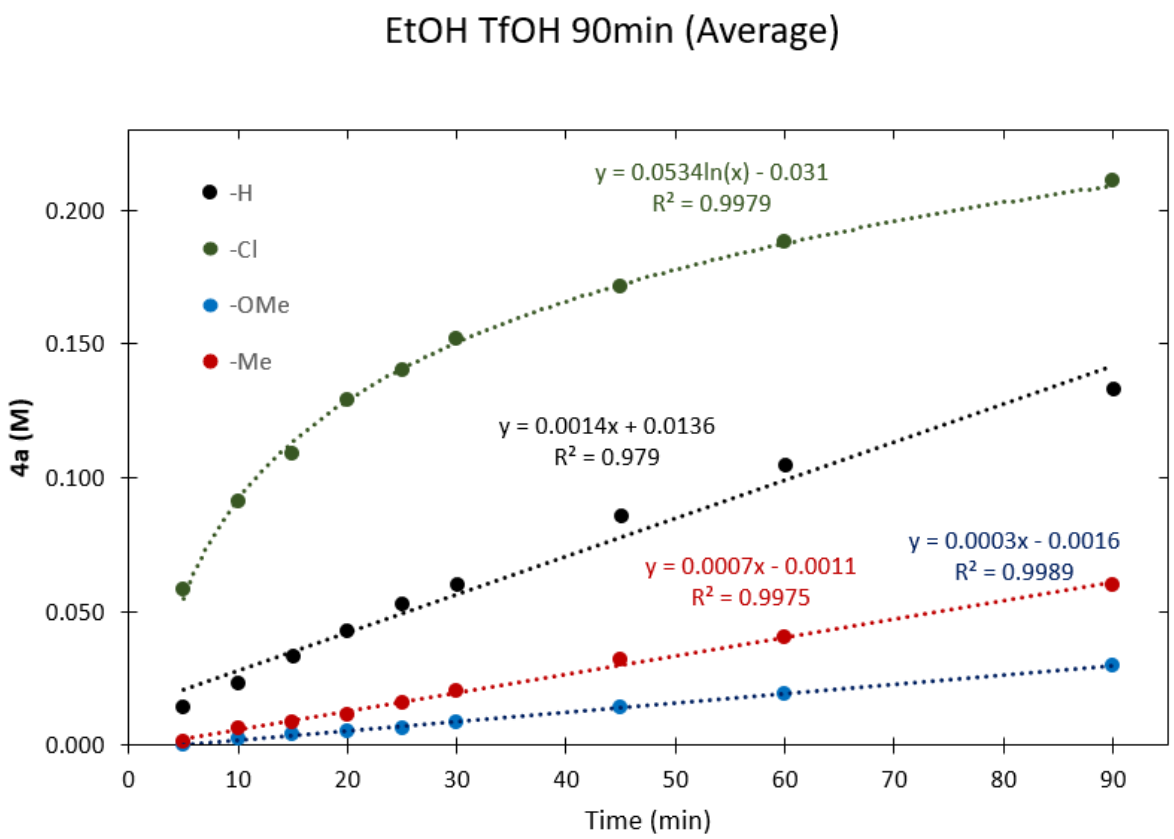


Figure S23: Average reaction progression over 30 min and 90 min for phosphonium salt **3a-3a‴** used to obtain the initial reaction rate for relative rate values. Yields were determined at the given timepoints using ^{1}H NMR in CD_3OD with triphenylmethane as the internal standard.

Table S11: Relative Initial Rates (30 min) ($rate_X/rate_H$) of Phosphonium Salts **3a-3a‴** under Standard Reaction Conditions.

Relative Rate:	
-Cl	1.89
-H	1.00
-Me	0.37
-OMe	0.16

Analysis: The investigation into the relative initial rates for the ligand-coupling reaction shows a correlation between reaction rate and electrophilicity at the phosphorus center. The more electron deficient phosphonium salt resulted in a relative rate of 1.89 while more electron rich phosphonium salts resulted in slower relative rates of reaction compared to the standard (-H) phosphonium. Since each phosphonium derivative results in an average 87%+ yield of **4a**, byproduct formation is not dramatically impacting the rate of product formation. This agrees with the hypothesis that the rate determining step is EtOH addition to the phosphorus center to form the phosphorane intermediate (**[Int-III·2H]**$^{2+}$).

9. Alkoxide Investigation

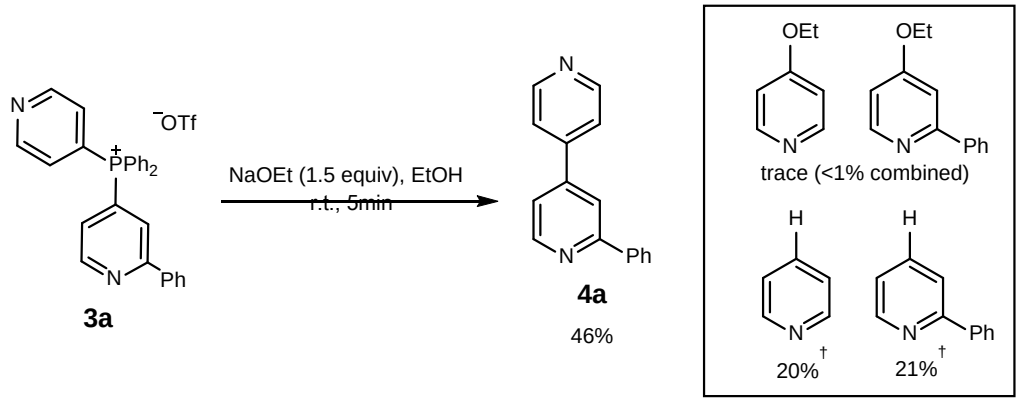


Figure S24. Reaction of phosphonium salt **3a** with NaOEt in EtOH at room temperature. Reaction was performed to investigate if ligand coupling occurs at lower temperatures with a stronger nucleophile (alkoxide vs alcohol). A mixture of products was observed, including 46% desired C-C bond formation (**4a**) along with undesired C-H products (41% combined). *Yield obtained by ^{1}H NMR using 1,3,5-trimethoxybenzene as internal standard. †Yield was obtained via GC/FID using 1,3,5-trimethoxybenzene as internal standard (Response Factors: pyridine: 1.46; 2-phenylpyridine: 0.597).

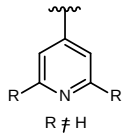
Procedure for Alkoxide Investigation:

An oven dried 8 mL vial with a septa cap was charged with NaH (60% dispersion in mineral oil, 15 mg, 0.38 mmol) and 1,3,5-trimethoxybenzene (42 mg, 0.25 mmol). The vial was placed under a nitrogen atmosphere, cooled to −78 ºC, and then EtOH (0.63 mL) was added. The vial was allowed to warm to 0 ºC and stirred for 30 minutes. The reaction was then warmed to room temperature and the cap was briefly removed and the phosphonium salt **3a** (142 mg, 0.25 mmol) was added in one portion. The reaction was subjected to three rapid cycles of vacuum/nitrogen backfill and the reaction stirred for 5 minutes at room temperature (phosphonium salt **3a** not detected by LCMS after 5 minutes). 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 (Na_2SO_4), filtered and concentrated *in vacuo*. Flash column chromatography (basic alumina: 10% EtOAc in hexanes to 20% EtOAc in hexanes) afforded **4a** as a white crystalline solid (27 mg, 0.12 mmol, 46% yield). (Characterization of **4a** product shown in Ligand-Coupling Reactions to Make Heterobiaryls)

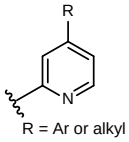
Analysis: The investigation into reaction of a stronger nucleophile (alkoxide vs alcohol) with phosphonium salt **3a** gave results consistent with a rate limiting step of phosphorane formation (**[Int-III·2H]$^{2+}$**) for the standard acidic conditions ligand-coupling reaction. Since the calculated barrier for C-C bond formation is only 30 kcal/mol from **[Int-III]** as long as **[Int-III]** is formed, one would expect to observe C-C bond formation at temperatures lower than 80 ºC. By using an alkoxide as the nucleophile to form **[Int-III]** we remove this potential barrier from the reaction coordinate (alkoxide attack on the phosphonium center was computed to be barrierless Figure S14). The result of this experiment giving 41% of **4a** when ran at room temperature indicates that in the standard acidic conditions it is the alcohol addition to form **[Int-III·2H]$^{2+}$** that is the rate limiting step and it is this step that requires higher temperatures.

10. Challenges and Limitations

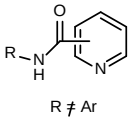
Salt Formation: Challenges/Limitations



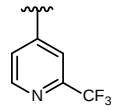
-Unable to form trifyl salt during activation step; No desired phosphonium observed



-Ar and HetAr: <25% desired salt yield (^{1}H NMR yield using trimethoxybenzene as internal standard)
-Alkyl: No nucleophilic addition observed (consistent with previously reported literature (*92*))

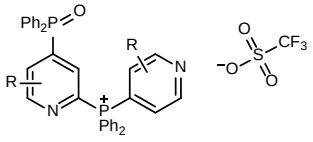


-Undesired side reaction with trifyl activated amide



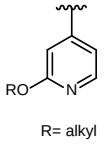
-Unable to form trifyl salt during activation step; No desired phosphonium observed

Pseudodimer: Tf-salt exchange can occur resulting in phosphine attacking another molecule of itself. Most often due to a lack of steric/electron bias between the two pyridines. This undesired side reaction can often be eliminated by increasing the temperature for the phosphine addition step.(See 3f for example)

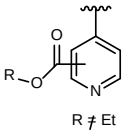


Pseudodimer

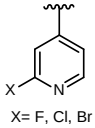
Ligand-coupling: Challenges/Limitations



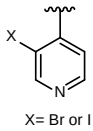
-Slow reaction rates with TFE/TfOH conditions



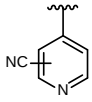
-Slow reaction rate with TFE/TfOH; transesterification under EtOH/acid



-S_nAr with alcohol solvent observed



-Dehalogenation observed under ligand-coupling conditions



-Slow reaction rate with TFE/TfOH conditions

Notes:

-The ligand-coupling reaction was typically able to achieve the desired heterobiaryl product with yields varying based on the pyridine substitutuents over substitution elsewhere in the molecule.

-Ligand-coupling together 2 deficient pyridines (3 or more EWG directly attached to the pyridines) have been seen to give lower than expected yields for the ligand coupled product.

-An excess of basic nitrogens (5+ between the two coupling partners) results in slower reaction rates.

-Ligand-couplings with pyrimidines resulted in formation undesired C-O bond formation regardless of acid used.

Figure S25. Challenges and limitations for phosphonium salt formation and ligand-coupling reaction.

11. Additional Examples

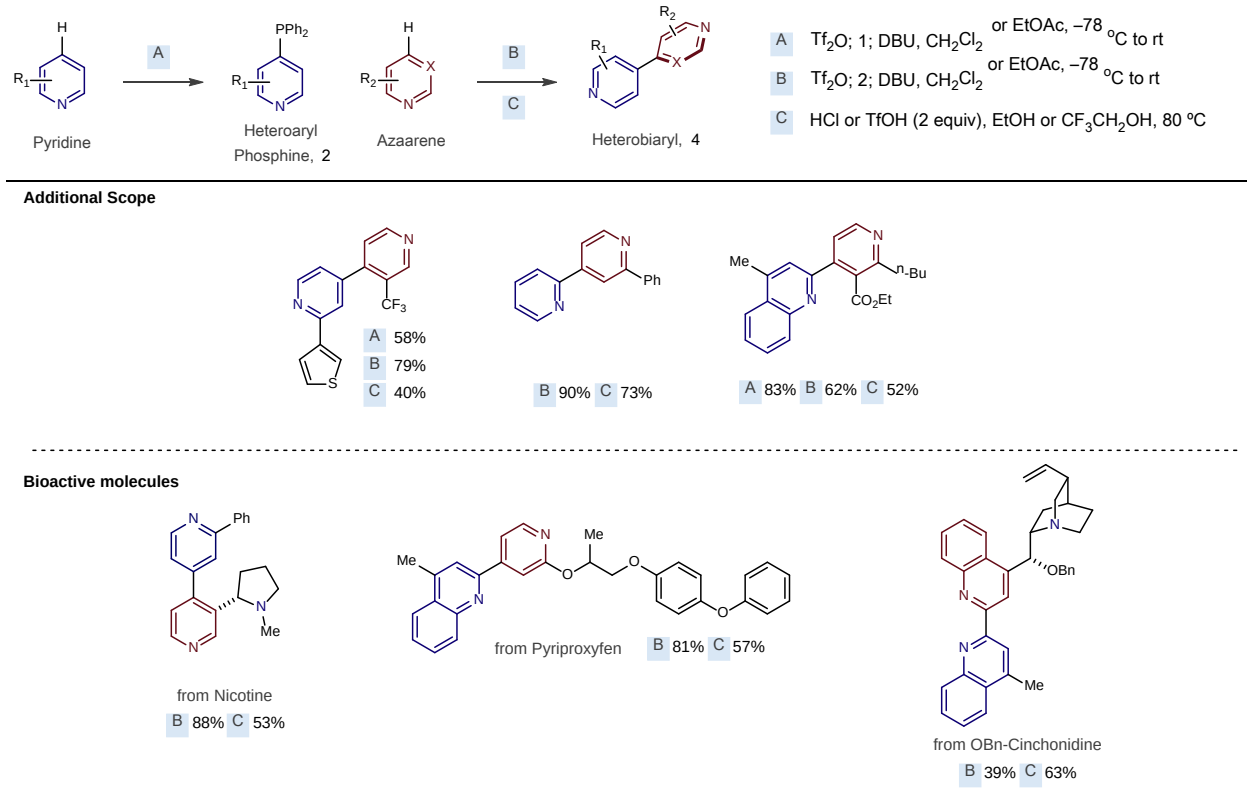
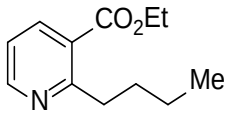


Figure S26. Additional examples of phosphorus ligand-coupling.

12. Experimental Procedures

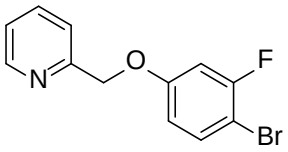
12a. Preparation of Heterocyclic Phosphonium Salt Precursors

Ethyl 2-butylnicotinate



An oven-dried 100 mL round bottom flask was charged with $ZnCl_2$ (1.91 g, 14.00 mmol) and anhydrous THF (28 mL). The colorless solution was cooled to 0 °C, n-BuLi (2.5 M in hexanes, 5.60 mL, 14.00 mmol) was added dropwise, and the reaction mixture was stirred for 1 hour. The resulting n-butylzinc chloride solution (14.00 mmol) was added dropwise to a 50 mL round bottom flask charged with ethyl 2-bromonicotinate (1.61 g, 7.00 mmol), $Pd(PPh_3)_4$ (81 mg, 0.07 mmol), and 7 mL of anhydrous THF. After 3 hours of stirring the reaction mixture at room temperature 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: CH_2Cl_2 to 5% EtOAc in CH_2Cl_2) to provide the title compound as a light yellow oil (680 mg, 3.29 mmol, 47% yield). IR υ_{max}/cm^{-1} (film): 3047, 2957, 2932, 2871, 1722, 1583, 1567, 1442, 1365, 1274, 1249, 1136, 1095, 1079, 1040, 765; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.63 (1H, dd, *J* = 4.8, 1.6 Hz), 8.13 (1H, dd, *J* = 1.8, 7.9 Hz), 7.18 (1H, dd, *J* = 4.8, 7.8 Hz), 4.37 (2H, q, *J* = 7.2 Hz), 3.14 (2H, t, *J* = 8.0 Hz), 1.73-1.65 (2H, m), 1.47-1.38 (5H, m), 0.94 (3H, t, *J* = 7.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 166.81, 163.42, 151.66, 138.33, 125.74, 120.64, 61.29, 36.84, 32.26, 22.89, 14.21, 13.96; *m/z* HRMS (DART) found $[M+H]^+$ 208.1349, $C_{12}H_{18}NO_2^+$ requires 208.1338.

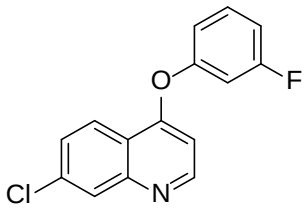
2-((4-Bromo-3-fluorophenoxy)methyl)pyridine



An oven dried 100 mL round bottom was charged with 2-(chloromethyl)pyridine hydrochloride (2.46 g, 15.00 mmol), 4-bromo-3-fluorophenol (2.87 g, 15.00 mmol), K_2CO_3 (6.22 g, 45.00 mmol) and CH_3CN (30 mL), and the mixture was refluxed overnight. After cooling to room temperature, the mixture was poured into water (50 mL) and extracted with EtOAc (3 × 50 mL). The combined organic layer was dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The crude material was purified by flash chromatography (silica gel: 16% EtOAc in hexanes to 33% EtOAc in hexanes) to give 2-((4-bromo-3-fluorophenoxy)methyl)pyridine as a white amorphous powder (4.07 g, 14.40 mmol, 96% yield). mp 56–58 °C; IR υ_{max}/cm^{-1} (film): 3096, 3067, 3024, 2921, 1595, 1587, 1574, 1488, 1479, 1458, 1435, 1416, 1379, 1323, 1301, 1285, 1266, 1239, 1176, 1168, 1154, 1146, 1124, 1061, 1055, 1028, 995, 969, 850, 839, 829, 796, 761, 754, 747; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.60 (1H, d, *J* = 4.8 Hz), 7.71 (1H, t, *J* = 7.7

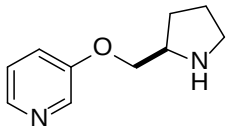
Hz), 7.45 (1H, d, *J* = 7.8 Hz), 7.39 (1H, t, *J* = 8.6 Hz), 7.23 (1H, dd, *J* = 6.8, 5.6 Hz), 6.78 (1H, dd, *J* = 10.3, 2.3 Hz), 6.68 (1H, dd, *J* = 8.9, 2.8 Hz), 5.16 (2H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.40 (d, *J* = 245.4 Hz), 158.88 (d, *J* = 9.8 Hz), 156.16, 149.35, 136.85, 133.39 (d, *J* = 1.8 Hz), 122.86, 121.30, 112.00 (d, *J* = 3.2 Hz), 103.93 (d, *J* = 25.6 Hz), 99.85 (d, *J* = 21.1 Hz), 71.12; ^{19}F NMR (365 MHz, $CDCl_3$) δ: -104.97 (t, *J* = 9.0 Hz); *m/z* HRMS (DART) found $[M+H]^+$ 281.9935, $C_{12}H_{10}BrFNO^+$ requires 281.9930.

7-Chloro-4-(3-fluorophenoxy)quinoline



An oven dried 80 mL pressure tube was charged with 4,7-dichloroquinoline (1.19 g, 6.00 mmol), and 3-fluorophenol (1.63 mL, 18.00 mmol). The flask was subjected to three cycles of vacuum/nitrogen backfill. The mixture was heated at 170 °C for 30 minutes, cooled to room temperature and diluted with CH_2Cl_2. The suspension was washed with an aqueous solution of NaOH (6M), the organic layer was separated and washed with H_2O (3 x 25 mL). The organic extract was dried ($MgSO_4$), filtered and concentrated *in vacuo* to provide the title compound as a pink crystalline solid (1.398 g, 5.10 mmol, 85% yield). mp 78-80 ºC; IR ν_{max}/cm^{-1} (film): 3013, 1612, 1378, 1161, 1135, 876, 819; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.71 (1H, d, *J* = 5.2 Hz), 8.26 (1H, d, *J* = 8.9 Hz), 8.10 (1H, d, *J* = 2.0 Hz), 7.54 (1H, dd, *J* = 11.0, 6.9 Hz), 7.47-7.41 (1H, m), 7.05-6.98 (2H, m), 6.93 (1H, dt, *J* = 9.4, 4.6 Hz), 6.61 (1H, d, *J* = 5.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 163.55 (d, *J* = 248.9 Hz), 162.32, 155.22 (d, *J* = 10.5 Hz), 152.26, 150.33, 136.30, 131.19 (d, *J* = 9.5 Hz), 128.19, 127.32, 123.20, 119.79, 116.55 (d, *J* = 3.4 Hz), 112.83 (d, *J* = 21.0 Hz), 108.87 (d, *J* = 24.1 Hz), 104.81; ^{19}F NMR (365 MHz, $CDCl_3$) δ: –109.43 (q, *J* = 7.1 Hz); *m/z* HRMS (DART) found $[M+H]^+$ 274.0426, $C_{15}H_{10}ClFNO^+$ requires 274.0429.

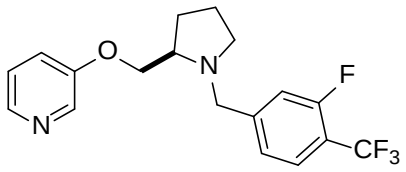
(*R*)-3-(Pyrrolidin-2-ylmethoxy)pyridine



Prepared according to Holladay's report (*93*) using Boc-D-Prolinol (4.03 g, 20.00 mmol), 3-hydroxypyridine (1.50 g, 30.00 mmol), diethyl azodicarboxylate (4.72 mL, 30.00 mmol), and PPh_3 (7.87 g, 30.00 mmol), and THF (100 mL). To provide the title compound as an orange oil (2.42 g, 13.60 mmol, 68% yield). IR ν_{max}/cm^{-1} (film): 3034, 2957, 2871, 1688, 1585, 1485, 1129, 1112, 1013; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.31 (1H, t, *J* = 3.6 Hz), 8.21 (1H, t, *J* = 3.0

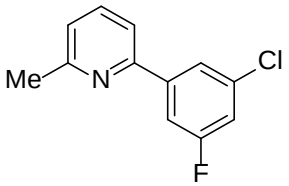
Hz), 7.20-7.19 (2H, m), 3.99-3.90 (2H, m), 3.60 (1H, m), 3.08-2.96 (3H, m), 2.02-1.92 (1H, m), 1.90-1.75 (2H, m), 1.63-1.54 (1H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 154.85, 142.23, 138.01, 123.74, 121.07, 70.73, 57.26, 48.31, 27.71, 24.98; *m/z* HRMS (DART) found $[M+H]^+$ 179.1179, $C_{10}H_{15}N_2O^+$ requires 179.1187.

(*R*)-3-((1-(3-Fluoro-4-(trifluoromethyl)benzyl)pyrrolidin-2-yl)methoxy)pyridine



An oven-dried 100 mL round bottom flask was charged with **(***R***)**-3-(pyrrolidin-2-ylmethoxy)pyridine (1.62 g, 9.10 mmol), 3-fluoro-4-(trifluoromethyl)benzaldehyde (1.40 mL, 10.00 mmol), and sodium triacetoxyhydroborate (3.86 g, 18.20 mmol). The flask was subjected to three cycles of vacuum/nitrogen backfill. CH_2Cl_2 (45 mL) was added to the reaction flask along with glacial AcOH (1.05 mL). After 1 hour stirring at room temperature, the reaction was quenched with a saturated solution of NH_4Cl (30 mL) and diluted with CH_2Cl_2 and the organic layer was separated. The aqueous layer was basified with $NaHCO_3$ 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 gradient elution: 2% MeOH in CH_2Cl_2 to 6% MeOH in CH_2Cl_2) to provide the title compound as an orange oil (2.50 g, 7.10 mmol, 78% yield). IR ν_{max}/cm $^{-1}$ (film): 3060, 2966, 2875, 2797, 1629, 1485, 961, 946, 830, 533; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.29 (1H, d, *J* = 2.8 Hz), 8.21 (1H, dd, *J* = 4.5, 1.2 Hz), 7.50 (1H, t, *J* = 7.6 Hz), 7.23-7.13 (4H, m), 4.20 (1H, d, *J* =14.1 Hz), 4.01-3.90 (2H, m), 3.57 (1H, d, *J* = 14.2 Hz), 3.09-3.04 (1H, m), 3.00-2.96 (1H, m), 2.30 (1H, q, *J* = 2.3 Hz), 2.11-2.02 (1H, m), 1.88-1.70 (3H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.83 (dq, *J* = 255.8, 2.4 Hz), 155.02, 147.52 (d, *J* = 7.2 Hz), 142.22, 137.98, 126.89-126.83 (2C, m), 122.68 (dq, *J* = 271.7, 0.8 Hz), 123.79, 123.67 (d, *J* = 3.4 Hz), 120.97, 116.52 (d, *J* = 20.7 Hz), 71.92, 62.52, 58.94, 54.80, 28.51, 23.24; ^{19}F NMR (365 MHz, $CDCl_3$) δ: –61.15 (d, *J* = 12.8 Hz), –115.05 (m); *m/z* HRMS (DART) found $[M+H]^+$ 355.1454, $C_{18}H_{19}F_4N_2O^+$ requires 355.1428.

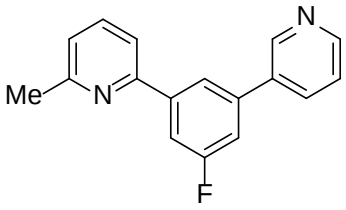
2-(3-Chloro-5-fluorophenyl)-6-methylpyridine



An oven dried round bottom flask was charged with 2-bromo-6-methylpyridine (1.14 mL, 10.00 mmol), (3-chloro-5-fluorophenyl)boronic acid (2.62 g, 15.00 mmol), $Pd(OAc)_2$ (34 mg, 0.15 mmol), K_3PO_4 (4.25 g, 20.00 mmol), 2-propanol (50 mL), and H_2O (50 mL). The mixture

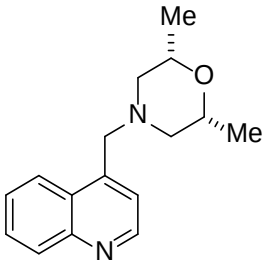
was heated at 80 °C overnight before being cooled to room temperature and diluted with CH_2Cl_2. The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (2x). The combined organic extracts were dried ($MgSO_4$), filtered and concentrated *in vacuo*. The crude material was purified by flash column chromatography (silica gel, gradient elution: 0.5% EtOAc in hexanes to 2% EtOAc in hexanes) followed by a second flash column (silica gel, gradient elution: 1.5% EtOAc in hexanes to 2% EtOAc in hexanes) afforded the title compound as a white solid (1.64 g, 7.40 mmol, 74% yield). mp 34-35 ºC; IR ν_{max}/cm^{-1} (film): 3087, 2923, 1607, 1573, 1432, 1388, 1311, 880, 790; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.79 (1H, s), 7.69-7.60 (2H, m), 7.48 (1H, d, *J* = 7.7 Hz), 7.18-7.08 (2H, m), 2.62 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 162.83 (d, *J* = 248.5 Hz), 158.49, 153.66 (d, *J* = 2.6 Hz), 142.74 (d, *J* = 8.4 Hz), 136.87, 135.11 (d, *J* = 10.8 Hz), 122.68 (d, *J* = 3.1 Hz), 122.54, 117.25, 115.94 (d, *J* = 25.1 Hz), 112.12 (d, *J* = 22.9 Hz), 24.43; ^{19}F NMR (365 MHz, $CDCl_3$) δ: -110.81 (t, *J* = 9.1 Hz); *m/z* HRMS (DART) found $[M+H]^+$ 222.0494, $C_{12}H_{10}ClFN^+$ requires 222.0480.

2-(3-Fluoro-5-(pyridin-3-yl)phenyl)-6-methylpyridine



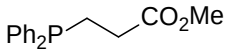
Prepared according to an established procedure (*12*) using 2-(3-chloro-5-fluorophenyl)-6-methylpyridine (1.64 g, 7.40 mmol), pyridin-3-ylboronic acid (1.0 g, 8.13 mmol), $Pd_2(dba)_3$ (68 mg, 0.074 mmol), tricyclohexylphosphane (50 mg, 0.18 mmol), aqueous K_3PO_4 (1.26 M, 10 mL, 12.60 mmol) and 1,4-dioxanes (20 mL). Flash column chromatography (silica gel, 40% EtOAc in hexanes) afforded the title compound as an off white solid (979 mg, 3.71 mmol, 50% yield). mp 110-111 ºC; IR ν_{max}/cm^{-1} (film): 3039, 2917, 1572, 1447, 1437, 1341, 1174, 869, 791; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.91 (1H, d, *J* = 2.5 Hz), 8.64 (1H, dd, *J* = 4.8, 1.6 Hz), 8.00 (1H, t, *J* = 1.6 Hz), 7.94 (1H, ddd, *J* = 7.7, 2.5, 1.6 Hz), 7.74 (1H, ddd, *J* = 9.7, 2.4, 1.6 Hz), 7.68 (1H, t, *J* = 7.7 Hz), 7.56 (1H, d, *J* = 7.7 Hz), 7.40 (1H, ddd, *J* = 7.7, 4.8, 0.8 Hz), 7.31 (1H, ddd, *J* = 9.4, 2.5, 1.6 Hz), 7.16 (1H, d, *J* = 7.7 Hz), 2.64 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 163.44 (d, *J* = 246.0 Hz) 158.52, 154.80 (d, *J* = 2.7 Hz), 148.96, 148.16, 142.61 (d, *J* = 8.1 Hz), 140.06 (d, *J* = 8.1 Hz), 136.93, 135.35 (d, *J* = 2.2 Hz), 134.25, 123.43, 122.34, 121.26 (d, *J* = 2.5 Hz), 117.49, 113.98 (d, *J* = 22.6 Hz), 113.32 (d, *J* = 22.8 Hz), 24.53; ^{19}F NMR (365 MHz, $CDCl_3$) δ: -112.31 (t, *J* = 9.7 Hz); *m/z* HRMS (DART) found $[M+H]^+$ 265.1136, $C_{17}H_{14}FN_2^+$ requires 265.1136.

(*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, 15.00 mmol), *cis*-2,6,-dimethylmorpholine (2.03 mL, 16.50 mmol), and sodium triacetoxyhydroborate (6.36 g, 30.00 mmol). The flask was subjected to three cycles of vacuum/nitrogen backfill. DCM (75 mL) was added to the reaction flask along with glacial AcOH (1.73 mL). After 1.0 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, 11.60 mmol, 77% yield). IR ν_{max}/cm^{-1} (film): 3035, 2971, 2868, 2813, 2774, 980, 815, 662, 645, 591; ^{1}H 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: 150.03, 148.34, 143.60, 129.89, 129.11, 127.62, 126.26, 124.17, 121.37, 71.65 (2C), 59.62, 19.01; *m/z* HRMS (DART) found $[M+H]^+$ 257.1647, $C_{16}H_{20}N_2O^+$ requires 257.1648.

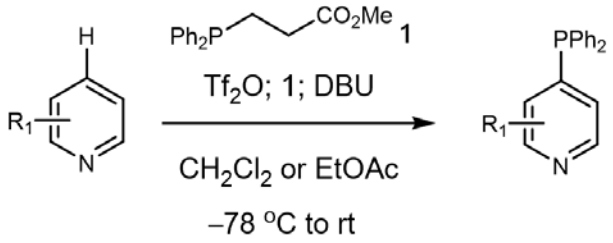
Methyl 3-(diphenylphosphaneyl)propanoate (1)



Prepared according to Alonso's report (*30*). An oven-dried round bottomed flask was charged with diphenylphosphane (17.4 mL, 100 mmol) under a nitrogen atmosphere. Methyl acrylate (9.0 mL, 100 mmol), previously degassed via N_2 sparging, was added dropwise at room temperature over 15 minutes. The reaction was stirred for 16 hours at room temperature before concentrating *in vacuo*. The crude material was purified by flash chromatography (silica gel: 9% EtOAc in hexanes) afforded the title compound as a colorless oil (24.26 g, 89.10 mmol, 89% yield). IR ν_{max}/cm^{-1} (film): 3053, 2949, 1735, 1481, 1433, 1353, 1221, 1164, 736, 695; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.47-7.39 (4H, m), 7.38-7.30 (6H, m), 3.65 (3H, s), 2.46-2.31 (4H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 173.05 (d, *J* = 15.3 Hz), 137.52 (d, *J* = 13.0 Hz), 132.39 (d, *J* = 19.2 Hz), 128.47, 128.22 (d, *J* = 6.6 Hz), 51.33, 30.21 (d, *J* = 19.8 Hz), 22.69 (d, *J* =12.2 Hz); ^{31}P (162 MHz, $CDCl_3$) δ: –15.76; *m/z* HRMS (DART) found $[M+H]^+$ 273.1057, $C_{16}H_{18}O_2P^+$ requires 273.1039.

12b. Preparation of Heteroaryl Phosphines

General Procedure A



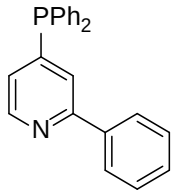
An oven dried 8 mL vial (≤ 0.5 mmol scale) or a round bottom flask (> 0.5 mmol scale) equipped with a stir bar was charged with the heterocycle (1.0 equiv) and placed under a nitrogen atmosphere. CH_2Cl_2 (0.1 M) was added, the reaction vessel cooled to –78 ºC and Tf_2O (1.0 equiv) was added dropwise over 5 minutes. The reaction was stirred for 30 minutes before the mixture was warmed to –50 ºC and then methyl 3-(diphenylphosphaneyl)propanoate (1.1 equiv) was added dropwise as a solution (2.0 M in CH_2Cl_2). The reaction was subjected to three rapid cycles of vacuum / nitrogen backfill and was stirred for a further 30 minutes at –50 ºC. The reaction was cooled to –78 ºC and DBU (3.0 equiv) was added dropwise via syringe, the cooling bath was removed and the reaction was allowed to warm to room temperature while stirring for approximately 2 hours. The reaction was diluted with H_2O and then extracted with CH_2Cl_2 (3x). The combined organic extracts were dried ($MgSO_4$), filtered and concentrated *in vacuo*. The residue was purified by flash column chromatography under the stated conditions to provide the heteroaryl phosphine product.

Notes.

1) To maximize the yield vigorous stirring is required.

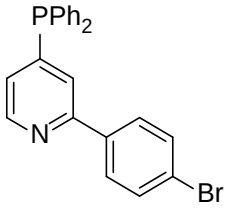
2) For long term storage (>2 weeks) it is best to keep the heteroaryl phosphine product in a –20 °C fridge.

4-(Diphenylphosphaneyl)-2-phenylpyridine (2a)



Prepared according to general procedure A using 2-phenylpyridine (2.13 mL, 14.90 mmol), Tf_2O (2.50 mL, 14.90 mmol), methyl 3-(diphenylphosphaneyl)propanoate (4.44 g, 16.30 mmol), DBU (6.67 mL, 44.70 mmol) and CH_2Cl_2 (149 mL). Crude (to determine the inherent regioselectivity a separate reaction was ran with 1eq DBU instead of 3eq resulting in a pre-fragmented phosphonium salt. See crude ^{31}P NMR for structure) regiomeric ratio 13.3:1.0 (4-position:2-position). Flash column chromatography (silica gel, gradient elution: 1% Et_2O in toluene to 2.5% Et_2O in toluene) afforded the title compound as a white solid (3.59 g, 10.57 mmol, 71% yield). mp 73-74 ºC; IR ν_{max}/cm^{-1} (film): 3053, 1570, 1434, 1373, 1026, 907, 837, 733, 693; ^1H NMR (400 MHz, $CDCl_3$) δ: 8.63 (1H, dd, *J* = 5.1, 2.4 Hz), 7.92 (2H, d, *J* = 7.5 Hz), 7.65 (1H, d, *J* = 7.5 Hz) 7.50-7.35 (13H, m), 7.06 (1H, dd, *J* = 6.2, 5.1 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 156.79 (d, *J* = 5.1 Hz), 149.48 (d, *J* = 17.5 Hz), 149.12 (d, *J* = 4.2 Hz), 139.04, 134.93 (d, *J* = 10.1 Hz), 134.09 (d, *J* = 20.4 Hz), 129.44, 128.94, 128.76 (d, *J* = 7.5 Hz), 128.62, 126.86, 125.48 (d, *J* = 13.5 Hz), 124.13 (d, *J* = 18.0 Hz); ^{31}P (162 MHz, $CDCl_3$) δ: -6.38; *m/z* HRMS (DART) found $[M+H]^+$ 340.1271, $C_{23}H_{19}NP^+$ requires 340.1250.

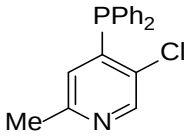
2-(4-Bromophenyl)-4-(diphenylphosphaneyl)pyridine (2b)



Prepared according to general procedure A using 2-(4-bromophenyl)pyridine (2.20 g, 9.40 mmol), Tf_2O (1.58 mL, 9.40 mmol), methyl 3-(diphenylphosphaneyl)propanoate (2.82 g, 10.34 mmol), DBU (4.21 mL, 28.20 mmol) and CH_2Cl_2 (94 mL). Crude (to determine the inherent regioselectivity a separate reaction was ran with 1eq DBU instead of 3eq resulting in a pre-fragmented phosphonium salt. See crude ^{31}P NMR for structure.) regiomeric ratio 13.9:1.0 (4-position:2-position). Flash column chromatography (silica gel: 1% ether in toluene) afforded the title compound as a white solid (2.40 g, 5.75 mmol, 61% yield). mp 120-123 ºC; IR ν_{max}/cm^{-1} (film): 3056, 1580, 1462, 1431, 1403, 1366, 1070, 826, 741, 694; ^1H NMR (400 MHz, $CDCl_3$) δ: 8.61 (1H, dd, *J* = 5.0, 2.4 Hz), 7.79 (2H, d, *J* = 8.6 Hz), 7.61 (1H, d, *J* = 7.3 Hz), 7.55 (2H, d, *J* = 8.6 Hz), 7.48-7.36 (10H, m), 7.06 (1H, t, *J* = 5.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 155.52 (d, *J* = 5.3 Hz), 149.85 (d, *J* = 18.3 Hz), 149.12 (d, *J* = 4.1 Hz), 137.81, 134.77 (d, *J* = 9.9 Hz), 134.07 (d, *J* = 20.6 Hz), 131.70, 129.49, 128.78 (d, *J* = 7.6 Hz), 128.37, 125.73 (d, *J* = 13.0 Hz),

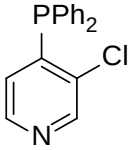
123.77 (d, J = 18.4 Hz), 123.45; ^{31}P (162 MHz, $CDCl_3$) δ: -6.35; *m/z* HRMS (DART) found $[M+H]^+$ 418.1046, $C_{23}H_{18}BrNP^+$ requires 418.1036.

5-Chloro-4-(diphenylphosphino)-2-methylpyridine (2c)



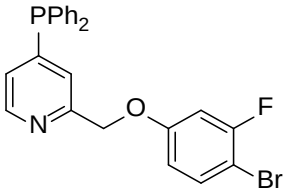
Prepared according to general procedure A using 5-chloro-2-methylpyridine (333 mg, 2.60 mmol), Tf_2O (437 μL, 2.60 mmol), methyl 3-(diphenylphosphino)propanoate (779 mg, 2.86 mmol), DBU (1.17 mL, 7.80 mmol) and CH_2Cl_2 (26 mL). Flash chromatography (silica gel: 9% EtOAc in hexanes to 16% EtOAc in hexanes) afforded the title compound as a white amorphous powder (524 mg, 1.69 mmol, 65% yield). mp 112–114 °C; IR υ_{max}/cm^{-1} (film): 3052, 2990, 2921, 1563, 1477, 1441, 1434, 1323, 1127, 749, 744; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.42 (1H, d, J = 4.5 Hz), 7.44–7.37 (6H, m), 7.32–7.28 (4H, m), 6.48 (1H, d, J = 3.0 Hz), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 156.39, 148.01, 147.45 (d, J = 19.8 Hz), 134.15 (d, J = 20.7 Hz), 133.52 (d, J = 8.9 Hz), 133.28 (d, J = 22.2 Hz), 129.58, 128.87 (d, J = 7.6 Hz), 126.91, 23.93; ^{31}P NMR (162 MHz, $CDCl_3$) δ: –11.81; *m/z* HRMS (DART) found $[M+H]^+$ 312.0710, $C_{18}H_{16}ClNP^+$ requires 312.0709.

3-Chloro-4-(diphenylphosphino)pyridine (2d)



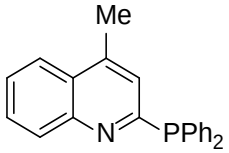
Prepared according to general procedure A using 3-chloropyridine (380 μL, 4.00 mmol), Tf_2O (672 μL, 4.00 mmol), methyl 3-(diphenylphosphino)propanoate (1.20 g, 4.40 mmol), DBU (1.80 mL, 12.00 mmol) and CH_2Cl_2 (40 mL). Flash chromatography (silica gel: CH_2Cl_2 to 5% EtOAc in CH_2Cl_2 afforded the title compound as a white powder (1.08 g, 3.64 mmol, 91% yield). mp 66-68 °C; IR υ_{max}/cm^{-1} (film): 3047, 1568, 1478, 1447, 1433, 1392, 1265, 1181, 1119, 1095, 1077, 1029, 836, 744; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.54 (1H, d, J = 4.4 Hz), 8.32 (1H, dd, J = 4.9, 0.8 Hz), 7.46–7.36 (6H, m), 7.34–7.27 (4H, m), 6.64 (1H, ddd, J = 5.0, 2.8, 0.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 148.85, 147.70 (d, J = 20.5 Hz), 147.34, 136.20 (d, J = 22.2 Hz), 134.14 (d, J = 20.9 Hz), 133.29 (d, J = 9.1 Hz), 129.66, 128.91 (d, J = 7.8 Hz), 127.35; ^{31}P NMR (162 MHz, $CDCl_3$) δ: –11.94; *m/z* LRMS (ESI + APCI) found $[M+H]^+$ 298.1, $C_{17}H_{14}ClNP^+$ requires 298.1.

2-((4-Bromo-3-fluorophenoxy)methyl)-4-(diphenylphosphino)pyridine (2e)



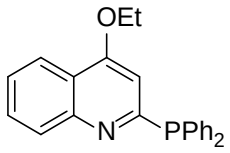
Prepared according to general procedure A using 2-((4-bromo-3-fluorophenoxy)methyl)pyridine (1.41 g, 5.00 mmol), Tf_2O (840 μL, 5.00 mmol), methyl 3-(diphenylphosphino)propanoate (1.50 g, 5.50 mmol), DBU (2.25 mL, 15.00 mmol) and CH_2Cl_2 (50 mL). Flash chromatography (silica gel: 16% EtOAc in hexanes) afforded the title compound as a white amorphous powder (1.96 g, 4.20 mmol, 84% yield). mp 125–127 °C; IR υ_{max}/cm^{-1} (film): 3091, 3068, 2915, 1603, 1580, 1540, 1490, 1476, 1470, 1447, 1435, 1431, 1375, 1294, 1242, 1168, 1149, 1094, 1062, 1027, 991, 949, 887, 853, 831, 804, 747, 731; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.50–8.48 (1H, m), 7.42–7.27 (11H, m), 7.22–7.20 (1H, m), 7.05–7.02 (1H, m), 6.64 (1H, dd, *J* = 10.2, 2.8 Hz), 6.56 (1H, ddd, *J* = 8.9, 2.8, 1.0 Hz), 5.13 (2H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.36 (d, *J* = 245.5 Hz), 158.60 (d, *J* = 9.7 Hz), 155.60 (d, *J* = 4.2 Hz), 150.34 (d, *J* = 18.4 Hz), 148.87 (d, *J* = 4.3 Hz), 134.60 (d, *J* = 9.8 Hz), 134.12 (d, *J* = 20.4 Hz), 133.32 (d, *J* = 1.9 Hz), 129.58, 128.83 (d, *J* = 7.5 Hz), 126.30 (d, *J* = 14.9 Hz), 124.69 (d, *J* = 15.9 Hz), 112.01 (d, *J* = 3.2 Hz), 104.02 (d, *J* = 25.4 Hz), 99.87 (d, *J* = 21.2 Hz), 70.83; ^{19}F NMR (365 MHz, $CDCl_3$) δ: -105.03 (t, *J* = 8.2 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ: –6.50; *m/z* HRMS (DART) found $[M+H]^+$ 466.0399, $C_{24}H_{19}BrFNOP^+$ requires 466.0372.

2-(Diphenylphosphino)-4-methylquinoline (2f)



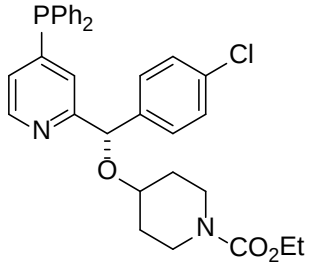
Prepared according to general procedure A using 4-methylquinoline (793 μL, 6.00 mmol), Tf_2O (1.01 mL, 6.00 mmol), methyl 3-(diphenylphosphino)propanoate (1.80 g, 6.60 mmol), DBU (2.70 mL, 18.00 mmol) and CH_2Cl_2 (60 mL). Flash chromatography (silica gel: 16% EtOAc in hexanes) afforded the title compound as a white amorphous powder (1.63 g, 4.98 mmol, 83% yield). mp 99–102 °C; IR υ_{max}/cm^{-1} (film): 3058, 2953, 2926, 2858, 1727, 1576, 1541, 1497, 1479, 1444, 1435, 1431, 761, 751, 739; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.17 (1H, d, *J* = 8.4 Hz), 7.96 (1H, d, *J* = 8.3 Hz), 7.72–7.68 (1H, m), 7.58–7.54 (1H, m), 7.50–7.46 (4H, m), 7.40–7.37 (6H, m), 7.06 (1H, s), 2.58 (3H, d, *J* = 0.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 164.19 (d, *J* = 3.8 Hz), 148.32 (d, *J* = 15.3 Hz), 143.42 (d, *J* = 2.8 Hz), 136.40 (d, *J* = 11.4 Hz), 134.11 (d, *J* = 19.4 Hz), 130.24, 129.17, 128.86, 128.48 (d, *J* = 7.0 Hz), 126.88, 126.53, 124.88 (d, *J* = 14.6 Hz), 123.60, 18.71; ^{31}P NMR (162 MHz, $CDCl_3$) δ: –2.45; *m/z* HRMS (DART) found $[M+H]^+$ 328.1254, $C_{22}H_{19}NP^+$ requires 328.1255.

2-(Diphenylphosphaneyl)-4-ethoxyquinoline (2g)



Prepared according to general procedure A, using 4-ethoxyquinoline (500 mg, 3.00 mmol), Tf_2O (500 μL, 3.00 mmol), methyl-3-(diphenylphosphaneyl)propanoate (900 mg, 3.30 mmol), DBU (1.35 mL, 9.00 mmol), and CH_2Cl_2 (60 mL). The crude material was purified by flash chromatography (silica gel: 15% EtOAc in hexanes) to provide the title compound as a white crystalline solid (880 mg, 2.46 mmol, 82% yield). mp 114-118 ^oC; IR ν_{max}/cm^{-1} (film): 3058, 2975, 1482, 1231, 1115, 1018, 696; ^1H NMR (400 MHz, $CDCl_3$) δ: 8.18 (1H, dd, *J* = 8.8, 1.2 Hz), 8.05 (1H, d, *J* = 8.2 Hz), 7.70-7.64 (1H, m), 7.51-7.39 (5H, m); 7.38-7.31 (6H, m), 6.49 (1H, d, *J* = 0.6 Hz), 3.94 (2H, q, *J* = 7.0 Hz), 1.41 (3H, t, *J* = 7.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 165.60 (d, *J* = 4.7 Hz), 160.96 (d, *J* = 3.5 Hz), 149.60 (d, *J* = 16.9 Hz), 136.56 (d, *J* = 11.9 Hz), 134.10 (d, *J* = 19.4 Hz), 129.73, 129.15, 128.92, 128.49 (d, *J* = 7.0 Hz), 125.72, 121,72, 120.23, 104.02, 63.69, 14.22 ^{31}P NMR (162 MHz, $CDCl_3$) δ: −1.06; *m/z* HRMS (DART) found $[M+H]^+$ 358.1349 $C_{23}H_{21}N_2OP^+$ requires 358.1355.

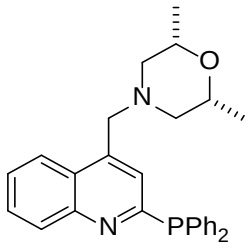
Ethyl (*S*)-4-((4-chlorophenyl)(4-(diphenylphosphaneyl)pyridin-2-yl)methoxy)piperidine-1-carboxylate (2h)



Prepared according to general procedure A using ethyl (*S*)-4-((4-chlorophenyl)(pyridin-2-yl)methoxy)piperidine-1-carboxylate (1.026 g, 2.74 mmol), Tf_2O (0.46 mL, 2.74 mmol), methyl 3-(diphenylphosphaneyl)propanoate (820 mg, 3.01 mmol), DBU (1.22 mL, 8.21 mmol) and CH_2Cl_2 (27.5 mL). Flash column chromatography (silica gel, gradient elution: 45% EtOAc in hexanes to 50% EtOAc in hexanes) afforded the title compound as a tan oil (1.19 g, 2.13 mmol, 78% yield). IR ν_{max}/cm^{-1} (film): 3052, 2981, 2928, 1692, 1577, 1489, 1434, 1381, 1272, 1227, 1087, 742; ^1H NMR (400 MHz, $CDCl_3$) δ: 8.37 (1H, ddd, *J* = 5.1, 2.3, 0.8 Hz), 7.41-7.19 (15H, m), 6.95 (1H, m), 5.52 (1H, s), 4.10 (2H, q, *J* = 7.2 Hz), 3.61-3.45 (3H, m), 3.25-3.06 (2H, m), 1.80-1.67 (1H, m), 1.63-1.38 (3H, m), 1.23 (3H, t, *J* = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 161.03 (d, *J* = 4.2 Hz), 155.36, 150.31 (d, *J* = 18.2 Hz), 148.31 (d, *J* = 4.2 Hz), 139.82, 134.79 (d, *J* = 10.1 Hz), 134.76 (d, *J* = 10.1 Hz), 134.12 (d, *J* = 20.7 Hz), 134.01 (d, *J* = 20.7 Hz), 133.31, 129.51 (d, *J* = 2.8 Hz), 128.72 (d, *J* = 7.6 Hz), 128.45, 128.14, 125.75 (d, *J* = 15.0 Hz), 123.83 (d, *J* = 15.6 Hz), 80.72, 72.23, 61.13, 40.69, 30.80, 30.66, 14.64; ^{31}P NMR (162 MHz,

$CDCl_3$) δ: –6.35; *m/z* HRMS (DART) found $[M+H]^+$ 559.1947, $C_{32}H_{33}ClN_2O_3P^+$ requires 559.1917.

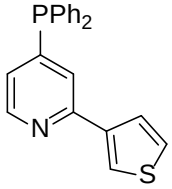
(*2R, 6S*)-4-((2-(Diphenylphosphaneyl)quinolin-4-yl)methyl)-2,6-dimethylmorpholine (2i)



Prepared according to general procedure A, using (*2R, 6S*)-2,6-dimethyl-4-(quinolin-4-ylmethyl)morpholine (1.28 g, 5.00 mmol), Tf_2O (840 μL, 5.00 mmol), methyl-3-(diphenylphosphaneyl)propanoate (1.50 g, 5.50 mmol), DBU (2.25 mL, 15.00 mmol), and CH_2Cl_2 (50 mL). Crude material was purified by flash chromatography (silica gel: 15% EtOAc in hexanes) to provide the title compound as a white amorphous solid (1.42 g, 3.25 mmol, 65% yield). IR ν_{max}/cm^{-1} (film): 3054, 2971, 2932, 2868, 2811, 2236, 570, 566, 542, 537, 529; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.95 (1H, d, *J* = 8.5 Hz), 7.88 (1H, d, *J* = 8.0 Hz), 7.48 (1H, m), 7.33 (1H, m), 7.30-7.24 (4H, m), 7.20-7.12 (6H, m), 7.07 (1H, s), 3.59 (2H, s), 3.35-3.24 (2H, m), 2.37 (2H, d, *J* = 10.4 Hz), 1.57 (2H, t, *J* = 10.7 Hz), 0.90 (6H, d, *J* = 6.3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 164. 39 (d, *J* = 3.7 Hz), 148.59 (d, *J* = 15.1 Hz), 142.58 (d, *J* = 2.7 Hz), 136.39 (d, *J* = 11.3 Hz), 134.05 (d, *J* = 19.5 Hz) 130.26, 129.12, 128.90, 128.45 (d, *J* = 6.9 Hz), 126.5, 125.96, 123.94 (d, *J* = 14.5 Hz), 123.45, 71.46, 59.42, 58.82, 18.94; ^{31}P NMR (162 MHz, $CDCl_3$) δ: –2.22; *m/z* HRMS (DART) found $[M+H]^+$ 441.2065, $C_{28}H_{30}N_2OP^+$ requires 441.2090.

Additional Examples: Characterization

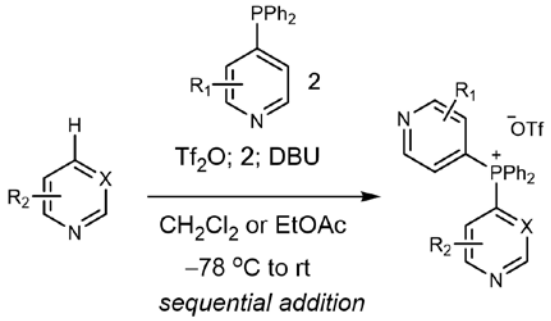
4-(Diphenylphosphaneyl)-2-(thiophen-3-yl)pyridine



Prepared according to general procedure A using 2-(thiophen-3-yl)pyridine (967 mg, 6.00 mmol), Tf_2O (1.0 mL, 6.00 mmol), methyl 3-(diphenylphosphaneyl)propanoate (1.80 g, 6.60 mmol), DBU (2.7 mL, 18.00 mmol) and CH_2Cl_2 (60 mL). Flash column chromatography (silica gel, gradient elution: toluene to 2% Et_2O in toluene) afforded the title compound as a white solid (1.19 g, 3.44 mmol, 58% yield). mp 102-104 ºC; IR ν_{max}/cm^{-1} (film): 3115, 3065, 3014, 1576, 1475, 1435, 1430, 1378, 793, 744, 694; ^1H NMR (400 MHz, $CDCl_3$) δ: 8.55, (1H, dd, *J* = 5.0,

2.4 Hz), 7.82 (1H, dd, *J* = 3.0, 1.0 Hz), 7.55 (1H, dd, *J* = 5.0, 1.0 Hz), 7.51 (1H, d, *J* = 7.3 Hz), 7.47-7.37 (10H, m), 7.34 (1H, dd, *J* = 5.1, 3.0 Hz), 6.99 (1H, app t, *J* = 5.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 152.84 (d, *J* = 5.3 Hz), 149.44 (d, *J* = 17.5 Hz), 149.03 (d, *J* = 4.3 Hz), 141.75, 134.87 (d, *J* = 10.1 Hz), 134.09 (d, *J* = 20.3 Hz), 129.45, 128.76 (d, *J* = 7.6 Hz), 126.14 (d, *J* = 15.1 Hz), 125.17 (d, *J* = 13.7 Hz), 123.92, 123.73 (2C); ^{31}P (162 MHz, $CDCl_3$) δ: –6.67; *m/z* HRMS (DART) found $[M+H]^+$ 346.0840, $C_{21}H_{17}NP^+$ requires 346.0814.

12c. Preparation of Heteroaryl Phosphonium Salts
General Procedure B

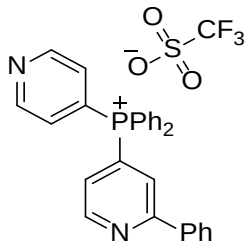


An oven dried 8 mL vial (≤ 0.5 mmol scale) or a round bottom flask (> 0.5 mmol scale) equipped with a stir bar was charged with the heterocycle (1.0 equiv) and placed under a nitrogen atmosphere. CH_2Cl_2 (0.1 M) was added, the reaction vessel cooled to –78 ºC and Tf_2O (1.0 equiv) was added dropwise over 5 minutes. The reaction was stirred for 30 minutes before the mixture was warmed to –50 ºC and then the heteroaryl phosphine (1.1 equiv) was added in one portion as a solid or dropwise as a solution (2.0 M in CH_2Cl_2). The reaction was subjected to three rapid cycles of vacuum / nitrogen backfill and was stirred for a further 30 minutes at –50 ºC. The reaction was cooled to –78 ºC and 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 diluted with CH_2Cl_2 and washed with H_2O (3x). The organic layer was dried ($MgSO_4$), filtered and concentrated *in vacuo* to approximately 2-10 mL (depending on the scale of the reaction). The concentrated reaction mixture was added dropwise to an excess of chilled Et_2O (0 ºC) that was then placed in a –20 ºC refrigerator for approximately 2-12 hours. The 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) 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.
2) To maximize the yield vigorous stirring is required.
3) Filtration can be done as soon as the precipitate settles.
4) In cases where an oil forms instead of a solid it is recommended to decant using Et_2O (0 ºC) instead of washing on a frit.

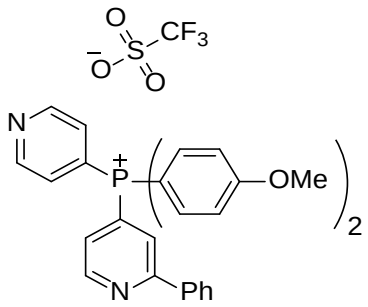
5) In general, CH_2Cl_2 results in the best yields for pyridine salt formation and EtOAc should be used for diazine salt formation for best results.
6) Et_2O typically works best for crashing out the phosphonium salt, however crashing out with 50:50 Et_2O:hexanes or hexanes have been seen to improve isolation of the phosphonium salt.
7) At lower temperatures (–78 °C) on select substrates pseudodimer formation was observed, raising the temperature (–50 °C or –30 °C) generally eliminated this undesired side reaction.

Diphenyl(2-phenylpyridin-4-yl)(pyridin-4-yl)phosphonium trifluoromethanesulfonate (3a)



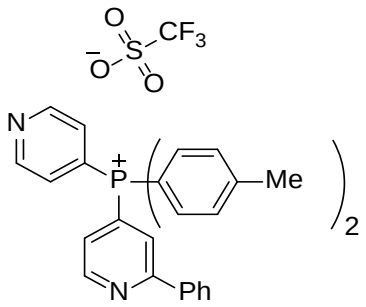
Prepared according to general procedure B using pyridine (119 μL, 1.50 mmol), Tf_2O (250 μL, 1.50 mmol), 4-(diphenylphosphaneyl)-2-phenylpyridine (560 mg, 1.65 mmol), DBU (224 μL, 1.50 mmol) and CH_2Cl_2 (15 mL). After the purification procedure (solid was dissolved in approximately 2-10 mL of CH_2Cl_2 and the solution was again added dropwise to an excess of chilled Et_2O (0 °C). The mixture was then placed in –20 °C refrigerator for 5 hour. The resulting suspension was filtered on a frit and the solid was washed with chilled Et_2O (0 °C) and dried *in vacuo* to provide the pure phosphonium salt), the title compound was isolated as a white solid (702 mg, 1.24 mmol, 83% yield). mp 73 °C; IR ν_{max}/cm^{-1} (film): 3059, 1573, 1440, 1262, 1223, 1150, 1109, 1030; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.09 (1H, app t, *J* = 5.1 Hz), 9.03 (2H, app t, *J* = 5.1 Hz), 7.99-7.87 (4H, m) 7.87-7.78 (5H, m), 7.77-7.63 (6H, m), 7.57 (1H, dd, *J* = 13.1, 5.1 Hz), 7.48-7.41 (3H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.99 (d, *J* = 10.4 Hz), 151.60 (d, *J* = 11.8 Hz), 151.49 (d, *J* = 10.3 Hz), 136.49 (d, *J* = 1.6 Hz), 136.35 (d, *J* = 3.0 Hz), 134.29 (d, *J* = 10.7 Hz), 130.93 (d, *J* = 13.3 Hz), 130.14, 128.75, 127.40 (d, *J* = 84.4 Hz), 126.98 (d, *J* = 8.2 Hz), 126.89, 126.39 (d, *J* = 84.3 Hz), 125.18 (d, *J* = 8.3 Hz), 122.96 (d, *J* = 8.9 Hz), 120.38 (q, *J* = 321.4 Hz), 113.59 (d, *J* = 89.4 Hz); ^{19}F NMR (365 MHz, $CDCl_3$) δ: –78.14; ^{31}P NMR (162 MHz, $CDCl_3$) δ: 21.76; *m/z* HRMS (ESI + APCI) found $[M\text{-}OTf]^+$ 417.1537, $C_{28}H_{22}N_2P^+$ requires 417.1521.

Bis(4-methoxyphenyl)(2-phenylpyridin-4-yl)(pyridin-4-yl)phosphonium trifluoromethanesulfonate (3a′)



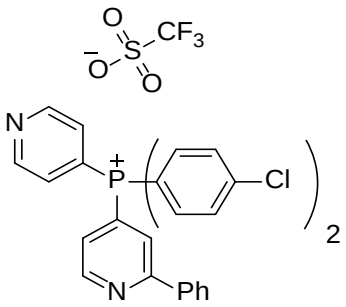
Prepared according to general procedure B using pyridine (24 μL, 0.30 mmol), Tf_2O (50 μL, 0.30 mmol), 4-(bis(4-methoxyphenyl)phosphaneyl)-2-phenylpyridine (prepared from diethyl phosphate and 1-bromo-4-chlorobenzene using Gessner's, Han's, and Bergbreiter's reports followed by general procedure A (*93-96*). (135 mg, 0.33 mmol), DBU (46 μL, 0.30 mmol) and CH_2Cl_2 (3 mL). After the purification procedure (solid was dissolved in approximately 2-10 mL of CH_2Cl_2 and the solution was again added dropwise to an excess of chilled Et_2O (0 °C). The mixture was then placed in –20 °C refrigerator for 5 hour. The resulting suspension was filtered on a frit and the solid was washed with chilled Et_2O (0 °C) and dried *in vacuo* to provide the pure phosphonium salt), the title compound was isolated as a white crystalline solid (136 mg, 0.22 mmol, 72% yield). mp 73-74 ºC; IR ν_{max}/cm^{-1} (film): 3046, 2934, 1592, 1573, 1536, 754, 563, 556; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.10-8.93 (3H, m), 7.95-7.86 (2H, m), 7.79 (1H, d, *J* = 14.1 Hz), 7.66-7.55 (6H, m), 7.53-7.42 (4H, m), 7.34-7.27 (4H, m), 3.95 (6H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 166.00 (d, *J* = 3.0 Hz), 159.39 (d, *J* = 10.4), 151.78 (d, *J* = 10.7 Hz), 151.74 (d, *J* = 10.0 Hz), 136.88 (d, *J* = 1.7 Hz), 136.65 (d, *J* = 12.4 Hz), 130.56, 129.27 (d, *J* = 85.2 Hz), 129.15, 128.39 (d, *J* = 85.4 Hz), 127.22, 127.06 (d, *J* = 7.7 Hz), 125.16 (d, *J* = 8.3 Hz), 123.09 (d, *J* = 8.7 Hz), 120.76 (q, *J* = 321.2 Hz), 117.14 (d, *J* = 14.5 Hz), 103.51 (d, *J* = 98.2 Hz), 56.19; ^{19}F NMR (365 MHz, $CDCl_3$) δ: –78.20; ^{31}P NMR (162 MHz, $CDCl_3$) δ: 20.74; *m/z* LRMS (ESI + APCI) found $[M\text{-}OTf]^+$ 477.2, $C_{30}H_{26}N_2O_2P^+$ requires 477.2.

(2-phenylpyridin-4-yl)(pyridin-4-yl)di-p-tolylphosphonium trifluoromethanesulfonate (3a′′)



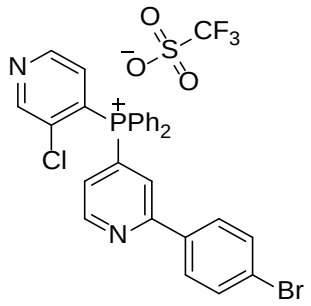
Prepared according to general procedure B using pyridine (60 μL, 0.75 mmol), Tf_2O (126 μL, 0.75 mmol), 4-(di-p-tolylphosphaneyl)-2-phenylpyridine (prepared from di(p-tolyl)phopshine using Alonso's report (*30*) and general procedure A) (312 mg, 0.83 mmol), DBU (112 μL, 0.75 mmol) and CH_2Cl_2 (7.5 mL). After the purification procedure (solid was dissolved in approximately 2-10 mL of CH_2Cl_2 and the solution was again added dropwise to an excess of chilled Et_2O (0 °C). The mixture was then placed in –20 °C refrigerator for 5 hour. The resulting suspension was filtered on a frit and the solid was washed with chilled Et_2O (0 °C) and dried *in vacuo* to provide the pure phosphonium salt), the title compound was isolated as a brown crystalline solid (375 mg, 0.63 mmol, 84% yield). mp 70-71 ºC; IR ν_{max}/cm^{-1} (film): 2936, 2861, 1574, 1444, 547, 543, 538, 528; ^1H NMR (400 MHz, $CDCl_3$) δ: 9.15-8.93 (3H, m), 7.97-7.87 (2H, m), 7.82 (1H, d, *J* = 14.4 Hz), 7.72-7.44 (14H, m), 2.55 (6H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.34 (d, *J* = 10.3 Hz), 151.83 (d, *J* = 10.8), 151.63 (d, *J* = 9.9 Hz), 148.52 (d, *J* = 3.3 Hz), 136.79, 134.46 (d, *J* = 11.2 Hz), 131.96 (d, *J* = 13.6 Hz), 130.52, 129.10, 128.31 (d, *J* = 84.5 Hz), 127.67 (d, *J* = 75.5 Hz), 127.30, 127.20, 125.33 (d, *J* = 8.4 Hz), 123.17 (d, *J* = 8.7), 120.64 (q, *J* = 321.0 Hz), 110.34 (d, *J* = 92.3 Hz), 21.92; ^{19}F NMR (365 MHz, $CDCl_3$) δ: –78.29; ^{31}P NMR (162 MHz, $CDCl_3$) δ: 21.61; *m/z* LRMS (ESI + APCI) found $[M\text{-}OTf]^+$ 445.2, $C_{30}H_{26}N_2P^+$ requires 445.2.

Bis(4-chlorophenyl)(2-phenylpyridin-4-yl)(pyridin-4-yl)phosphonium trifluoromethanesulfonate (3a′′′)



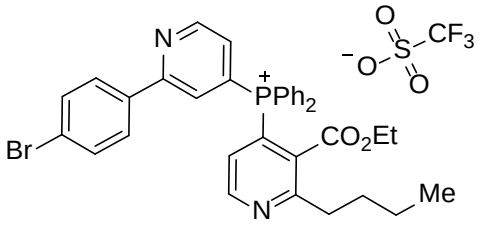
Prepared according to general procedure B using pyridine (84 μL, 1.00 mmol), Tf_2O (168 μL, 1.00 mmol), 4-(bis(4-chlorophenyl)phosphaneyl)-2-phenylpyridine (prepared from diethyl phosphate and 1-bromo-4-chlorobenzene using Gessner's, Han's, and Bergbreiter's reports followed by general procedure A (*94-96*)) (449 mg, 1.10 mmol), NEt_3 (140 μL, 1.10 mmol) and CH_2Cl_2 (10 mL). After the purification procedure (solid was dissolved in approximately 2-10 mL of CH_2Cl_2 and the solution was again added dropwise to an excess of chilled Et_2O (0 °C). The mixture was then placed in –20 °C refrigerator for 5 hour. The resulting suspension was filtered on a frit and the solid was washed with chilled Et_2O (0 °C) and dried *in vacuo* to provide the pure phosphonium salt), the title compound was isolated as a yellow crystalline solid (366 mg, 0.57 mmol, 57% yield). mp 88-90 ºC; IR ν_{max}/cm^{-1} (film): 3046, 2974, 2844, 1592, 1536, 727, 560, 555; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.21-8.97 (3H, m), 8.00-7.91 (2H, m), 7.87 (1H, d, *J* = 14.3 Hz), 7.84-7.61 (10H, m), 7.57-7.43 (4H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.71 (d, *J* = 10.4 Hz), 152.04 (d, *J* = 11.0), 152.00 (d, *J* = 10.2 Hz), 144.30 (d, *J* = 3.9 Hz), 136.67 (d, *J* = 1.8 Hz), 136.09 (d, *J* = 11.9 Hz), 132.01 (d, *J* = 12.4 Hz), 131.79 (d, *J* = 14.3 Hz), 130.74, 129.43 (d, *J* = 13.5 Hz), 129.20, 127.09 (d, *J* = 85.0 Hz), 127.04 (d, *J* = 83.2), 125.78, 125.26 (d, *J* = 8.7 Hz), 123.27 (d, *J* = 9.0), 120.58 (q, *J* = 321.0 Hz), 112.22 (d, *J* = 92.7 Hz); ^{19}F NMR (365 MHz, $CDCl_3$) δ: –78.40; ^{31}P NMR (162 MHz, $CDCl_3$) δ: 21.96; *m/z* LRMS (ESI + APCI) found $[M\text{-}OTf]^+$ 485.1, $C_{28}H_{20}Cl_2N_2P^+$ requires 485.1.

(2-(4-Bromophenyl)pyridin-4-yl)(3-chloropyridin-4-yl)diphenylphosphonium trifluoromethanesulfonate (3b)



Prepared according to general procedure B using 3-chloropyridine (95 μL, 1.00 mmol), Tf_2O (168 μL, 1.00 mmol), 2-(4-Bromophenyl)-4-(diphenylphosphaneyl)pyridine (460 mg, 1.10 mmol), DBU (149 μL, 1.00 mmol) and CH_2Cl_2 (10 mL). After the purification procedure, the title compound was isolated as a white solid (556 mg, 0.82 mmol, 82% yield). mp 94-96 ºC; IR ν_{max}/cm^{-1} (film): 3062, 1579, 1439, 1258, 1223, 1149, 1107, 1029, 724; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.04 (1H, app t, *J* = 5.4 Hz), 8.97-8.82 (2H, m), 8.02 (1H, d, *J* = 14.5 Hz), 7.96-7.85 (4H, m), 7.84-7.72 (8H, m), 7.64-7.52 (3H, m), 7.41 (1H, dd, *J* = 15.1, 5.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.30 (d, *J* = 10.8 Hz), 151.78 (d, *J* = 11.1 Hz), 151.59 (d, *J* = 5.1 Hz), 150.33 (d, *J* = 10.1 Hz), 136.46 (d, *J* = 3.0 Hz), 135.67 (d, *J* = 1.7 Hz), 134.51, 134.27, 132.14, 131.17 (d, *J* = 13.6 Hz), 130.91 (d, *J* = 8.4 Hz), 128.93, 127.66 (d, *J* = 85.7 Hz), 125.57 (d, *J* = 88.3 Hz), 125.33 (d, *J* = 8.5 Hz), 125.13, 123.02 (d, *J* = 9.1 Hz), 120.57 (q, *J* = 321.2 Hz), 113.39 (d, *J* = 90.4 Hz); ^{19}F NMR (365 MHz, $CDCl_3$) δ: -78.18; ^{31}P (162 MHz, $CDCl_3$) δ: 22.17; *m/z* HRMS (ESI + APCI) found $[M\text{-}OTf]^+$ 529.0239, $C_{28}H_{20}BrClN_2P^+$ requires 529.0236.

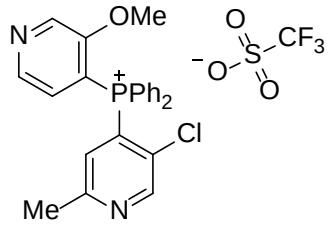
(2-(4-Bromophenyl)pyridin-4-yl)(2-butyl-3-(ethoxycarbonyl)pyridin-4-yl)diphenylphosphonium trifluoromethanesulfonate (3c)



Prepared according to general procedure B (except that after 2-(4-bromophenyl)-4-(diphenylphosphino)pyridine was added, the reaction mixture was stirred for 30 min at -30 °C) using ethyl 2-butylnicotinate (300.4 mg, 1.45 mmol), Tf_2O (244 μL, 1.45 mmol), 2-(4-bromophenyl)-4-(diphenylphosphino)pyridine (667 mg, 1.60 mmol), DBU (218 μL, 1.45 mmol) and CH_2Cl_2 (14.5 mL). After the purification procedure, the title compound was isolated as a white amorphous powder (831 mg, 1.07 mmol, 74% yield). mp 212-214 °C; IR υ_{max}/cm^{-1} (film): 3045, 2950, 2927, 2870, 1706, 1787, 1578, 1547, 1538, 1463, 1440, 1435, 1404, 1369, 1291, 1275, 1258, 1223, 1177, 1152, 1136, 1105, 1069, 1030, 1013, 1004, 816, 751, 727, 721, 697, 685; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.04-9.00 (2H, m), 7.94-7.84 (5H, m), 7.80-7.69 (8H, m), 7.60-7.54 (3H, m), 7.33 (1H, dd, *J* = 15.7, 5.0 Hz), 3.51 (2H, q, *J* = 7.2 Hz), 3.07 (2H, t, *J* = 7.8 Hz), 1.82-1.74 (2H, m), 1.41 (2H, sext, *J* = 7.4 Hz), 0.99-0.93 (6H, m); ^{13}C NMR (100 MHz,

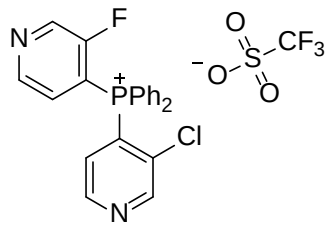
$CDCl_3$) δ: 166.34 (d, *J* = 3.7 Hz), 164.12 (d, *J* = 6.3 Hz), 157.79 (d, *J* = 10.6 Hz), 153.20 (d, *J* = 11.6 Hz), 151.37 (d, *J* = 11.0 Hz), 135.91 (d, *J* = 2.9 Hz), 135.84 (d, *J* = 1.7 Hz), 134.53 (d, *J* = 10.5 Hz), 132.17, 130.65 (d, *J* = 13.3 Hz), 129.71 (d, *J* = 86.4 Hz), 128.79, 128.50 (d, *J* = 4.9 Hz), 127.95 (d, *J* = 9.5 Hz), 126.79 (d, *J* = 83.3 Hz), 125.40 (d, *J* = 8.1 Hz), 125.07, 123.09 (d, *J* = 8.8 Hz), 120.66 (q, *J* = 319.6 Hz), 115.84 (d, *J* = 90.5 Hz), 63.18, 37.27 (d, *J* = 1.5 Hz), 31.87, 22.62, 13.75, 13.26; ^{19}F NMR (365 MHz, $CDCl_3$) δ: −78.19; ^{31}P NMR (162 MHz, $CDCl_3$) δ: 27.28; *m/z* HRMS (ESI + APCI) found $[M\text{-}OTf]^+$ 623.1460, $C_{35}H_{33}BrN_2O_2P^+$ requires 623.1463.

(5-Chloro-2-methylpyridin-4-yl)(3-methoxypyridin-4-yl)diphenylphosphonium trifluoromethanesulfonate (3d)



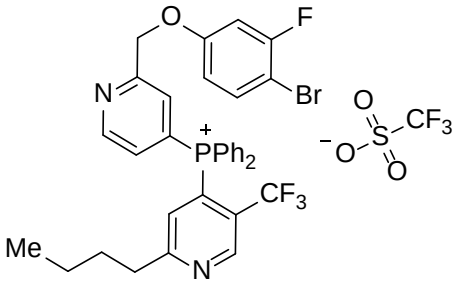
Prepared according to general procedure B (except that after 5-chloro-4-(diphenylphosphino)-2-methylpyridine was added, the reaction mixture was stirred for 30 min at −30 °C) using 3-methoxypyridine (202 μL, 2.00 mmol), Tf_2O (336 μL, 2.00 mmol), 5-chloro-4-(diphenylphosphino)-2-methylpyridine (686 mg, 2.20 mmol), DBU (300 μL, 2.00 mmol) and CH_2Cl_2 (20 mL). After the purification procedure, the title compound was isolated as an amorphous white powder (842 mg, 1.48 mmol, 74% yield). mp 182-186 °C; IR υ_{max}/cm^{-1} (film): 3060, 2951, 1570, 1544, 1483, 1460, 1439, 1411, 1380, 1326, 1300, 1258, 1222, 1140, 1103, 1087, 1072, 1043, 1029, 998, 914, 823, 808, 753, 722, 688, 646; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.74 (1H, d, *J* = 6.6 Hz), 8.70 (1H, d, *J* = 6.7 Hz), 8.62 (1H, t, *J* = 4.6 Hz), 7.91-7.87 (2H, m), 7.81-7.76 (4H, m), 7.72-7.67 (4H, m), 7.39 (1H, dd, *J* = 15.2, 5.0 Hz), 7.26 (1H, d, *J* = 15.6 Hz), 3.72 (3H, s), 2.65 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 160.05 (d, *J* = 10.2 Hz), 155.60, 150.83 (d, *J* = 5.7 Hz), 144.17 (d, *J* = 11.3 Hz), 136.64 (d, *J* = 4.5 Hz), 135.91 (d, *J* = 3.1 Hz), 134.11 (d, *J* = 11.2 Hz), 130.81 (d, *J* = 13.7 Hz), 130.79 (d, *J* = 2.2 Hz), 129.12 (d, *J* = 8.1 Hz), 127.68 (d, *J* = 6.8 Hz), 126.35 (d, *J* = 90.1 Hz), 120.68 (q, *J* = 319.6 Hz), 114.06 (d, *J* = 92.0 Hz), 113.45 (d, *J* = 88.4 Hz), 57.39 (dd, *J* = 4.6, 5.9 Hz), 24.19; ^{19}F NMR (365 MHz, $CDCl_3$) δ: −78.26; ^{31}P NMR (162 MHz, $CDCl_3$) δ: 21.15; *m/z* HRMS (ESI + APCI) found $[M\text{-}OTf]^+$ 419.1099, $C_{24}H_{21}ClN_2OP^+$ requires 419.1080.

(3-Chloro-pyridin-4-yl)(3-fluoropyridin-4-yl)diphenylphosphonium trifluoromethanesulfonate (3e)

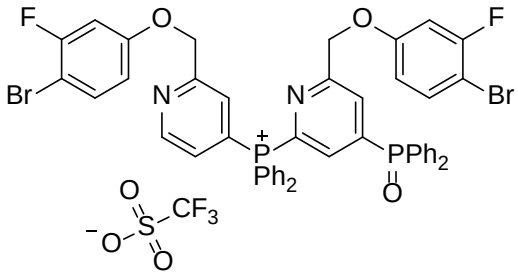


Prepared according to general procedure B (except that after the initial extraction the aqueous layer was extracted an additional 3 times with CH_2Cl_2 and then the combined organic was washed once with water prior to concentration) using 3-fluoropyridine (43 μL, 0.50 mmol), Tf_2O (84 μL, 0.50 mmol), 3-chloro-4-(diphenylphosphino)pyridine (164 mg, 0.55 mmol), DBU (75 μL, 0.50 mmol) and CH_2Cl_2 (5.0 mL). After the purification procedure (concentrated CH_2Cl_2 solution of crude product was added dropwise to an excess of 50% Et_2O in hexanes instead of Et_2O), the title compound was isolated as a pale yellow solid (148 mg, 0.27 mmol, 54% yield). mp 59-62 °C; IR υ_{max}/cm^{-1} (film): 3085, 3024, 1586, 1546, 1472, 1440, 1403, 1282, 1247, 1225, 1201, 1184, 1154, 1132, 1106, 1030, 996, 749; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.99-8.71 (4H, m), 8.02-7.68 (2H, m), 7.83-7.57 (9H, m), 7.45 (1H, dd, *J* = 15.4, 4.8 Hz); ^{13}C NMR (100 MHz, CD_3OD) δ: 160.39 (d, *J* = 264.3Hz), 153.28 (d, *J* = 5.2 Hz), 151.07 (d, *J* = 10.4 Hz), 149.09 (dd, *J* = 10.7, 5.3 Hz), 141.83 (dd, *J* = 24.0, 4.1 Hz), 137.73 (d, *J* = 3.2 Hz), 136.19 (d, *J* = 2.0 Hz), 135.86 (d, *J* = 11.7 Hz), 132.22 (d, *J* = 14.1 Hz), 131.34 (d, *J* = 8.7 Hz), 129.60 (d, *J* = 3.8 Hz), 127.07 (d, *J* = 91.3 Hz), 121.73 (d, *J* = 319.0 Hz), 116.20 (dd, *J* = 87.5, 13.3 Hz), 115.76 (d, *J* = 13.3 Hz); ^{19}F NMR (365 MHz, CD_3OD) δ: –79.79, –111.00; ^{31}P NMR (162 MHz, $CDCl_3$) δ: 19.61 (d, *J* = 4.0 Hz); *m/z* LRMS (ESI + APCI) found $[M\text{-}OTf]^+$ 393.1, $C_{22}H_{16}ClFN_2OP^+$ requires 393.1.

(2-((4-Bromo-3-fluorophenoxy)methyl)pyridin-4-yl)(2-butyl-5-(trifluoromethyl)pyridin-4-yl)diphenylphosphonium trifluoromethanesulfonate and (6-((4-bromo-3-fluorophenoxy)methyl)-4-(diphenylphosphoryl)pyridin-2-yl)(2-((4-bromo-3-fluorophenoxy)methyl)pyridin-4-yl)diphenylphosphonium (3f)



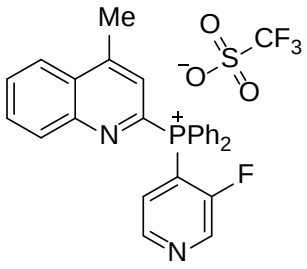
Pseudodimer Impurity



5.6:1

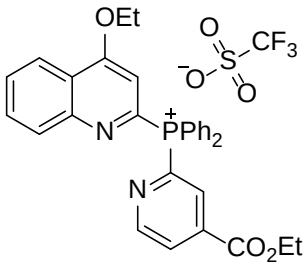
Prepared according to general procedure B using 2-butyl-5-(trifluoromethyl)pyridine (93 mg, 0.46 mmol), Tf_2O (77 μL, 0.46 mmol), 2-((4-bromo-3-fluorophenoxy)methyl)-4-(diphenylphosphino)pyridine (234 mg, 0.50 mmol), DBU (68 μL, 0.46 mmol) and CH_2Cl_2 (4.6 mL). After the purification procedure, the title compounds were isolated as a mixture (crude: 3.7:1; pure: 5.6:1) as a white amorphous powder (204 mg). The mixture was carried forward through the ligand coupling step. IR υ_{max}/cm^{-1} (film): 3063, 2959, 2932, 2872, 1603, 1578, 1532, 1486, 1439, 1384, 1320, 1259, 1223, 1143, 1120, 1106, 1029, 997, 968, 945, 909, 848, 834, 727; Major, ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.16 (1H, d, *J* = 7.3 Hz), 9.03 (1H, t, *J* = 5.2 Hz), 7.93-7.90 (2H, m), 7.80-7.62 (10H, m), 7.36 (1H, t, *J* = 8.4 Hz), 7.21 (1H, d, *J* = 17.4 Hz), 6.63 (1H, dd, *J* = 10.0, 2.7 Hz), 6.58 (1H, dd, *J* = 8.7, 2.4 Hz), 5.33 (2H, s), 2.94 (2H, t, *J* = 7.7 Hz), 1.66 (2H, qn, *J* = 7.6 Hz), 1.31 (2H, sext, *J* = 7.5 Hz), 0.87 (3H, t, *J* = 7.3 Hz); Major, ^{13}C NMR (100 MHz, $CDCl_3$) δ: 170.37 (d, *J* = 9.8 Hz), 159.21 (d, *J* = 245.9 Hz), 158.88 (d, *J* = 10.3 Hz), 157.97 (d, *J* = 9.8 Hz), 151.53 (d, *J* = 10.7 Hz), 150.06 (m), 136.40 (d, *J* = 3.0 Hz), 134.56 (d, *J* = 7.7 Hz), 133.52, 130.93 (d, *J* = 13.4 Hz), 130.24 (d, *J* = 8.5 Hz), 128.43 (d, *J* = 84.9 Hz), 126.52 (d, *J* = 8.5 Hz), 124.46 (d, *J* = 8.8 Hz), 124.17 (d, *J* = 4.1 Hz), 123.82 (d, *J* = 79.6 Hz), 122.48 (qd, *J* = 273.8, 2.3 Hz), 120.56 (q, *J* = 319.5 Hz), 114.65 (d, *J* = 89.3 Hz), 111.81 (d, *J* = 3.0 Hz), 103.90 (d, *J* = 25.5 Hz), 100.22 (d, *J* = 21.1 Hz), 70.00 (d, *J* = 1.5 Hz), 37.94, 30.25, 22.14, 13.63; Major, ^{19}F NMR (365 MHz, $CDCl_3$) δ: –53.41 (d, *J* = 1.7 Hz), –78.35, –104.68 (t, *J* = 8.4 Hz); Major, ^{31}P NMR (162 MHz, $CDCl_3$) δ: 26.97 (d, *J* = 2.4 Hz); *m/z* HRMS (ESI + APCI) found $[M\text{-}OTf]^+$ 667.1166, $C_{34}H_{29}BrF_4N_2OP^+$ requires 667.1137.

(3-Fluoropyridin-4-yl)(4-methylquinolin-2-yl)diphenylphosphonium trifluoromethanesulfonate (3g)



Prepared according to general procedure B, using 3-fluoropyridine (171 μL, 2.00 mmol), Tf_2O (336 μL, 2.00 mmol), 2-(diphenylphosphaneyl)-4-methylquinoline (720 mg, 2.20 mmol), DBU (300 μL, 2.00 mmol), and CH_2Cl_2 (20 mL). After purification procedure, the title compound was provided as a light brown crystalline solid (660 mg, 1.16 mmol, 58% yield). mp 65-66 °C IR ν_{max}/cm^{-1} (film): 3064, 1545, 1505, 997, 857, 688; ^1H NMR (400 MHz, $CDCl_3$) δ: 8.88-8.83 (2H, m), 8.19 (1H, d, *J* = 8.2 Hz), 8.14 (1H, d, *J* = 8.2 Hz), 7.95-7.78 (13H, m), 7.41 (1H, dt, *J* = 14.2, 5.1 Hz), 2.88 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.98 (d, *J* = 265.8 Hz), 149.37 (d, *J* = 11.4 Hz), 148.49 (d, *J* = 23.9 Hz), 148.15 (dd, *J* = 9.9, 6.4 Hz), 142.67 (d, *J* = 120.2 Hz), 139.85 (dd, *J* = 22.9, 3.8 Hz), 136.27 (d, *J* = 31.1 Hz), 134.67 (d, *J* = 10.6 Hz), 131.68, 130.92 (d, *J* = 13.4 Hz), 130.65 (d, *J* = 1.2 Hz), 130.54, 129.45 (d, *J* = 3.1 Hz), 128.86 (dd, *J* = 7.0, 1.7 Hz), 125.22 (d, *J* = 27.1 Hz), 124.61 (d, *J* = 1.4 Hz), 120.79 (q, *J* = 321.1 Hz), 116.43 (dd, *J* = 84.7, 13.9 Hz), 114.84 (d, *J* = 88.9 Hz), 19.19 (d, *J* = 1.6 Hz); ^{19}F NMR (365 MHz, $CDCl_3$) δ: –78.25, –109.74 (d, *J* = 6.6 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ: 11.79; *m/z* HRMS (ESI + APCI) found $[M\text{-}OTf]^+$ 423.1454, $C_{27}H_{21}FN_2P^+$ requires 423.1426.

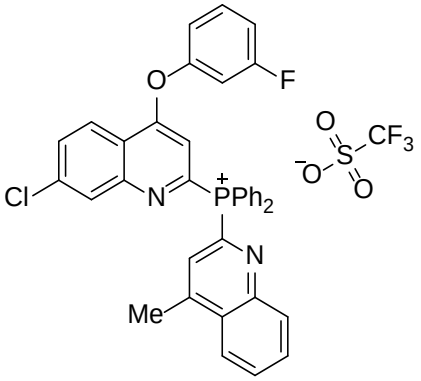
(4-(Ethoxycarbonyl)pyridin-2-yl)(4-ethoxyquinolin-2-yl)diphenylphosphonium trifluoromethanesulfonate (3h)



Prepared according to general procedure B, using 4- picolyl acid ethyl ester (150 μL, 1.00 mmol), Tf_2O (168 μL, 1.00 mmol), 2-(diphenylphosphaneyl)-4-ethoxyquinoline (392 mg, 1.10 mmol), DBU (150 μL, 1.00 mmol), and CH_2Cl_2 (10 mL). After purification procedure, (concentrated CH_2Cl_2 solution of crude product was added dropwise to an excess of 50% Et_2O in hexanes instead of Et_2O) the title compound was provided as a light brown amorphous solid (400 mg, 0.61 mmol, 61% yield). IR ν_{max}/cm^{-1} (film): 3064, 2986, 1729, 1476, 942, 851, 557, 537; ^1H NMR (400 MHz, $CDCl_3$) δ: 9.19 (1H, d, *J* = 4.8 Hz), 8.48 (1H, d, *J* = 5.8 Hz), 8.35 (1H, d, *J* =

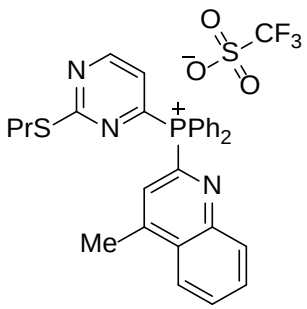
8.3 Hz), 8.31-8.25 (1H, m), 8.05 (1H, d, *J* = 8.5 Hz), 7.93-7.66 (12H, m), 7.18 (1H, d, *J* = 6.2 Hz), 4.40 (2H, q, *J* = 7.1 Hz), 4.22 (2H, q, *J* = 7.0 Hz), 1.51 (3H, t, *J* = 7.0 Hz), 1.35 (3H, t, *J* = 7.1 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 163.46 (d, *J* = 14.2 Hz), 163.15 (d, *J* = 2.7 Hz), 153.32 (d, *J* = 20.0 Hz), 149.59 (d, *J* = 25.9 Hz), 145.87 (d, *J* = 120.4 Hz), 145.13 (d, *J* = 119.0 Hz), 139.52 (d, *J* = 10.4 Hz), 135.75 (d, *J* = 3.1 Hz), 134.91 (d, *J* = 9.9 Hz), 131.83, 131.26 (d, *J* = 24.2 Hz), 130.45 (d, *J* = 13.0 Hz), 129.31 (d, *J* = 18.0 Hz), 127.48 (d, *J* = 3.5 Hz), 122.66, 121.93 (d, *J* = 2.5 Hz), 120.78 (q, *J* = 321.0 Hz), 116.87 (d, *J* = 87.9 Hz), 106.06, 105.78, 65.83, 62.74, 14.04, 13.92; ^{19}F NMR (365 MHz, $CDCl_3$) δ: –78.25; ^{31}P NMR (162 MHz, $CDCl_3$) δ: 9.58; *m/z* HRMS (ESI + APCI) found $[M\text{-}OTf]^+$ 507.1919, $C_{31}H_{28}N_2O_3P^+$ requires 507.1832.

(7-Chloro-4-(3-fluorophenoxy)quinolin-2-yl)(4-methylquinolin-2-yl)diphenylphosphonium trifluoromethanesulfonate (3i)



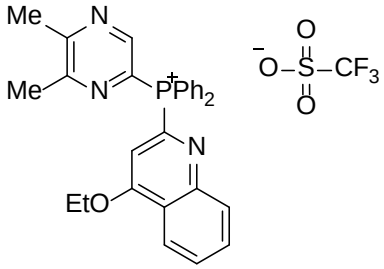
Prepared according to general procedure B, using 7-chloro-4-(3-fluorophenoxy)quinoline (244 mg, 0.89 mmol), Tf_2O (151 μL, 0.89 mmol), 2-(diphenylphosphaneyl)-4-methylquinoline (320 mg, 0.99 mmol), DBU (133 μL, 0.89 mmol), and CH_2Cl_2 (9 mL). After purification procedure, the title compound was provided as a brown amorphous solid (330 mg, 0.47 mmol, 53% yield). IR ν_{max}/cm^{-1} (film): 3067, 1607, 666, 605, 579, 544, 532; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.41 (1H, d, *J* = 9.0 Hz), 8.16-8.14 (2H, m), 7.92-7.67 (15H, m), 7.54 (1H, d, *J* = 4.6 Hz), 7.31 (1H, q, *J* = 5.8 Hz), 7.10 (1H, d, *J* = 5.6 Hz), 6.98 (1H, dd, *J* = 8.2, 1.8 Hz), 6.92-6.84 (2H, m), 2.78 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 163.16 (d, *J* = 249.9 Hz), 162.90 (d, *J* = 13.9 Hz), 153.49 (d, *J* = 10.4 Hz), 150.56 (d, *J* = 25.7 Hz), 148.76 (d, *J* = 10.6 Hz), 148.15 (d, *J* = 8.6 Hz), 147.67 (d, *J* = 132.3 Hz), 143.40 (d, *J* = 114.9 Hz), 138.65, 135.63 (d, *J* = 3.1 Hz), 134.76 (d, *J* = 9.8 Hz), 131.75 (d, *J* = 9.4 Hz), 131.56, 130.77, 130.66, 130.35 (d, *J* = 12.9 Hz), 128.87 (d, *J* = 3.0 Hz), 128.57 (d, *J* = 1.0 Hz), 128.56, 126.04 (d, *J* = 25.7 Hz), 124.47 (d, *J* = 1.3 Hz), 123.78, 120.77 (q, *J* = 321.2 Hz), 119.87 (d, *J* = 2.5 Hz), 116.91 (d, *J* = 87.7 Hz), 117.03 (d, *J* = 3.5 Hz), 113.69 (d, *J* = 20.9 Hz), 109.23 (d, *J* = 27.4 Hz), 108.87 (d, *J* = 24.2 Hz), 19.14 (d, *J* = 1.5 Hz) ; ^{19}F NMR (365 MHz, $CDCl_3$) δ: –78.19, –108.64 (q, *J* = 8.3 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ: 8.06; *m/z* HRMS (ESI + APCI) found $[M\text{-}OTf]^+$ 599.1450, $C_{38}H_{27}ClFN_2OP^+$ requires 599.1467.

(4-Methylquinolin-2-yl)diphenyl(2-(propylthio)pyrimidin-4-yl)phosphonium trifluoromethanesulfonate (3j)



Prepared according to general procedure B (except the stirring time after the addition of the heteroaryl phosphine was 45 minutes instead of 30 minutes) using 2-(propylthio)pyrimidine (154 mg, 1.00 mmol), Tf_2O (168 μL, 1.00 mmol), 2-(diphenylphosphaneyl)-4-methylquinoline (360 mg, 1.10 mmol), DBU (149, 1.00 mmol) and EtOAc (5 mL). After the purification procedure, the title compound was isolated as a brown solid (433 mg, 0.72 mmol, 72% yield). mp 52-54 ºC; IR ν_{max}/cm^{-1} (film): 3064, 2963, 1576, 1544, 1526, 1439, 1259, 1143, 1029, 727; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.91 (1H, dd, *J* = 7.6, 4.8 Hz), 8.21-8.12 (2H, m), 7.95-7.87 (3H, m), 7.87-7.80 (5H, m), 7.80-7.73 (4H, m), 7.70 (1H, dd, *J* = 6.0, 4.8 Hz), 7.65 (1H, d, *J* = 4.8 Hz), 2.93 (2H, t, *J* = 7.3 Hz), 2.83 (3H, s), 1.53 (2H, sext, *J* = 7.3 Hz), 0.84 (3H, t, *J* = 7.3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 174.98 (d, *J* = 18.0 Hz), 159.91 (d, *J* = 7.3 Hz), 154.41 (d, *J* = 111.9 Hz), 148.87 (d, *J* = 10.7 Hz), 148.51 (d, *J* = 23.4 Hz), 142.36 (d, *J* = 117.1 Hz), 136.04 (d, *J* = 3.0 Hz), 134.99 (d, *J* = 9.9 Hz), 131.72, 130.77-130.43 (3C, m), 129.12 (d, *J* = 3.0 Hz), 125.98 (d, *J* = 26.5 Hz), 124.51 (d, *J* = 1.2 Hz), 123.11 (d, *J* = 19.6 Hz), 120.74 (q, *J* = 321.1 Hz), 115.21 (d, *J* = 87.3 Hz), 33.05, 22.02, 19.18 (d, *J* = 1.5 Hz), 13.23; ^{19}F NMR (365 MHz, $CDCl_3$) δ: –78.21; ^{31}P (162 MHz, $CDCl_3$) δ: 9.49; *m/z* HRMS (ESI + APCI) found $[M\text{-}OTf]^+$ 480.1673, $C_{29}H_{27}N_3PS^+$ requires 480.1663.

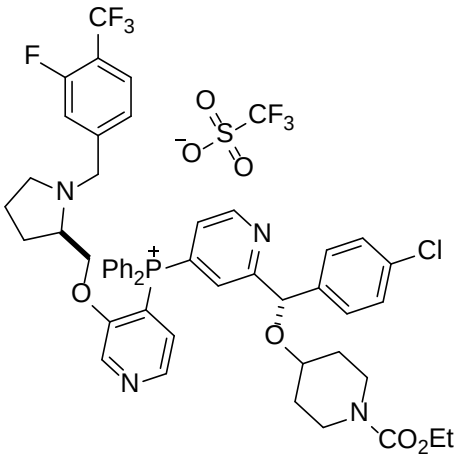
(5,6-Dimethylpyrazin-2-yl)(4-ethoxyquinolin-2-yl)diphenylphosphonium trifluoromethanesulfonate (3k)



Prepared according to general procedure B using 2,3-dimethylpyrazine (128 μL, 1.20 mmol), Tf_2O (336 μL, 1.20 mmol), 2-(diphenylphosphino)-4-ethoxyquinoline (472 mg, 1.32 mmol), DBU (180 μL, 1.20 mmol) and CH_2Cl_2 (12 mL). After the purification procedure (concentrated CH_2Cl_2 solution of crude product was added dropwise to an excess of hexanes instead of Et_2O and placed at room temperature overnight), the title compound was isolated as a light brown amorphous powder (663 mg, 1.08 mmol, 90% yield). mp 145-148 °C; IR υ_{max}/cm^{-1}

(film): 3066, 2989, 1571, 1551, 1507, 1438, 1410, 1385, 1354, 1316, 1260, 1222, 1192, 1145, 1108, 1029, 997, 771, 751, 728, 707; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.67 (1H, s), 8.35 (1H, d, *J* = 8.4 Hz), 8.04 (1H, d, *J* = 8.5 Hz), 7.90-7.81 (7H, m), 7.77-7.70 (5H, m), 7.26 (1H, d, *J* = 6.1 Hz), 4.25 (2H, q, *J* = 7.0 Hz), 2.73 (3H, s), 2.69 (3H, s), 1.52 (3H, t, *J* = 7.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 163.27 (d, *J* = 14.0 Hz), 159.36 (d, *J* = 3.4 Hz), 156.13 (d, *J* = 15.5 Hz), 149.50 (d, *J* = 25.9 Hz), 147.83 (d, *J* = 23.3 Hz), 144.83 (d, *J* = 118.6 Hz), 136.09 (d, *J* = 83.7 Hz), 135.67 (d, *J* = 3.0 Hz), 134.74 (d, *J* = 9.9 Hz), 131.76, 130.37 (d, *J* = 12.9 Hz), 129.38, 129.16, 122.50, 121.80 (d, *J* = 2.4 Hz), 120.73 (q, *J* = 319.6 Hz), 116.49 (d, *J* = 87.7 Hz), 105.64 (d, *J* = 29.0 Hz), 65.66, 22.76, 22.42, 14.01; ^{19}F NMR (365 MHz, $CDCl_3$) δ: –78.26; ^{31}P NMR (162 MHz, $CDCl_3$) δ: 7.50; *m/z* HRMS (ESI + APCI) found $[M\text{-}OTf]^+$ 464.1931, $C_{29}H_{27}N_3OP^+$ requires 464.1892.

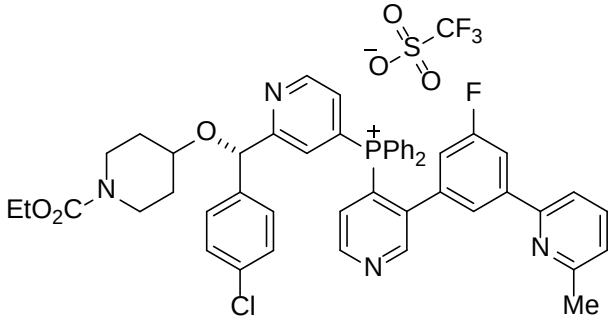
(2-((*S*)-(4-Chlorophenyl)((1-(ethoxycarbonyl)piperidin-4-yl)oxy)methyl)pyridin-4-yl)(3-(((*R*)-1-(3-fluoro-4-(trifluoromethyl)benzyl)pyrrolidin-2-yl)methoxy)pyridin-4-yl)diphenylphosphonium trifluoromethanesulfonate (3l)



Prepared according to general procedure B, using (*R*)-3-((1-(3-fluoro-4-(trifluoromethyl)benzyl)pyrrolidin-2-yl)methoxy)pyridine (177 mg, 0.50 mmol), Tf_2O (85 μL, 0.50 mmol), ethyl (*S*)-4-((4-chlorophenyl)(4-(diphenylphosphaneyl)pyridin-2-yl)methoxy)piperidine-1-carboxylate (307 mg, 0.55 mmol), DBU (75 μL, 0.89 mmol), and CH_2Cl_2 (5 mL). After the purification procedure (concentrated CH_2Cl_2 solution of crude product was added dropwise to an excess of 50% Et_2O in hexanes instead of Et_2O), the title compound was provided as a brown amorphous solid (370 mg, 0.35 mmol, 70% yield). IR ν_{max}/cm^{-1} (film): 3061, 2950, 2873, 825, 560, 557, 535, 528; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.90 (1H, t, *J* = 5.1 Hz), 8.74 (1H, d, *J* = 6.4 Hz), 8.57 (1H, t, *J* = 4.4 Hz), 7.92-7.45 (13H, m), 7.36-7.27 (4H, m), 7.14-6.96 (3H, m), 5.72 (1H, s), 4.21-4.04 (3H, m), 3.89-3.78 (1H, m), 3.69-3.44 (4H, m), 3.32-3.05 (3H, m), 2.85-2.65 (1H, m), 2.24-1.94 (2H, br), 1.83-1.63 (3H, m), 1.48-1.35 (4H, m), 1.34-1.16 (4H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 164.41 (d, *J* = 9.9 Hz), 159.67 (dq, *J* = 256.0, 2.4 Hz), 155.43, 155.18, 151.30 (d, *J* = 10.5 Hz), 144.50 (d, *J* = 11.4 Hz), 138.69, 136.28-136.10 (m), 134.25-134.02 (m, 2C), 132.57, 131.94 (dd, *J* = 14.6, 4.6 Hz), 131.03 (dd, *J* = 13.4, 7.7 Hz), 128.89, 128.86 (d, *J* = 15.3 Hz), 128.69 (d, *J* = 4.8 Hz), 128.59 (d, *J* = 85.2 Hz), 128.52 (d, *J* = 70.8 Hz), 128.32, 127.31-127.08 (m), 125.56 (d, *J* = 8.6 Hz), 123.15 (d, *J* = 9.4 Hz), 122.51 (dq,

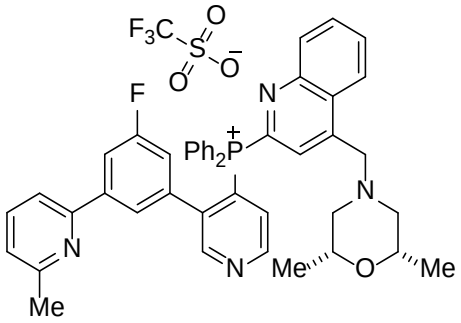
J = 271.8, 1.9 Hz), 120.63 (q, *J* = 320.7 Hz), 114.79 (dd, *J* = 81.0, 28.2 Hz), 113.05 (d, *J* = 88.0 Hz), 72.56, 61.37, 57.85, 54.02, 53.99, 40.82, 40.76, 31.46, 30.43, 29.67, 27.89, 22.63, 14.66; ^{19}F NMR (365 MHz, $CDCl_3$) δ: –61.18 (d, *J* = 13.2 Hz), –78.25, –113.33-115.80 (m); ^{31}P NMR (162 MHz, $CDCl_3$) δ: 21.01; *m/z* HRMS (ESI + APCI) found $[M\text{-}OTf]^+$ 911.3094, $C_{50}H_{49}ClF_4N_4O_4P^+$ requires 911.3116.

(*S*)-(2-((4-Chlorophenyl)((1-(ethoxycarbonyl)piperidin-4-yl)oxy)methyl)pyridin-4-yl)(3-(3-fluoro-5-(6-methylpyridin-2-yl)phenyl)pyridin-4-yl)diphenylphosphonium trifluoromethanesulfonate (3m)



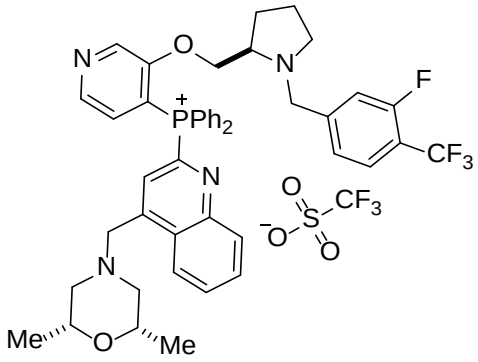
Prepared according to general procedure B using 2-(3-fluoro-5-(pyridin-3-yl)phenyl)-6-methylpyridine (132 mg, 0.50 mmol), Tf_2O (84 μL, 0.50 mmol), ethyl (S)-4-((4-chlorophenyl)(4-(diphenylphosphaneyl)pyridin-2-yl)methoxy)piperidine-1-carboxylate (308 mg, 0.55 mmol), DBU (75 μL, 0.50 mmol) and CH_2Cl_2 (5 mL). After the purification procedure, the title compound was isolated as a white solid (305 mg, 0.31 mmol, 63% yield). mp 103-109 ºC; IR ν_{max}/cm^{-1} (film): 3063, 2928, 1687, 1438, 1261, 1224, 1149, 1030, 796; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.00 (1H, app t, *J* = 4.7 Hz), 8.82 (1H, d, *J* = 7.0 Hz), 8.74 (1H, app t, *J* = 5.3 Hz), 7.81-7.72 (2H, m), 7.71-7.60 (9H, m), 7.58-7.47 (3H, m), 7.44 (1H, d, *J* = 9.8 Hz), 7.28 (1H, s), 7.29-7.19 (6H, m), 7.07 (1H, d, *J* = 7.6 Hz), 7.02 (1H, d, *J* = 7.7 Hz), 6.46 (1H, d, *J* = 8.3 Hz) 5.62 (1H, s), 4.09 (2H, q, *J* = 7.2 Hz), 3.62-3.44 (3H, m), 3.17-3.02 (2H, m), 2.44 (3H, s), 1.73-1.59 (2H, m), 1.48-1.33 (2H, m), 1.23 (3H, t, *J* = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 163.84 (d, *J* = 9.9 Hz), 162.21 (d, *J* = 249.4 Hz), 158.45, 155.36, 153.28 (d, *J* = 7.8 Hz), 152.76 (d, *J* = 2.2 Hz), 150.98-150.64 (2C, m), 141.63 (d, *J* = 7.8 Hz), 140.06 (d, *J* = 7.2 Hz), 138.47, 137.34, 136.68-136.51 (m), 136.01-135.82 (m), 134.63-134.36 (m), 133.90, 130.80 (d, *J* =13.3 Hz), 128.74 (d, *J* = 83.4 Hz), 128.72, 128.62 (d, *J* = 9.0 Hz), 128.43, 125.91 (d, *J* = 8.1 Hz), 124.96 (d, *J* = 83.9 Hz), 124.06, 123.52 (d, *J* = 9.0 Hz), 122.95, 120.73 (q, *J* = 321.2 Hz), 117.38, 116.4 (d, *J* = 23.3 Hz), 115.36 (d, *J* = 88.8 Hz), 115.12 (d, *J* = 88.8 Hz), 114.44 (d, *J* = 22.2 Hz), 79.76, 72.91, 61.24, 40.78, 40.70, 31.32, 30.27, 24.50, 14.63 ; ^{19}F NMR (365 MHz, $CDCl_3$) δ: -110.66 (t, *J* = 9.4 Hz), -78.16; ^{31}P (162 MHz, $CDCl_3$) δ: 20.63; *m/z* HRMS (ESI + APCI) found $[M\text{-}OTf]^+$ 821.2852, $C_{49}H_{44}ClFN_4O_3P^+$ requires 821.2824.

(4-(((2*R*, 6*S*)-2,6-Dimethylmorpholino)methyl)quinolin-2-yl)(3-(3-fluoro-5-(6-methylpyridin-2-yl)phenyl)pyridin-4-yl)diphenylphosphonium trifluoromethanesulfonate (3n)



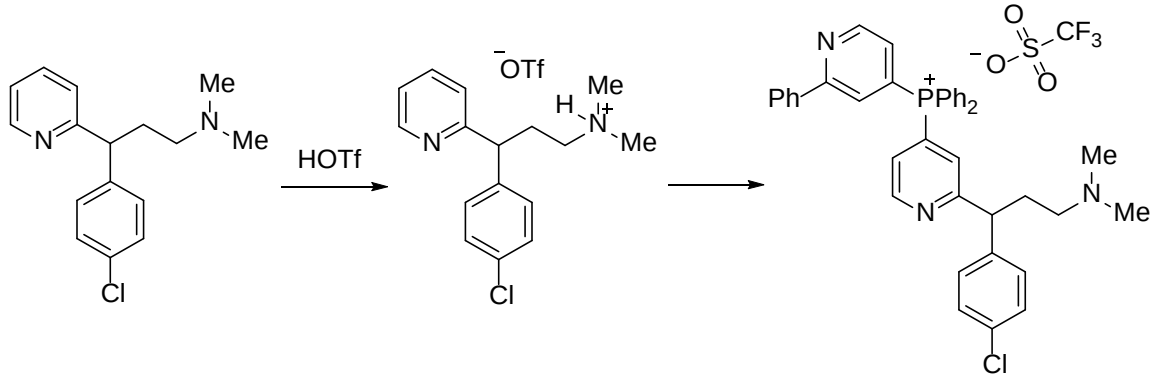
Prepared according to general procedure B using 2-(3-fluoro-5-(pyridin-3-yl)phenyl)-6-methylpyridine (132 mg, 0.50 mmol), Tf_2O (84 μL, 0.50 mmol), (2*R*, 6*S*)-4-((2-(diphenylphosphaneyl)quinolin-4-yl)methyl)-2,6-dimethylmorpholine (242 mg, 0.55 mmol), DBU (75 μL, 0.50 mmol) and CH_2Cl_2 (5 mL). After the purification procedure, the title compound was isolated as an off white solid (317 mg, 0.37 mmol, 74% yield). mp 106-111 ºC; IR ν_{max}/cm^{-1} (film): 3063, 2971, 2930, 2856, 1575, 1439, 1263, 1223, 1143, 1030, 728; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.03 (1H, app t, *J* = 4.7 Hz), 8.75 (1H, d, *J* = 6.8 Hz), 8.12 (1H, d, *J* = 8.4 Hz), 8.02-7.89 (6H, m), 7.88-7.75 (6H, m), 7.59 (1H, t, *J* = 7.7 Hz), 7.55-7.36 (4H, m), 7.05 (1H, d, *J* = 7.7 Hz), 6.93 (1H, s), 6.64 (1H, d, *J* = 7.8 Hz), 6.31 (1H, d, *J* = 8.2 Hz), 3.75 (2H, s), 3.43-3.21 (2H, m), 2.52-2.38 (5H, m), 1.83 (2H, t, *J* = 10.2 Hz) , 1.07 (6H, d, *J* = 6.3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 162.04 (d, *J* = 249.4 Hz), 158.29, 152.53 (d, *J* = 7.4 Hz), 152.27 (d, *J* = 2.5 Hz), 150.80 (d, *J* = 10.5 Hz), 148.33 (d, *J* = 23.0), 147.71 (br), 144.34 (d, *J* = 118.4 Hz), 141.49 (d, *J* = 8.0 Hz), 139.73 (d, *J* = 7.3 Hz), 137.38-137.20 (m), 137.12, 136.08 (d, *J* = 3.1 Hz), 135.06 (d, *J* = 9.8 Hz), 131.61, 130.76 (d, *J* = 12.9 Hz), 130.22 (2C, m), 128.95 (d, *J* = 9.7 Hz), 128.39 (d, *J* = 85.0 Hz), 127.11 (d, *J* = 3.4 Hz), 123.26, 123.04 (d, *J* = 2.5 Hz), 122.91, 122.44 (d, *J* = 28.4 Hz) 120.85 (q, *J* = 321.3 Hz), 116.58 (d, *J* = 86.4 Hz), 116.55, 116.00 (d, *J* = 23.4 Hz), 113.76 (d, *J* = 22.6 Hz), 71.62, 59.29, 57.36, 24.58, 18.86; ^{19}F NMR (365 MHz, $CDCl_3$) δ: –78.07, –111.47 (t, *J* = 10.2 Hz); ^{31}P (162 MHz, $CDCl_3$) δ: 11.94; *m/z* HRMS (ESI + APCI) found $[M\text{-}OTf]^+$ 703.2979, $C_{45}H_{41}FN_4OP^+$ requires 703.3002.

(4-(((*2S, 6R*)-2,6-Dimethylmorpholino)methyl)quinolin-2-yl)(3-(((*R*)-1-(3-fluoro-4-(trifluoromethyl)benzyl)pyrrolidin-2-yl)methoxy)pyridin-4-yl)diphenylphosphonium trifluoromethanesulfonate (3o)



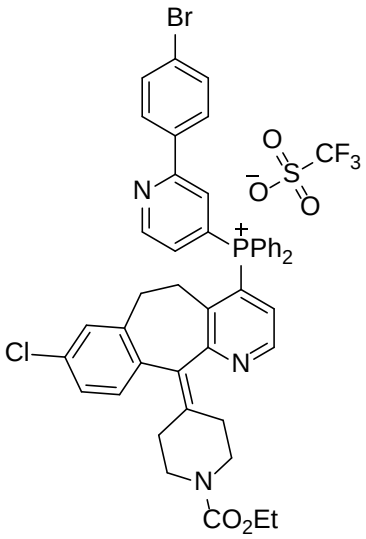
Prepared according to general procedure B, using (*R*)-3-((1-(3-fluoro-4-(trifluoromethyl)benzyl)pyrrolidin-2-yl)methoxy)pyridine (177 mg, 0.50 mmol), Tf_2O (85 μL, 0.50 mmol), (*2R, 6S*)-4-((2-(diphenylphosphaneyl)quinolin-4-yl)methyl)-2,6-dimethylmorpholine (242 mg, 0.55 mmol), DBU (75 μL, 0.89 mmol), and CH_2Cl_2 (5 mL). After the purification procedure (concentrated CH_2Cl_2 solution of crude product was added dropwise to an excess of 50% Et_2O in hexanes instead of Et_2O), the title compound was provided as a brown amorphous solid (310 mg, 0.33 mmol, 66% yield). IR ν_{max}/cm^{-1} (film): 3061, 3012, 2974, 2935, 2875, 2818, 1630, 1440, 909, 689, 665, 636, 603; ^1H NMR (400 MHz, $CDCl_3$) δ: 8.75 (1H, d, *J* = 6.6 Hz), 8.65-8.60 (1H, m), 8.23 (1H, dd, *J* = 7.9, 0.7 Hz), 8.15 (1H, d, *J* = 8.4 Hz), 7.98-7.69 (13H, m), 7.34 (1H, t, *J* = 7.7 Hz), 7.12 (1H, dd, *J* = 19.6, 9.8 Hz), 6.85-6.69 (2H, m), 4.10-3.91 (4H, m), 3.53-3.40 (2H, m), 3.34 (1H, d, *J* = 14.2 Hz), 2.80 (1H, d, *J* = 13.8 Hz), 2.65-2.51 (3H, m), 2.07-1.87 (3H, m), 1.87-1.74 (1H, m), 1.69-1.54 (1H, m), 1.47-1.25 (3H, m), 1.11 (6H, app t, *J* = 5.9 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.46 (dq, *J* = 257.36 257.4, 2.3 Hz), 155.69, 148.76 (d, *J* = 23.1 Hz), 148.24, (d, *J* = 11.2 Hz), 144.40 (d, *J* = 10.2 Hz), 143.96 (d, *J* = 120.6 Hz), 136.87 (m), 135.79 (m), 134.55-134.19 (m), 131.76, 130.66 (d, *J* = 13.2 Hz), 130.63, 129.17, 128.57, 128.27 (d, *J* = 73.9 Hz), 127.00-126.76 (m, 2C), 124.03, 123.86, 123.63 (d, *J* = 3.6 Hz), 122.37, 122.50 (dq, *J* = 273.6 Hz), 120.76 (q, *J* = 318.4 Hz), 116.78 (dd, *J* = 89.6, 3.1 Hz), 116.11 (dd, *J* = 91.4, 1.4 Hz), 114.57 (d, *J* = 86.2 Hz), 73.54, 71.64, 62.21, 59.64, 59.39 (d, *J* = 4.7 Hz), 58.10, 54.07, 27.83, 22.56, 19.96 (d, *J* = 3.2 Hz); ^{19}F NMR (365 MHz, $CDCl_3$) δ: –61.13 (d, *J* = 13.74 13.7 Hz), –78.14, –114.39- (–)115.04 (m); ^{31}P NMR (162 MHz, $CDCl_3$) δ: 12.52; *m/z* HRMS (ESI + APCI) found $[M\text{-}OTf]^+$ 793.3407, $C_{46}H_{46}F_4N_4O_2P^+$ requires 793.3295.

(2-(1-(4-Chlorophenyl)-3-(dimethylamino)propyl)pyridin-4-yl)diphenyl(2-phenylpyridin-4-yl)phosphonium trifluoromethanesulfonate (3p)



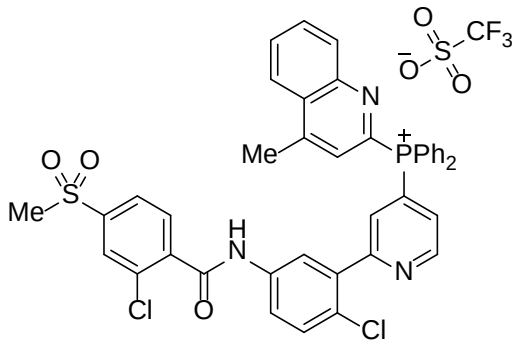
Chlorphenamine (412.2 mg, 1.50 mmol) was dissolved in Et_2O (3 mL) and cooled to 0 ºC. Trifluoromethanesulfonic acid (134 μL, 1.50 mmol) was added dropwise, the ice bath was removed and the solution was stirred for 10 minutes at room temperature. The solution was concentrated *in vacuo* and the resulting acid salt was subjected to general procedure B (except that after 4-(diphenylphosphino)-2-phenylpyridine was added, the reaction mixture was stirred for 30 min at −78 °C) using Tf_2O (252 μL, 1.50 mmol), 4-(diphenylphosphino)-2-phenylpyridine (560 mg, 1.65 mmol), DBU (450 μL, 3.00 mmol) and CH_2Cl_2 (15 mL). After the purification procedure, the title compound was isolated as a white amorphous powder (714 mg, 0.95 mmol, 63% yield). mp 130-133 °C; IR υ_{max}/cm^{-1} (film): 3060, 1574, 1489, 1468, 1440, 1378, 1259, 1223, 1150, 1124, 1109, 1028, 729, 636; ^1H NMR (400 MHz, $CDCl_3$) δ: 9.05 (1H, d, *J* = 5.2 Hz), 9.00 (1H, t, *J* = 5.2 Hz), 7.95-7.87 (4H, m), 7.80-7.77 (5H, m), 7.70-7.65 (4H, m), 7.52-7.45 (5H, m), 7.39 (1H, dd, *J* = 13.0, 4.8 Hz), 7.27 (2H, d, *J* = 8.3 Hz), 7.17 (2H, d, *J* = 8.3 Hz), 4.46 (1H, t, *J* = 7.4 Hz), 3.07-2.93 (2H, m), 2.83-2.76 (1H, m), 2.69 (6H, s), 2.44-2.35 (1H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 164.22 (d, *J* = 9.6 Hz), 159.31 (d, *J* = 10.3 Hz), 151.77 (d, *J* = 10.9 Hz), 151.36 (d, *J* = 10.5 Hz), 139.50, 136.68 (d, *J* = 1.6 Hz), 136.48 (d, *J* = 2.5 Hz), 134.56 (d, *J* = 10.6 Hz), 133.05, 131.13, 130.99, 130.53, 129.42, 129.06, 128.98, 127.58 (d, *J* = 83.9 Hz), 127.27 (d, *J* = 83.6 Hz), 127.13, 125.31 (d, *J* = 8.3 Hz), 125.09 (d, *J* = 8.2 Hz), 123.20 (d, *J* = 8.8 Hz), 120.40 (q, *J* = 318.7 Hz), 114.01 (d, *J* = 88.9 Hz), 56.27, 49.15, 43.36, 29.65; ^{19}F NMR (365 MHz, $CDCl_3$) δ: −78.30; ^{31}P NMR (162 MHz, $CDCl_3$) δ: 22.06; *m/z* HRMS (ESI + APCI) found $[M\text{-}OTf]^+$ 612.2328, $C_{39}H_{36}ClN_3P^+$ requires 612.2335.

(2-(4-Bromophenyl)pyridin-4-yl)(8-chloro-11-(1-(ethoxycarbonyl)piperidin-4-ylidene)-6,11-dihydro-5H-benzo[5,6]cyclohepta[1,2-b]pyridin-4-yl)diphenylphosphonium trifluoromethanesulfonate (3q)



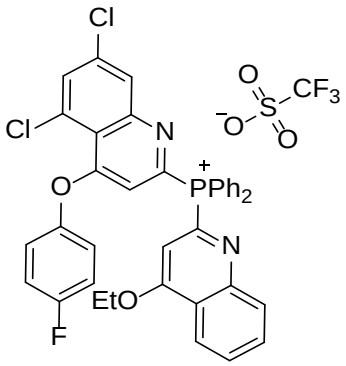
Prepared according to general procedure B using loratadine (383 mg, 1.00 mmol), Tf_2O (168 μL, 1.00 mmol), 2-(4-Bromophenyl)-4-(diphenylphosphaneyl)pyridine (460 mg, 1.10 mmol), DBU (149 μL, 1.00 mmol) and CH_2Cl_2 (10 mL). After the purification procedure, the title compound was isolated as an off white solid (770 mg, 0.81 mmol, 81% yield). mp 159-164 ºC; IR ν_{max}/cm^{-1} (film): 3055, 2981, 1687, 1438, 1262, 1223, 1109, 1030, 730; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.01 (1H, app t, *J* = 5.1 Hz), 8.73 (1H, app t, *J* = 4.7 Hz), 8.05-7.62 (13H, m), 7.60-7.40 (3H, m) 7.16 (1H, dd, *J* = 7.7, 5.1 Hz), 7.06 (2H, s), 6.63 (1H, s), 4.06 (2H, q, *J* = 6.8 Hz), 3.80-3.57 (2H, m), 3.40-3.16 (3H, m) 2.74 (1H, d, *J* = 17.4 Hz), 2.63-2.09 (5H, m), 1.60-1.39 (1H, m), 1.20 (3H, t, *J* = 7.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 163.34 (d, *J* = 8.5 Hz), 158.14 (d, *J* = 10.5 Hz), 155.15, 151.83 (d, *J* = 10.9 Hz), 149.26 (d, *J* = 11.6 Hz), 139.30, 136.53, 136.46-136.12 (2C, m), 135.45 (d, *J* = 1.4 Hz), 134.26 (d, *J* = 10.6 Hz), 133.83, 133.37, 132.17-131.89 (2C, m), 131.41, 131.20 (d, *J* = 13.2 Hz), 129.64, 128.71, 128.64 (d, *J* = 83.6 Hz), 127.54 (d, *J* = 10.3 Hz), 126.28, 125.35 (d, *J* = 8.3 Hz), 125.14 (d, *J* = 82.3 Hz), 122.94 (d, *J* = 8.9 Hz), 120.48 (q, *J* = 321.4 Hz), 114.84 (d, *J* = 88.2 Hz), 114.39 (d, *J* = 88.1 Hz), 61.17, 44.48, 44.34, 30.52, 30.43-30.10 (2C, m), 29.30, 14.45; ^{19}F NMR (365 MHz, $CDCl_3$) δ: –78.15; ^{31}P (162 MHz, $CDCl_3$) δ: 20.87; *m/z* HRMS (ESI + APCI) found $[M\text{-}OTf]^+$ 798.1693, $C_{45}H_{39}BrClN_3O_2P^+$ requires 798.1652.

(2-(2-Chloro-5-(2-chloro-4-(methylsulfonyl)benzamido)phenyl)pyridin-4-yl)(4-methylquinolin-2-yl)diphenylphosphonium trifluoromethanesulfonate (3r)



Prepared according to general procedure B (except the stirring time after the addition of Tf_2O was 2 hours instead of 30 minutes, the stirring time after the addition of the phosphine was 1.5 hours instead of 30 minutes, and after the addition of DBU the reaction was allowed to slowly warm from –78 ºC to 0 ºC over 3 hours instead of warming from –78 ºC to room temperature over approximately 15-30 minutes) using vismodegib (506 mg, 1.20 mmol), Tf_2O (200 μL, 1.20 mmol), 2-(diphenylphosphaneyl)-4-methylquinoline (432 mg, 1.32 mmol), DBU (180 μL, 1.20 mmol) and CH_2Cl_2 (30 mL). After the purification procedure (concentrated CH_2Cl_2 solution was added dropwise to an excess of Et_2O at room temperature. The resulting suspension was immediately filtered on a frit and the solid was washed with room temperature Et_2O. The solid was dissolved in approximately 5 mL CH_2Cl_2 and this process was repeated (4x) before the solid was dried *in vacuo* to provide the pure phosphonium salt), the title compound was isolated as a pale yellow solid (592 mg, 0.66 mmol, 55% yield). mp 119-125 ºC; IR ν_{max}/cm^{-1} (film): 3255, 3062, 1681, 1575, 1539, 1439, 1364, 1315, 1274, 1246, 1152, 1029, 726; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.90 (1H, s), 8.98 (1H, app t, *J* = 5.1 Hz), 8.24-8.09 (3H, m), 8.01-7.59 (18H, m), 7.56 (1H, d, *J* = 4.8 Hz), 7.31-7.23 (1H, m), 2.93 (3H, s), 2.77 (3H, s) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 164.27, 157.96 (d, *J* = 10.9 Hz), 150.87 (d, *J* = 10.6 Hz), 148.76 (d, *J* = 10.9 Hz), 148.46 (d, *J* = 23.0 Hz), 142.65 (d, *J* = 118.3), 142.04, 140.23, 137.66, 136.79 (d, *J* = 1.6 Hz), 136.05 (d, *J* = 2.7 Hz), 134.58 (d, *J* = 10.3 Hz), 132.23, 131.83, 130.92-130.42 (2C, m), 130.29, 129.85, 128.77 (d, *J* = 3.1 Hz), 128.46 (d, *J* = 83.7 Hz), 128.59-128.24 (3C, m), 126.35, 125.82 (d, *J* = 7.6 Hz), 125.59, 125.10 (d, *J* = 27.0 Hz), 124.31, 123.07, 122.38, 120.24 (d, *J* = 320.9 Hz), 115.31 (d, *J* = 87.8 Hz), 44.14, 19.05 (d, *J* = 1.4 Hz); ^{19}F NMR (365 MHz, $CDCl_3$) δ: –78.30; ^{31}P (162 MHz, $CDCl_3$) δ: 13.30; *m/z* HRMS (ESI + APCI) found $[M\text{-}OTf]^+$ 746.1185, $C_{41}H_{31}Cl_2N_3O_3PS^+$ requires 746.1201.

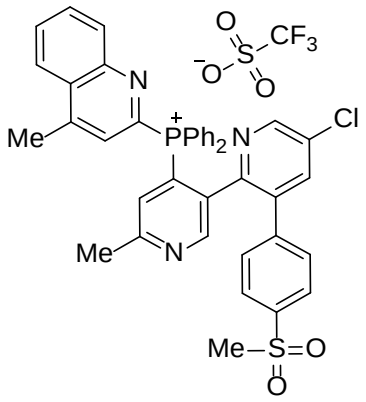
(5,7-Dichloro-4-(4-fluorophenoxy)quinolin-2-yl)(4-ethoxyquinolin-2-yl)diphenylphosphonium trifluoromethanesulfonate (3s)



Prepared according to general procedure B, using 5,7-dichloro-4-(4-fluorophenoxy)quinoline

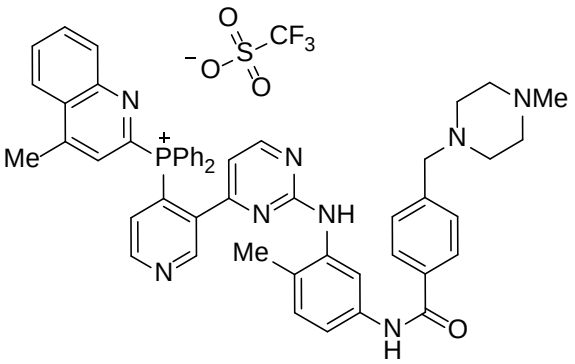
(308 mg, 1.00 mmol), Tf_2O (168 μL, 1.00 mmol), 2-(diphenylphosphaneyl)-4-ethoxyquinoline (392 mg, 1.10 mmol), DBU (150 μL, 1.00 mmol), and EtOAc (10 mL). After the purification procedure (concentrated CH_2Cl_2 solution of crude product was added dropwise to an excess of 50% Et_2O in hexanes instead of Et_2O), the title compound was provided as a brown amorphous solid (400 mg, 0.49 mmol, 49% yield). IR ν_{max}/cm^{-1} (film): 3070, 2989, 2248, 855, 834, 646, 594, 572; ^1H NMR (400 MHz, $CDCl_3$) δ: 8.31 (1H, d, *J* = 8.1 Hz), 8.02 (1H, d, *J* = 2.1 Hz), 7.87-7.64 (14H, m), 7.16-7.04 (3H, m), 7.00 (1H, d, *J* = 6.4 Hz), 6.96-6.88 (2H, m), 4.14 (2H, q, *J* = 7.0 Hz), 1.47 (3H, t, *J* = 7.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 164.34 (d, *J* = 12.9 Hz), 153.30 (d, *J* = 14.0 Hz), 160.27 (d, *J* = 246.1 Hz), 151.68 (d, *J* = 25.5 Hz), 149.24 (d, *J* = 25.4 Hz), 148.30 (d, *J* = 117.4 Hz), 148.14 (d, *J* = 2.8 Hz), 144.56 (d, *J* = 116.9 Hz), 136.97, 135.54 (d, *J* = 2.9 Hz), 134.68 (d, *J* = 10.0 Hz), 132.24, 131.67, 131.09 (d, *J* = 1.2 Hz), 130.27 (d, *J* = 13.0 Hz), 129.13, 127.99, 122.77 (d, *J* = 8.6 Hz), 122.45, 121.56 (d, *J* = 2.3 Hz), 120.64 (q, *J* = 321.3 Hz), 118.17 (d, *J* = 2.3 Hz), 117.21, 116.96, 116.51 (d, *J* = 87.5 Hz), 110.93 (d, *J* = 26.9 Hz), 105.92 (d, *J* = 29.0 Hz), 65.51, 13.93; ^{19}F NMR (365 MHz, $CDCl_3$) δ: –78.19, –114.90- (–)115.01 (m); ^{31}P NMR (162 MHz, $CDCl_3$) δ: 8.41; *m/z* HRMS (ESI + APCI) found $[M\text{-}OTf]^+$ 663.1166, $C_{38}H_{27}Cl_2FN_2O_2P^+$ requires 663.1199.

(5-Chloro-6'-methyl-3-(4-(methylsulfonyl)phenyl)-[2,3'-bipyridin]-4'-yl)(4-methylquinolin-2-yl)diphenylphosphonium trifluoromethanesulfonate (3t)



Prepared according to general procedure B except with NaOAc added with phosphine, using 5-chloro-6'-methyl-3-(4-(methylsulfonyl)phenyl)-2,3'-bipyridine (538 mg, 1.50 mmol), Tf_2O (255 μL, 1.50 mmol), 2-(diphenylphosphaneyl)-4-methylquinoline (540 mg, 1.65 mmol), DBU (225 μL, 1.50 mmol), NaOAc (123 mg, 1.50 mmol) and CH_2Cl_2 (15 mL). After the purification procedure (concentrated CH_2Cl_2 solution was added dropwise to an excess of Et_2O at room temperature. The resulting suspension was immediately filtered on a frit and the solid was washed with room temperature Et_2O. The solid was dissolved in approximately 5 mL CH_2Cl_2 and this process was repeated (3x) before the solid was dried *in vacuo* to provide the pure phosphonium salt), the title compound was provided as a yellow crystalline solid (840 mg, 1.04 mmol, 69% yield). mp 165-170 ^oC; IR ν_{max}/cm^{-1} (film): 3060, 1576, 1312, 770, 721, 547; ^1H NMR (400 MHz, $CDCl_3$) δ: 8.24 (1H, d, *J* = 7.0 Hz), 8.12-7.93 (8H, m), 7.87-7.67 (9H, m), 7.62-7.55 (3H, m), 7.30-7.23 (2H, m), 3.17 (3H, s), 2.74 (3H, s), 2.60 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 160.87 (d, *J* = 11.1 Hz), 152.08 (d, *J* = 7.2 Hz), 148.24 (d, *J* = 11.1 Hz), 147.98 (d, *J* = 2.1 Hz), 147.32 (d, *J* = 24.0 Hz), 147.15 (d, *J* = 125.9 Hz), 146.15, 141.55, 141.15, 138.54, 135.30, 135.29, 135.13 (d, *J* = 3.0 Hz), 134.85 (d, *J* = 9.4 Hz), 133.39 (d, *J* = 3.2 Hz), 131.95, 131.71, 130.71 (d, *J* = 10.1 Hz), 130.23, 130.07 (d, *J* = 6.3 Hz), 129.74 (d, *J* = 1.3 Hz), 128.92 (d, *J* = 87.0 Hz), 128.36, 128.12 (d, *J* = 3.1 Hz), 124.45, 123.53 (d, *J* = 26.9 Hz), 120.83 (q, *J* = 321.2 Hz), 119.37 (d, *J* = 88.5 Hz), 44.14, 24.62, 18.84 (d, *J* = 1.6 Hz); ^{19}F NMR (365 MHz, $CDCl_3$) δ: −78.15; ^{31}P NMR (162 MHz, $CDCl_3$) δ: 16.31; *m/z* HRMS (ESI + APCI) found $[M\text{-}OTf]^+$ 684.1666 $C_{40}H_{32}ClN_3O_2PS^+$ requires 684.1641.

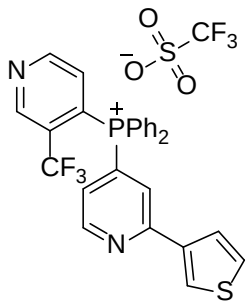
(3-(2-((2-Methyl-5-(4-((4-methylpiperazin-1-yl)methyl)benzamido)phenyl)amino)pyrimidin-4-yl)pyridin-4-yl)(4-methylquinolin-2-yl)diphenylphosphonium trifluoromethanesulfonate (3u)



Prepared according to general procedure B (except that the stirring time after addition of Tf_2O was 2 hours instead of 30 minutes, the stirring time after addition of 2-(diphenylphosphino)-4-methylquinoline was 1.5 hours instead of 30 minutes, and after the addition of DBU the reaction was allowed to slowly warm from –78 ºC to 0 ºC over 3 hours instead of warming from –78 ºC to room temperature over approximately 15-30 minutes) using (1*S*,2*S*,4*S*,5*R*)-2-((*R*)-(benzyloxy)(quinolin-4-yl)methyl)-5-vinylquinuclidine (592 mg, 1.20 mmol), Tf_2O (200 μL, 1.20 mmol), 2-(diphenylphosphino)-4-methylquinoline (432 mg, 1.32 mmol), DBU (180 μL, 1.20 mmol) and CH_2Cl_2 (30 mL). After the purification procedure (concentrated CH_2Cl_2 solution was added dropwise to an excess of Et_2O at room temperature. The resulting suspension was immediately filtered on a frit and the solid was washed with room temperature Et_2O. The solid was dissolved in approximately 5 mL CH_2Cl_2 and this process was repeated (3x) before the solid was dried *in vacuo* to provide the pure phosphonium salt), the title compound was isolated as a yellow amorphous powder (710 mg, 0.73 mmol, 61% yield). mp 155-158 °C; IR υ_{max}/cm^{-1} (film): 3316, 3056, 2795, 1662, 1568, 1527, 1505, 1474, 1450, 1406, 1254, 1222, 1149, 1104, 1028, 857, 815, 752, 726, 689; ^1H NMR (400 MHz, $CDCl_3$) δ: 9.52 (1H, d, *J* = 6.4 Hz), 9.04 (1H, dd, *J* = 4.8, 4.4 Hz), 8.53 (1H, s), 8.23 (1H, d, *J* = 5.1 Hz), 8.01–7.99 (1H, m), 7.87-7.59 (15H, m), 7.52 (1H, d, *J* = 4.8 Hz), 7.45 (1H, dd, *J* = 4.3, 2.0 Hz), 7.39 (2H, d, *J* = 8.2 Hz), 7.28 (1H, dd, *J* = 15.7, 5.1 Hz), 7.22 (1H, d, *J* = 5.2 Hz), 7.06 (1H, d, *J* = 1.9 Hz), 6.92 (1H, d, *J* = 8.5 Hz), 5.51 (1H, s), 3.54 (2H, s), 2.77-2.51 (14H, m), 1.50 (3H, s); ^{13}C NMR (100 MHz, CD_3CN) δ: 166.21, 161.17, 159.55 (d, *J* = 1.1 Hz), 159.01, 154.33 (d, *J* = 1.1 Hz), 152.10 (d, *J* = 6.3 Hz), 149.77 (d, *J* = 11.3 Hz), 149.43, 148.63, 148.38, 148.10, 142.66, 137.94, 136.82, 136.06 (d, *J* = 2.1 Hz), 135.71 (d, *J* = 9.3 Hz), 135.33 (d, *J* = 85.6 Hz), 132.86 (d, *J* = 9.8 Hz), 132.23, 131.02 (d, *J* = 12.7 Hz), 130.44 (d, *J* = 4.4 Hz), 129.85, 129.45 (d, *J* = 3.0 Hz), 128.45, 126.72, 126.06 (d, *J* = 84.5 Hz), 125.56 (d, *J* = 1.0 Hz), 123.30, 123.04, 122.31 (d, *J* = 90.6 Hz), 122.01 (q, *J* = 319.1 Hz), 117.99, 115.59, 110.10, 62.06, 55.02, 51.51, 44.62, 18.95 (d, *J* = 1.6 Hz), 17.29; ^{19}F NMR (365 MHz, $CDCl_3$) δ: –78.13; ^{31}P NMR (162 MHz, $CDCl_3$) δ: 18.51; *m/z* HRMS (ESI + APCI) found $[M\text{-}OTf]^+$ 819.3695, $C_{51}H_{48}N_8OP^+$ requires 819.3689.

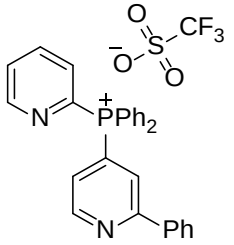
Additional Examples Characterization

Diphenyl(2-(thiophen-3-yl)pyridin-4-yl)(3-(trifluoromethyl)pyridin-4-yl)phosphonium trifluoromethanesulfonate



Prepared according to general procedure B using 3-(trifluoromethyl)pyridine (144 μL, 1.25 mmol), Tf_2O (210 μL, 1.25 mmol), 4-(diphenylphosphaneyl)-2-(thiophen-3-yl)pyridine (475 mg, 1.375 mmol), DBU (187 μL, 1.25 mmol) and CH_2Cl_2 (12.5 mL). After the purification procedure, the title compound was isolated as an off white solid (633 mg, 0.99 mmol, 79% yield). mp 92-97 ºC; IR ν_{max}/cm^{-1} (film): 3094, 1575, 1439, 1323, 1258, 1223, 1140, 1118, 1029, 723; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.26 (1H, d, *J* = 6.4 Hz), 9.19 (1H, br s), 8.96 (1H, t, *J* = 5.5 Hz), 8.08 (1H, dd, *J* = 3.1, 1.3 Hz), 7.96-7.87 (3H, m), 7.84-7.68 (8H, m), 7.64-7.55 (2H, m), 7.46 (1H, ddd, *J* = 13.4, 5.1, 1.5 Hz), 7.36 (1H, dd, *J* = 5.1, 3.1 Hz) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 156.24 (d, *J* = 10.2 Hz), 155.33 (d, *J* = 10.8 Hz), 151.58 (d, *J* = 10.2 Hz), 150.37-150.10 (m), 139.67 (d, *J* =1.9 Hz), 136.46 (d, *J* = 3.0 Hz), 134.75 (d, *J* = 10.7 Hz), 131.58 (d, *J* = 8.7 Hz), 131.00 (d, *J* = 13.7 Hz), 128.34 (d, *J* = 85.1 Hz), 127.14, 126.91, 126.85 (qd, *J* = 33.0, 3.8 Hz), 126.09, 124.35 (d, *J* = 8.3 Hz), 124.11 (d, *J* = 80.2 Hz), 123.13 (d, *J* = 9.0 Hz), 122.37 (qd, 275.6, 2.9 Hz), 120.59 (q, *J* = 321.4 Hz), 114.77 (d, *J* = 89.9 Hz); ^{19}F NMR (365 MHz, $CDCl_3$) δ: –78.30, –53.70 (d, *J* = 2.6 Hz); ^{31}P (162 MHz, $CDCl_3$) δ: 26.91; *m/z* HRMS (ESI + APCI) found $[M\text{-}OTf]^+$ 491.1888, $C_{27}H_{19}F_3N_2PS^+$ requires 491.0959.

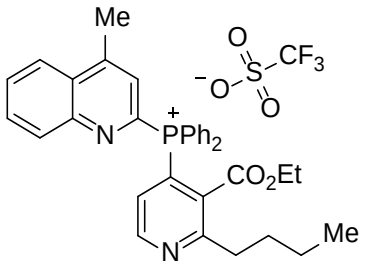
Diphenyl(2-phenylpyridin-4-yl)(pyridin-2-yl)phosphonium trifluoromethanesulfonate



Prepared according to general procedure B (except that the reaction was warmed to –30 ºC prior to the addition of the heteroaryl phosphine instead –50 ºC) using 2-phenylpyridine (1.29 mL, 9.0 mmol), Tf_2O (1.5 mL, 9.00 mmol), 2-(diphenylphosphaneyl)pyridine (2.61 g, 9.90 mmol), DBU (1.35 mL, 9.00 mmol) and CH_2Cl_2 (90 mL). After the purification procedure, the title compound was isolated as a white solid (4.59 g, 8.11 mmol, 90% yield). mp 110-114 ºC; IR ν_{max}/cm^{-1} (film): 3064, 1572, 1439, 1378, 1263, 1223, 1149, 1110, 1030, 728, 689, 637; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.06-8.97 (2H, m), 8.23-8.15 (1H, m), 8.01 (1H, d, *J* = 13.9 Hz), 7.97-7.66

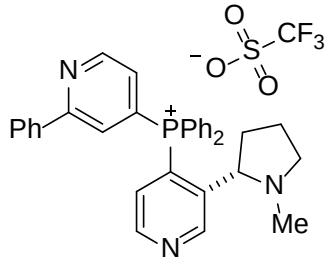
(14 H, m), 7.56 (1H, dd, *J* = 12.8 Hz, 5.1 Hz), 7.50-7.39 (3H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.54 (d, *J* = 10.2 Hz), 152.37 (d, *J* = 19.8 Hz), 150.97 (d, *J* = 10.8 Hz), 142.67 (d, *J* = 120.96 Hz), 138.57 (d, *J* = 10.8 Hz), 136.64 (d, *J* = 1.5 Hz), 135.90 (d, *J* = 2.9 Hz), 134.27 (d, *J* = 10.3 Hz), 132.10 (d, *J* = 25.1 Hz), 130.55 (d, *J* = 13.1 Hz), 129.95, 128.81 (d, *J* = 84.2 Hz), 128.67 (2C), 126.74, 125.24 (d, *J* = 7.9 Hz), 123.39 (d, *J* = 8.2 Hz), 120.43 (q, *J* = 321.3 Hz), 114.76 (d, *J* = 88.6 Hz); ^{19}F NMR (365 MHz, $CDCl_3$) δ: –78.16; ^{31}P (162 MHz, $CDCl_3$) δ: 13.94; *m/z* HRMS (ESI + APCI) found $[M\text{-}OTf]^+$ 417.1545, $C_{28}H_{22}N_2P^+$ requires 417.1521.

(2-Butyl-3-(ethoxycarbonyl)pyridin-4-yl)(4-methylquinolin-2-yl)diphenylphosphonium trifluoromethanesulfonate



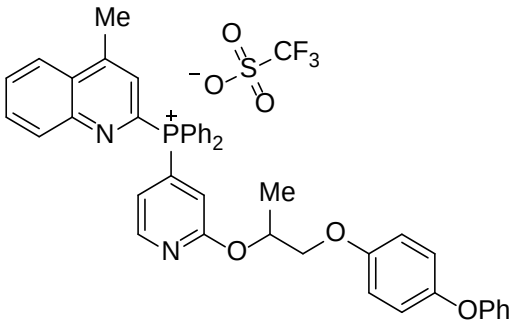
Prepared according to general procedure B (except that after 2-(diphenylphosphino)-4-methylquinoline was added, the reaction mixture was stirred for 30 min at -30 °C) using ethyl 2-butylnicotinate (248.8 mg, 1.20 mmol), Tf_2O (336 μL, 1.20 mmol), 2-(diphenylphosphino)-4-methylquinoline (432 mg, 1.32 mmol), DBU (180 μL, 1.20 mmol) and CH_2Cl_2 (12 mL). After the purification procedure, the title compound was isolated as a white amorphous powder (505 mg, 0.74 mmol, 62% yield). mp 135-138 °C; IR υ_{max}/cm^{-1} (film): 3062, 2958, 2871, 1703, 1577, 1547, 1504, 1438, 1367, 1259, 1223, 1149, 1100, 1030, 998, 912, 857, 753, 724; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.98 (1H, t, *J* = 4.7 Hz), 8.17 (1H, d, *J* = 8.4 Hz), 8.13 (1H, d, *J* = 8.4 Hz), 7.92-7.71 (13H, m), 7.20 (1H, dd, *J* = 15.2, 5.0 Hz), 3.33 (2H, q, *J* = 7.1 Hz), 3.09 (2H, t, *J* = 7.8 Hz), 2.85 (3H, s), 1.82-1.75 (2H, m), 1.42 (2H, sext, *J* = 7.4 Hz), 0.95 (3H, t, *J* = 7.3 Hz), 0.78 (3H, t, *J* = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 166.54 (d, *J* = 3.2 Hz), 163.85 (d, *J* = 6.1 Hz), 152.74 (d, *J* = 11.6 Hz), 148.51 (d, *J* = 11.1 Hz), 147.85, 147.61, 145.86, 144.63, 135.53 (d, *J* = 3.0 Hz), 134.61 (d, *J* = 9.8 Hz), 130.64 (d, *J* = 98.2 Hz), 130.38 (d, *J* = 12.9 Hz), 129.24 (d, *J* = 83.9 Hz), 129.04 (d, *J* = 4.1 Hz), 128.68 (d, *J* = 3.1 Hz), 127.82 (d, *J* = 9.4 Hz), 124.52 (d, *J* = 1.3 Hz), 124.26, 120.81 (q, *J* = 319.8 Hz), 117.58 (d, *J* = 87.7 Hz), 62.83, 37.33 (d, *J* = 1.4 Hz), 31.99, 22.66, 19.14 (d, *J* = 1.5 Hz), 13.76, 13.01; ^{19}F NMR (365 MHz, $CDCl_3$) δ: –78.15; ^{31}P NMR (162 MHz, $CDCl_3$) δ: 19.61; *m/z* HRMS (ESI + APCI) found $[M\text{-}OTf]^+$ 533.2438, $C_{34}H_{34}N_2O_2P^+$ requires 533.2358.

(*S*)-(3-(1-Methylpyrrolidin-2-yl)pyridin-4-yl)diphenyl(2-phenylpyridin-4-yl)phosphonium trifluoromethanesulfonate



Prepared according to general procedure B (except that after 4-(diphenylphosphino)-2-phenylpyridine was added, the reaction mixture was stirred for 30 min at -78 °C) using (-)-nicotine (193 μL, 1.20 mmol), Tf_2O (336 μL, 1.20 mmol), 4-(diphenylphosphino)-2-phenylpyridine (448 mg, 1.32 mmol), DBU (180 μL, 1.20 mmol) and CH_2Cl_2 (12 mL). After the purification procedure, the title compound was isolated as a yellow amorphous powder (751 mg, 1.06 mmol, 88% yield). mp 169-173 °C; IR υ_{max}/cm^{-1} (film): 3060, 2944, 2786, 1571, 1536, 1484, 1467, 1441, 1399, 1377, 1258, 1223, 1150, 1107, 1029, 909, 775, 723, 690; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.36 (1H, d, *J* = 7.2 Hz), 9.09 (1H, t, *J* = 5.2 Hz), 8.83 (1H, d, *J* = 4.8 Hz), 7.95-7.80 (13H, m), 7.65 (1H, ddd, *J* = 12.9, 5.0, 1.2 Hz), 7.47-7.45 (3H, m), 7.25 (1H, dd, *J* = 15.8, 5.1 Hz), 3.05 (1H, t, *J* = 7.2 Hz), 2.95 (1H, t, *J* = 8.1 Hz), 2.00–1.93 (1H, m), 1.81–1.69 (4H, m), 1.46-1.34 (2H, m), 1.05-0.96 (1H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.19 (d, *J* = 10.2 Hz), 152.92 (d, *J* = 8.1 Hz), 151.98 (d, *J* = 10.8 Hz), 150.20 (d, *J* = 10.7 Hz), 144.01 (d, *J* = 6.7 Hz), 136.61 (d, *J* = 1.7 Hz), 136.38 (t, *J* = 3.6 Hz), 134.41 (dd, *J* = 0.8, 10.6 Hz), 131.27 (dd, *J* = 2.4, 13.1 Hz), 130.51, 129.18 (d, *J* = 83.1 Hz), 129.07, 127.84 (d, *J* = 10.0 Hz), 127.07, 125.33 (d, *J* = 8.0 Hz), 124.54 (d, *J* = 81.4 Hz), 123.03 (d, *J* = 8.6 Hz), 120.70 (q, *J* = 319.5 Hz), 115.12 (dd, *J* = 19.9, 88.0 Hz), 66.11 (d, *J* = 5.3 Hz), 55.82, 39.26, 35.25, 22.84; ^{19}F NMR (365 MHz, $CDCl_3$) δ: –78.13; ^{31}P NMR (162 MHz, $CDCl_3$) δ: 20.39; *m/z* HRMS (ESI + APCI) found $[M\text{-}OTf]^+$ 500.2265, $C_{33}H_{31}N_3P^+$ requires 500.2256.

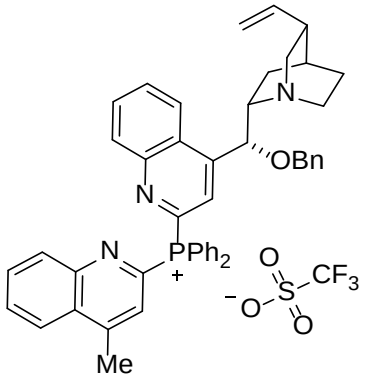
(4-Methylquinolin-2-yl)(2-((1-(4-phenoxyphenoxy)propan-2-yl)oxy)pyridin-4-yl)diphenylphosphonium trifluoromethanesulfonate



Prepared according to general procedure B (except that after 2-(diphenylphosphino)-4-methylquinoline was added, the reaction mixture was stirred for 30 min at –78 °C) using pyriproxyfen (424 mg, 1.32 mmol), Tf_2O (222 μL, 1.32 mmol), 2-(diphenylphosphino)-4-methylquinoline (475 mg, 1.45 mmol), DBU (198 μL, 1.32 mmol) and CH_2Cl_2 (13 mL). After

the purification procedure, the title compound was isolated as a white amorphous powder (856 mg, 1.07 mmol, 81% yield). mp 75–78 °C; IR υ_{max}/cm^{-1} (film): 3063, 2983, 1585, 1541, 1503, 1488, 1438, 1399, 1340, 1311, 1260, 1218, 1150, 1108, 1076, 1029, 997, 988, 910, 872, 857, 845, 754, 725; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.55 (1H, t, *J* = 5.4 Hz), 8.19 (2H, dd, *J* = 7.6, 2.0 Hz), 7.94-7.89 (3H, m), 7.86-7.74 (9H, m), 7.65 (1H, d, *J* = 4.4 Hz), 7.32-7.26 (3H, m), 7.05-6.87 (8H, m), 5.69 (1H, sext, *J* = 5.4 Hz), 4.19-4.10 (2H, m), 2.85 (3H, s), 1.51 (3H, d, *J* = 6.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 163.54 (d, *J* = 15.7 Hz), 158.11, 154.71, 150.25, 149.36 (d, *J* = 12.1 Hz), 148.98 (d, *J* = 10.8 Hz), 148.50 (d, *J* = 22.8 Hz), 143.42 (d, *J* = 117.2 Hz), 136.07 (d, *J* = 2.9 Hz), 134.63 (d, *J* = 10.2 Hz), 131.76, 130.80 (d, *J* = 83.2 Hz), 130.76 (d, *J* = 12.9 Hz), 130.57, 129.46, 128.93 (d, *J* = 3.0 Hz), 125.45, 125.18, 124.47 (d, *J* = 1.2 Hz), 122.39, 120.78 (q, *J* = 319.6 Hz), 120.52, 119.42 (d, *J* = 8.0 Hz), 117.44, 116.99 (d, *J* = 9.6 Hz), 115.58, 115.50 (d, *J* = 87.4 Hz), 71.33, 70.51, 19.14 (d, *J* = 1.4 Hz), 16.42; ^{19}F NMR (365 MHz, $CDCl_3$) δ: –78.30; ^{31}P NMR (162 MHz, $CDCl_3$) δ: 13.27; *m/z* HRMS (ESI + APCI) found $[M\text{-}OTf]^+$ 647.2502, $C_{42}H_{36}N_2O_3P^+$ requires 647.2464.

(4-((1*R*)-(Benzyloxy)((1*R*,4*R*)-5-vinylquinuclidin-2-yl)methyl)quinolin-2-yl)(4-methylquinolin-2-yl)diphenylphosphonium trifluoromethanesulfonate

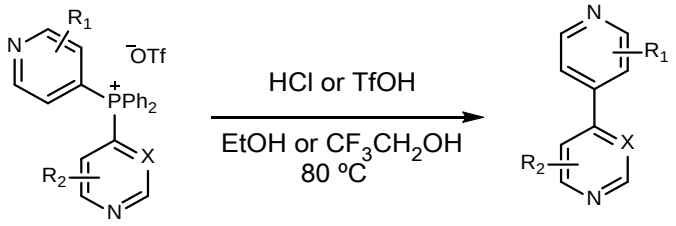


Prepared according to general procedure B (except that the stirring time after addition of 2-(diphenylphosphino)-4-methylquinoline was 1 hour instead of 30 minutes) using (1*S*,2*S*,4*S*,5*R*)-2-((*R*)-(benzyloxy)(quinolin-4-yl)methyl)-5-vinylquinuclidine (769 mg, 2.00 mmol), Tf_2O (336 μL, 2.00 mmol), 2-(diphenylphosphino)-4-methylquinoline (720 mg, 2.20 mmol), DBU (300 μL, 2.00 mmol) and CH_2Cl_2 (20 mL). After the purification procedure (concentrated CH_2Cl_2 solution was added dropwise to an excess of chilled Et_2O (0 °C). The mixture was then placed in a –20 °C refrigerator for approximately 1 hour. The resulting suspension was filtered on a frit and the solid was washed with chilled Et_2O (0 °C). The solid was redissolved in approximately 10 mL of CH_2Cl_2 and was precipitated a second time via dropwise addition to an excess of chilled Et_2O (0 °C). The resulting suspension was filtered on a frit, the solid washed with chilled Et_2O (0 °C) and dried *in vacuo* to provide the pure phosphonium salt), the title compound was isolated as a white amorphous powder (671 mg, 0.78 mmol, 39% yield). mp 178-181 °C; IR υ_{max}/cm^{-1} (film): 3062, 2939, 2323, 1576, 1505, 1438, 1261, 1222, 1148, 1110, 1029, 997, 859, 754, 727, 636; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.82 (1H, d, *J* = 7.4 Hz), 8.23 (1H, d, *J* = 9.4 Hz), 8.16-8.10 (2H, m), 7.94-7.26 (16H, m), 7.21-7.11 (3H, m), 6.98 (2H, d, *J* = 7.1 Hz), 6.45 (1H, br s), 5.75-5.67 (1H, m), 5.05-5.00 (2H, m), 4.65 (1H, d, *J* = 11.1 Hz), 4.36 (1H, d, *J* = 11.1 Hz), 3.81 (1H, br s), 3.54 (1H, br s), 3.42 (1H, dd, *J* = 12.3, 11.5 Hz), 3.12-3.05 (2H, m), 2.80 (3H, s), 2.70-2.64 (1H, m),

2.09-1.64 (5H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 149.02 (d, *J* = 22.5 Hz), 148.48 (d, *J* = 10.4 Hz), 148.28 (d, *J* = 23.0 Hz), 145.52 (d, *J* = 10.2 Hz), 145.35, 144.49, 143.76 (d, *J* = 83.9 Hz), 137.21, 135.91, 135.57 (t, *J* = 3.7 Hz), 134.97 (d, *J* = 9.7 Hz), 134.79 (d, *J* = 9.7 Hz), 131.91, 131.45, 131.14, 130.29 (d, *J* = 12.8 Hz), 130.23 (d, *J* = 15.0 Hz), 128.88 (d, *J* = 3.0 Hz), 128.42, 128.01, 127.17, 126.37 (d, *J* = 2.9 Hz), 125.95 (d, *J* = 25.5 Hz), 124.47, 124.04, 120.51 (q, *J* = 319.1 Hz), 117.05 (d, *J* = 86.7 Hz), 117.03, 116.63 (d, *J* = 86.1 Hz), 74.86, 71.76, 60.05, 54.53, 43.86, 36.75, 26.44, 23.99, 19.09 (d, *J* = 1.2 Hz); ^{19}F NMR (365 MHz, $CDCl_3$) δ: –78.23; ^{31}P NMR (162 MHz, $CDCl_3$) δ: 8.74; *m/z* HRMS (ESI + APCI) found $[M\text{-}OTf]^+$ 710.3303, $C_{48}H_{45}N_3OP^+$ requires 710.3300.

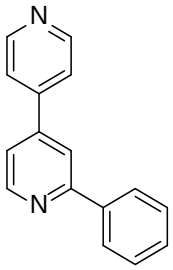
12d. Ligand-coupling Reactions to Make Heterobiaryls

General Procedure C



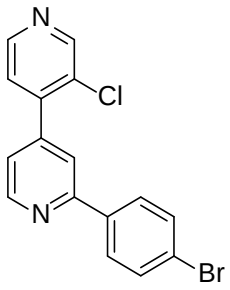
An oven dried 8 mL vial with a septa cap was charged with the phosphonium salt (1.0 equiv) and EtOH or TFE (0.4 M). The vial was subjected to three rapid cycles of vacuum / nitrogen backfill and then HCl or TfOH (2.0 equiv) was added via a syringe. The septa cap was quickly replaced with an unpierced one and the reaction was heated to 80 ºC for the stated time. The reaction was quenched with a saturated aqueous solution of Na_2CO_3 and the aqueous layer was 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 heterobiaryl.

2-Phenyl-4,4'-bipyridine (4a)



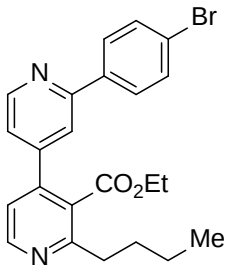
Prepared according to general procedure C using diphenyl(2-phenylpyridin-4-yl)(pyridin-4-yl)phosphonium trifluoromethanesulfonate (283 mg, 0.50 mmol), 4.0 M HCl in dioxanes (250 μL, 1.00 mmol), and EtOH (1.25 mL). The was reaction was heated to 80 ºC for 14 hours. Flash column chromatography (silica gel, gradient elution: 40% EtOAc in hexanes to 50% EtOAc in hexanes) afforded the title compound as an off white solid (102 mg, 0.44 mmol, 88% yield). mp 64-65 ºC; IR ν_{max}/cm^{-1} (film): 3029, 1590, 1532, 1472, 1444, 1389, 1225, 808, 770, 731, 687; ^1H NMR (400 MHz, $CDCl_3$) δ: 8.87-8.59 (3H, m), 8.02 (2H, d, *J* = 7.2 Hz), 7.88 (1H, s), 7.62-7.32 (6H, m) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.34, 150.51, 150.34, 146.25, 145.67, 138.78, 129.21, 128.71, 126.86, 121.34, 119.70, 118.16; *m/z* HRMS (DART) found $[M+H]^+$ 233.1092, $C_{16}H_{13}N_2^+$ requires 233.1073.

2-(4-Bromophenyl)-3'-chloro-4,4'-bipyridine (4b)



Prepared according to general procedure C using (2-(4-bromophenyl)pyridin-4-yl)(3-chloropyridin-4-yl)diphenylphosphonium trifluoromethanesulfonate (340 mg, 0.50 mmol), 4.0 M HCl in dioxanes (250 μL, 1.00 mmol), and EtOH (1.25 mL). The was reaction was heated to 80 ºC for 17 hrs. Flash column chromatography (silica gel: 25% EtOAc in hexanes) afforded the title compound as a white solid (111 mg, 0.32 mmol, 64% yield). mp 153-154 ºC; IR ν_{max}/cm^{-1} (film): 3053, 1603, 1579, 1552, 1461, 1412, 1376, 1111, 1006, 831, 741; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.79 (1H, d, *J* = 5.0 Hz), 8.74 (1H, s), 8.60 (1H, d, *J* = 4.9 Hz), 7.91 (2H, d, *J* = 8.5 Hz), 7.77 (1H, s), 7.61 (2H, d, *J* = 8.5 Hz), 7.37-7.28 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 156.61, 150.35, 149.96, 148.15, 145.03, 144.91, 137.56, 131.92, 129.72, 128.46, 124.53, 123.87, 122.03, 120.01; *m/z* HRMS (DART) found $[M+H]^+$ 344.9812, $C_{16}H_{11}BrN_2^+$ requires 344.9789.

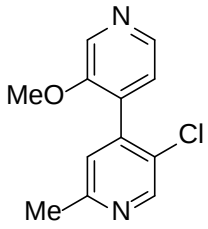
Ethyl 2'-(4-bromophenyl)-2-butyl-[4,4'-bipyridine]-3-carboxylate (4c)



Prepared according to general procedure C using (2-(4-bromophenyl)pyridin-4-yl)(2-butyl-3-(ethoxycarbonyl)pyridin-4-yl)diphenylphosphonium trifluoromethanesulfonate (155 mg, 0.20 mmol), trifluoromethanesulfonic acid (36 μL, 0.40 mmol) and EtOH (0.5 mL) at 80 °C for 14 hours. Flash column chromatography (silica gel: 16% EtOAc in hexanes to 33% EtOAc in hexanes) afforded the title compound as a colorless oil (67 mg, 0.15 mmol, 76% yield). IR υ_{max}/cm^{-1} (film): 3051, 2956, 2929, 2870, 1722, 1601, 1589, 1575, 1537, 1491, 1475, 1455, 1405, 1379, 1258, 1138, 1099, 1071, 1045, 1008, 825; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.73 (1H, d, *J* = 5.0 Hz), 8.68 (1H, d, *J* = 5.0 Hz), 7.90 (2H, d, *J* = 8.3 Hz), 7.71 (1H, s), 7.60 (2H, d, *J* = 8.3 Hz), 7.26 (1H, d, *J* = 5.8 Hz), 7.18 (1H, d, *J* = 5.0 Hz), 4.11 (2H, q, *J* = 7.2 Hz), 2.89 (2H, t, *J* = 7.8 Hz), 1.76 (2H, qn, *J* = 7.6 Hz), 1.42 (2H, sext, *J* = 7.4 Hz), 1.00 (3H, t, *J* = 7.2 Hz), 0.94 (3H, t, *J* = 7.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 167.97, 160.08, 156.52, 150.14, 149.95, 147.22, 145.26, 137.49, 131.99, 128.40, 127.85, 123.92, 121.29, 120.68, 119.21, 61.69, 36.02,

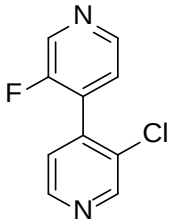
31.93, 22.66, 13.86, 13.60; *m/z* HRMS (DART) found $[M+H]^+$ 439.1029, $C_{23}H_{23}BrN_2O_2^+$ requires 439.1021.

5-Chloro-3'-methoxy-2-methyl-4,4'-bipyridine (4d)



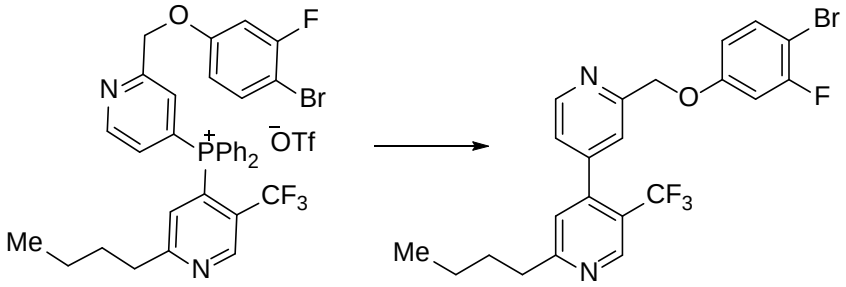
Prepared according to general procedure C using (5-chloro-2-methylpyridin-4-yl)(3-methoxypyridin-4-yl)diphenylphosphonium trifluoromethanesulfonate (285 mg, 0.50 mmol), trifluoromethanesulfonic acid (89 μL, 1.00 mmol) and EtOH (1.25 mL) at 80 °C for 14 hours. Flash column chromatography (silica gel: 50% EtOAc in hexanes) afforded the title compound as a colorless crystalline solid (77 mg, 0.33 mmol, 65% yield). mp 105-108 °C; IR υ_{max}/cm^{-1} (film): 3029, 2968, 2938, 2842, 1582, 1556, 1506, 1492, 1469, 1441, 1379, 1360, 1312, 1306, 1291, 1269, 1256, 1239, 1213, 1195, 1101, 1017, 846, 833; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.52 (1H, s), 8.39 (1H, s), 8.33 (1H, d, *J* = 4.7 Hz), 7.09 (1H, d, *J* = 4.7 Hz), 7.05 (1H, s), 3.88 (3H, s), 2.54 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 156.62, 152.18, 148.70, 142.83, 142.52, 134.21, 133.11, 128.01, 124.66, 124.11, 56.18, 23.74; *m/z* HRMS (DART) found $[M+H]^+$ 235.0664, $C_{12}H_{12}ClN_2O^+$ requires 235.0638.

3-Chloro-3'-fluoro-4,4'-bipyridine (4e)



Prepared according to general procedure C using (3-chloro-pyridin-4-yl)(3-fluoropyridin-4-yl)diphenylphosphonium trifluoromethanesulfonate (136 mg, 0.25 mmol), 4.0M HCl in dioxane (125 μL, 0.50 mmol) and EtOH (0.625 mL) at 80 °C for 23 hours. Flash column chromatography (silica gel: 40% EtOAc in hexanes to 50% EtOAc in hexanes) followed by flash column chromatography (neutral alumina: 20% EtOAc in hexanes to 40% EtOAc in hexanes) afforded the title compound as a white crystalline solid (34 mg, 0.16 mmol, 65% yield). mp 92-94 °C; IR υ_{max}/cm^{-1} (film): 3021, 1578, 1470, 1413, 1398, 1268, 1217, 1202, 1176, 1110, 1027, 830, 752; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.69 (1H, s), 8.60-8.44 (3H, m), 7.29-7.17 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 155.86 (d, *J* = 259.5 Hz), 150.15, 147.84, 145.81 (d, *J* = 5.4 HZ), 139.81, 139.05 (d, *J* = 24.1 Hz), 131.57 (d, *J* = 13.0 Hz), 130.70, 124.97, 124.63; ^{19}F NMR (365 MHz, $CDCl_3$) δ: –128.06 (d, *J* = 5.5 Hz); *m/z* LRMS (ESI + APCI) found $[M+H]^+$ 209.0, $C_{10}H_7ClFN_2^+$ requires 209.0.

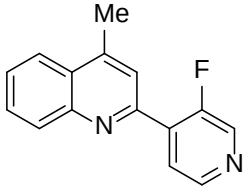
2'-((4-Bromo-3-fluorophenoxy)methyl)-2-butyl-5-(trifluoromethyl)-4,4'-bipyridine (4f)



isolated as mixture see 3f

Prepared according to general procedure C using (2-((4-bromo-3-fluorophenoxy)methyl)pyridin-4-yl)(2-butyl-5-(trifluoromethyl)pyridin-4-yl)diphenylphosphonium trifluoromethanesulfonate (204 mg, isolated as a mixture see 3f), Trifluoromethanesulfonic acid (45 μL, 0.50 mmol) and EtOH (0.625 mL) at 80 °C for 12 hours. Flash column chromatography (silica gel: 2% EtOAc in CH_2Cl_2 to 5% EtOAc in CH_2Cl_2) afforded the title compound as a white amorphous powder (63 mg, 0.13 mmol, 29% yield over two steps). mp 79-81 °C; IR υ_{max}/cm^{-1} (film): 3027, 2958, 2924, 2875, 2860, 1597, 1589, 1564, 1539, 1492, 1467, 1452, 1426, 1415, 1380, 1323, 1292, 1268, 1249, 1189, 1177, 1153, 1130, 1101, 1089, 1057, 1032, 974, 942, 902, 855, 843, 820; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.88 (1H, s), 8.68 (1H, d, *J* = 5.0 Hz), 7.44-7.38 (2H, m), 7.22 (1H, d, *J* = 4.8 Hz), 7.08 (1H, s), 6.78 (1H, dd, *J* = 10.2, 2.8 Hz), 6.69 (1H, dd, *J* = 8.9, 2.8 Hz), 5.22 (2H, s), 2.88 (2H, t, *J* = 7.7 Hz), 1.74 (2H, qn, *J* = 7.3 Hz), 1.40 (2H, sext, *J* = 7.5 Hz), 0.94 (3H, t, *J* = 7.3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 166.90, 159.44 (d, *J* = 245.7 Hz), 158.68 (d, *J* = 9.7 Hz), 156.50, 149.21, 147.06 (q, *J* = 5.5 Hz), 146.29, 146.23 (q, *J* = 1.8 Hz), 133.47 (d, *J* = 1.7 Hz), 123.90, 123.50 (q, *J* = 272.3 Hz), 122.27 (d, *J* = 1.1 Hz), 121.38 (q, *J* = 30.6 Hz), 120.59, 111.98 (d, *J* = 3.2 Hz), 103.98 (d, *J* = 25.6 Hz), 100.11 (d, *J* = 21.2 Hz), 70.86, 37.99, 31.58, 22.44, 13.83; ^{19}F NMR (365 MHz, $CDCl_3$) δ: −56.55, −104.87 (t, *J* = 8.4 Hz); *m/z* HRMS (DART) found $[M+H]^+$ 483.0690, $C_{22}H_{20}BrF_4N_2O^+$ requires 483.0695.

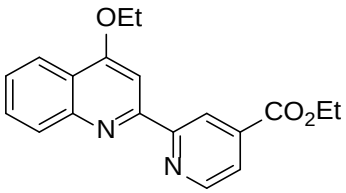
2-(3-Fluoropyridin-4-yl)-4-methylquinoline (4g)



Prepared according to general procedure C, using (3-fluoropyridin-4-yl)(4-methylquinolin-2-yl)diphenylphosphonium trifluoromethanesulfonate (286 mg, 0.50 mmol), 4.0M HCl in dioxane (250 μL, 1.00 mmol), and EtOH (1.25 mL) at 80 °C for 12 hours. The crude material was purified by flash chromatography (silica gel gradient elution: 25% EtOAc in hexanes to 50% EtOAc in hexanes) to provide the title compound as a white crystalline solid (68 mg, 0.31 mmol, 57% yield). mp 94-95 °C; IR ν_{max}/cm^{-1} (film): 3038, 2968, 1464, 1350, 1277, 1235, 746; ^{1}H

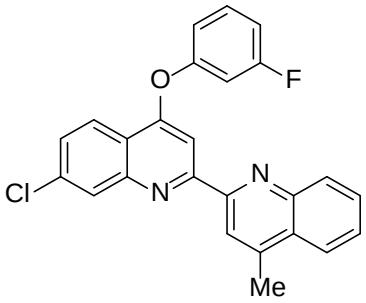
NMR (400 MHz, $CDCl_3$) δ: 8.62 (1H, d, *J* = 2.8 Hz), 8.59 (1H, dd, *J* = 4.9, 0.9 Hz), 8.19 (1H, dd, *J* = 8.4, 0.5 Hz), 8.10 (1H, dd, *J* = 7.3, 5.0 Hz), 8.05 (1H, dd, *J* = 8.4, 0.9 Hz), 7.80-7.75 (2H, m), 7.66-7.62 (1H, m), 2.80 (3H, d, *J* = 0.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 157.28 (d, *J* = 258.8 Hz); 158.84 (d, *J* = 2.0 Hz), 148.09, 146.25 (d, *J* = 5.1 Hz), 145.16, 139.33 (d, *J* = 26.1 Hz), 134.60 (d, *J* = 9.5 Hz), 130.50, 129.74, 127.79, 127.20, 124.58, 123.74, 122.69 (d, *J* = 8.2 Hz), 19.00; ^{19}F NMR (365 MHz, $CDCl_3$) δ: –131.61 (d, *J* = 7.5 Hz); *m/z* HRMS (DART) found $[M+H]^+$ 239.0973, $C_{15}H_{12}FN_2^+$ requires 239.0979.

Ethyl 2-(4-ethoxyquinolin-2-yl)isonicotinate (4h)



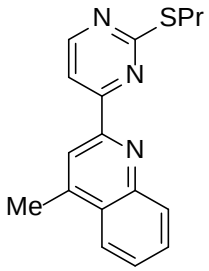
Prepared according to general procedure C, using (4-(ethoxycarbonyl)pyridin-2-yl)(4-ethoxyquinolin-2-yl)diphenylphosphonium trifluoromethanesulfonate (164 mg, 0.25 mmol), trifluoromethanesulfonic acid (42 μL, 0.50 mmol), and EtOH (0.63 mL) at 80 °C for 12 hours. The crude material was purified by flash chromatography (silica gel: 10% EtOAc in hexanes to 25% EtOAc in hexanes) to provide the title compound as a white crystalline solid (38 mg, 0.12 mmol, 47% yield). mp 102-104 °C; IR ν_{max}/cm^{-1} (film): 3038, 2968, 1464, 1350, 1277, 1235, 746; ^1H NMR (400 MHz, $CDCl_3$) δ: 9.18 (1H, s), 8.84 (1H,d, *J* = 5.0 Hz), 8.26 (1H,dd, *J* = 3.16 3.2, 1.2 Hz), 8.15 (1H, d, *J* = 8.4 Hz), 7.97 (1H, s), 7.97 (1H, dd, *J* = 5.0, 1.6 Hz), 7.71-7.70 (1H, m), 7.56-7.49 (1H, m), 4.55-4.38 (4H, m), 1.62 (3H, t, *J* = 7.0 Hz), 1.47 (3H, t, *J* = 7.1 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 165.36, 162.43, 157.71, 156.56, 149.59, 148.98, 138.80, 129.89, 129.35, 125.93, 123.05, 121.94, 121.54, 121.16, 98.12, 64.34, 61.83, 14.55, 14.29; *m/z* HRMS (DART) found $[M+H]^+$ 323.1386, $C_{19}H_{19}N_2O_3^+$ requires 323.1390.

7-Chloro-4-(3-fluorophenoxy)-4'-methyl-2,2'-biquinoline (4i)



Prepared according to general procedure C, using (7-chloro-4-(3-fluorophenoxy)quinolin-2-yl)(4-methylquinolin-2-yl)diphenylphosphonium trifluoromethanesulfonate (187 mg, 0.25 mmol), trifluoromethanesulfonic acid (42 μL, 0.50 mmol), and (2,2,2)-Trifluoroethanol (0.63 mL) at 80°C for 12 hours. The crude material was purified by flash chromatography (silica gel, 10% EtOAc in hexanes) to provide the title compound as a white crystalline solid (70 mg, 0.17 mmol, 67% yield). mp 208-210 °C; IR ν_{max}/cm^{-1} (film): 3068, 1615, 1094, 947, 831, 755, 526; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.60 (1H, d, *J* = 0.8 Hz), 8.28 (1H, d, *J* = 8.9 Hz), 8.25 (1H, d, *J* = 1.8 Hz), 8.13 (1H, s), 8.07 (1H, dd, *J* = 8.4, 0.7 Hz), 8.03 (1H, dd, *J* = 8.3, 0.9 Hz), 7.69 (1H, m), 7.60-7.53 (2H, m), 7.47 (1H, td, *J* = 12.2, 7.5 Hz), 7.10-6.99 (3H, m), 2.83 (3H, d, *J* = 0.9 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 163.60 (d, *J* = 248.4 Hz), 161.43, 158.99, 155.76 (d, *J* = 10.6 Hz), 154.93, 150.04, 147.57, 145.07, 136.33, 131.10, (d, *J* = 9.6 Hz), 130.50, 129.22, 128.57, 128.54, 127.50, 126.90, 123.75, 123.26, 120.13, 119.70, 116.32 (d, *J* = 3.4 Hz), 112.44 (d, *J* = 21.1 Hz), 108.65 (d, *J* = 24.2 Hz), 108.65 (d, *J* = 24.2 Hz), 103.43, 18.95; ^{19}F NMR (365 MHz, $CDCl_3$) δ: –109.72-(–)109.79 (m); *m/z* HRMS (DART) found $[M+H]^+$ 415.1024, $C_{25}H_{17}ClFN_2O^+$ requires 415.1008.

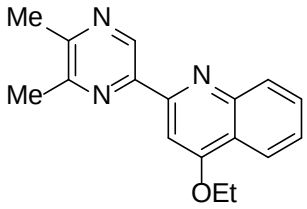
4-Methyl-2-(2-(propylthio)pyrimidin-4-yl)quinoline (4j)



Prepared according to general procedure C using (4-Methylquinolin-2-yl)diphenyl(2-(propylthio)pyrimidin-4-yl)phosphonium trifluoromethanesulfonate (149 mg, 0.25 mmol), trifluoromethanesulfonic acid (44 μL, 0.50 mmol), and EtOH (0.63 mL). The was reaction was heated to 80 °C for 5.5 hours. Flash column chromatography (silica gel: 5% EtOAc in hexanes) followed by a second flash column (silica gel, gradient elution: 3% EtOAc in hexanes to 5% EtOAc in hexanes) afforded the title compound as a white solid (27 mg, 0.091 mmol, 37% yield). mp 57-58 °C; IR ν_{max}/cm^{-1} (film): 2925, 1557, 1539, 1505, 1417, 1352, 1317, 1194, 1160,

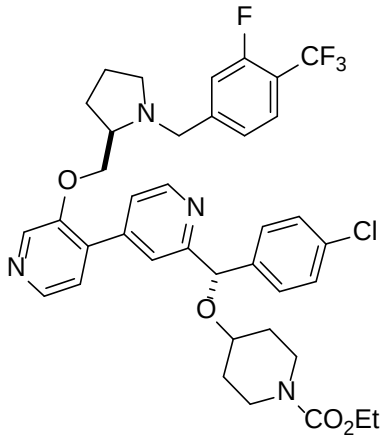
782; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.67 (1H, d, *J* = 4.7 Hz), 8.40 (1H, s), 8.23 (1H, d, *J* = 4.7 Hz), 8.17 (1H, d, *J* = 8.1 Hz), 8.03 (1H, d, *J* = 8.1 Hz), 7.75 (1H, t, *J* = 7.0 Hz), 7.61 (1H, t, *J* = 7.0 Hz), 3.26 (2H, t, *J* = 7.1 Hz), 2.80 (3H, s), 1.88 (2H, sext, *J* = 7.1 Hz), 1.13 (3H, t, *J* = 7.1 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 172.21, 163.22, 158.12, 153.22, 147.70, 145.37, 130.61, 129.53, 128.96, 127.37, 123.80, 119.29, 112.97, 33.04, 22.72, 19.02, 13.62; *m/z* LRMS (ESI + APCI) found $[M+H]^+$ 296.2, $C_{17}H_{18}N_3S^+$ requires 296.1.

2-(5,6-Dimethylpyrazin-2-yl)-4-ethoxyquinoline (4k)



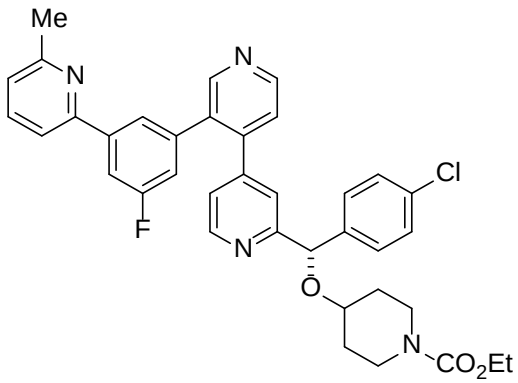
Prepared according to general procedure C using (5,6-dimethylpyrazin-2-yl)(4-ethoxyquinolin-2-yl)diphenylphosphonium trifluoromethanesulfonate (154 mg, 0.25 mmol), trifluoromethanesulfonic acid (67 μL, 0.75 mmol) and EtOH (625 μL) at 100 °C for 14 hours. Flash column chromatography (silica gel: 33% EtOAc in hexanes) afforded the title compound as a gray amorphous powder (16 mg, 0.06 mmol, 23% yield). mp 189-191 °C; IR υ_{max}/cm^{-1} (film): 3080, 2999, 2977, 2919, 1615, 1586, 1500, 1472, 1460, 1445, 1420, 1402, 1376, 1359, 1347, 1273, 1249, 1232, 1185, 1156, 1114, 1105, 1089, 1027, 993, 953, 919, 861, 837, 818, 784, 777, 767; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.52 (1H, s), 8.24 (1H, d, *J* = 8.2 Hz), 8.10 (1H, d, *J* = 8.4 Hz), 7.86 (1H, s), 7.71 (1H, dd, *J* = 7.2, 7.1 Hz), 7.50 (1H, dd, *J* = 7.8, 7.3 Hz), 4.42 (2H, q, *J* = 7.0 Hz), 2.64 (3H, s), 2.62 (3H, s), 1.61 (3H, t, *J* = 7.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 162.28, 156.03, 152.39, 150.85, 149.00, 148.17, 140.21, 129.87, 129.28, 125.77, 121.89, 121.37, 97.86, 64.26, 22.23, 22.02, 14.55; *m/z* LRMS (DART) found $[M+H]^+$ 280.2, $C_{17}H_{18}N_3O^+$ requires 280.1.

Ethyl 4-((*S*)-(4-chlorophenyl)(3'-(((*R*)-1-(3-fluoro-4-(trifluoromethyl)benzyl)pyrrolidin-2-yl)methoxy)-[4,4'-bipyridin]-2-yl)methoxy)piperidine-1-carboxylate (4l)



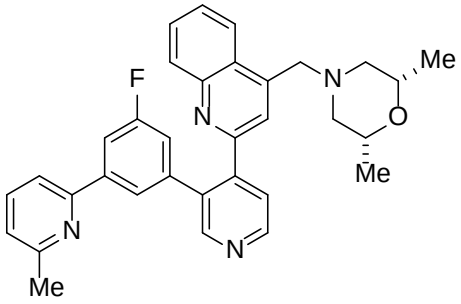
Prepared according to general procedure C, using (2-((*S*)-(4-chlorophenyl)((1-(ethoxycarbonyl)piperidin-4-yl)oxy)methyl)pyridin-4-yl)(3-(((*R*)-1-(3-fluoro-4-(trifluoromethyl)benzyl)pyrrolidin-2-yl)methoxy)pyridin-4-yl)diphenylphosphonium trifluoromethanesulfonate (106 mg, 0.10 mmol), trifluoromethanesulfonic acid (25 μL, 0.30 mmol), and EtOH (0.25 mL) at 80 °C for 72 hours. The crude material was purified by flash chromatography (silica gel: 2% MeOH in CH_2Cl_2) followed by a second flash chromatography column (silica gel: 2% MeOH in CH_2Cl_2) to provide the title compound as a faint brown oil (43 mg, 0.06 mmol, 60% yield). IR ν_{max}/cm^{-1} (film): 3055, 2928, 2872, 1689, 1629, 1604, 1586, 1564, 1502, 964, 766, 645, 619, 534; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.40 (1H, d, *J* = 5.5 Hz), 8.35-8.25 (2H, m), 7.62 (1H, s), 7.40-7.34 (1H, s), 7.40-7.34 (3H, m), 7.24 (1H, t, *J* = 1.7 Hz), 7.22 (2H, m), 6.93-6.85 (2H, m), 5.60 (1H, s), 4.05 (2H, q, *J* = 7.1 Hz), 3.95 (2H, d, *J* = 5.4 Hz), 3.79-3.62 (3H, m), 3.57 (1H, m), 3.17-3.04 (3H, m), 2.86-2.72 (2H, m), 2.10 (1H, q, *J* = 8.4 Hz), 1.96-1.47 (5H, m), 1.25-1.12 (6H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 161.94, 159.72 (dq, *J* = 255.5, 2.3 Hz), 155.47, 151.76 (m), 148.82, 147.49 (d, *J* = 7.2 Hz), 144.64, 143.16, 140.14, 135.40, 134.77, 133.47, 128.65, 128.08, 126.75 (2C, m), 122.64 (dq, *J* = 270.5, 1.1 Hz), 123.86 (m), 123.22 (d, *J* = 3.4 Hz), 122.58, 116.09 (d, *J* = 20.7 Hz), 72.80, 62.61, 61.28, 58.75, 54.74, 41.07, 40.99, 31.16, 31.01, 29.67, 28.59, 23.26, 14.66; ^{19}F NMR δ: –61.13 (d, *J* = 12.8 Hz), –114.89-(–)115.21 (m); *m/z* HRMS (DART) found $[M+H]^+$ 727.2688, $C_{38}H_{40}ClF_4N_4O_4^+$ requires 727.2669.

Ethyl (*S*)-4-((4-chlorophenyl)(3'-(3-fluoro-5-(6-methylpyridin-2-yl)phenyl)-[4,4'-bipyridin]-2-yl)methoxy)piperidine-1-carboxylate (4m)



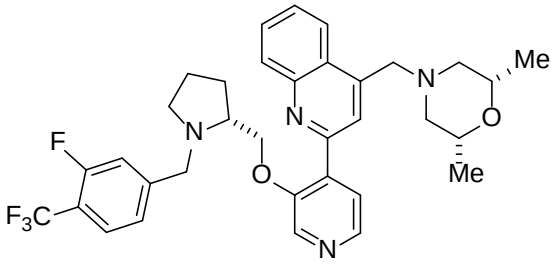
Prepared according to general procedure C using (*S*)-(2-((4-chlorophenyl)((1-(ethoxycarbonyl)piperidin-4-yl)oxy)methyl)pyridin-4-yl)(3-(3-fluoro-5-(6-methylpyridin-2-yl)phenyl)pyridin-4-yl)diphenylphosphonium trifluoromethanesulfonate (97 mg, 0.10 mmol), trifluoromethanesulfonic acid (26.5 μL, 0.30 mmol), and EtOH (0.25 mL). The was reaction was heated to 80 ºC for 26 hours. Flash column chromatography (the crude reaction mixture was dissolved in 5 mL of CH_2Cl_2 and then 1 mL of trifluoroacetic acid was added, the mixture was loaded onto a silica column and then gradient elution: CH_2Cl_2 to 3% MeOH in CH_2Cl_2) followed by a second flash column (the crude reaction mixture was dissolved in 5 mL of CH_2Cl_2 and then 1 mL of trifluoroacetic acid was added, the mixture was loaded onto a silica column and then gradient elution: CH_2Cl_2 to 2% MeOH in CH_2Cl_2) followed by preparatory thin layer chromatography (silica gel: 3% MeOH in CH_2Cl_2 afforded the title compound as a colorless oil (41 mg, 0.07 mmol, 65% yield). IR ν_{max}/cm^{-1} (film): 3060, 2953, 2925, 1690, 1585, 1576, 1432, 1384, 1228, 1087, 751; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.74 (2H, br s), 8.54 (1H, d, *J* = 5.0 Hz), 7.69 (1H, d, *J* = 9.9 Hz), 7.60-7.50 (2H, m), 7.35 (1H, d, *J* = 4.2 Hz), 7.24-7.15 (3H, m), 7.13-7.04 (5H, m), 6.84 (1H, d, *J* = 8.7 Hz), 5.47 (1H, s), 4.09 (2H, q, *J* = 7.2 Hz), 3.63-3.49 (2H, m), 3.49-3.38 (1H, m), 3.16-3.03 (2H, m), 2.58 (3H, s), 1.72-1.55 (2H, m), 1.54-1.36 (2H, m), 1.23 (3H, t, *J* = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 162.95 (d, *J* = 246.7 Hz), 161.95, 158.64, 155.38, 154.23 (d, *J* = 2.9 Hz), 151.02, 149.66-149.29 (2C, m), 147.16, 145.05, 142.20 (d, *J* = 7.8 Hz), 139.54, 138.93 (d, *J* = 8.3 Hz), 136.94, 134.56, 133.30, 128.52, 127.81, 124.11-123.81 (2C, m), 122.47, 122.44, 120.99, 117.20, 116.54 (d, *J* = 22.6 Hz), 113.28 (d, *J* = 22.7 Hz), 80.38, 72.19, 61.19, 40.78, 40.72, 30.88, 30.68, 24.62, 14.66; ^{19}F NMR (365 MHz, $CDCl_3$) δ: -112.23; *m/z* HRMS (ESI) found $[M+H]^+$ 637.2391, $C_{37}H_{35}ClFN_4O_3^+$ requires 637.2376.

(2*R*, 6*S*)-4-((2-(3-(3-fluoro-5-(6-methylpyridin-2-yl)phenyl)pyridin-4-yl)quinolin-4-yl)methyl)-2,6-dimethylmorpholine (4n)



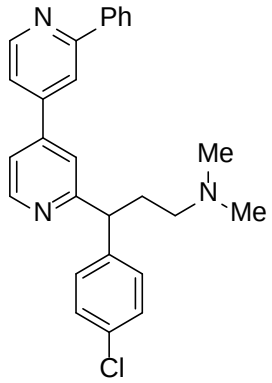
Prepared according to general procedure C (except an additional 18 μL, 0.20 mmol of trifluoromethanesulfonic acid was added after 40.5 hours) using (4-(((2*R*, 6*S*)-2,6-dimethylmorpholino)methyl)quinolin-2-yl)(3-(3-fluoro-5-(6-methylpyridin-2-yl)phenyl)pyridin-4-yl)diphenylphosphonium trifluoromethanesulfonate (85 mg, 0.10 mmol), trifluoromethanesulfonic acid (35 μL, 0.40 mmol), and EtOH (0.25 mL). The was reaction was heated to 80 ºC for 58.5 hours. Flash column chromatography (silica gel: 60% EtOAc in hexanes) followed by a second flash column (silica gel, gradient elution: 1% MeOH in CH_2Cl_2 to 2.5% MeOH in CH_2Cl_2) afforded the title compound as a colorless oil (23.7 mg, 0.046 mmol, 46%). IR ν_{max}/cm^{-1} (film): 3063, 2972, 2928, 1586, 1455, 1430, 1344, 1083, 757; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.81 (2H, br s), 8.27-8.15 (2H, m), 7.85-7.73 (3H, m), 7.68 (1H, d, *J* = 9.9 Hz), 7.58 (1H, t, *J* = 7.6 Hz), 7.51 (1H, t, *J* = 7.7 Hz), 7.23 (1H, d, *J* = 7.7 Hz), 7.15-7.03 (2H, m), 6.92 (1H, d, *J* = 9.0 Hz), 3.63 (2H, s), 3.54-3.38 (2H, m), 2.50 (3H, s), 2.40 (2H, d, *J* = 11.5 Hz), 1.63 (2H, t, *J* = 10.5 Hz), 1.00 (6H, d, *J* = 6.3 Hz) ^{13}C NMR (100 MHz, $CDCl_3$) δ: 162.86 (d, *J* = 246.4), 158.62, 156.36, 154.36 (d, *J* = 2.7 Hz), 150.76, 149.56, 148.57, 146.77, 143.77, 142.18 (d, *J* = 8.6 Hz), 139.74 (d, *J* = 8.2 Hz), 136.94, 134.58, 130.19, 129.63, 126.87, 126.64, 124.68, 124.24, 123.95 (d, *J* = 2.7 Hz), 122.63, 122.40, 117.22, 116.79 (d, *J* = 22.5 Hz), 113.16 (d, *J* = 22.7 Hz), 71.51, 59.81, 59.38, 24.51, 18.83; ^{19}F NMR (365 MHz, $CDCl_3$) δ: -112.28 (t, *J* = 9.3 Hz); *m/z* HRMS (ESI) found $[M+H]^+$ 519.2572, $C_{33}H_{32}FN_4O^+$ requires 519.2555.

(*2S, 6R*)-4-((2-(3-(((*R*)-1-(3-Fluoro-4-(trifluoromethyl)benzyl)pyrrolidin-2-yl)methoxy)pyridin-4-yl)quinolin-4-yl)methyl)-2,6-dimethylmorpholine (4o)



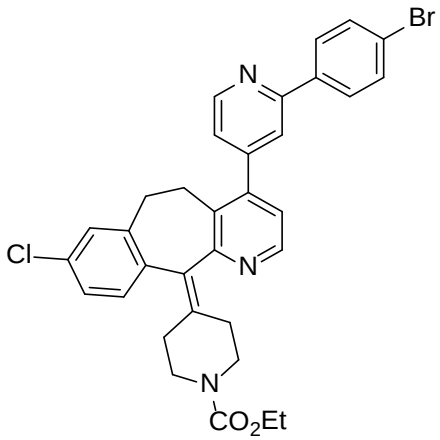
Prepared according to general procedure C, using (4-(((*2S, 6R*)-2,6-dimethylmorpholino)methyl)quinolin-2-yl)(3-(((*R*)-1-(3-fluoro-4-(trifluoromethyl)benzyl)pyrrolidin-2-yl)methoxy)pyridin-4-yl)diphenylphosphonium trifluoromethanesulfonate (94 mg, 0.10 mmol), 4.0M HCl in dioxane (100 μL, 0.40 mmol), and EtOH (0.25 mL) at 80 ºC for 72 hours. The crude material was purified by flash chromatography (silica gel: 2% MeOH in CH_2Cl_2) to provide the title compound as a brown amorphous solid (30 mg, 0.05 mmol, 49% yield). IR ν_{max}/cm^{-1} (film): 3063, 2971, 2930, 2871, 2813, 1629, 1587, 1545, 693, 653, 602, 550, 531, 526; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.50-8.39 (2H, m), 8.23 (1H, d, *J* = 8.3 Hz), 8.11 (1H, d, *J* = 8.4 Hz), 7.85 (1H, s), 7.75 (1H, d, *J* = 4.8 Hz), 7.71 (1H, m), 7.56 (1H, m), 7.29 (1H, t, *J* = 7.7 Hz), 6.97-6.87 (2H, m), 4.21-4.06 (2H, m), 4.01 (1H, d, *J* = 14.16 14.2 Hz), 3.80 (2H, d, *J* = 1.8 Hz), 3.73-3.61 (2H, m), 3.30 (1H, d, *J* = 14.2 Hz), 3.08-2.97 (1H, m), 2.91-2.80 (1H, m), 2.79 (2H, d, *J* = 11.5 Hz), 2.15 (1H, q, *J* = 6.2 Hz), 2.06-1.94 (1H, m), 1.86 (2H, q, *J* = 10.6 Hz), 1.78-1.65 (3H, m), 1.14 (6H, d, *J* = 6.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.57 (dq, *J* = 253.8, 2.1 Hz), 154.01, 152.42, 148.39, 147.22 (d, *J* = 5.5 Hz), 143.38, 143.23, 136.59, 135.72, 130.16, 129.47, 126.94-126.32 (m, 4C), 124.75, 124.17, 123.30 (d, *J* = 3.3 Hz), 122.97, 122.62 (dq, *J* = 273.1, 1.0 Hz), 116.89 (d, *J* = 20.6 Hz), 73.11, 71.67 (d, *J* = 2.2 Hz), 62.43, 60.13, 59.69 (d, *J* = 8.4 Hz), 58.86, 54.66, 28.60, 23.29, 19.88 (d, *J* = 1.1 Hz); ^{19}F NMR δ: –61.10 (d, *J* = 12.9 Hz), –114.67- (–)115.23 (m); *m/z* HRMS (DART) found $[M+H]^+$ 609.2839, $C_{34}H_{37}F_4N_4O_2^+$ requires 609.2847.

3-(4-Chlorophenyl)-N,N-dimethyl-3-(2'-phenyl-[4,4'-bipyridin]-2-yl)propan-1-amine (4p)



Prepared according to general procedure C using (2-(1-(4-chlorophenyl)-3-(dimethylamino)propyl)pyridin-4-yl)diphenyl(2-phenylpyridin-4-yl)phosphonium trifluoromethanesulfonate (381 mg, 0.50 mmol), trifluoromethanesulfonic acid (134 μL, 1.50 mmol) and EtOH (1.25 mL) at 80 °C for 12 hours. Flash column chromatography (silica gel: 9% MeOH in CH_2Cl_2) afforded the title compound as a light yellow oil (179 mg, 0.42 mmol, 84% yield). IR υ_{max}/cm^{-1} (film): 3410, 3027, 2940, 2856, 2815, 2766, 2430, 2203, 1590, 1533, 1488, 1467, 1445, 1379, 1261, 1089, 1025, 1014, 907, 829, 775, 756, 727, 694; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.74 (1H, d, *J* = 4.9 Hz), 8.68 (1H, d, *J* = 4.9 Hz), 8.01 (2H, d, *J* = 7.4 Hz), 7.87 (1H, s), 7.49–7.33 (8H, m), 7.25 (2H, d, *J* = 8.6 Hz), 4.29 (1H, t, *J* = 7.4 Hz), 2.70–2.34 (10H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 163.01, 158.27, 150.26, 150.06, 146.48, 146.27, 141.11, 138.76, 132.47, 129.21, 129.15, 128.66, 126.88, 120.96, 119.79, 119.49, 118.23, 56.90, 49.98, 44.25, 31.30; *m/z* HRMS (DART) found $[M+H]^+$ 428.1921, $C_{27}H_{27}ClN_3^+$ requires 428.1894.

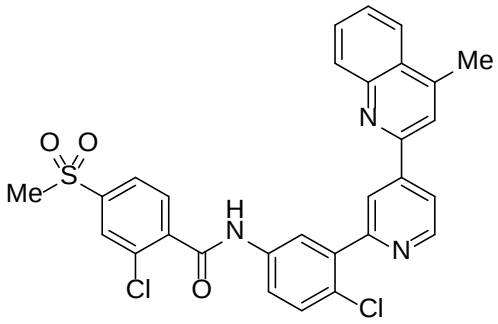
Ethyl 4-(4-(2-(4-bromophenyl)pyridin-4-yl)-8-chloro-5,6-dihydro-11H-benzo[5,6]cyclohepta[1,2-b]pyridin-11-ylidene)piperidine-1-carboxylate (4q)



Prepared according to general procedure C using (2-(4-bromophenyl)pyridin-4-yl)(8-chloro-11-(1-(ethoxycarbonyl)piperidin-4-ylidene)-6,11-dihydro-5H-benzo[5,6]cyclohepta[1,2-b]pyridin-4-yl)diphenylphosphonium trifluoromethanesulfonate (237 mg, 0.25 mmol), trifluoromethanesulfonic acid (44 μL, 0.50 mmol), and EtOH (625 μL). The was reaction was

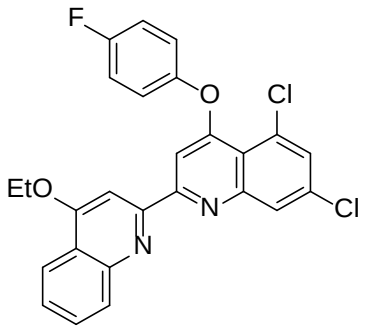
heated to 80 ºC for 30 hrs. Flash column chromatography (basic alumina, gradient elution: 20% EtOAc in hexanes to 40% EtOAc in hexanes) afforded the title compound as a white solid (133 mg, 0.22 mmol, 87% yield). mp 95-98 ºC; IR ν_{max}/cm^{-1} (film): 3050, 2972, 2922, 1690, 1578, 1473, 1428, 1222, 1008, 826, 729; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.77 (1H, d, *J* = 5.0 Hz), 8.49 (1H, d, *J* = 5.0 Hz), 7.91 (2H, d, *J* = 8.6 Hz), 7.66-7.58 (3H, m), 7.21-7.14 (3H, m), 7.12 (1H, s) 7.06 (1H, d, *J* = 5.0 Hz), 4.14 (2H, q, *J* = 7.2 Hz), 3.82 (2H, br s), 3.41-3.29 (1H, m), 3.27-3.12 (3H, m), 2.88-2.72 (2H, m), 2.56-2.35 (3H, m), 2.34-2.20 (1H, m), 1.26 (3H, t, *J* = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.73, 156.58, 155.34, 149.87, 147.81, 147.09, 146.77, 138.50, 137.53, 137.34, 135.89, 134.11, 133.01, 131.90, 131.21, 130.30, 129.60, 128.41, 126.07, 123.84, 122.53, 121.87, 119.70, 61.24, 44.69, 44.57, 32.12, 30.60, 30.51, 27.48, 14.48; *m/z* HRMS (DART) found $[M+H]^+$ 614.1235, $C_{33}H_{30}BrClN_3O_2^+$ requires 614.1204.

2-Chloro-N-(4-chloro-3-(4-(4-methylquinolin-2-yl)pyridin-2-yl)phenyl)-4-(methylsulfonyl)benzamide (4r)



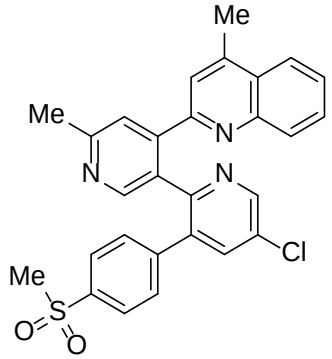
Prepared according to general procedure C using (2-(2-chloro-5-(2-chloro-4-(methylsulfonyl)benzamido)phenyl)pyridin-4-yl)(4-methylquinolin-2-yl)diphenylphosphonium trifluoromethanesulfonate (224 mg, 0.25 mmol), 4.0 M HCl in dioxanes (125 μL, 0.50 mmol), and (2,2,2)-Trifluoroethanol (625 μL). The was reaction was heated to 80 ºC for 37 hours. Flash column chromatography (silica gel was packed in hexanes and neutralized with NEt_3 then gradient elution: CH_2Cl_2 to 1.5% MeOH in CH_2Cl_2) followed by a second flash column (basic alumina, gradient elution: CH_2Cl_2 to 2% MeOH in CH_2Cl_2) and the resulting solid was washed on a frit with 200 mL of Et_2O and then 25 mL of chilled CH_2Cl_2 (0 ºC). The title compound was isolated as a white solid (73 mg, 0.13 mmol, 52% yield). decomp. 270-275 ºC; IR ν_{max}/cm^{-1} (film): 3318, 3018, 2992, 2914, 1689, 1539, 1299, 1152, 1030, 816, 751; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.99, (1H, s), 8.89 (1H, d, *J* = 5.2 Hz), 8.28 (1H, d, *J* = 5.2 Hz), 8.21 (1H, s), 8.18-8.07 (4H, m), 8.02 (1H, dd, *J* = 8.0, 1.5 Hz), 7.94 (1H, d, *J* = 8.0 Hz), 7.87-7.76 (2H, m), 7.72-7.59 (2H, m), 3.36 (3H, s), 2.79 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 163.87, 156.84, 152.95, 150.28, 147.31, 146.12, 146.03, 143.13, 140.84, 139.31, 137.65, 130.97, 130.44, 130.08-129.82 (3C, m), 128.10, 127.60, 127.16, 125.99, 125.91, 124.21, 122.35, 121.81, 125.99, 125.91, 124.21, 122.35, 121.81, 121.07, 120.42, 119.31, 43.09, 18.39; *m/z* HRMS (ESI + APCI) found $[M+H]^+$ 562.0766, $C_{29}H_{22}Cl_2N_3O_3S^+$ requires 562.0753.

5,7-Dichloro-4'-ethoxy-4-(4-fluorophenoxy)-2,2'-biquinoline (4s)



Prepared according to general procedure C, using (5,7-dichloro-4-(4-fluorophenoxy)quinolin-2-yl)(4-ethoxyquinolin-2-yl)diphenylphosphonium trifluoromethanesulfonate (203 mg, 0.25 mmol), trifluoromethanesulfonic acid (42 μL, 0.50 mmol), and (2,2,2)-Trifluoroethanol (625 μL) at 80 °C for 36 hours. The crude material was suspended in a 5mL CH_2Cl_2 and filtered over a frit with cold CH_2Cl_2 to provide the title compound as a white crystalline solid (69 mg, 0.15 mmol, 58% yield). mp 235-238 °C; IR ν_{max}/cm^{-1} (film): 3065, 2978, 1430, 1296, 1214, 1117, 733; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.24 (1H, d, *J* = 8.2 Hz), 8.19-8.12 (2H, m), 8.10 (1H, s), 7.97 (1H, d, *J* = 8.4 Hz), 7.67 (1H, t, *J* = 7.3 Hz), 7.60 (1H, d, *J* = 1.8 Hz), 7.51 (1H, t, *J* = 15.0 Hz), 7.24 (4H, m), 4.47 (2H, q, *J* = 7.0 Hz), 1.64 (3H, t, *J* = 7.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 162.60, 162.32, 159.93 (d, *J* = 243.8 Hz), 158.99, 155.89, 151.37, 150.39 (d, *J* = 2.7 Hz), 148.69, 134.94, 130.24, 129.86, 129.67, 129.42, 128.18, 126.26, 122.87 (d, *J* = 8.5 Hz), 121.94, 121.77, 118.42, 116.98 (d, *J* = 23.6 Hz), 105.31, 98.17, 64.38, 14.55; ^{19}F NMR δ: –117.56 (m); *m/z* HRMS (DART) found $[M+H]^+$ 479.0709, $C_{26}H_{18}Cl_2FN_2O_2^+$ requires 479.0724.

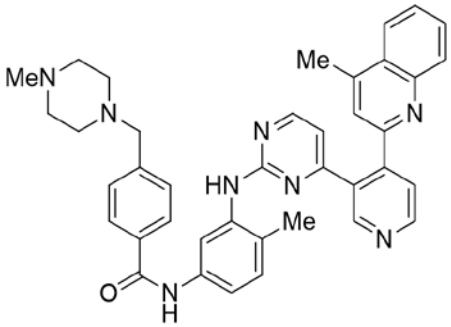
2-(5-Chloro-6'-methyl-3-(4-(methylsulfonyl)phenyl)-[2,3'-bipyridin]-4'-yl)-4-methylquinoline (4t)



Prepared according to general procedure C, using (5-chloro-6'-methyl-3-(4-(methylsulfonyl)phenyl)-[2,3'-bipyridin]-4'-yl)(4-methylquinolin-2-yl)diphenylphosphonium trifluoromethanesulfonate (83 mg, 0.10 mmol), trifluoromethanesulfonic acid (26 μL, 0.30 mmol), and EtOH (0.25 mL) at 80 °C for 22 hours. The crude material was purified by flash

chromatography (silica gel gradient elution: 3% MeOH in CH_2Cl_2 to 4% MeOH in CH_2Cl_2) to provide the title compound as a white crystalline solid (40 mg, 0.08 mmol, 80% yield). mp 286-290 ^oC; IR ν_{max}/cm^{-1} (film): 3034, 2926, 1506, 1264, 1034, 873, 863; ^1H NMR (400 MHz, $CDCl_3$) δ: 8.69-8.59 (2H, m), 7.96 (1H, d, *J* = 8.0 Hz), 7.68-7.43 (6H, m), 7.35 (1H, s), 6.94-6.81 (3H, m), 3.00 (3H, s), 2.67 (3H, s), 2.61 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.16, 154.96, 154.07, 151.54, 147.94, 147.32, 147.11, 145.21, 143.07, 139.47, 136.47, 136.03, 130.77, 130.59, 130.02, 129.61, 129.56, 127.08, 126.92, 126.75, 123.57, 122.81, 120.92, 44.39, 24.42, 18.78; *m/z* HRMS (DART) found $[M+H]^+$ 500.1175, $C_{28}H_{23}ClN_3O_2S^+$ requires 500.1194.

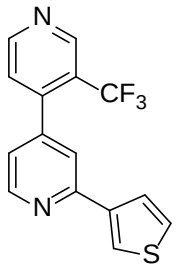
_N_-(4-Methyl-3-((4-(4-(4-methylquinolin-2-yl)pyridin-3-yl)pyrimidin-2-yl)amino)phenyl)-4-((4-methylpiperazin-1-yl)methyl)benzamide (4u)



Prepared according to general procedure C using (3-(2-((2-methyl-5-(4-((4-methylpiperazin-1-yl)methyl)benzamido)phenyl)amino)pyrimidin-4-yl)pyridin-4-yl)(4-methylquinolin-2-yl)diphenylphosphonium trifluoromethanesulfonate (97 mg, 0.10 mmol), trifluoromethanesulfonic acid (36 μL, 0.40 mmol) and EtOH (0.25 mL) at 80 °C for 48 hours. Flash column chromatography by three times (silica gel: 30% toluene, 3% MeOH and 1% Et_3N in CH_2Cl_2) afforded the title compound as a colorless oil (26 mg, 0.04 mmol, 41% yield). IR υ_{max}/cm^{-1} (film): 3249, 3036, 2933, 2796, 1663, 1572, 1553, 1525, 1505, 1446, 1406, 1349, 1287, 1204, 1162, 1138, 1010, 906, 816, 758, 730; ^1H NMR (400 MHz, $CDCl_3$) δ: 9.02 (1H, s), 8.83 (1H, d, *J* = 5.0 Hz), 8.26 (1H, d, *J* = 5.1 Hz), 8.09 (1H, s), 7.96–7.87 (5H, m), 7.72 (1H, d, *J* = 5.0 Hz), 7.66 (1H, t, *J* = 7.5 Hz), 7.55 (1H, t, *J* = 7.4 Hz), 7.48–7.44 (3H, m), 7.09–7.06 (2H, m), 6.83 (1H, s), 6.62 (1H, d, *J* = 5.1 Hz), 3.56 (2H, s), 2.57–2.29 (14H, m), 2.13 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 165.33, 164.51, 160.07, 157.95, 156.20, 150.85, 150.62, 147.78, 147.57, 144.55, 142.50, 137.36, 136.47, 133.86, 132.78, 130.60, 129.99, 129.67, 129.24, 127.14, 127.12, 126.91, 124.53, 123.66, 123.51, 122.41, 115.13, 112.72, 112.53, 62.52, 55.08, 53.12, 45.99, 18.74, 17.32; *m/z* HRMS (ESI + APCI) found $[M+H]^+$ 635.3221, $C_{39}H_{39}N_8O^+$ requires 635.3247.

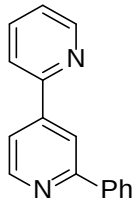
Additional Examples: Characterization

2-(Thiophen-3-yl)-3'-(trifluoromethyl)-4,4'-bipyridine



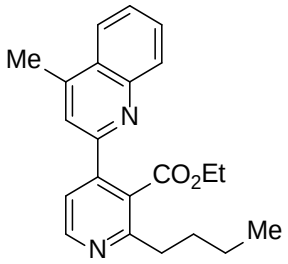
Prepared according to general procedure C using diphenyl(2-(thiophen-3-yl)pyridin-4-yl)(3-(trifluoromethyl)pyridin-4-yl)phosphonium trifluoromethanesulfonate (320 mg, 0.50 mmol), trifluoromethanesulfonic acid (88 μL, 1.00 mmol), and EtOH (1.25 mL). The reaction was heated to 80 ºC for 11 hrs. Flash column chromatography (silica gel, gradient elution: 20% EtOAc in hexanes to 30% EtOAc in hexanes) afforded the title compound as a colorless oil (61 mg, 0.20 mmol, 40% yield). IR ν_{max}/cm^{-1} (film): 3047, 1589, 1540, 1329, 1280, 1265, 1133, 1095, 1029, 907, 730; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.03 (1H, s), 8.87 (1H, d, *J* = 5.0 Hz), 8.70 (1H, d, *J* = 5.1 Hz), 7.95 (1H, dd, *J* = 3.1, 1.2 Hz), 7.66 (1H, dd, *J* = 5.1, 1.2 Hz), 7.57 (1H, s), 7.41 (1H, dd, *J* = 5.1, 3.1 Hz), 7.32 (1H, d, *J* = 5.0 Hz), 7.14 (1H, dd, *J* = 5.0, 1.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 153.57, 153.00, 149.56, 147.51 (q, *J* = 5.6 Hz), 146.54 (q, *J* = 1.9 Hz), 145.53, 141.45, 126.59, 126.04, 125.02, 124.08 (q, *J* = 30.4 Hz), 123.92 (2C), 123.27 (q, *J* = 274.0 Hz), 120.93 (q, *J* = 1.6 Hz) ; ^{19}F NMR (365 MHz, $CDCl_3$) δ: –56.8; *m/z* HRMS (DART) found $[M+H]^+$ 307.0535, $C_{15}H_{10}F_3N_2S^+$ requires 307.0511.

2'-Phenyl-2,4'-bipyridine



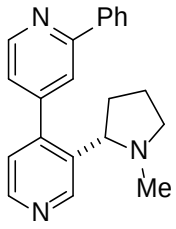
Prepared according to general procedure C using diphenyl(2-phenylpyridin-4-yl)(pyridin-2-yl)phosphonium trifluoromethanesulfonate (142 mg, 0.25 mmol), 4.0 M HCl in dioxanes (125 μL, 0.5 mmol), and EtOH (0.5 mL). The was reaction was heated to 80 ºC for 24 hours. Flash column chromatography (silica gel was packed in hexanes and neutralized with NEt_3 then gradient elution: 10% EtOAc in hexanes to 25% EtOAc in hexanes) afforded the title compound as a tan oil (42 mg, 0.18 mmol, 73%). The spectroscopic data is in agreement with a previously reported synthesis (*31*).

Ethyl 2-butyl-4-(4-methylquinolin-2-yl)nicotinate



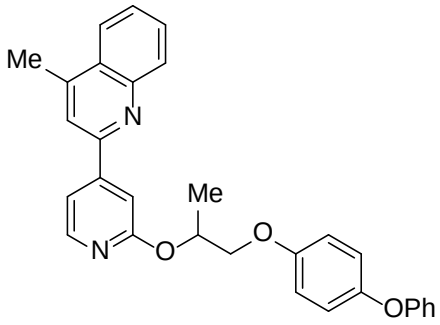
Prepared according to general procedure C using (2-butyl-3-(ethoxycarbonyl)pyridin-4-yl)(4-methylquinolin-2-yl)diphenylphosphonium trifluoromethanesulfonate (341 mg, 0.50 mmol), trifluoromethanesulfonic acid (89 μL, 1.00 mmol) and EtOH (1.25 mL) at 80 °C for 21 hours. Flash column chromatography (silica gel: 16% EtOAc in toluene) afforded the title compound as a light yellow oil (91 mg, 0.26 mmol, 52% yield). IR υ_{max}/cm^{-1} (film): 3060, 2956, 2930, 2870, 1724, 1597, 1576, 1546, 1507, 1447, 1413, 1364, 1256, 1151, 1131, 1093, 1049, 1022, 839, 758; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.67 (1H, d, *J* = 5.1 Hz), 8.06 (1H, d, *J* = 8.4 Hz), 8.00 (1H, d, *J* = 8.3 Hz), 7.71 (1H, dd, *J* = 8.2, 7.1 Hz), 7.57 (1H, dd, *J* = 8.0, 7.2 Hz), 7.54 (1H, s), 7.47 (1H, d, *J* = 5.1 Hz), 4.22 (2H, q, *J* = 7.2 Hz), 2.94 (2H, t, *J* = 7.9 Hz), 2.74 (3H, s), 1.83-1.75 (2H, m), 1.43 (2H, sext, *J* = 7.5 Hz), 1.07 (3H, t, *J* = 7.2 Hz), 0.94 (3H, t, *J* = 7.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 168.89, 160.31, 154.90, 149.88, 147.42, 146.25, 145.49, 130.09, 129.69, 128.07, 127.34, 126.90, 123.63, 120.46, 120.41, 61.22, 35.94, 31.96, 22.72, 18.87, 13.86, 13.85; *m/z* HRMS (DART) found $[M+H]^+$ 349.1960, $C_{22}H_{25}N_2O_2^+$ requires 349.1916.

(*S*)-3'-(1-Methylpyrrolidin-2-yl)-2-phenyl-4,4'-bipyridine



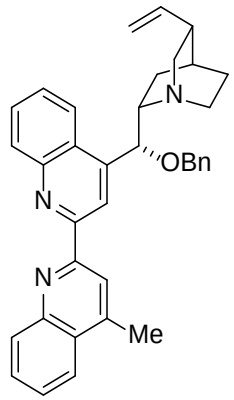
Prepared according to general procedure C using (*S*)-(3-(1-methylpyrrolidin-2-yl)pyridin-4-yl)diphenyl(2-phenylpyridin-4-yl)phosphonium trifluoromethanesulfonate (325 mg, 0.50 mmol), trifluoromethanesulfonic acid (134 μL, 1.50 mmol) and EtOH (1.25 mL) at 80 °C for 12 hours. Flash column chromatography (silica gel: 2.5% MeOH in CH_2Cl_2 to 5% MeOH in CH_2Cl_2) afforded the title compound as a yellow amorphous solid (84 mg, 0.265 mmol, 53% yield). mp 85–88 °C; IR υ_{max}/cm^{-1} (film): 3030, 2960, 2937, 2872, 2831, 2770, 1604, 1585, 1577, 1557, 1532, 1467, 1442, 1408, 1390, 1358, 1217, 1182, 1151, 1062, 1039, 1023, 836, 780, 750, 701; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.97 (1H, s), 8.75 (1H, d, *J* = 4.9 Hz), 8.54 (1H, d, *J* = 4.9 Hz), 8.02 (2H, d, *J* = 7.4 Hz), 7.62 (1H, s), 7.50-7.40 (3H, m), 7.13 (1H, d, *J* = 4.9 Hz), 7.09 (1H, d, *J* = 4.9 Hz), 3.18-3.12 (2H, m), 2.18-2.03 (5H, m), 1.98-1.86 (1H, m), 1.80-1.66 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 157.40, 150.26, 149.54, 147.57, 147.48, 146.85, 138.74, 136.03, 129.30, 128.81, 126.86, 122.84, 121.89, 120.26, 65.27, 56.64, 40.28, 35.64, 22.79; *m/z* HRMS (DART) found $[M+ H]^+$ 316.1827, $C_{21}H_{22}N_3^+$ requires 316.1814.

4-Methyl-2-(2-((1-(4-phenoxyphenoxy)propan-2-yl)oxy)pyridin-4-yl)quinoline



Prepared according to general procedure C using (4-methylquinolin-2-yl)(2-((1-(4-phenoxyphenoxy)propan-2-yl)oxy)pyridin-4-yl)diphenylphosphonium trifluoromethanesulfonate (80 mg, 0.10 mmol), trifluoromethanesulfonic acid (18 μL, 0.20 mmol) and EtOH (0.25 mL) at 80 °C for 48 hours. Flash column chromatography (silica gel: 2.5% EtOAc in CH_2Cl_2 to 5% EtOAc in CH_2Cl_2) afforded the title compound as a colorless oil (27 mg, 0.06 mmol, 57% yield). IR υ_{max}/cm^{-1} (film): 3063, 2924, 2870, 1595, 1541, 1502, 1487, 1461, 1418, 1403, 1377, 1345, 1304, 1282, 1265, 1217, 1158, 1134, 1119, 1102, 1072, 1042, 995, 976, 919, 890, 871, 836, 757; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.31 (1H, d, *J* = 4.9 Hz), 8.18 (1H, d, *J* = 8.4 Hz), 8.01 (1H, d, *J* = 8.3 Hz), 7.76-7.66 (3H, m), 7.59 (1H, t, *J* = 7.6 Hz), 7.51 (1H, s), 7.29 (2H, t, *J* = 7.8 Hz), 7.05-6.94 (7H, m), 5.72-5.65 (1H, m), 4.25 (1H, dd, *J* = 9.9, 5.4 Hz), 4.13 (1H, dd, *J* = 9.8, 4.8 Hz), 2.77 (3H, s), 1.54 (3H, d, *J* = 6.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 164.03, 158.47, 155.21, 154.26, 150.23, 149.95, 147.98, 147.35, 145.33, 130.55, 129.61, 129.55, 127.84, 126.79, 123.63, 122.36, 120.74, 119.32, 117.57, 115.77, 115.20, 109,69, 71.07, 69.56, 19.01, 17.06; *m/z* HRMS (DART) found $[M+H]^+$ 463.2017, $C_{30}H_{27}N_2O_3^+$ requires 463.2022.

(1*R*,4*R*,5*R*)-2-((*R*)-(Benzyloxy)(4'-methyl-[2,2'-biquinolin]-4-yl)methyl)-5-vinylquinuclidine



Prepared according to general procedure C using (4-((1*R*)-(benzyloxy)((1*R*,4*R*)-5-vinylquinuclidin-2-yl)methyl)quinolin-2-yl)(4-methylquinolin-2-yl)diphenylphosphonium trifluoromethanesulfonate (215 mg, 0.25 mmol), trifluoromethanesulfonic acid (67 μL, 0.75 mmol) and EtOH (625 μL) at 80 °C for 15 hours. Purified by flash column chromatography three rounds (basic Al_2O_3: 33% EtOAc in hexanes) to afford the title compound as a colorless oil (83 mg, 0.16 mmol, 63% yield). IR υ_{max}/cm^{-1} (film): 3064, 3031, 2927, 2862, 1594, 1548, 1503,

1452, 1422, 1406, 1297, 1263, 1221, 1161, 1084, 1046, 1027, 990, 907, 883, 863, 815, 756, 728, 697; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.02 (1H, s), 8.69 (1H, s), 8.32 (1H, d, *J* = 8.4 Hz), 8.29-8.23 (2H, m), 8.05 (1H, d, *J* = 8.3 Hz), 7.80–7.74 (2H, m), 7.61-7.59 (2H, m), 7.47-7.32 (5H, m), 5.82-5.74 (1H, m), 5.37 (1H, br s), 4.93 (2H, dd, *J* = 17.2, 10.4 Hz), 4.59 (1H, d, *J* = 11.2 Hz), 4.47 (1H, d, *J* = 11.2 Hz), 3.50-3.44 (1H, m), 3.33 (1H, br s), 3.13-3.07 (1H, m), 2.85 (3H, s), 2.73-2.62 (2H, m), 2.26 (1H, br s), 1.97-1.92 (1H, m), 1.81-1.74 (3H, m), 1.53-1.47 (1H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 156.22, 155.79, 148.49, 147.86, 146.76, 144.71, 142.02, 138.00, 130.88, 130.68, 129.07, 129.03, 128.42, 128.35, 128.20, 127.69, 126.83, 126.68, 126.59, 123.70, 123.46, 119.81, 117.56, 114.06, 81.94, 71.49, 60.75, 57.04, 43.03, 40.12, 27.93, 27.77, 22.95, 18.94; *m/z* HRMS (DART) found $[M+H]^+$ 526.2885, $C_{36}H_{36}N_3O^+$ requires 526.2858.

13. Thermochemical Data and Absolute Energy Values

To compare Gibbs free energies along the reaction coordinate, a correction for the change in standard state from gas phase at 1 atm to a 1 M solution was applied to all species ($G_{corr}^{1M} = RT \cdot \ln(\frac{V_o}{V})$ = +2.36 kcal/mol). For V_0, we considered the molar volume of an ideal gas at 353.15 K to be 28.98 l mol^{-1}.

Table S12. Thermochemical data including absolute energies, zero-point energies (ZPE), T·S and Gibbs free energies along the reaction pathway from **Int-III** at the ωB97X-D/6-31+G(d) level. All values include quasi-harmonic corrections.

System	E (hartree)	ZPE (hartree)	T·S (hartree)	G (hartree)
[Int-III]-Py,OMe,ax-a	-1414.803437	0.390381	0.095766	-1414.475791
[Int-III]-Py,OMe,ax-b	-1414.802529	0.389765	0.096565	-1414.476040
[Int-III]-Py,Py,ax-a	-1414.788634	0.390262	0.095984	-1414.461209
[Int-III]-Ph,OMe,ax-a	-1414.801268	0.390497	0.095671	-1414.473414
[Int-III]-Ph,OMe,ax-b	-1414.800387	0.390040	0.095921	-1414.473112
[Int-III]-Py,Ph,ax-a	-1414.786059	0.390239	0.096125	-1414.458766
[Int-III]-Ph,Ph,ax-a	-1414.781281	0.389897	0.096750	-1414.454850
[TS-I]-Py,OMe,ax-a	-1414.752347	0.388220	0.095681	-1414.426872
[TS-I]-Ph,OMe,ax-a	-1414.741220	0.388277	0.095699	-1414.415713
[TS-I]-Py,Ph,ax-a	-1414.747257	0.387285	0.097162	-1414.423702
[Int-IV]-Py,Ph,ax-a	-1414.794151	0.389786	0.096332	-1414.467431
[TS-II]-Py,Ph,ax-a	-1414.793916	0.388976	0.095692	-1414.467943
[Int-V]-Py,OMe,ax-a	-1414.859381	0.389933	0.098695	-1414.534274
[Int-V]-Py,OMe,ax-b	-1414.858316	0.389556	0.099600	-1414.534274
[Int-V]-Ph,OMe,ax-a	-1414.859671	0.389243	0.100234	-1414.536442
[Int-V]-Ph,OMe,ax-b	-1414.858745	0.389953	0.098822	-1414.533744
[Int-V]-Py,Ph,ax-a	-1414.860239	0.389670	0.099092	-1414.535600
BiPy	-495.239050	0.160415	0.054965	-495.120680
Phosph-Ph,Ph,OMe	-919.605000	0.227880	0.070212	-919.427423
PhPy	-479.205617	0.172111	0.055245	-479.075605
Phosph-Py,Ph,OMe	-935.639914	0.216869	0.068537	-935.472293

Table S13. Absolute energies and Gibbs free energies along the reaction pathway from **Int-III** at the DLPNO-CCSD(T)/cc-pV(DT)Z//ωB97X-D/6-31+G(d) level. All values include quasi-harmonic corrections.

System	E (hartree)	G (hartree)	G_{rel} (kcal/mol)
[Int-III]-Py,OMe,ax-a	-1413.318548	-1412.990902	0.1
[Int-III]-Py,OMe,ax-b	-1413.317477	-1412.990987	0.0
[Int-III]-Py,Py,ax-a	-1413.306330	-1412.978904	7.6
[Int-III]-Ph,OMe,ax-a	-1413.315975	-1412.988121	1.8
[Int-III]-Ph,OMe,ax-b	-1413.315659	-1412.988383	1.6
[Int-III]-Py,Ph,ax-a	-1413.304320	-1412.977027	8.8
[Int-III]-Ph,Ph,ax-a	-1413.300163	-1412.973731	10.8
[TS-I]-Py,OMe,ax-a	-1413.267942	-1412.942467	30.4
[TS-I]-Ph,OMe,ax-a	-1413.257852	-1412.932345	36.8
[TS-I]-Py,Ph,ax-a	-1413.263204	-1412.939650	32.2
[Int-IV]-Py,Ph,ax-a	-1413.305916	-1412.979196	7.4
[TS-II]-Py,Ph,ax-a	-1413.304702	-1412.978730	7.7
[Int-V]-Py,OMe,ax-a	-1413.366873	-1413.041765	-31.9
[Int-V]-Py,OMe,ax-b	-1413.365225	-1413.041183	-31.5
[Int-V]-Ph,OMe,ax-a	-1413.366836	-1413.043607	-33.0
[Int-V]-Ph,OMe,ax-b	-1413.365545	-1413.040544	-31.1
[Int-V]-Py,Ph,ax-a	-1413.367564	-1413.042925	-32.6
BiPy	-494.727418	-494.609049	-
Phosph-Ph,Ph,OMe	-918.625005	-918.447428	-
BiPy + **Phosph-Ph,Ph,OMe**	-1413.352423	-1413.056477	-38.7 (G_{corr}^{1M} included)
PhPy	-478.692700	-478.562689	-
Phosph-Py,Ph,OMe	-934.660342	-934.492721	-
PhPy + **Phosph-Py,Ph,OMe**	-1413.353042	-1413.05541	-38.1 (G_{corr}^{1M} included)

Table S14. Absolute energies and Gibbs free energies along the reaction pathway from **Int-III** at the ωB97X-D/def2-QZVPP//ωB97X-D/6-31+G(d) level. All values include quasi-harmonic corrections.

System	E (hartree)	G (hartree)	G_{rel} (kcal/mol)
[Int-III]-Py,OMe,ax-a	-1415.256868	-1414.929222	0.1
[Int-III]-Py,OMe,ax-b	-1415.255945	-1414.929455	0.0
[Int-III]-Py,Py,ax-a	-1415.244831	-1414.917405	7.6
[Int-III]-Ph,OMe,ax-a	-1415.254623	-1414.926769	1.7
[Int-III]-Ph,OMe,ax-b	-1415.253758	-1414.926482	1.9
[Int-III]-Py,Ph,ax-a	-1415.242494	-1414.915201	8.9
[Int-III]-Ph,Ph,ax-a	-1415.237355	-1414.910923	11.6
[TS-I]-Py,OMe,ax-a	-1415.209182	-1414.883708	28.7
[TS-I]-Ph,OMe,ax-a	-1415.198305	-1414.872798	35.6
[TS-I]-Py,Ph,ax-a	-1415.205324	-1414.881770	29.9
[Int-IV]-Py,Ph,ax-a	-1415.248970	-1414.922253	4.5
[TS-II]-Py,Ph,ax-a	-1415.247531	-1414.921559	5.0
[Int-V]-Py,OMe,ax-a	-1415.309483	-1414.984375	-34.5
[Int-V]-Py,OMe,ax-b	-1415.308302	-1414.984260	-34.4
[Int-V]-Ph,OMe,ax-a	-1415.309784	-1414.986554	-35.8
[Int-V]-Ph,OMe,ax-b	-1415.308775	-1414.983775	-34.1
[Int-V]-Py,Ph,ax-a	-1415.309791	-1414.985151	-34.9
BiPy	-495.422409	-495.304039	-
Phosph-Ph,Ph,OMe	-919.872786	-919.695209	-
BiPy + **Phosph-Ph,Ph,OMe**	-1415.295195	-1414.999248	-41.4 (G^{1M}_{corr} included)
PhPy	-479.383436	-479.253424	-
Phosph-Py,Ph,OMe	-935.913465	-935.745844	-
PhPy + **Phosph-Py,Ph,OMe**	-1415.296901	-1414.999268	-41.4 (G^{1M}_{corr} included)

Table S15. Thermochemical data including absolute energies, zero-point energies (ZPE), T·S and Gibbs free energies along the reaction pathway from **[Int-III·H]$^+$** at the ωB97X-D/6-31+G(d) level. All values include quasi-harmonic corrections.

System	E (hartree)	ZPE (hartree)	T·S (hartree)	G (hartree)
[Int-III·H]$^+$-PyH$^+$,OMe,ax-a	-1415.262121	0.404638	0.095855	-1414.920109
[Int-III·H]$^+$-PyH$^+$,OMe,ax-b	-1415.263469	0.404777	0.095922	-1414.921433
[Int-III·H]$^+$-Py,OMe,ax-a	-1415.260058	0.404555	0.096047	-1414.918301
[Int-III·H]$^+$-Py,OMe,ax-b	-1415.255477	0.404475	0.095756	-1414.913564
[Int-III·H]$^+$-Py,OMe,ax-c	-1415.257792	0.405108	0.095342	-1414.914975
[Int-III·H]$^+$-Py,PyH$^+$,ax-a	-1415.248032	0.404674	0.095901	-1414.906052
[Int-III·H]$^+$-Py,PyH$^+$,ax-b	-1415.249944	0.404386	0.096363	-1414.908535
[Int-III·H]$^+$-Ph,OMe,ax-a	-1415.255391	0.404550	0.095345	-1414.913106
[Int-III·H]$^+$-PyH$^+$,Ph,ax-a	-1415.247341	0.404111	0.096617	-1414.906360
[Int-III·H]$^+$-PyH$^+$,Ph,ax-b	-1415.246798	0.403983	0.096930	-1414.906200
[Int-III·H]$^+$-Ph,Ph,ax-a	-1415.237385	0.403956	0.097217	-1414.897084
[TS-I·H]$^+$-Py,OMe,ax-a	-1415.229298	0.402314	0.095970	-1414.889798
[TS-I·H]$^+$-Ph,OMe,ax-a	-1415.218953	0.403480	0.094704	-1414.877465
[TS-I·H]$^+$-Py,Ph,ax-a	-1415.220149	0.402099	0.096364	-1414.881090
[Int-IV·H]$^+$-Py,OMe,ax-a*	-1415.288257	0.404398	0.096500	-1414.946932
[Int-IV·H]$^+$-Py,OMe,ax-b	-1415.291214	0.404355	0.096727	-1414.950053
[Int-IV·H]$^+$-Ph,OMe,ax-a	-1415.282840	0.404072	0.096590	-1414.941851
[Int-IV·H]$^+$-Ph,OMe,ax-b	-1415.285992	0.404052	0.097358	-1414.945697
[Int-IV·H]$^+$-Py,Ph,ax-a	-1415.288417	0.403684	0.097399	-1414.948300
[TS-II·H]$^+$-Py,OMe,ax-a	-1415.282237	0.403121	0.096600	-1414.942537
[TS-II·H]$^+$-Ph,OMe,ax-a	-1415.279125	0.402521	0.097169	-1414.940420
[TS-II·H]$^+$-Py,Ph,ax-a	-1415.279596	0.403239	0.095948	-1414.939287
[Int-V·H]$^+$-Py,OMe,ax-a*	-1415.314386	0.403894	0.100227	-1414.976601
[Int-V·H]$^+$-Ph,OMe,ax-a	-1415.314710	0.404168	0.099293	-1414.975817
[Int-V·H]$^+$-Py,Ph,ax-a*	-1415.315627	0.403783	0.099682	-1414.977268
[BiPy·H]$^+$	-495.693964	0.174416	0.055238	-495.561679
Phosph-Ph,Ph,OMe	-919.605000	0.227880	0.070212	-919.427423
[PhPy·H]$^+$	-479.662889	0.186174	0.055538	-479.518906
Phosph-Py,Ph,OMe	-935.639914	0.216869	0.068537	-935.472293

*These systems showed $\nu_i < 35$ cm^{-1}. These imaginary frequencies were inverted to their respective positive values before the QHA entropic corrections were computed as seen in previous examples. (*97*)

Table S16. Absolute energies and Gibbs free energies along the reaction pathway from **[Int-III·H]+** at the DLPNO-CCSD(T)/cc-pV(DT)Z//ωB97X-D/6-31+G(d) level. All values include quasi-harmonic corrections.

System	E (hartree)	G (hartree)	G_{rel} (kcal/mol)
[Int-III·H]$^+$-PyH$^+$,OMe,ax-a	-1413.776342	-1413.434331	0.6
[Int-III·H]$^+$-PyH$^+$,OMe,ax-b	-1413.777378	-1413.435342	0.0
[Int-III·H]$^+$-Py,OMe,ax-a	-1413.774234	-1413.432478	1.8
[Int-III·H]$^+$-Py,OMe,ax-b	-1413.769657	-1413.427744	4.8
[Int-III·H]$^+$-Py,OMe,ax-c	-1413.771195	-1413.428379	4.4
[Int-III·H]$^+$-Py,PyH$^+$,ax-a	-1413.764070	-1413.422091	8.3
[Int-III·H]$^+$-Py,PyH$^+$,ax-b	-1413.767048	-1413.425639	6.1
[Int-III·H]$^+$-Ph,OMe,ax-a	-1413.768895	-1413.426609	5.5
[Int-III·H]$^+$-PyH$^+$,Ph,ax-a	-1413.764661	-1413.423680	7.3
[Int-III·H]$^+$-PyH$^+$,Ph,ax-b	-1413.764384	-1413.423786	7.3
[Int-III·H]$^+$-Ph,Ph,ax-a	-1413.754571	-1413.414270	13.2
[TS-I·H]$^+$-Py,OMe,ax-a	-1413.743709	-1413.404209	19.5
[TS-I·H]$^+$-Ph,OMe,ax-a	-1413.734467	-1413.392979	26.6
[TS-I·H]$^+$-Py,Ph,ax-a	-1413.734881	-1413.395823	24.8
[Int-IV·H]$^+$-Py,OMe,ax-a*	-1413.799816	-1413.458491	-14.5
[Int-IV·H]$^+$-Py,OMe,ax-b	-1413.802370	-1413.461209	-16.2
[Int-IV·H]$^+$-Ph,OMe,ax-a	-1413.795050	-1413.454061	-11.7
[Int-IV·H]$^+$-Ph,OMe,ax-b	-1413.797667	-1413.457372	-13.8
[Int-IV·H]$^+$-Py,Ph,ax-a	-1413.800840	-1413.460723	-15.9
[TS-II·H]$^+$-Py,OMe,ax-a	-1413.789622	-1413.449922	-9.1
[TS-II·H]$^+$-Ph,OMe,ax-a	-1413.786764	-1413.448059	-8.0
[TS-II·H]$^+$-Py,Ph,ax-a	-1413.786334	-1413.446025	-6.7
[Int-V·H]$^+$-Py,OMe,ax-a*	-1413.821310	-1413.483525	-30.2
[Int-V·H]$^+$-Ph,OMe,ax-a	-1413.820113	-1413.481220	-28.8
[Int-V·H]$^+$-Py,Ph,ax-a*	-1413.822152	-1413.483793	-30.4
[BiPy·H]$^+$	-495.182152	-495.049867	-
Phosph-Ph,Ph,OMe	-918.625005	-918.447428	-
[BiPy·H]$^+$ + Phosph-Ph,Ph,OMe	-1413.807157	-1413.497295	-36.5 (G_{corr}^{1M} included)
[PhPy·H]$^+$	-479.149345	-479.005362	-
Phosph-Py,Ph,OMe	-934.660342	-934.492721	-
[PhPy·H]$^+$ + Phosph-Py,Ph,OMe	-1413.809687	-1413.498083	-37.0 (G_{corr}^{1M} included)

*These systems showed ν_i < 35 cm^{-1}. These imaginary frequencies were inverted to their respective positive values before the QHA entropic corrections were computed as seen in previous examples (*97*).

Table S17. Absolute energies and Gibbs free energies along the reaction pathway from **[Int-III·H]+** at at the ωB97X-D/def2-QZVPP//ωB97X-D/6-31+G(d) level. All values include quasi-harmonic corrections.

System	E (hartree)	G (hartree)	G_{rel} (kcal/mol)
[Int-III·H]$^+$-PyH$^+$,OMe,ax-a	-1415.720913	-1415.378902	0.8
[Int-III·H]$^+$-PyH$^+$,OMe,ax-b	-1415.722258	-1415.380222	0.0
[Int-III·H]$^+$-Py,OMe,ax-a	-1415.718735	-1415.376979	2.0
[Int-III·H]$^+$-Py,OMe,ax-b	-1415.714218	-1415.372305	5.0
[Int-III·H]$^+$-Py,OMe,ax-c	-1415.716455	-1415.373639	4.1
[Int-III·H]$^+$-Py,PyH$^+$,ax-a	-1415.709362	-1415.367383	8.1
[Int-III·H]$^+$-Py,PyH$^+$,ax-b	-1415.711284	-1415.369875	6.5
[Int-III·H]$^+$-Ph,OMe,ax-a	-1415.714124	-1415.371838	5.3
[Int-III·H]$^+$-PyH$^+$,Ph,ax-a	-1415.708852	-1415.367871	7.8
[Int-III·H]$^+$-PyH$^+$,Ph,ax-b	-1415.708315	-1415.367717	7.8
[Int-III·H]$^+$-Ph,Ph,ax-a	-1415.699327	-1415.359026	13.3
[TS-I·H]$^+$-Py,OMe,ax-a	-1415.691404	-1415.351903	17.8
[TS-I·H]$^+$-Ph,OMe,ax-a	-1415.681360	-1415.339872	25.3
[TS-I·H]$^+$-Py,Ph,ax-a	-1415.683835	-1415.344777	22.2
[Int-IV·H]$^+$-Py,OMe,ax-a*	-1415.749250	-1415.407922	-17.4
[Int-IV·H]$^+$-Py,OMe,ax-b	-1415.752260	-1415.411095	-19.4
[Int-IV·H]$^+$-Ph,OMe,ax-a	-1415.743890	-1415.402903	-14.2
[Int-IV·H]$^+$-Ph,OMe,ax-b	-1415.747130	-1415.406836	-16.7
[Int-IV·H]$^+$-Py,Ph,ax-a	-1415.749470	-1415.409353	-18.3
[TS-II·H]$^+$-Py,OMe,ax-a	-1415.739550	-1415.399850	-12.3
[TS-II·H]$^+$-Ph,OMe,ax-a	-1415.736760	-1415.398055	-11.2
[TS-II·H]$^+$-Py,Ph,ax-a	-1415.736814	-1415.396505	-10.2
[Int-V·H]$^+$-Py,OMe,ax-a*	-1415.769264	-1415.431479	-32.2
[Int-V·H]$^+$-Ph,OMe,ax-a	-1415.769772	-1415.430879	-31.8
[Int-V·H]$^+$-Py,Ph,ax-a*	-1415.770107	-1415.431748	-32.3
[BiPy·H]$^+$	-495.882458	-495.750173	-
Phosph-Ph,Ph,OMe	-919.872786	-919.695209	-
[BiPy·H]$^+$ + Phosph-Ph,Ph,OMe	-1415.755244	-1415.445382	-38.5 (G^{1M}_{corr} included)
[PhPy·H]$^+$	-479.845825	-479.701842	-
Phosph-Py,Ph,OMe	-935.913465	-935.745844	-
[PhPy·H]$^+$ + Phosph-Py,Ph,OMe	-1415.75929	-1415.447686	-40.0 (G^{1M}_{corr} included)

*These systems showed ν_i < 35 cm^{-1}. These imaginary frequencies were inverted to their respective positive values before the QHA entropic corrections were computed as seen in previous examples (*97*).

Table S18. Thermochemical data including absolute energies, zero-point energies (ZPE), T·S and Gibbs free energies along the reaction pathway from **[Int-III·2H]$^{2+}$** at the ωB97X-D/6-31+G(d) level. All values include quasi-harmonic corrections.

System	E (hartree)	ZPE (hartree)	T·S (hartree)	G (hartree)
[Int-III·2H]$^{2+}$-PyH^{+},OMe,ax-a	-1415.715045	0.419114	0.096169	-1415.358797
[Int-III·2H]$^{2+}$-PyH^{+},OMe,ax-b	-1415.711031	0.419045	0.095727	-1415.354450
[Int-III·2H]$^{2+}$-PyH^{+},OMe,ax-c	-1415.713255	0.418916	0.096062	-1415.357040
[Int-III·2H]$^{2+}$-PyH^{+},PyH^{+},ax-a	-1415.706212	0.419258	0.095755	-1415.349458
[Int-III·2H]$^{2+}$-Ph,OMe,ax-a	-1415.708399	0.419425	0.095324	-1415.351204
[Int-III·2H]$^{2+}$-Ph,OMe,ax-b	-1415.706755	0.419581	0.095533	-1415.349573
[Int-III·2H]$^{2+}$-PyH^{+},Ph,ax-a	-1415.698106	0.418680	0.096493	-1415.342438
[Int-III·2H]$^{2+}$-PyH^{+},Ph,ax-b	-1415.697383	0.418818	0.096644	-1415.341718
[Int-III·2H]$^{2+}$-Ph,Ph,ax-a	-1415.689310	0.418363	0.097117	-1415.334496
[TS-I·2H]$^{2+}$-PyH^{+},OMe,ax-a	-1415.682140	0.417530	0.095393	-1415.326982
[TS-I·2H]$^{2+}$-PyH^{+},OMe,ax-b	-1415.686916	0.417186	0.096003	-1415.332533
[TS-I·2H]$^{2+}$-Ph,OMe,ax-a	-1415.670386	0.417010	0.095543	-1415.315861
[TS-I·2H]$^{2+}$-PyH^{+},Ph,ax-a	-1415.681170	0.416331	0.097009	-1415.328257
[TS-I·2H]$^{2+}$-Ph,Ph,ax-a	-1415.661334	0.416101	0.096741	-1415.308530
[Int-IV·2H]$^{2+}$-PyH^{+},OMe,ax-a	-1415.739754	0.418595	0.097298	-1415.384856
[Int-IV·2H]$^{2+}$-PyH^{+},OMe,ax-b	-1415.742543	0.418177	0.095240	-1415.386770
[Int-IV·2H]$^{2+}$-Ph,OMe,ax-a	-1415.730395	0.418574	0.096589	-1415.374822
[Int-IV·2H]$^{2+}$-PyH^{+},Ph,ax-a	-1415.740873	0.418274	0.098334	-1415.387006
[TS-II·2H]$^{2+}$-PyH^{+},OMe,ax-a	-1415.734212	0.417525	0.096379	-1415.379855
[TS-II·2H]$^{2+}$-Ph,OMe,ax-a	-1415.727262	0.417335	0.095933	-1415.372721
[TS-II·2H]$^{2+}$-PyH^{+},Ph,ax-a	-1415.731725	0.418091	0.095632	-1415.376324
[Int-V·2H]$^{2+}$-PyH^{+},OMe,ax-a	-1415.765251	0.418693	0.099081	-1415.411556
[Int-V·2H]$^{2+}$-Ph,OMe,ax-a	-1415.767800	0.418564	0.098581	-1415.413736
[Int-V·2H]$^{2+}$-PyH^{+},Ph,ax-a	-1415.766283	0.417841	0.099483	-1415.41356
[BiPy·2H]$^{2+}$	-496.142980	0.188377	0.055558	-495.996855
Phosph-Ph,Ph,OMe	-919.605000	0.227880	0.070212	-919.427423
[PhPy·H]$^{+}$	-479.662889	0.186174	0.055538	-479.518906
Phosph-PyH^{+},Ph,OMe	-936.091213	0.230776	0.069174	-935.910036

Table S19. Absolute energies and Gibbs free energies along the reaction pathway from **[Int-III·2H]$^{2+}$** at the DLPNO-CCSD(T)/cc-pV(DT)Z//ωB97X-D/6-31+G(d) level. All values include quasi-harmonic corrections.

System	E (hartree)	G (hartree)	G_{rel} (kcal/mol)
[Int-III·2H]$^{2+}$-PyH^{+},OMe,ax-a	-1414.223227	-1413.866979	0.0
[Int-III·2H]$^{2+}$-PyH^{+},OMe,ax-b	-1414.223209	-1413.866629	0.2
[Int-III·2H]$^{2+}$-PyH^{+},OMe,ax-c	-1414.211964	-1413.855749	7.0
[Int-III·2H]$^{2+}$-PyH^{+},PyH^{+},ax-a	-1414.220429	-1413.863674	2.1
[Int-III·2H]$^{2+}$-Ph,OMe,ax-a	-1414.219198	-1413.862003	3.1
[Int-III·2H]$^{2+}$-Ph,OMe,ax-b	-1414.218356	-1413.861174	3.6
[Int-III·2H]$^{2+}$-PyH^{+},Ph,ax-a	-1414.213688	-1413.858020	5.6
[Int-III·2H]$^{2+}$-PyH^{+},Ph,ax-b	-1414.212305	-1413.856639	6.5
[Int-III·2H]$^{2+}$-Ph,Ph,ax-a	-1414.203378	-1413.848565	11.6
[TS-I·2H]$^{2+}$-PyH^{+},OMe,ax-a	-1414.194715	-1413.839557	17.2
[TS-I·2H]$^{2+}$-PyH^{+},OMe,ax-b	-1414.199208	-1413.844825	13.9
[TS-I·2H]$^{2+}$-Ph,OMe,ax-a	-1414.181410	-1413.826885	25.2
[TS-I·2H]$^{2+}$-PyH^{+},Ph,ax-a	-1414.192702	-1413.839788	17.1
[TS-I·2H]$^{2+}$-Ph,Ph,ax-a	-1414.173224	-1413.820421	29.2
[Int-IV·2H]$^{2+}$-PyH^{+},OMe,ax-a	-1414.248486	-1413.893588	-16.7
[Int-IV·2H]$^{2+}$-PyH^{+},OMe,ax-b	-1414.251141	-1413.895368	-17.8
[Int-IV·2H]$^{2+}$-Ph,OMe,ax-a	-1414.238513	-1413.882940	-10.0
[Int-IV·2H]$^{2+}$-PyH^{+},Ph,ax-a	-1414.250426	-1413.896559	-18.6
[TS-II·2H]$^{2+}$-PyH^{+},OMe,ax-a	-1414.238504	-1413.884147	-10.8
[TS-II·2H]$^{2+}$-Ph,OMe,ax-a	-1414.231879	-1413.877338	-6.5
[TS-II·2H]$^{2+}$-PyH^{+},Ph,ax-a	-1414.235758	-1413.880357	-8.4
[Int-V·2H]$^{2+}$-PyH^{+},OMe,ax-a	-1414.269254	-1413.915559	-30.5
[Int-V·2H]$^{2+}$-Ph,OMe,ax-a	-1414.272460	-1413.918397	-32.3
[Int-V·2H]$^{2+}$-PyH^{+},Ph,ax-a	-1414.270115	-1413.917392	-31.6
[BiPy·2H]$^{2+}$	-495.630016	-495.483890	-
Phosph-Ph,Ph,OMe	-918.625005	-918.447428	-
[BiPy·2H]$^{2+}$ + Phosph-Ph,Ph,OMe	-1414.255021	-1413.931318	-38.0
[PhPy·H]$^{+}$	-479.149345	-479.005362	-
Phosph-PyH^{+},Ph,OMe	-935.111488	-934.930311	-
[PhPy·H]$^{+}$ + Phosph-PyH^{+},Ph,OMe	-1414.260833	-1413.935673	-40.7

Table S20. Absolute energies and Gibbs free energies along the reaction pathway from **[Int-III·2H]$^{2+}$** at the ωB97X-D/def2-QZVPP//ωB97X-D/6-31+G(d) level. All values include quasi-harmonic corrections.

System	E (hartree)	G (hartree)	G_{rel} (kcal/mol)
[Int-III·2H]$^{2+}$-PyH^{+},OMe,ax-a	-1416.178948	-1415.822700	0.0
[Int-III·2H]$^{2+}$-PyH^{+},OMe,ax-b	-1416.175069	-1415.818489	2.6
[Int-III·2H]$^{2+}$-PyH^{+},OMe,ax-c	-1416.177246	-1415.821031	1.0
[Int-III·2H]$^{2+}$-PyH^{+},PyH^{+},ax-a	-1416.172628	-1415.815873	4.3
[Int-III·2H]$^{2+}$-Ph,OMe,ax-a	-1416.172269	-1415.815074	4.8
[Int-III·2H]$^{2+}$-Ph,OMe,ax-b	-1416.170770	-1415.813588	5.7
[Int-III·2H]$^{2+}$-PyH^{+},Ph,ax-a	-1416.164642	-1415.808974	8.6
[Int-III·2H]$^{2+}$-PyH^{+},Ph,ax-b	-1416.163978	-1415.808312	9.0
[Int-III·2H]$^{2+}$-Ph,Ph,ax-a	-1416.156198	-1415.801385	13.4
[TS-I·2H]$^{2+}$-PyH^{+},OMe,ax-a	-1416.149376	-1415.794218	17.9
[TS-I·2H]$^{2+}$-PyH^{+},OMe,ax-b	-1416.154105	-1415.799722	14.4
[TS-I·2H]$^{2+}$-Ph,OMe,ax-a	-1416.137733	-1415.783208	24.8
[TS-I·2H]$^{2+}$-PyH^{+},Ph,ax-a	-1416.149430	-1415.796516	16.4
[TS-I·2H]$^{2+}$-Ph,Ph,ax-a	-1416.130386	-1415.777583	28.3
[Int-IV·2H]$^{2+}$-PyH^{+},OMe,ax-a	-1416.205900	-1415.851003	-17.8
[Int-IV·2H]$^{2+}$-PyH^{+},OMe,ax-b	-1416.208740	-1415.852962	-19.0
[Int-IV·2H]$^{2+}$-Ph,OMe,ax-a	-1416.196260	-1415.840681	-11.3
[Int-IV·2H]$^{2+}$-PyH^{+},Ph,ax-a	-1416.207000	-1415.853131	-19.1
[TS-II·2H]$^{2+}$-PyH^{+},OMe,ax-a	-1416.196888	-1415.842531	-12.4
[TS-II·2H]$^{2+}$-Ph,OMe,ax-a	-1416.190437	-1415.835897	-8.3
[TS-II·2H]$^{2+}$-PyH^{+},Ph,ax-a	-1416.194030	-1415.838630	-10.0
[Int-V·2H]$^{2+}$-PyH^{+},OMe,ax-a	-1416.224969	-1415.871275	-30.5
[Int-V·2H]$^{2+}$-Ph,OMe,ax-a	-1416.227757	-1415.873694	-32.0
[Int-V·2H]$^{2+}$-PyH^{+},Ph,ax-a	-1416.225502	-1415.872779	-31.4
[BiPy·2H]$^{2+}$	-496.336457	-496.190331	-
Phosph-Ph,Ph,OMe	-919.872786	-919.695209	-
[BiPy·2H]$^{2+}$ + Phosph-Ph,Ph,OMe	-1416.209243	-1415.88554	-37.1
[PhPy·H]$^{+}$	-479.845825	-479.701842	-
Phosph-PyH^{+},Ph,OMe	-936.369964	-936.188787	-
[PhPy·H]$^{+}$ + Phosph-PyH^{+},Ph,OMe	-1416.215789	-1415.890629	-40.3

Table S21. Thermochemical data including absolute energies, zero-point energies (ZPE), T·S and Gibbs free energies of MeO-Py couplings in **[TS-I·2H]$^{2+}$** at the ωB97X-D/6-31+G(d) level. All values include quasi-harmonic corrections.

System	E (hartree)	ZPE (hartree)	T·S (hartree)	G (hartree)
[TS-I·2H]$^{2+}$-Ph,OMe,ax-MeOPyH^{+}	-1415.689234	0.416703	0.096262	-1415.335433
[TS-I·2H]$^{2+}$-PyH^{+},OMe,ax-MeOPyH^{+}	-1415.690099	0.416664	0.096017	-1415.336133

Table S22. Absolute energies and Gibbs free energies of MeO-Py couplings in **[TS-I·2H]$^{2+}$** at the DLPNO-CCSD(T)/cc-pV(DT)Z//ωB97X-D/6-31+G(d) level. All values include quasi-harmonic corrections.

System	E (hartree)	G (hartree)	G_{rel} (kcal/mol)
[TS-I·2H]$^{2+}$-Ph,OMe,ax-MeOPyH^{+}	-1414.191043	-1413.837243	18.7
[TS-I·2H]$^{2+}$-PyH^{+},OMe,ax-MeOPyH^{+}	-1414.192949	-1413.838983	17.6

14. Cartesian Coordinates

Pathway Int-III

[Int-III]-Ph,OMe,ax-a

C	2.315747	-3.417517	-1.115310
C	1.440619	-2.344070	-1.268153
C	1.282964	-1.401310	-0.245374
C	2.040581	-1.546387	0.923994
C	2.944378	-2.596978	1.060555
H	2.409980	-4.148771	-1.913493
H	0.889607	-2.238012	-2.195396
H	1.929633	-0.842839	1.743166
H	3.535904	-2.679936	1.968110
P	0.103553	0.015200	-0.425152
C	0.797043	1.718886	-0.282781
C	0.131824	2.804624	-0.852873
C	2.014516	1.961707	0.350028
C	0.693003	4.071806	-0.738183
H	-0.804460	2.684519	-1.388656
C	2.502326	3.264709	0.392182
H	2.591944	1.166153	0.809297
H	0.181518	4.931944	-1.163249
H	3.455038	3.470747	0.874086
C	-0.463581	-0.078578	1.423789
C	-0.497817	1.000784	2.310738
C	-0.981181	-1.303552	1.876946
C	-1.014133	0.863610	3.604123
H	-0.127338	1.977097	2.012236
C	-1.495534	-1.450693	3.160581
H	-0.983283	-2.168409	1.214802
C	-1.512602	-0.361156	4.035118
H	-1.024238	1.722849	4.270440

H	-1.884624	-2.414332	3.480248
H	-1.913300	-0.469674	5.039681
C	3.075982	-3.543191	0.045612
H	3.768879	-4.372712	0.158371
O	0.392176	0.098425	-2.197727
C	-1.662043	-0.231739	-0.940527
C	-2.063466	-1.332623	-1.696403
C	-2.648482	0.666434	-0.530024
C	-3.413772	-1.486498	-1.996127
H	-1.356386	-2.073861	-2.050402
C	-3.966569	0.441733	-0.911939
H	-2.415883	1.530015	0.085700
H	-3.745620	-2.349535	-2.568472
H	-4.743073	1.143719	-0.617917
N	-4.362260	-0.618230	-1.626882
C	1.656341	0.420409	-2.738894
H	1.772961	-0.113523	-3.689780
H	1.739225	1.499483	-2.932265
H	2.489239	0.127041	-2.084061
N	1.860360	4.315399	-0.129664

[Int-III]-Ph,OMe,ax-b

C	-1.655786	-1.441348	3.080806
C	-1.098831	-1.296519	1.814272
C	-0.475761	-0.103184	1.412843
C	-0.450491	0.949062	2.332521
C	-1.008312	0.814050	3.608292
H	-2.127844	-2.380288	3.359672
H	-1.157082	-2.137873	1.124791
H	-0.000212	1.901642	2.069296
H	-0.970091	1.651461	4.300905
P	0.120136	0.027334	-0.425527
C	1.138544	-1.529096	-0.286793
C	1.878955	-1.807940	0.863866
C	1.192470	-2.463300	-1.321805
C	2.639809	-2.971409	0.918334
H	1.870630	-1.148047	1.724577
C	1.951826	-3.618189	-1.156129
H	0.664387	-2.302764	-2.253906
H	3.237631	-3.186928	1.800369
H	1.983162	-4.363592	-1.947033
C	0.987554	1.635847	-0.220801
C	2.158091	1.739137	0.534123
C	0.484804	2.771196	-0.864056
C	2.815069	2.963359	0.648655
H	2.570951	0.872376	1.040904
C	1.127552	3.999458	-0.725633
H	-0.405080	2.705119	-1.483666
C	2.296194	4.098366	0.028596
H	3.730940	3.027050	1.229856
H	0.718957	4.877014	-1.219294
H	2.803032	5.054435	0.127446
C	-1.610189	-0.380997	3.988982
H	-2.043574	-0.487888	4.980060
O	0.430132	0.088733	-2.193216

C	-1.658472	0.000818	-0.951131
C	-2.191942	-1.040811	-1.709197
C	-2.525386	1.015258	-0.541136
C	-3.550227	-1.024406	-2.012076
H	-1.581141	-1.864182	-2.061816
C	-3.860392	0.956158	-0.925145
H	-2.186980	1.843228	0.074691
H	-3.986035	-1.838245	-2.586749
H	-4.543890	1.749284	-0.631866
N	-4.383741	-0.045276	-1.642895
C	1.727756	0.291944	-2.712007
H	1.817456	-0.263891	-3.653357
H	1.907392	1.356986	-2.915165
H	2.520193	-0.061484	-2.036480
N	2.677613	-3.878727	-0.063806

[Int-III]-Ph,Ph,ax-a

C	-1.325289	2.897121	-2.172103
C	-1.079356	1.648364	-1.600273
C	-0.342619	1.579541	-0.408380
C	0.069193	2.783977	0.177633
C	-0.263150	3.990160	-0.443030
H	-1.867526	2.967350	-3.113062
H	-1.474196	0.759171	-2.082365
H	0.641302	2.798450	1.101338
H	0.030308	4.935309	0.009900
P	0.003468	-0.023882	0.494490
C	-1.902143	-0.387529	0.462558
C	-2.758176	0.562795	1.043801
C	-2.493089	-1.502361	-0.138098
C	-4.140452	0.409184	1.027844
H	-2.339461	1.448046	1.520692
C	-3.882867	-1.663660	-0.163989
H	-1.883761	-2.273826	-0.599098
H	-4.773883	1.163875	1.487770
H	-4.311300	-2.541174	-0.642329
C	1.900688	0.407138	0.623832
C	2.539569	0.869463	-0.538400
C	2.708199	0.164917	1.742288
C	3.914166	1.090012	-0.583801
H	1.961354	1.065101	-1.439229
C	4.088382	0.384755	1.707040
H	2.262843	-0.202332	2.660279
H	4.372042	1.451504	-1.501462
H	4.684359	0.189787	2.595711
O	0.051777	-0.188779	2.140977
C	0.453284	-1.486926	-0.544166
C	0.521137	-1.491713	-1.939052
C	0.782749	-2.668201	0.130810
C	0.905934	-2.662872	-2.588892
H	0.290177	-0.612142	-2.529941
C	1.149742	-3.788849	-0.609577
H	0.759468	-2.731394	1.215578
H	0.967343	-2.683963	-3.674817
H	1.403067	-4.716703	-0.101381
C	-0.832750	-0.915831	2.996303
H	-0.222548	-1.226243	3.849056
H	-1.647490	-0.275937	3.345091
H	-1.246314	-1.801709	2.508785
N	-0.936907	4.063710	-1.611221
N	1.215094	-3.804475	-1.951239
C	4.698705	0.849253	0.544998
H	5.771685	1.021215	0.516144
C	-4.711770	-0.709953	0.417408
H	-5.791509	-0.833278	0.396867

[Int-III]-Py,OMe,ax-a

C	3.388156	-1.685919	-1.935969
C	2.045705	-1.417462	-1.672534
C	1.687543	-0.322439	-0.880950
C	2.692639	0.503716	-0.366074
C	4.031175	0.255015	-0.661335
H	3.652290	-2.550879	-2.538517
H	1.287341	-2.072969	-2.085863
H	2.442852	1.346589	0.272717
H	4.798172	0.917351	-0.269165
P	-0.080329	0.013633	-0.457375
C	0.394446	-0.076592	1.435516
C	0.859988	-1.299687	1.939423
C	0.398908	0.990748	2.333134
C	1.278549	-1.401477	3.257575
H	0.900258	-2.185954	1.309317
C	0.840519	0.798424	3.643547
H	0.072577	1.985349	2.045770
H	1.635996	-2.352057	3.647333
H	0.842880	1.633095	4.341794
C	-1.329126	-1.342776	-0.273929
C	-2.138215	-1.419188	0.866957
C	-1.488316	-2.309288	-1.274402
C	-3.090525	-2.426909	0.998667
H	-2.033685	-0.694143	1.668083
C	-2.413554	-3.340134	-1.124873
H	-0.901156	-2.254218	-2.183725
C	-3.222744	-3.398214	0.008110
H	-3.720377	-2.455967	1.883474
H	-2.508702	-4.090749	-1.904734
H	-3.954202	-4.194376	0.117605
C	4.383794	-0.846109	-1.440094
H	5.428948	-1.049979	-1.656692
O	-0.332988	0.079967	-2.226774
C	-0.686116	1.751566	-0.345319
C	-1.927993	2.061930	0.205941
C	0.076846	2.799303	-0.861463
C	-2.341858	3.390773	0.225332
H	-2.580800	1.299506	0.618262
C	-0.418539	4.096076	-0.777580
H	1.040163	2.627003	-1.331324
H	-3.311146	3.649690	0.644543
H	0.168216	4.926684	-1.162238
N	-1.607981	4.404453	-0.246114
C	-1.575096	0.442944	-2.792935
H	-1.621269	1.525029	-2.981440
H	-1.684747	-0.082209	-3.749329
H	-2.430840	0.170095	-2.159187
N	1.274977	-0.371159	4.118635

[Int-III]-Py,OMe,ax-b

C	-0.118078	4.150337	-0.720723
C	0.232478	2.807317	-0.840690
C	-0.566596	1.815648	-0.262973
C	-1.734352	2.183309	0.408878
C	-2.095811	3.526231	0.507584
H	0.517222	4.912137	-1.164358
H	1.127550	2.539109	-1.394991
H	-2.374612	1.432787	0.862093
H	-3.012024	3.797493	1.025025
P	-0.082297	0.053227	-0.458960
C	-1.422063	-1.241686	-0.349895
C	-1.625763	-2.165645	-1.375779
C	-2.263401	-1.328250	0.761198
C	-2.622764	-3.127021	-1.237361
H	-1.033877	-2.143299	-2.282602
C	-3.258509	-2.300226	0.788779
H	-2.161884	-0.663965	1.612573
H	-2.774225	-3.865911	-2.020361
H	-3.933012	-2.360433	1.639202
C	0.361578	-0.203724	1.427081
C	0.715347	-1.491104	1.856183
C	0.459660	0.803894	2.386502
C	1.118864	-1.707933	3.165497
H	0.682410	-2.339179	1.174912
C	0.877399	0.495585	3.682076
H	0.225605	1.838202	2.155279
H	1.389380	-2.708075	3.497054
H	0.951797	1.283493	4.428997
C	-1.284646	4.513370	-0.048414
H	-1.562744	5.560360	0.036581
O	-0.326214	0.176598	-2.223836
C	1.667254	-0.362958	-0.881840
C	2.703980	0.399708	-0.332653
C	1.981173	-1.451640	-1.699941
C	4.032342	0.093397	-0.618451
H	2.485736	1.237955	0.323743
C	3.312631	-1.777569	-1.955537
H	1.196976	-2.057292	-2.140523
H	4.825552	0.706658	-0.199444
H	3.542374	-2.636743	-2.580039
C	-1.538025	0.655988	-2.768245
H	-1.491300	1.740908	-2.937674
H	-1.705329	0.158103	-3.730923
H	-2.407987	0.450590	-2.127860
C	4.341207	-1.002029	-1.423849
H	5.378002	-1.250716	-1.633684
N	1.203272	-0.734803	4.086364
N	-3.441111	-3.201389	-0.182431

[Int-III]-Py,Ph,ax-a

C	0.136943	4.007863	-0.435808
C	0.330311	2.760870	0.156775
C	-0.239177	1.613440	-0.401705
C	-1.011447	1.733358	-1.562060
C	-1.167399	2.971767	-2.180235
H	0.570443	4.893654	0.020484
H	0.927356	2.690589	1.062548
H	-1.508423	0.865451	-1.985952
H	-1.748718	3.046095	-3.095308
P	-0.028219	-0.009151	0.479076
C	0.361665	-1.490099	-0.558736
C	0.338062	-1.517663	-1.951981
C	0.720352	-2.661497	0.111025
C	0.672051	-2.701065	-2.603814
H	0.074280	-0.645401	-2.540469
C	1.024594	-3.795919	-0.633024
H	0.766392	-2.705515	1.196056
H	0.667070	-2.740330	-3.690526
H	1.297112	-4.719947	-0.128778
C	-1.941422	-0.300113	0.444111
C	-2.768339	0.716701	0.949676
C	-2.565575	-1.449194	-0.049911
C	-4.154207	0.595822	0.959913
H	-2.323365	1.628140	1.346015
C	-3.958633	-1.577859	-0.050466
H	-1.979425	-2.273845	-0.444442
C	-4.758365	-0.557094	0.453188
H	-4.764582	1.402063	1.359493
H	-4.412839	-2.482511	-0.447574
H	-5.840933	-0.654967	0.452486
C	-0.599120	4.113334	-1.614493
H	-0.736521	5.082101	-2.087364
O	0.023360	-0.178365	2.124082
C	1.913082	0.289658	0.626184
C	2.617531	0.610301	-0.542852
C	2.693689	0.119681	1.772141
C	3.999211	0.743414	-0.519380
H	2.101890	0.762914	-1.488295
C	4.078246	0.275666	1.705020
H	2.243183	-0.132754	2.725044
H	4.540057	0.992621	-1.429974
H	4.682149	0.145889	2.601205
N	4.741934	0.582490	0.586028
C	-0.915195	-0.818037	2.991625
H	-0.347736	-1.068582	3.891995
H	-1.733683	-0.143013	3.253985
H	-1.319493	-1.734378	2.554919
N	1.006787	-3.831648	-1.971099

[Int-III]-Py,Py,ax-a

C	-1.204604	2.937772	-2.189234
C	-1.028056	1.704357	-1.566951
C	-0.231894	1.596003	-0.421158
C	0.338999	2.751526	0.119318
C	0.126290	3.993420	-0.477495
H	-1.804535	3.002141	-3.092965
H	-1.528442	0.831950	-1.977369
H	0.952788	2.692222	1.014565
H	0.562639	4.884716	-0.034869
P	0.004584	-0.017209	0.472668
C	-1.931172	-0.273062	0.471654
C	-2.749570	0.737574	0.995005
C	-2.594000	-1.391240	-0.034814
C	-4.129861	0.595068	0.988841
H	-2.320215	1.647344	1.409364
C	-3.988052	-1.447078	-0.006981
H	-2.054946	-2.233643	-0.456805
H	-4.763771	1.379353	1.396961
H	-4.503784	-2.317022	-0.408705
C	1.934401	0.300056	0.607877
C	2.719407	0.184220	1.757203
C	2.630496	0.588085	-0.574537
C	4.101478	0.358112	1.680060
H	2.274885	-0.038953	2.720127
C	4.009840	0.742052	-0.560102
H	2.108793	0.698215	-1.522496
H	4.709369	0.271025	2.578688
H	4.544896	0.965404	-1.480752
C	-0.632903	4.086750	-1.642221
H	-0.785728	5.051468	-2.118585
O	0.054200	-0.188337	2.116879
C	0.348200	-1.514998	-0.541685
C	0.299717	-1.543463	-1.937304
C	0.686699	-2.678368	0.157854
C	0.584879	-2.723131	-2.623584
H	0.048983	-0.651657	-2.503169
C	0.961059	-3.858566	-0.530337
H	0.741120	-2.670877	1.244269
H	0.550255	-2.732155	-3.709772
H	1.217523	-4.757108	0.024464
C	-0.874730	-0.843437	2.983696
H	-0.296619	-1.115486	3.870788
H	-1.686197	-0.170307	3.271766
H	-1.288595	-1.749669	2.534511
C	0.910422	-3.883935	-1.923475
H	1.127620	-4.802878	-2.461229
N	4.757641	0.633018	0.548578
N	-4.762022	-0.479526	0.492333

[TS-I]-Ph,OMe,ax-a (ν_i = -513.72 cm^{-1})

C	-3.754887	1.199015	1.167711
C	-2.455609	1.241611	0.670706
C	-1.978697	0.204970	-0.140394
C	-2.836859	-0.849360	-0.482370
C	-4.134487	-0.886423	0.021416
H	-4.109775	2.007280	1.800473
H	-1.833229	2.092998	0.919587
H	-2.517129	-1.645375	-1.144720
H	-4.785608	-1.713768	-0.245136
P	-0.324515	0.287115	-0.869618
C	0.645633	-1.191595	-0.860898
C	1.983961	-1.065350	-1.394332
C	0.141460	-2.545958	-0.917128
C	2.764957	-2.191995	-1.532909
H	2.416739	-0.094033	-1.610740
C	1.027337	-3.581541	-1.088376
H	-0.894348	-2.775422	-0.703025
H	3.801630	-2.072138	-1.846586
H	0.647861	-4.601244	-1.035601
C	0.642330	-0.748906	1.114436
C	1.923257	-0.462702	1.584046
C	-0.277765	-1.310145	2.003545
C	2.273651	-0.681700	2.916020
H	2.672900	-0.064462	0.899872
C	0.060556	-1.535717	3.339783
H	-1.276994	-1.583437	1.669493
H	3.277870	-0.443620	3.260068
H	-0.674992	-1.961681	4.018823
C	-4.593522	0.131206	0.854234
H	-5.605490	0.098802	1.247840
O	-0.623712	0.738550	-2.419944
C	0.617121	1.792255	-0.427853
C	0.698000	2.296198	0.871680
C	1.280196	2.487668	-1.440275
C	1.422299	3.461996	1.093638
H	0.227852	1.801693	1.712644
C	1.997671	3.634140	-1.107158
H	1.255006	2.155358	-2.471001
H	1.487967	3.872666	2.097534
H	2.533380	4.178515	-1.880282
C	-1.281461	-0.134893	-3.346312
H	-2.360453	-0.138351	-3.163012
H	-1.082855	0.269404	-4.340400
H	-0.884980	-1.153160	-3.281909
N	2.349071	-3.460811	-1.354093
C	1.337142	-1.215547	3.803184
H	1.603954	-1.392573	4.842056
N	2.071557	4.127102	0.131733

[TS-I]-Py,OMe,ax-a (ν_i = -506.35 cm^{-1})

C	-4.112573	-0.852588	-0.465694
C	-2.811696	-0.649864	-0.917767
C	-1.725860	-0.909059	-0.070499
C	-1.954313	-1.413267	1.213013
C	-3.256670	-1.625716	1.654753
H	-4.948642	-0.639564	-1.125264
H	-2.651485	-0.302792	-1.934517
H	-1.131383	-1.642848	1.878527
H	-3.424982	-2.017158	2.653751
P	-0.074295	-0.624376	-0.747385
C	1.288893	-1.469167	0.104446
C	2.212948	-2.137984	-0.711621
C	1.465791	-1.485685	1.493918
C	3.294924	-2.807263	-0.146159
H	2.096955	-2.134043	-1.790571
C	2.541178	-2.167889	2.053743
H	0.789837	-0.952091	2.150374
H	4.007739	-3.312514	-0.791275
H	2.665095	-2.174080	3.132697
C	0.159769	1.309537	0.820695
C	1.348661	1.679281	1.445141
C	-1.017970	1.797669	1.388413
C	1.316868	2.456796	2.598496
H	2.313034	1.373807	1.041091
C	-0.959549	2.575166	2.541695
H	-1.991794	1.590657	0.948289
H	2.242499	2.737099	3.098386
H	-1.874859	2.950232	2.996498
C	-4.336599	-1.335245	0.822336
H	-5.352090	-1.494904	1.173913
O	-0.144022	-1.389799	-2.188476
C	0.310746	1.043991	-1.188543
C	-0.666239	1.942955	-1.752787
C	1.667031	1.350688	-1.573240
C	-0.245260	3.154381	-2.250145
H	-1.728075	1.733561	-1.693827
C	1.951263	2.597894	-2.082692
H	2.475605	0.650262	-1.389530
H	-0.995446	3.867433	-2.589847
H	2.990004	2.854561	-2.287854
C	-0.593806	-2.747680	-2.322307
H	-1.681402	-2.764679	-2.434306
H	-0.121813	-3.143226	-3.223302
H	-0.303080	-3.357086	-1.460874
N	0.184105	2.905340	3.158332
N	1.040904	3.542870	-2.396128
C	3.458368	-2.827454	1.236846
H	4.300387	-3.353038	1.678547

[TS-I]-Py,Ph,ax-a (ν_i = -420.54 cm^{-1})

C	4.565217	0.633785	0.467208
C	3.190821	0.801820	0.595559
C	2.316038	-0.230838	0.226829
C	2.835787	-1.429310	-0.275480
C	4.214471	-1.591669	-0.406880
H	5.236538	1.437665	0.755464
H	2.799660	1.739516	0.983584
H	2.174689	-2.239255	-0.568056
H	4.610546	-2.523052	-0.801293
P	0.520029	0.006149	0.410440
C	-0.354877	-1.305757	-0.400419
C	-0.461155	-2.575419	0.254366
C	-0.513946	-1.342295	-1.821278
C	-0.989592	-3.639488	-0.442585
H	-0.205148	-2.689277	1.303232
C	-1.046642	-2.476135	-2.398652
H	-0.294281	-0.478993	-2.440216
H	-1.136569	-4.587088	0.073381
H	-1.240565	-2.478590	-3.470272
C	0.217351	1.669289	-0.209187
C	0.682169	2.030929	-1.477508
C	-0.445655	2.603245	0.592227
C	0.450837	3.318861	-1.955245
H	1.226856	1.319522	-2.093017
C	-0.655748	3.893407	0.116175
H	-0.803953	2.323213	1.578088
C	-0.216436	4.248821	-1.159640
H	0.801233	3.595672	-2.945315
H	-1.168556	4.619868	0.739931
H	-0.389295	5.254959	-1.531528
C	5.077800	-0.563625	-0.035510
H	6.151715	-0.692269	-0.139742
O	0.230018	-0.017705	1.984669
C	-2.028112	-0.169862	0.351366
C	-2.716115	-0.631621	1.473124
C	-2.792189	0.495681	-0.607397
C	-4.083796	-0.395847	1.599351
H	-2.205230	-1.185638	2.260421
C	-4.155381	0.689201	-0.405585
H	-2.339937	0.869290	-1.527284
H	-4.624976	-0.745934	2.477650
H	-4.754923	1.214686	-1.147883
N	-4.811945	0.258465	0.682999
C	1.146944	-0.551654	2.963690
H	1.969011	0.148199	3.128651
H	0.556751	-0.657116	3.874434
H	1.531481	-1.526182	2.655279
N	-1.325537	-3.624022	-1.749662

[Int-IV]-Py,Ph,ax-a

C	-0.713544	3.345354	-1.814735
C	-0.000283	2.278447	-1.273699
C	-0.458343	1.660220	-0.104294
C	-1.628980	2.111348	0.519276
C	-2.329783	3.183150	-0.023935
H	-0.356402	3.825131	-2.721268
H	0.908741	1.936839	-1.760828
H	-1.995805	1.628960	1.420407
H	-3.234647	3.534756	0.463193
P	0.380628	0.199565	0.528817
C	-1.859197	-1.213564	-0.030744
C	-2.375796	-1.463193	1.244140
C	-2.765528	-0.795564	-1.005480
C	-3.731790	-1.273432	1.482900
H	-1.745246	-1.799435	2.060359
C	-4.105714	-0.633070	-0.669860
H	-2.450316	-0.590359	-2.022319
H	-4.139407	-1.461985	2.473263
H	-4.815727	-0.300120	-1.423273
C	2.158886	0.408466	0.308872
C	2.999912	-0.572721	-0.225290
C	2.699595	1.614213	0.782854
C	4.371769	-0.338980	-0.294766
H	2.606795	-1.512374	-0.594972
C	4.069939	1.836925	0.711895
H	2.054037	2.380034	1.205476
C	4.906706	0.860283	0.170594
H	5.021358	-1.101045	-0.715519
H	4.482874	2.772784	1.076751
H	5.977326	1.036076	0.112213
C	-1.875476	3.797445	-1.191194
H	-2.427991	4.631618	-1.614644
O	0.088249	0.297057	2.112089
C	-0.357580	-1.364076	-0.329444
C	0.220069	-2.645358	0.210476
C	0.014995	-1.248023	-1.781889
C	1.018441	-3.452690	-0.544346
H	-0.020256	-2.941827	1.226644
C	0.845593	-2.148279	-2.388865
H	-0.359716	-0.410159	-2.362265
H	1.392643	-4.366683	-0.080934
H	1.086715	-1.979419	-3.439556
N	1.407569	-3.255930	-1.836933
C	0.761291	-0.550007	3.066380
H	0.602332	-0.080775	4.037512
H	0.324542	-1.550497	3.057954
H	1.832377	-0.602905	2.850600
N	-4.600531	-0.858345	0.552526

[TS-II]-Py,Ph,ax-a (ν_i = -141.39 cm^{-1})

C	-0.956398	3.203774	-1.856514
C	-0.165043	2.202625	-1.298211
C	-0.537643	1.620270	-0.080560
C	-1.701954	2.044448	0.573102
C	-2.481253	3.051212	0.012552
H	-0.664550	3.654670	-2.800606
H	0.739166	1.884468	-1.809903
H	-2.004519	1.588446	1.510986
H	-3.381344	3.380459	0.523761
P	0.380842	0.210838	0.561551
C	-1.806246	-1.286974	-0.059168
C	-2.319883	-1.509463	1.221960
C	-2.711294	-0.870639	-1.036209
C	-3.670774	-1.292658	1.465378
H	-1.688717	-1.841346	2.039634
C	-4.046134	-0.678828	-0.694918
H	-2.399931	-0.686742	-2.058248
H	-4.075669	-1.458819	2.460825
H	-4.754497	-0.344466	-1.449221
C	2.144854	0.521383	0.314207
C	3.033457	-0.473825	-0.105194
C	2.628897	1.795525	0.648771
C	4.393510	-0.188340	-0.205475
H	2.682658	-1.467204	-0.360188
C	3.988389	2.070953	0.550112
H	1.948352	2.573903	0.983981
C	4.870966	1.079660	0.119213
H	5.078485	-0.962674	-0.538643
H	4.357402	3.059835	0.806473
H	5.932430	1.297295	0.038168
C	-2.112647	3.627657	-1.203233
H	-2.726982	4.409577	-1.641082
O	0.102248	0.330325	2.154426
C	-0.314872	-1.458281	-0.357017
C	0.268166	-2.713791	0.194818
C	0.089427	-1.315318	-1.780806
C	1.172305	-3.456374	-0.509504
H	-0.023877	-3.041255	1.187853
C	1.025799	-2.140361	-2.346857
H	-0.318226	-0.505462	-2.378217
H	1.569696	-4.356098	-0.038346
H	1.311898	-1.946943	-3.381559
N	1.629390	-3.207843	-1.768207
C	0.779441	-0.538477	3.083846
H	0.528946	-0.160171	4.075222
H	0.426336	-1.566678	2.977417
H	1.862420	-0.492844	2.933086
N	-4.537464	-0.876186	0.533658

[Int-V]-Ph,OMe,ax-a

C	-5.038904	0.165013	0.572451
C	-3.663563	0.311461	0.722801
C	-2.840544	0.452385	-0.403278
C	-3.415246	0.444203	-1.677441
C	-4.794587	0.286092	-1.829354
H	-5.671660	0.058145	1.449604
H	-3.227224	0.314609	1.719351
H	-2.786544	0.562811	-2.557592
H	-5.232370	0.277293	-2.823905
P	-1.018408	0.667845	-0.269244
C	2.675382	0.936262	-0.321576
C	2.567161	1.315494	1.021022
C	2.872458	1.965041	-1.250576
C	2.656379	2.659755	1.362704
H	2.396595	0.581994	1.801966
C	2.951474	3.280491	-0.809142
H	2.987262	1.754258	-2.309373
H	2.563099	2.960635	2.403590
H	3.111415	4.083317	-1.525095
C	2.583667	-0.485927	-0.740713
C	3.028032	-1.512198	0.103732
C	2.040135	-0.830019	-1.985856
C	2.937824	-2.844919	-0.289155
H	3.464896	-1.272445	1.069366
C	1.950206	-2.163044	-2.378654
H	1.661942	-0.055222	-2.647147
H	3.289125	-3.626462	0.379087
H	1.517215	-2.410239	-3.344334
C	-5.605334	0.148678	-0.705352
H	-6.679476	0.029887	-0.820784
O	-0.885525	1.780271	0.964079
C	-0.612172	-0.829699	0.712539
C	-0.742228	-2.083679	0.108934
C	-0.119583	-0.787391	2.016653
C	-0.382884	-3.218364	0.825100
H	-1.114109	-2.187757	-0.907502
C	0.214087	-1.982761	2.648335
H	0.006584	0.152852	2.542203
H	-0.474688	-4.201334	0.369490
H	0.599070	-1.969034	3.665511
C	-0.778255	3.147327	0.561754
H	-1.739186	3.516175	0.182503
H	-0.500181	3.717257	1.450845
H	-0.009098	3.274588	-0.209133
N	2.848264	3.643915	0.475749
C	2.399477	-3.175522	-1.532153
H	2.324868	-4.216195	-1.836027
N	0.091008	-3.186351	2.078074

[Int-V]-Ph,OMe,ax-b

C	-4.828339	-0.918902	-0.081358
C	-3.543346	-0.570044	0.324380
C	-2.753823	0.278384	-0.465639
C	-3.279602	0.765892	-1.669060
C	-4.567678	0.417711	-2.076340
H	-5.430620	-1.576654	0.539628
H	-3.156043	-0.964405	1.260146
H	-2.677724	1.419675	-2.296954
H	-4.961343	0.800891	-3.013803
P	-1.057039	0.836743	-0.028912
C	2.578650	1.087398	-0.552443
C	2.594349	1.518286	0.778452
C	2.513336	2.081805	-1.535183
C	2.519900	2.877425	1.058641
H	2.636518	0.810357	1.599380
C	2.446560	3.416299	-1.154131
H	2.522337	1.831206	-2.591588
H	2.514321	3.217829	2.091485
H	2.393928	4.194631	-1.911902
C	2.598624	-0.355126	-0.903750
C	3.278436	-1.282816	-0.103467
C	1.915153	-0.818265	-2.036548
C	3.280195	-2.636181	-0.431293
H	3.824913	-0.947550	0.773921
C	1.917709	-2.171736	-2.364052
H	1.355411	-0.121886	-2.655166
H	3.814266	-3.340886	0.200417
H	1.374196	-2.513032	-3.241116
C	-5.342249	-0.425024	-1.282111
H	-6.344936	-0.701042	-1.597724
O	-1.282109	1.992150	1.144375
C	-0.454401	-0.605058	0.945936
C	-0.478401	-1.890573	0.396513
C	0.178513	-0.447034	2.179907
C	0.109739	-2.937446	1.095856
H	-0.945809	-2.087604	-0.564670
C	0.735477	-1.559829	2.803314
H	0.247617	0.524827	2.659479
H	0.098384	-3.942474	0.681090
H	1.227449	-1.452323	3.767367
C	-2.269015	1.872273	2.173586
H	-2.216716	0.900054	2.675174
H	-2.059238	2.663767	2.896745
H	-3.271903	2.014478	1.757841
N	2.442196	3.829086	0.120177
C	2.600921	-3.085699	-1.563113
H	2.599660	-4.142660	-1.815570
N	0.709737	-2.792797	2.284957

[Int-V]-Py,OMe,ax-a

C	0.423761	-1.650182	2.682169
C	-0.106699	-0.611322	1.915987
C	-0.473916	-0.834580	0.586604
C	-0.304767	-2.111563	0.036191
C	0.216199	-3.149407	0.803599
H	0.711843	-1.463593	3.713683
H	-0.224123	0.374718	2.354580
H	-0.573466	-2.297837	-1.002381
H	0.347261	-4.133837	0.362380
P	-1.134663	0.472949	-0.517270
C	-2.934865	0.084655	-0.430504
C	-3.617270	-0.186701	-1.619650
C	-3.636670	0.064321	0.782408
C	-4.980783	-0.489293	-1.600047
H	-3.084800	-0.162007	-2.568433
C	-4.997839	-0.224043	0.802132
H	-3.115677	0.273890	1.714320
H	-5.501785	-0.703726	-2.529428
H	-5.536275	-0.235535	1.746222
C	2.729024	-0.230023	-0.662953
C	2.266988	-0.701094	-1.896132
C	3.383765	-1.148218	0.162860
C	2.477728	-2.031154	-2.238514
H	1.723835	-0.059195	-2.582123
C	3.541914	-2.460067	-0.269224
H	3.784063	-0.857917	1.128915
H	2.117065	-2.408542	-3.192301
H	4.047877	-3.182316	0.366848
C	0.586824	-2.918988	2.129460
H	1.005786	-3.725037	2.726095
O	-1.014554	1.753904	0.547734
C	2.514974	1.178772	-0.242231
C	2.422787	1.530747	1.107468
C	2.379675	2.209590	-1.177770
C	2.197994	2.858392	1.451443
H	2.495562	0.786824	1.893547
C	2.161157	3.508300	-0.732737
H	2.458144	2.022616	-2.244077
H	2.112947	3.139640	2.498308
H	2.057080	4.317086	-1.451984
C	-1.374528	3.030953	0.023995
H	-2.456062	3.088621	-0.153657
H	-1.095258	3.771908	0.775960
H	-0.841767	3.243233	-0.911329
N	3.104861	-2.912818	-1.450291
N	2.067915	3.846907	0.558742
C	-5.670824	-0.505488	-0.390291
H	-6.733085	-0.734728	-0.372699

[Int-V]-Py,OMe,ax-b

C	4.606564	0.574220	-2.014765
C	3.299621	0.867371	-1.624281
C	2.756709	0.306562	-0.461125
C	3.549268	-0.560359	0.304869
C	4.853107	-0.855542	-0.083927
H	5.013170	1.014926	-2.921018
H	2.695896	1.536474	-2.234256
H	3.148079	-1.011748	1.208467
H	5.457124	-1.528766	0.518681
P	1.036113	0.803796	-0.033600
C	0.457795	-0.664801	0.913485
C	-0.161808	-0.531830	2.159828
C	0.498533	-1.929718	0.310894
C	-0.712700	-1.642283	2.800579
H	-0.220440	0.442639	2.637814
C	-0.054910	-3.037014	0.947427
H	0.964327	-2.055860	-0.664429
H	-1.186449	-1.522301	3.771575
H	-0.017722	-4.009838	0.464500
C	-2.590672	-0.334576	-0.913680
C	-3.234717	-1.309284	-0.147201
C	-1.915521	-0.764871	-2.060182
C	-3.181233	-2.637253	-0.555440
H	-3.786145	-1.049093	0.751017
C	-1.921834	-2.116378	-2.383861
H	-1.368114	-0.068554	-2.687788
H	-3.679025	-3.405177	0.031640
H	-1.396147	-2.464387	-3.269825
C	5.383846	-0.287873	-1.244027
H	6.401201	-0.521518	-1.546746
O	1.231737	1.953846	1.155710
C	-2.598115	1.096232	-0.518905
C	-2.562775	2.117593	-1.472875
C	-2.610978	1.477742	0.825370
C	-2.525925	3.440672	-1.048838
H	-2.572307	1.898515	-2.536197
C	-2.563715	2.828879	1.148120
H	-2.628988	0.740300	1.620785
H	-2.498933	4.244747	-1.780320
H	-2.555023	3.137334	2.190698
C	2.219205	1.842596	2.184265
H	3.215849	2.046235	1.778576
H	1.972082	2.596673	2.935466
H	2.212305	0.851835	2.650846
N	-2.543143	-3.052537	-1.656240
N	-2.519043	3.809651	0.238383
C	-0.662016	-2.896639	2.196337
H	-1.097401	-3.760620	2.691427

[Int-V]-Py,Ph,ax-a

C	-0.962812	-1.353586	2.717852
C	-0.072042	-1.095700	1.675255
C	-0.332006	-1.571050	0.385925
C	-1.507355	-2.301806	0.157703
C	-2.387616	-2.572338	1.201224
H	-0.747778	-0.974873	3.713765
H	0.826050	-0.519224	1.877730
H	-1.740373	-2.661962	-0.842069
H	-3.292821	-3.142013	1.008667
P	0.729887	-1.194750	-1.063569
C	-2.155403	1.390310	-0.371867
C	-2.443032	0.807749	-1.610145
C	-3.039266	1.126997	0.677988
C	-3.575563	0.012954	-1.739611
H	-1.789620	0.946237	-2.465474
C	-4.146373	0.318338	0.446551
H	-2.888735	1.553647	1.664769
H	-3.806350	-0.450427	-2.695835
H	-4.841978	0.108369	1.255319
C	2.291499	-0.658874	-0.263181
C	2.678978	0.676045	-0.406855
C	3.103210	-1.533221	0.471796
C	3.846165	1.143896	0.198623
H	2.065872	1.357779	-0.993080
C	4.276776	-1.072264	1.061492
H	2.813360	-2.575015	0.586336
C	4.645950	0.269270	0.930932
H	4.131048	2.187094	0.090739
H	4.902522	-1.756028	1.629226
H	5.559409	0.628686	1.397545
C	-2.118570	-2.095247	2.484942
H	-2.811766	-2.296231	3.297511
O	1.071597	-2.787983	-1.465847
C	-0.961384	2.252657	-0.179350
C	-0.457353	3.043810	-1.216769
C	-0.298078	2.316358	1.049745
C	0.651445	3.849071	-0.980135
H	-0.927010	3.062418	-2.195341
C	0.807438	3.148527	1.183857
H	-0.617976	1.718438	1.896553
H	1.045800	4.475937	-1.776207
H	1.336533	3.197867	2.132411
N	1.286045	3.914933	0.196658
C	1.741735	-2.977844	-2.712077
H	1.782197	-4.055228	-2.888017
H	1.195534	-2.495821	-3.532745
H	2.764397	-2.581996	-2.673930
N	-4.428538	-0.235913	-0.738219

Pathway [Int-III·H]$^+$

[Int-III·H]$^+$-Ph,OMe,ax-a

C	-2.015260	0.324709	3.206934
C	-1.539885	0.497267	1.912042
C	-0.424321	-0.211756	1.435903
C	0.186907	-1.114638	2.309274
C	-0.285720	-1.296272	3.613826
H	-2.879159	0.891229	3.545279
H	-2.052448	1.203402	1.260036
H	1.041222	-1.708341	1.998258
H	0.212295	-2.006615	4.269174
P	0.051381	0.058446	-0.412929
C	1.586310	-0.981852	-0.299232
C	2.755647	-0.476444	0.274797
C	1.603619	-2.267625	-0.850646
C	3.896856	-1.251849	0.288134
H	2.798839	0.512980	0.715493
C	2.761788	-3.012968	-0.798171
H	0.734056	-2.697076	-1.334488
H	4.839961	-0.925817	0.708254
H	2.849964	-4.016545	-1.194710
C	0.259626	1.884599	-0.223810
C	-0.120278	2.759986	-1.248961
C	0.804540	2.419025	0.950824
C	0.016592	4.136938	-1.090774
H	-0.518410	2.371112	-2.178768
C	0.977478	3.793590	1.091954
H	1.095487	1.769559	1.770366
C	0.572498	4.657473	0.076323
H	-0.302920	4.801323	-1.888762
H	1.417007	4.187158	2.004162
H	0.690900	5.731235	0.193556
C	-1.385258	-0.577217	4.068437
H	-1.753339	-0.717061	5.081418
O	0.361487	0.129834	-2.173417
C	-1.567562	-0.688064	-0.931115
C	-1.926919	-1.960814	-0.486660
C	-2.481224	0.004322	-1.724800
C	-3.153546	-2.489173	-0.874730
H	-1.278653	-2.544802	0.159947
C	-3.699662	-0.597351	-2.025351
H	-2.274742	0.998035	-2.104669
H	-3.438348	-3.488712	-0.555673
H	-4.433175	-0.063048	-2.624197
N	-4.041749	-1.827079	-1.624606
C	1.578556	0.593007	-2.727263
H	2.248956	-0.248086	-2.953431
H	1.353744	1.120051	-3.661643
H	2.111927	1.290236	-2.066694
N	3.863938	-2.486817	-0.236687
H	4.714204	-3.047675	-0.214176

[Int-III·H]$^+$-Ph,Ph,ax-a

C	-1.453349	2.873058	-2.183898
C	-1.173336	1.640021	-1.603863
C	-0.445528	1.606483	-0.415476
C	-0.073909	2.821583	0.156785
C	-0.441370	4.004539	-0.477899
H	-1.994040	2.920395	-3.125850
H	-1.536411	0.733831	-2.079127
H	0.492037	2.863845	1.082970
H	-0.180432	4.962991	-0.036021
P	-0.045404	0.035315	0.503519
C	-1.904883	-0.485082	0.425297
C	-2.855389	0.432952	0.903219
C	-2.380740	-1.693896	-0.090247
C	-4.217916	0.158368	0.868930
H	-2.529256	1.387188	1.313651
C	-3.750324	-1.976772	-0.133978
H	-1.700238	-2.450079	-0.469406
H	-4.926112	0.890599	1.248570
H	-4.088058	-2.925192	-0.544292
C	1.839291	0.509517	0.624972
C	2.473164	0.962376	-0.542408
C	2.641993	0.304976	1.754153
C	3.842641	1.212883	-0.583002
H	1.896248	1.129486	-1.450018
C	4.016818	0.552383	1.722252
H	2.196920	-0.052203	2.676440
H	4.298825	1.568405	-1.503662
H	4.611627	0.387416	2.617545
O	-0.023614	-0.027447	2.148760
C	0.526379	-1.435865	-0.495974
C	0.573327	-1.482423	-1.892272
C	0.988563	-2.538310	0.234842
C	1.082129	-2.602551	-2.515655
H	0.229626	-0.660385	-2.508770
C	1.477852	-3.639762	-0.431569
H	0.976954	-2.549023	1.320321
H	1.158951	-2.709637	-3.590374
H	1.848788	-4.528618	0.063058
C	-0.916211	-0.687390	3.051173
H	-0.318486	-0.903327	3.940566
H	-1.747282	-0.031118	3.320125
H	-1.302262	-1.622509	2.639881
N	-1.106721	4.044868	-1.637581
N	1.512976	-3.637760	-1.775551
C	4.623845	1.008480	0.554739
H	5.693023	1.202612	0.529318
C	-4.673437	-1.053453	0.344438
H	-5.737681	-1.271302	0.310690
H	1.885784	-4.455971	-2.253921

[Int-III·H]$^{+}$-Py,OMe,ax-a

C	-3.174512	-2.570094	0.754661
C	-2.340498	-1.458802	0.652652
C	-1.277794	-1.455524	-0.254753
C	-1.057217	-2.581571	-1.054333
C	-1.871497	-3.704814	-0.927008
H	-4.006899	-2.552897	1.452713
H	-2.530139	-0.600836	1.289496
H	-0.255709	-2.584812	-1.787709
H	-1.680285	-4.578813	-1.543441
P	-0.189143	0.016634	-0.432217
C	1.595835	-0.175962	-0.936694
C	2.315702	0.909403	-1.448940
C	2.257109	-1.395623	-0.749435
C	3.651257	0.755886	-1.753348
H	1.855825	1.876625	-1.612891
C	3.588644	-1.506542	-1.084722
H	1.753830	-2.261485	-0.333489
H	4.272561	1.550407	-2.147103
H	4.162343	-2.418068	-0.975036
C	0.483089	-0.045156	1.398528
C	0.440169	-1.175108	2.217396
C	1.215544	1.042666	1.892701
C	1.086358	-1.163267	3.453239
H	-0.083933	-2.077814	1.920136
C	1.828304	0.965474	3.136460
H	1.319495	1.960720	1.318781
H	1.048110	-2.042140	4.093334
H	2.391958	1.812353	3.521538
C	-2.935585	-3.699375	-0.026582
H	-3.579615	-4.569959	0.062368
O	-0.424797	0.037077	-2.183831
C	-0.952759	1.685874	-0.218802
C	-1.621324	2.020506	0.966045
C	-0.877079	2.639189	-1.241072
C	-2.218787	3.269046	1.114771
H	-1.678475	1.316953	1.790299
C	-1.441973	3.902089	-1.076344
H	-0.378192	2.397519	-2.172756
H	-2.749077	3.502721	2.033693
H	-1.356747	4.634734	-1.874097
C	-1.713147	0.048158	-2.771973
H	-2.498290	0.351800	-2.066618
H	-1.712235	0.759179	-3.606408
H	-1.965242	-0.948507	-3.156144
C	-2.122369	4.217341	0.097635
H	-2.574943	5.197494	0.220737
N	1.772866	-0.118059	3.924003
N	4.242602	-0.436344	-1.568097
H	5.228051	-0.533250	-1.805342

[Int-III·H]$^+$-Py,OMe,ax-b

C	2.862120	3.063058	-0.559659
C	2.194321	1.847885	-0.692762
C	0.885920	1.707970	-0.218438
C	0.245560	2.805694	0.360742
C	0.909305	4.026524	0.473378
H	3.882356	3.155786	-0.921618
H	2.699176	1.015520	-1.174960
H	-0.771727	2.727649	0.730618
H	0.397446	4.874507	0.919849
P	0.045123	0.092238	-0.453987
C	-1.841441	0.043140	-0.467336
C	-2.522814	-0.594722	-1.507915
C	-2.592113	0.619047	0.563267
C	-3.901605	-0.661070	-1.488287
H	-1.996899	-1.031605	-2.345922
C	-3.970293	0.563782	0.524788
H	-2.127831	1.104267	1.413177
H	-4.490486	-1.154306	-2.251192
H	-4.610887	1.003761	1.278525
C	0.011963	-0.384188	1.435431
C	-0.614776	-1.583123	1.803582
C	0.619767	0.330042	2.467000
C	-0.618417	-1.990911	3.129738
H	-1.101489	-2.216349	1.063485
C	0.568672	-0.157906	3.773745
H	1.146502	1.261257	2.285099
H	-1.106557	-2.919837	3.415968
H	1.043221	0.399344	4.578716
C	2.221048	4.156069	0.022038
H	2.740028	5.105783	0.117850
O	0.016641	0.336128	-2.208166
C	1.095015	-1.387560	-0.797794
C	2.275989	-1.555504	-0.064838
C	0.736469	-2.353545	-1.742238
C	3.094828	-2.659010	-0.289539
H	2.571891	-0.825027	0.683120
C	1.538695	-3.477103	-1.937297
H	-0.166014	-2.244458	-2.332315
H	4.018884	-2.763281	0.272319
H	1.237809	-4.228869	-2.661801
C	-0.522939	1.509482	-2.784117
H	0.248547	2.283803	-2.890600
H	-0.907277	1.254341	-3.778198
H	-1.352187	1.935114	-2.200320
C	2.722778	-3.629361	-1.218919
H	3.353060	-4.499223	-1.382517
N	-0.039072	-1.295338	4.120244
N	-4.576868	-0.078370	-0.485927
H	-5.594278	-0.126957	-0.491793

[Int-III·H]$^{+}$-Py,OMe,ax-c

C	-3.762729	0.558232	-1.982109
C	-2.399048	0.700994	-1.732341
C	-1.750490	-0.165540	-0.847013
C	-2.485146	-1.184084	-0.229362
C	-3.839252	-1.348879	-0.511326
H	-4.257424	1.251173	-2.657183
H	-1.854768	1.495533	-2.229660
H	-2.010172	-1.858541	0.477905
H	-4.390448	-2.156619	-0.037886
P	0.042095	0.031955	-0.445995
C	1.113672	-1.478257	-0.324811
C	2.428789	-1.396263	0.141086
C	0.630180	-2.714191	-0.768246
C	3.215321	-2.529683	0.163315
H	2.857361	-0.465115	0.492410
C	1.447420	-3.822491	-0.715046
H	-0.372389	-2.830058	-1.163924
H	4.241951	-2.542050	0.506542
H	1.141904	-4.811645	-1.031987
C	-0.382506	0.013950	1.453510
C	-1.187244	1.051727	1.944572
C	-0.017654	-0.964248	2.377567
C	-1.566386	1.071128	3.278263
H	-1.526570	1.854523	1.293179
C	-0.447197	-0.865036	3.702566
H	0.592756	-1.820182	2.107521
H	-2.188466	1.877893	3.659108
H	-0.161401	-1.629266	4.422296
C	-4.484436	-0.471358	-1.380823
H	-5.544851	-0.588062	-1.587297
O	0.309067	-0.039176	-2.204994
C	0.866242	1.683401	-0.315969
C	1.645865	2.012009	0.800390
C	0.722389	2.628792	-1.338491
C	2.272914	3.252410	0.888038
H	1.775002	1.305849	1.614614
C	1.317078	3.883707	-1.231411
H	0.155642	2.387081	-2.230112
H	2.887229	3.481690	1.754207
H	1.176896	4.611453	-2.025803
C	1.596795	-0.011599	-2.790771
H	1.951880	-1.031323	-2.995684
H	1.531777	0.532665	-3.739813
H	2.343348	0.493852	-2.162762
C	2.098752	4.197323	-0.121226
H	2.572834	5.171974	-0.044332
N	-1.207408	0.129226	4.165138
N	2.704111	-3.698206	-0.254453
H	3.297059	-4.526151	-0.228398

[Int-III·H]$^+$-Py,PyH$^+$,ax-a

C	-1.237121	2.895498	-2.191783
C	-1.028034	1.669288	-1.565877
C	-0.215759	1.585418	-0.429169
C	0.341427	2.754016	0.098018
C	0.097669	3.986860	-0.504679
H	-1.848647	2.942854	-3.088601
H	-1.512854	0.784474	-1.968750
H	0.968579	2.711624	0.984833
H	0.524623	4.888812	-0.075080
P	0.069872	-0.009272	0.469702
C	-1.903394	-0.272243	0.478648
C	-2.706604	0.742687	1.027424
C	-2.562394	-1.383355	-0.058734
C	-4.078099	0.635522	1.031189
H	-2.264331	1.636261	1.457983
C	-3.942354	-1.456734	-0.046644
H	-2.019843	-2.213570	-0.496101
H	-4.746237	1.382010	1.442398
H	-4.505875	-2.288416	-0.451468
C	1.979923	0.316447	0.594904
C	2.762039	0.191126	1.744430
C	2.671517	0.616297	-0.586396
C	4.143411	0.369586	1.668117
H	2.316858	-0.042686	2.704472
C	4.050639	0.773754	-0.569494
H	2.148928	0.732392	-1.532908
H	4.751992	0.275889	2.565371
H	4.585484	1.006452	-1.487738
C	-0.679777	4.057886	-1.658950
H	-0.856282	5.016301	-2.139608
O	0.088701	-0.158225	2.107580
C	0.383807	-1.517512	-0.530804
C	0.347215	-1.544528	-1.927198
C	0.697491	-2.685060	0.173590
C	0.615680	-2.730093	-2.609533
H	0.120332	-0.648484	-2.496068
C	0.956674	-3.869923	-0.512285
H	0.746555	-2.678287	1.260038
H	0.590396	-2.739366	-3.695854
H	1.195650	-4.771625	0.044926
C	-0.824872	-0.840368	2.972786
H	-0.233107	-1.130717	3.844226
H	-1.632376	-0.174713	3.288104
H	-1.240211	-1.738422	2.508618
C	0.914871	-3.895529	-1.905535
H	1.120327	-4.818516	-2.440788
N	4.797397	0.656628	0.538574
N	-4.654749	-0.455960	0.492407
H	-5.669902	-0.526309	0.496797

[Int-III·H]$^+$-Py,PyH$^+$,ax-b

C	1.164100	3.025138	-2.160211
C	1.022728	1.771135	-1.571224
C	0.265018	1.621041	-0.405013
C	-0.306241	2.750502	0.188334
C	-0.130014	4.011354	-0.378812
H	1.735931	3.125391	-3.078552
H	1.518567	0.916726	-2.022784
H	-0.886050	2.657838	1.103385
H	-0.563718	4.883366	0.102729
P	0.073303	-0.009841	0.446828
C	-1.893800	0.296129	0.575403
C	-2.580293	0.587570	-0.616563
C	-2.670854	0.147428	1.731899
C	-3.949015	0.720525	-0.633738
H	-2.048819	0.715889	-1.554778
C	-4.043979	0.289657	1.681229
H	-2.215058	-0.079937	2.686914
H	-4.526642	0.945438	-1.521782
H	-4.693082	0.190275	2.542688
C	1.989851	-0.289929	0.422923
C	2.837747	0.727486	0.880940
C	2.615986	-1.455099	-0.020747
C	4.213965	0.545489	0.873149
H	2.438003	1.670050	1.247902
C	4.007835	-1.547798	0.001194
H	2.049929	-2.306337	-0.385281
H	4.872374	1.334158	1.230394
H	4.496481	-2.454025	-0.350494
C	0.593045	4.148490	-1.562183
H	0.719300	5.128875	-2.013417
O	0.002759	-0.129522	2.084590
C	-0.325192	-1.515948	-0.530594
C	-0.230226	-1.593942	-1.921939
C	-0.752834	-2.632252	0.196761
C	-0.565708	-2.777024	-2.578277
H	0.100893	-0.741184	-2.506129
C	-1.072732	-3.817487	-0.462034
H	-0.839955	-2.583434	1.280096
H	-0.495522	-2.826578	-3.661484
H	-1.395713	-4.681564	0.112182
C	0.936417	-0.754849	2.972687
H	1.769584	-0.086187	3.200909
H	0.369304	-0.955721	3.884741
H	1.313808	-1.696916	2.568078
C	-0.982496	-3.891402	-1.851416
H	-1.236588	-4.813836	-2.366362
N	4.811073	-0.573413	0.436820
N	-4.641285	0.569140	0.511939
H	-5.653007	0.674136	0.489974

[Int-III·H]$^+$-PyH$^+$,OMe,ax-a

C	-1.368591	3.940951	-0.642092
C	-0.647976	2.761409	-0.815421
C	-1.107391	1.567178	-0.250636
C	-2.309753	1.561211	0.459941
C	-3.039240	2.739283	0.613218
H	-0.996547	4.864788	-1.076269
H	0.267557	2.779565	-1.400193
H	-2.694964	0.646315	0.898690
H	-3.977621	2.720004	1.160487
P	-0.142298	0.031411	-0.523167
C	-1.020598	-1.599096	-0.329415
C	-0.989003	-2.552651	-1.347806
C	-1.732458	-1.922508	0.827696
C	-1.636061	-3.770344	-1.157575
H	-0.483174	-2.361626	-2.286497
C	-2.378345	-3.152374	0.907057
H	-1.796704	-1.247754	1.674655
H	-1.599220	-4.529703	-1.934627
H	-2.953287	-3.405624	1.794102
C	0.459112	-0.082104	1.373244
C	1.203087	-1.212407	1.756551
C	0.292023	0.921460	2.334243
C	1.726107	-1.320741	3.023540
H	1.387771	-2.026454	1.061380
C	0.832708	0.783035	3.598688
H	-0.252862	1.833538	2.119956
H	2.303672	-2.167405	3.373267
H	0.735391	1.526311	4.380678
C	-2.566303	3.932809	0.071765
H	-3.131935	4.851696	0.199131
O	-0.474127	0.066948	-2.246366
C	1.641483	0.146847	-0.978707
C	2.429186	1.171354	-0.441727
C	2.231203	-0.798044	-1.823514
C	3.781104	1.261953	-0.764012
H	1.999232	1.909079	0.230307
C	3.591848	-0.723530	-2.117009
H	1.641003	-1.597997	-2.256952
H	4.375619	2.074413	-0.355405
H	4.040927	-1.472294	-2.763769
C	-1.794195	0.175934	-2.746376
H	-2.083413	1.229215	-2.858617
H	-1.822604	-0.305295	-3.730030
H	-2.536169	-0.317960	-2.104048
C	4.368323	0.309691	-1.595653
H	5.426113	0.372779	-1.835853
N	1.524953	-0.323593	3.907085
N	-2.330184	-4.077480	-0.057056
H	1.917702	-0.410726	4.841826

[Int-III·H]$^+$-PyH$^+$,OMe,ax-b

C	-3.639417	0.027374	-2.064320
C	-2.346560	0.427563	-1.740288
C	-1.523846	-0.457778	-1.044476
C	-2.044243	-1.710742	-0.717307
C	-3.339956	-2.024273	-1.113442
H	-4.300745	0.710386	-2.591944
H	-2.010432	1.417241	-2.028335
H	-1.469017	-2.444884	-0.161389
H	-3.754377	-3.002768	-0.883569
P	0.178978	0.035696	-0.509954
C	0.640000	1.804944	-0.233136
C	0.451275	2.747706	-1.251044
C	1.187187	2.231018	0.984401
C	0.783494	4.085467	-1.049734
H	0.050405	2.438891	-2.209728
C	1.552269	3.561414	1.172307
H	1.332140	1.536179	1.805508
H	0.613814	4.804213	-1.846492
H	1.991301	3.867428	2.117644
C	1.469971	-1.241875	-0.245612
C	2.566750	-1.006053	0.586875
C	1.375477	-2.458158	-0.929119
C	3.552487	-1.979465	0.741000
H	2.668929	-0.066632	1.120947
C	2.347971	-3.439751	-0.751940
H	0.550840	-2.644478	-1.611087
H	4.407041	-1.779172	1.381364
H	2.256979	-4.385655	-1.278595
O	0.529269	0.112836	-2.226426
C	-0.528460	-0.115324	1.346683
C	-1.498967	0.813397	1.762955
C	-0.227588	-1.156185	2.232523
C	-2.103876	0.703044	2.993290
H	-1.796619	1.640210	1.124502
C	-0.852900	-1.238418	3.461972
H	0.494360	-1.926068	1.986095
H	-2.853267	1.389839	3.366681
H	-0.656529	-2.018251	4.187065
C	1.844532	0.322154	-2.708673
H	2.340761	-0.636457	-2.908638
H	1.778007	0.887766	-3.644591
H	2.467343	0.893200	-2.007013
C	3.439869	-3.202033	0.081798
H	4.203953	-3.963751	0.210484
C	1.342394	4.494973	0.158807
H	1.613802	5.536077	0.310760
N	-4.141305	-1.177098	-1.769521
N	-1.761865	-0.314377	3.807112
H	-2.212500	-0.385100	4.716798

[Int-III·H]$^{+}$-PyH^{+},Ph,ax-a

C	1.072453	3.051448	-2.171410
C	0.971669	1.795003	-1.578970
C	0.246911	1.631048	-0.394355
C	-0.333466	2.747936	0.213263
C	-0.196636	4.011895	-0.357648
H	1.618769	3.163429	-3.103852
H	1.473301	0.949332	-2.040552
H	-0.889199	2.642500	1.141890
H	-0.635698	4.875340	0.134403
P	0.105168	-0.005567	0.453601
C	-1.880386	0.261859	0.593648
C	-2.648790	0.078968	1.751287
C	-2.579505	0.562240	-0.588665
C	-4.024589	0.195924	1.710669
H	-2.183784	-0.155182	2.700179
C	-3.950917	0.669714	-0.596402
H	-2.056971	0.719341	-1.527660
H	-4.666722	0.069273	2.573771
H	-4.537451	0.899895	-1.477240
C	2.002712	-0.289046	0.399368
C	2.607674	-1.480837	-0.012399
C	2.844364	0.753352	0.820936
C	3.998138	-1.625663	-0.016175
H	2.007681	-2.326166	-0.335596
C	4.228936	0.615711	0.826337
H	2.414617	1.695868	1.155217
C	4.813851	-0.578825	0.401691
H	4.438095	-2.562980	-0.347613
H	4.852594	1.441759	1.158840
H	5.895064	-0.689630	0.398112
C	0.493862	4.163035	-1.558858
H	0.589048	5.145687	-2.012803
O	0.027628	-0.124714	2.091709
C	-0.313859	-1.505258	-0.541791
C	-0.732613	-2.637226	0.159871
C	-0.252450	-1.581383	-1.931733
C	-1.060268	-3.785126	-0.553372
H	-0.806622	-2.640444	1.244160
C	-0.618285	-2.772881	-2.551210
H	0.067507	-0.743109	-2.541153
H	-1.378154	-4.680996	-0.025711
H	-0.587536	-2.850966	-3.635217
N	-1.013186	-3.865969	-1.888431
C	0.995645	-0.672135	2.994326
H	0.445573	-0.853445	3.920905
H	1.405940	-1.615139	2.626313
H	1.803866	0.038079	3.182455
N	-4.633667	0.484372	0.549564
H	-5.647201	0.571427	0.535089

[Int-III·H]$^+$-PyH$^+$,Ph,ax-b

C	0.552342	-2.818791	-2.553168
C	0.206673	-1.632422	-1.908212
C	0.311392	-1.536766	-0.518704
C	0.757773	-2.639343	0.218172
C	1.085742	-3.828828	-0.428771
H	0.475473	-2.881601	-3.635227
H	-0.138950	-0.791426	-2.500855
H	0.851905	-2.575915	1.300125
H	1.422038	-4.682515	0.153279
P	-0.094859	-0.027912	0.452248
C	1.879269	0.281286	0.589674
C	2.572516	0.541832	-0.605481
C	2.649388	0.175611	1.755539
C	3.940211	0.686442	-0.617475
H	2.048299	0.636152	-1.551974
C	4.021715	0.327827	1.710091
H	2.188696	-0.025467	2.714005
H	4.522171	0.889090	-1.508042
H	4.665262	0.260717	2.578821
C	-1.999402	-0.258171	0.409123
C	-2.629204	-1.434359	-0.009596
C	-2.816955	0.798257	0.842126
C	-4.022326	-1.549895	-0.010266
H	-2.044037	-2.287415	-0.339726
C	-4.204225	0.689607	0.850151
H	-2.367687	1.728488	1.185405
C	-4.814820	-0.489099	0.417637
H	-4.483186	-2.475205	-0.347021
H	-4.809713	1.525560	1.191355
H	-5.898146	-0.577047	0.416270
C	0.986941	-3.919857	-1.816504
H	1.247997	-4.845210	-2.322649
O	-0.016352	-0.145641	2.091262
C	-0.239323	1.609568	-0.426570
C	0.310343	2.745950	0.164808
C	-0.941979	1.773500	-1.620089
C	0.141338	3.979760	-0.457307
H	0.859290	2.693839	1.100802
C	-1.019024	3.042236	-2.185204
H	-1.441353	0.943810	-2.109670
H	0.544336	4.879573	0.000707
H	-1.537126	3.185128	-3.130161
N	-0.496397	4.138179	-1.621749
C	-0.977419	-0.725948	2.980931
H	-0.427652	-0.912694	3.906613
H	-1.799843	-0.034572	3.177617
H	-1.368379	-1.670322	2.595409
N	4.625283	0.576310	0.536974
H	5.636304	0.689033	0.519095

[TS-I·H]$^+$-Ph,OMe,ax-a (ν_i = -481.02 cm^{-1})

C	3.588336	-1.675086	1.149831
C	2.278469	-1.526965	0.704579
C	1.942271	-0.470450	-0.148763
C	2.941487	0.414590	-0.574161
C	4.248701	0.265384	-0.116778
H	3.835324	-2.499312	1.812537
H	1.536385	-2.246111	1.028490
H	2.725631	1.221707	-1.265037
H	5.011514	0.963892	-0.447945
P	0.261291	-0.297174	-0.806378
C	-0.429157	1.330412	-0.828500
C	-1.773135	1.457247	-1.339129
C	0.301618	2.567953	-0.696030
C	-2.371097	2.678804	-1.388625
H	-2.339422	0.590372	-1.658561
C	-0.359226	3.751807	-0.769088
H	1.356774	2.583134	-0.461508
H	-3.392953	2.818193	-1.720806
H	0.134134	4.704980	-0.623137
C	-0.495115	0.645562	1.149352
C	-1.818885	0.526496	1.572053
C	0.470181	1.047960	2.075329
C	-2.171606	0.748735	2.901615
H	-2.598997	0.257682	0.860957
C	0.126418	1.272122	3.409349
H	1.505596	1.189079	1.775026
H	-3.208003	0.641287	3.212334
H	0.893858	1.568446	4.120307
C	4.574129	-0.774649	0.749875
H	5.594191	-0.889441	1.105282
O	0.486796	-0.721375	-2.389381
C	-0.891375	-1.692834	-0.494293
C	-1.020164	-2.309712	0.751352
C	-1.671361	-2.177270	-1.545211
C	-1.896011	-3.381551	0.881124
H	-0.478356	-1.970085	1.625580
C	-2.541671	-3.237226	-1.301460
H	-1.618328	-1.749320	-2.538703
H	-1.996636	-3.881996	1.840355
H	-3.169611	-3.614474	-2.104256
C	1.206702	0.086099	-3.321937
H	2.281289	-0.104740	-3.239947
H	0.862654	-0.207075	-4.316046
H	1.005239	1.152747	-3.174750
N	-1.688139	3.802166	-1.059779
H	-2.145693	4.703614	-1.134238
C	-1.195052	1.118113	3.827858
H	-1.464566	1.296103	4.865591
N	-2.656219	-3.844069	-0.117487

[TS-I·H]$^{+}$-Py,OMe,ax-a (ν_i = -491.12 cm^{-1})

C	-3.936541	-1.624936	-0.499020
C	-2.686744	-1.183820	-0.925818
C	-1.614230	-1.125934	-0.025563
C	-1.804416	-1.535894	1.297935
C	-3.048783	-1.998088	1.713053
H	-4.763542	-1.652822	-1.202499
H	-2.554155	-0.884972	-1.961373
H	-1.000606	-1.486247	2.021124
H	-3.182708	-2.319292	2.741815
P	-0.028797	-0.548154	-0.695486
C	1.514129	-1.254029	-0.036671
C	2.523243	-1.524282	-0.971540
C	1.731749	-1.555791	1.312745
C	3.734199	-2.073619	-0.558108
H	2.370119	-1.307719	-2.024064
C	2.933431	-2.127617	1.716317
H	0.985781	-1.332926	2.065107
H	4.512362	-2.265435	-1.290980
H	3.085710	-2.363799	2.765387
C	0.055611	1.141567	0.941791
C	1.262823	1.521389	1.523037
C	-1.111205	1.540906	1.589105
C	1.255918	2.218897	2.727359
H	2.217942	1.288727	1.056919
C	-1.024044	2.237994	2.791335
H	-2.095371	1.325789	1.179170
H	2.193562	2.507403	3.198061
H	-1.929016	2.541182	3.313949
C	-4.118235	-2.036657	0.819156
H	-5.091151	-2.388701	1.150425
O	-0.063158	-1.248846	-2.187014
C	0.039050	1.150731	-1.162914
C	-1.150606	1.880927	-1.516877
C	1.286577	1.747352	-1.564340
C	-1.048821	3.173206	-1.927416
H	-2.134972	1.441652	-1.414324
C	1.311940	3.044453	-1.972914
H	2.219137	1.199607	-1.505991
H	-1.912572	3.784122	-2.160444
H	2.227443	3.557931	-2.241122
C	-0.176364	-2.664754	-2.381847
H	-1.209221	-2.911185	-2.644180
H	0.487780	-2.932730	-3.206516
H	0.113928	-3.227362	-1.488438
N	0.135716	2.574230	3.370106
N	0.164483	3.758209	-2.102934
H	0.209859	4.713568	-2.439132
C	3.938911	-2.382190	0.784444
H	4.879958	-2.819653	1.105821

[TS-I·H]$^{+}$-Py,Ph,ax-a (ν_i = -403.65 cm^{-1})

C	0.873757	3.213453	-2.015172

C	0.923629	1.919981	-1.500356
C	0.353664	1.649936	-0.252810
C	-0.227174	2.677068	0.495944
C	-0.247701	3.972077	-0.011898
H	1.302002	3.420066	-2.991689
H	1.409976	1.132279	-2.070555
H	-0.667470	2.468125	1.466551
H	-0.692202	4.772107	0.572936
P	0.433456	-0.021745	0.426467
C	-1.937864	0.050970	0.441955
C	-2.643323	-0.377434	1.564239
C	-2.659053	0.754722	-0.520781
C	-3.997304	-0.069207	1.686323
H	-2.162239	-0.951433	2.352930
C	-4.010120	1.018730	-0.317792
H	-2.189365	1.106557	-1.438580
H	-4.555358	-0.390957	2.564076
H	-4.578856	1.574951	-1.060903
C	2.228681	-0.383220	0.267728
C	2.682245	-1.575723	-0.304517
C	3.166454	0.563712	0.705950
C	4.050112	-1.821702	-0.431291
H	1.980394	-2.323990	-0.660968
C	4.529106	0.315941	0.583762
H	2.832321	1.501895	1.143714
C	4.973030	-0.879158	0.013761
H	4.390121	-2.750617	-0.880516
H	5.245739	1.055942	0.928848
H	6.037949	-1.070991	-0.085861
C	0.291273	4.238333	-1.271168
H	0.263031	5.248599	-1.669813
O	0.192265	-0.059448	2.011015
C	-0.415153	-1.318267	-0.438636
C	-0.665460	-2.556495	0.230383
C	-0.669292	-1.267666	-1.842001
C	-1.329815	-3.548895	-0.426123
H	-0.370222	-2.707470	1.262521
C	-1.338804	-2.297766	-2.435767
H	-0.375424	-0.416478	-2.443837
H	-1.581907	-4.496870	0.033205
H	-1.596343	-2.305532	-3.487794
N	-1.689075	-3.396419	-1.725125
C	1.097676	-0.637761	2.975596
H	0.496893	-0.772826	3.875790
H	1.478207	-1.602682	2.635004
H	1.922622	0.048655	3.175801
N	-4.687293	0.620770	0.768917
H	-2.166638	-4.157800	-2.196514

[Int-IV·H]$^{+}$-Ph,OMe,ax-a

C	1.998384	-3.602744	-0.191212
C	1.123224	-2.583881	-0.558756
C	1.499088	-1.264216	-0.306501
C	2.744465	-1.025786	0.283263
C	3.541913	-2.117949	0.607617
H	1.727428	-4.639332	-0.371950
H	0.181335	-2.838613	-1.031536
H	3.104022	-0.024503	0.491715
H	4.512789	-1.960894	1.069397
P	0.414948	0.119420	-0.755584
C	0.068851	1.370304	0.640963
C	-0.662685	2.479592	-0.082221
C	1.357876	1.917715	1.214446
C	-0.058484	3.631694	-0.425440
H	-1.682034	2.316185	-0.412344
C	1.868770	3.102670	0.838673
H	1.882886	1.339413	1.965537
H	-0.573767	4.401136	-0.989792
H	2.796412	3.483524	1.251481
C	-0.760140	0.629434	1.696915
C	-2.109163	0.927674	1.908536
C	-0.174406	-0.388360	2.462101
C	-2.858899	0.214145	2.842601
H	-2.594293	1.720683	1.350067
C	-0.923376	-1.104240	3.392411
H	0.875177	-0.639111	2.340831
H	-3.906770	0.462606	2.987794
H	-0.447718	-1.892302	3.969779
O	1.065185	0.914483	-1.973788
C	-1.146038	-0.473263	-1.417738
C	-1.973804	-1.296517	-0.640709
C	-1.557347	-0.057599	-2.689349
C	-3.204944	-1.703229	-1.143245
H	-1.663271	-1.631436	0.344402
C	-2.794221	-0.467773	-3.180026
H	-0.920919	0.581247	-3.292391
H	-3.842150	-2.345011	-0.542241
H	-3.113102	-0.144352	-4.166462
C	2.475381	1.148554	-2.185403
H	2.976663	0.203119	-2.405076
H	2.524359	1.808658	-3.050831
H	2.920651	1.634642	-1.315925
C	-3.616727	-1.287462	-2.409343
H	-4.580733	-1.605445	-2.796315
N	1.237011	3.922508	-0.068946
H	1.598094	4.852116	-0.230162
N	3.184269	-3.387148	0.385074
C	-2.272807	-0.810126	3.582198
H	-2.859178	-1.368842	4.306488

[Int-IV·H]$^{+}$-Ph,OMe,ax-b

C	2.821010	-2.945920	-0.251773
C	1.669960	-2.208110	-0.514766
C	1.746939	-0.817913	-0.443591
C	2.977816	-0.228777	-0.137627
C	4.064763	-1.061001	0.107897
H	2.789596	-4.031005	-0.298224
H	0.754441	-2.728442	-0.771779
H	3.106073	0.847767	-0.096352
H	5.032317	-0.631084	0.351944
P	0.330850	0.275462	-0.722654
C	-0.201733	1.300329	0.788028
C	-1.235270	2.250594	0.227681
C	0.976253	2.086556	1.314341
C	-0.970407	3.550951	0.004286
H	-2.201620	1.864073	-0.074811
C	1.142703	3.396276	1.058017
H	1.716833	1.577423	1.920049
H	-1.705171	4.215643	-0.436497
H	1.995612	3.949223	1.435955
C	-0.739202	0.290409	1.809882
C	-2.100197	0.218540	2.119947
C	0.136079	-0.608048	2.435147
C	-2.577331	-0.737935	3.015123
H	-2.806635	0.908183	1.671386
C	-0.340168	-1.566225	3.326396
H	1.202981	-0.573579	2.234774
H	-3.639899	-0.775989	3.239394
H	0.357671	-2.254722	3.795014
O	0.803827	1.392767	-1.756140
C	-1.088990	-0.592080	-1.400496
C	-1.675882	-1.665696	-0.713865
C	-1.673483	-0.106006	-2.576958
C	-2.826069	-2.260107	-1.222094
H	-1.249215	-2.039911	0.212157
C	-2.825121	-0.708355	-3.075504
H	-1.242246	0.740455	-3.102396
H	-3.276639	-3.093157	-0.690935
H	-3.274557	-0.331449	-3.989319
C	1.540185	1.074085	-2.962625
H	1.222012	0.115734	-3.380212
H	1.318543	1.879463	-3.662585
H	2.607205	1.053265	-2.732910
C	-3.399077	-1.784653	-2.401400
H	-4.298160	-2.252017	-2.792920
N	0.230545	4.127805	0.335077
H	0.347220	5.127293	0.247401
N	3.998172	-2.395756	0.061070
C	-1.701957	-1.639791	3.615311
H	-2.075681	-2.388311	4.308616

[Int-IV·H]$^{+}$-Py,OMe,ax-a

C	2.696558	-3.118611	-0.333102
C	1.634076	-2.274990	-0.645441
C	1.724495	-0.906070	-0.361985
C	2.895107	-0.387656	0.214394
C	3.951328	-1.238208	0.519269
H	2.618998	-4.179491	-0.551508
H	0.745739	-2.691062	-1.109093
H	2.992102	0.672159	0.424040
H	4.853926	-0.831995	0.965778
P	0.356562	0.193734	-0.765922
C	-0.235355	1.344611	0.630086
C	-1.266729	2.217929	-0.051456
C	0.903947	2.212104	1.122165
C	-0.991922	3.474721	-0.443402
H	-2.231035	1.796724	-0.311368
C	1.079908	3.475063	0.697395
H	1.596687	1.801884	1.847320
H	-1.716975	4.077491	-0.979151
H	1.906275	4.085598	1.044490
C	-0.793438	0.457819	1.746236
C	-2.152662	0.421558	2.055971
C	0.049581	-0.368412	2.496285
C	-2.601245	-0.435143	3.056963
H	-2.875850	1.042367	1.540654
C	-0.494511	-1.191102	3.475130
H	1.121971	-0.390908	2.333853
H	-3.660366	-0.473651	3.299551
H	0.153596	-1.841855	4.056786
C	3.851189	-2.603631	0.252018
H	4.677761	-3.265194	0.495195
O	0.758797	1.151221	-1.977351
C	-1.061178	-0.723994	-1.382262
C	-1.671095	-1.699708	-0.580124
C	-1.589853	-0.414832	-2.640383
C	-2.802801	-2.361842	-1.043465
H	-1.264629	-1.957728	0.393798
C	-2.724792	-1.082951	-3.093231
H	-1.122135	0.341195	-3.262339
H	-3.270264	-3.120852	-0.423292
H	-3.134064	-0.842641	-4.070031
C	2.096473	1.603848	-2.281199
H	2.722883	0.752675	-2.557212
H	1.981046	2.276124	-3.130876
H	2.521575	2.141039	-1.431721
C	-3.330994	-2.052787	-2.296969
H	-4.216181	-2.571635	-2.654019
N	-1.801191	-1.242651	3.760691
N	0.210491	4.086405	-0.177290
H	0.318508	5.071408	-0.374379

[Int-IV·H]$^{+}$-Py,OMe,ax-b

C	-4.111513	-0.881723	0.155697
C	-2.977325	-0.135772	-0.144419
C	-1.766888	-0.790081	-0.424254
C	-1.709824	-2.188449	-0.426979
C	-2.851047	-2.925461	-0.123864
H	-5.046685	-0.373482	0.371023
H	-3.040303	0.947952	-0.172161
H	-0.790941	-2.711385	-0.668988
H	-2.803455	-4.010307	-0.125895
P	-0.324561	0.230069	-0.754255
C	1.084296	-0.722100	-1.341800
C	1.698433	-0.339710	-2.540912
C	1.631355	-1.759937	-0.571329
C	2.840888	-1.006422	-2.975688
H	1.297391	0.477524	-3.132496
C	2.772947	-2.418465	-1.015199
H	1.179386	-2.056813	0.370973
H	3.313461	-0.708924	-3.907072
H	3.192718	-3.222430	-0.418044
C	0.727185	0.382862	1.783717
C	2.072641	0.294003	2.138610
C	-0.165351	-0.455674	2.459635
C	2.461139	-0.622454	3.111332
H	2.829651	0.918527	1.678948
C	0.321180	-1.339965	3.415129
H	-1.231505	-0.442781	2.256961
H	3.509092	-0.702420	3.389661
H	-0.364326	-2.001179	3.939254
C	-4.047025	-2.275069	0.174486
H	-4.934476	-2.855002	0.411676
O	-0.717107	1.312102	-1.859230
C	0.234708	1.334968	0.689541
C	-0.919035	2.188318	1.164585
C	1.308538	2.217689	0.094946
C	-1.039898	3.484828	0.829532
H	-1.678143	1.738637	1.794065
C	1.088347	3.510215	-0.205998
H	2.265558	1.781978	-0.168664
H	-1.877304	4.086121	1.166068
H	1.849341	4.125315	-0.673441
C	-1.487880	0.969551	-3.036367
H	-2.550525	0.980990	-2.786060
H	-1.262451	1.745469	-3.767641
H	-1.199500	-0.009280	-3.426832
N	1.614469	-1.440784	3.744566
N	-0.099051	4.141906	0.072475
C	3.376371	-2.044599	-2.215909
H	4.268849	-2.561577	-2.557023
H	-0.181943	5.138049	-0.072893

[Int-IV·H]$^{+}$-Py,Ph,ax-a

C	-1.513768	3.022570	-1.742693
C	-0.569117	2.115268	-1.273462
C	-0.696207	1.591472	0.019229
C	-1.763645	1.976633	0.838443
C	-2.702523	2.884725	0.358977
H	-1.414731	3.430964	-2.743992
H	0.259162	1.821013	-1.912273
H	-1.868884	1.567022	1.837989
H	-3.532346	3.183034	0.992798
P	0.407136	0.282432	0.556744
C	-1.698934	-1.296754	-0.080088
C	-2.316706	-1.516955	1.153773
C	-2.527241	-0.972882	-1.155145
C	-3.697882	-1.392888	1.256070
H	-1.749061	-1.768921	2.042906
C	-3.899161	-0.870385	-0.950644
H	-2.134533	-0.791366	-2.148975
H	-4.186122	-1.558168	2.213391
H	-4.550732	-0.611355	-1.781594
C	2.114002	0.698235	0.179466
C	3.090545	-0.293399	0.011574
C	2.476345	2.052676	0.143151
C	4.413400	0.072749	-0.211261
H	2.833882	-1.345478	0.061467
C	3.802951	2.408150	-0.079295
H	1.732821	2.830987	0.286830
C	4.769321	1.420283	-0.260790
H	5.166815	-0.697695	-0.344681
H	4.078722	3.457882	-0.110878
H	5.803854	1.700793	-0.437462
C	-2.580990	3.403260	-0.929796
H	-3.319432	4.108026	-1.301526
O	0.193123	0.180671	2.138722
C	-0.165455	-1.351012	-0.222368
C	0.418672	-2.525573	0.539097
C	0.313115	-1.379385	-1.659069
C	1.229127	-3.431823	-0.032939
H	0.152728	-2.657182	1.581372
C	1.142530	-2.326539	-2.129037
H	-0.004475	-0.596400	-2.338187
H	1.614955	-4.280564	0.520872
H	1.475178	-2.329579	-3.161052
N	1.629270	-3.345052	-1.345293
C	1.254095	-0.183788	3.054023
H	0.763121	-0.331257	4.015564
H	1.743757	-1.106260	2.735894
H	1.976021	0.633587	3.117448
N	-4.494083	-1.069363	0.230975
H	2.206109	-4.067858	-1.749938

[TS-I·H]$^{+}$-Ph,OMe,ax-a (ν_i = -255.96 cm^{-1})

C	3.068855	-2.772227	0.665464
C	1.930295	-2.203240	0.100958
C	1.894229	-0.819556	-0.069923
C	3.006091	-0.071388	0.334253
C	4.094183	-0.740352	0.883035
H	3.123453	-3.848727	0.805622
H	1.108301	-2.843301	-0.201547
H	3.037949	1.008444	0.220088
H	4.971683	-0.183311	1.200924
P	0.453472	0.103605	-0.684437
C	-0.531337	1.713872	0.614575
C	-1.400508	2.322883	-0.379964
C	0.545987	2.587543	1.056346
C	-1.057127	3.483135	-0.996148
H	-2.297506	1.812803	-0.711154
C	0.827244	3.743543	0.403882
H	1.161668	2.308181	1.903259
H	-1.659028	3.929283	-1.778915
H	1.641203	4.396923	0.695042
C	-1.125434	0.771297	1.631672
C	-2.507749	0.584312	1.719251
C	-0.293368	0.047440	2.498395
C	-3.045570	-0.318472	2.637041
H	-3.183538	1.144304	1.081206
C	-0.829750	-0.852567	3.412453
H	0.785914	0.165730	2.452925
H	-4.122756	-0.451790	2.686135
H	-0.166456	-1.409224	4.068765
O	0.992018	0.998547	-1.919786
C	-0.786524	-1.036799	-1.334178
C	-1.398525	-1.952700	-0.464187
C	-1.264666	-0.895350	-2.642874
C	-2.449082	-2.744693	-0.916932
H	-1.063938	-2.047202	0.566225
C	-2.319748	-1.689780	-3.086570
H	-0.822172	-0.167651	-3.316715
H	-2.913969	-3.456261	-0.240525
H	-2.682595	-1.580257	-4.104613
C	1.885584	0.472589	-2.923175
H	1.647738	-0.567362	-3.163613
H	1.751414	1.098268	-3.806778
H	2.915690	0.546240	-2.565299
C	-2.909056	-2.616342	-2.227806
H	-3.732685	-3.233028	-2.576738
N	0.060975	4.170013	-0.638127
H	0.272887	5.051557	-1.089071
N	4.135919	-2.067012	1.055909
C	-2.210656	-1.044156	3.481583
H	-2.629937	-1.751040	4.192241

[TS-II·H]$^+$-Py,OMe,ax-a (ν_i = -245.55 cm^{-1})

C	3.927798	-1.229217	1.140910
C	2.614527	-1.265463	0.682371
C	2.097094	-0.189423	-0.053679
C	2.906563	0.919245	-0.326996
C	4.218499	0.952340	0.140668
H	4.324281	-2.065434	1.709653
H	1.995140	-2.133376	0.896286
H	2.523374	1.753901	-0.906592
H	4.843461	1.814560	-0.074006
P	0.385498	-0.337352	-0.633452
C	-0.168027	1.273514	-1.234490
C	-0.802779	1.388581	-2.477065
C	-0.124389	2.378712	-0.371000
C	-1.357886	2.606980	-2.864504
H	-0.864059	0.533467	-3.144394
C	-0.680567	3.591530	-0.764472
H	0.342074	2.296107	0.608197
H	-1.841423	2.693242	-3.833492
H	-0.638068	4.444852	-0.093512
C	-1.376474	-0.189940	1.627143
C	-2.392667	0.761393	1.705412
C	-0.342661	-0.099309	2.565602
C	-2.320747	1.752497	2.681711
H	-3.240087	0.754685	1.029416
C	-0.362164	0.925344	3.501176
H	0.488677	-0.796978	2.566067
H	-3.103354	2.504586	2.744806
H	0.440615	1.010110	4.229220
C	4.728576	-0.118353	0.873889
H	5.752359	-0.088419	1.236397
O	0.404308	-1.345668	-1.906979
C	-1.371906	-1.258561	0.564198
C	-0.970577	-2.597712	0.958457
C	-2.398502	-1.233658	-0.461255
C	-1.344280	-3.682280	0.233672
H	-0.333255	-2.746263	1.822197
C	-2.723394	-2.358038	-1.152006
H	-2.865834	-0.300870	-0.753548
H	-1.034466	-4.689864	0.483972
H	-3.443956	-2.358398	-1.961403
C	1.429700	-1.260182	-2.915373
H	2.372270	-1.649359	-2.520426
H	1.088477	-1.881499	-3.744762
H	1.563640	-0.228767	-3.255125
N	-1.328096	1.852212	3.569568
N	-2.176668	-3.561147	-0.837457
C	-1.295661	3.707857	-2.011845
H	-1.730255	4.656044	-2.316095
H	-2.463660	-4.389304	-1.345180

[TS-II·H]$^+$-Py,Ph,ax-a (ν_i = -252.59 cm^{-1})

C	-1.496168	2.880512	-1.868123

C	-0.541913	2.044219	-1.294874
C	-0.724530	1.565759	0.009817
C	-1.869779	1.928024	0.730287
C	-2.817100	2.767481	0.151015
H	-1.347784	3.251253	-2.878342
H	0.341713	1.771529	-1.865828
H	-2.027281	1.552021	1.736321
H	-3.702740	3.046184	0.715006
P	0.384504	0.302232	0.659184
C	-1.689032	-1.440087	-0.142348
C	-2.217269	-1.592293	1.143444
C	-2.570441	-1.049592	-1.151044
C	-3.564121	-1.332069	1.360002
H	-1.597526	-1.884727	1.985354
C	-3.903414	-0.808429	-0.830773
H	-2.251412	-0.925821	-2.179817
H	-3.982369	-1.439524	2.357621
H	-4.595094	-0.491350	-1.607253
C	2.090748	0.819618	0.330150
C	3.079060	-0.167599	0.235762
C	2.445725	2.172043	0.231667
C	4.408685	0.192209	0.030670
H	2.816877	-1.216606	0.332036
C	3.775873	2.526179	0.025972
H	1.690226	2.948277	0.315290
C	4.755591	1.537850	-0.078802
H	5.171116	-0.577929	-0.043504
H	4.047668	3.574980	-0.052409
H	5.792346	1.818825	-0.242499
C	-2.634836	3.240454	-1.148194
H	-3.379535	3.890511	-1.599129
O	0.131561	0.435662	2.266273
C	-0.219464	-1.660183	-0.409673
C	0.384706	-2.821156	0.236651
C	0.291861	-1.420282	-1.751960
C	1.459044	-3.449050	-0.297989
H	-0.017782	-3.193447	1.171074
C	1.386902	-2.073472	-2.216320
H	-0.152066	-0.660166	-2.383538
H	1.929567	-4.304191	0.172410
H	1.814648	-1.871838	-3.191322
N	1.992347	-3.051101	-1.489143
C	0.812178	-0.481510	3.141977
H	0.439676	-0.269431	4.144694
H	0.585968	-1.517424	2.875191
H	1.892889	-0.309998	3.106236
N	-4.409815	-0.938605	0.399303
H	2.779294	-3.553708	-1.880523

[Int-V·H]$^{+}$-Ph,OMe,ax-a

C	-4.778680	-1.128326	-0.152476
C	-3.510362	-0.757626	0.281566
C	-2.770145	0.148910	-0.482378
C	-3.355726	0.633892	-1.653473
C	-4.633525	0.203019	-2.004416
H	-5.370439	-1.831462	0.428578
H	-3.116872	-1.179206	1.201595
H	-2.830859	1.336227	-2.296125
H	-5.103801	0.568289	-2.914109
P	-1.085618	0.783427	-0.051161
C	2.490978	1.125416	-0.574431
C	2.521585	1.552945	0.762934
C	2.299511	2.098332	-1.569379
C	2.333275	2.881819	1.067031
H	2.656867	0.852697	1.577727
C	2.120574	3.417051	-1.219834
H	2.295758	1.837743	-2.621196
H	2.324473	3.270806	2.077262
H	1.966008	4.212855	-1.937282
C	2.624941	-0.305902	-0.918836
C	3.393884	-1.164253	-0.121397
C	1.959981	-0.828621	-2.037137
C	3.500666	-2.514304	-0.440383
H	3.930050	-0.778058	0.740731
C	2.062261	-2.180794	-2.348298
H	1.332555	-0.188589	-2.650893
H	4.105162	-3.167000	0.183005
H	1.530046	-2.575437	-3.209220
O	-1.404673	1.963823	1.074156
C	-0.433563	-0.601680	0.967360
C	-0.380742	-1.892065	0.422569
C	0.156695	-0.368492	2.213101
C	0.235305	-2.928733	1.118016
H	-0.821613	-2.094046	-0.551748
C	0.772634	-1.407957	2.910667
H	0.142795	0.628578	2.645852
H	0.268271	-3.923880	0.682766
H	1.223181	-1.212273	3.880293
C	-2.394792	1.814200	2.098457
H	-2.319672	0.842702	2.597790
H	-2.212487	2.609576	2.824762
H	-3.397380	1.930746	1.674177
C	0.813780	-2.689349	2.365292
H	1.298142	-3.498202	2.905747
N	2.134540	3.770346	0.077781
H	1.995714	4.749184	0.319877
N	-5.343205	-0.664106	-1.275213
C	2.833843	-3.026535	-1.552499
H	2.912119	-4.082590	-1.795745

[Int-V·H]$^{+}$-Py,OMe,ax-a

C	-4.197082	-0.541386	-2.257752
C	-2.962541	-0.886103	-1.706198
C	-2.609474	-0.461688	-0.419055
C	-3.520068	0.318490	0.309410
C	-4.753646	0.659792	-0.237448
H	-4.454953	-0.874040	-3.259579
H	-2.267281	-1.489896	-2.286337
H	-3.264700	0.667710	1.306353
H	-5.451055	1.263074	0.337665
P	-0.968309	-1.009887	0.200863
C	-0.431853	0.438071	1.202784
C	0.308377	0.228284	2.372926
C	-0.593137	1.748511	0.734174
C	0.861605	1.303313	3.067191
H	0.453486	-0.781313	2.750579
C	-0.033739	2.822351	1.423185
H	-1.155406	1.940007	-0.176375
H	1.426213	1.122454	3.978274
H	-0.165979	3.831826	1.043165
C	2.315623	0.632506	-1.073622
C	2.995128	1.653960	-0.406819
C	1.374178	0.997588	-2.039666
C	2.709755	2.974640	-0.735101
H	3.747525	1.440224	0.345766
C	1.159768	2.347937	-2.290244
H	0.788298	0.254433	-2.571856
H	3.229633	3.783734	-0.228792
H	0.424347	2.652119	-3.030500
C	-5.093378	0.230921	-1.522405
H	-6.055562	0.502226	-1.948789
O	-1.314303	-2.148977	1.366711
C	2.562158	-0.793766	-0.755876
C	2.487511	-1.774131	-1.754652
C	2.848207	-1.196898	0.555792
C	2.671450	-3.099199	-1.427378
H	2.294927	-1.514939	-2.789187
C	3.021694	-2.534099	0.837269
H	2.908660	-0.482445	1.368139
H	2.625072	-3.908357	-2.145384
H	3.227421	-2.918232	1.828364
C	-2.305207	-1.950235	2.378081
H	-3.309893	-2.013007	1.946818
H	-2.172723	-2.754180	3.106172
H	-2.181209	-0.984263	2.879553
N	1.811569	3.331644	-1.660022
N	2.923938	-3.438648	-0.151905
C	0.694931	2.603413	2.592132
H	1.131729	3.441866	3.128098
H	3.050387	-4.423494	0.074337

[Int-V·H]$^{+}$-Py,Ph,ax-a

C	-1.115654	-1.319967	2.722471
C	-0.187492	-1.157901	1.692924
C	-0.474862	-1.608898	0.401105
C	-1.714482	-2.219750	0.157627
C	-2.633139	-2.396593	1.187705
H	-0.878547	-0.961107	3.720718
H	0.761827	-0.675937	1.907654
H	-1.968098	-2.557214	-0.845284
H	-3.587711	-2.873933	0.983361
P	0.633681	-1.385362	-1.044573
C	-2.036219	1.506075	-0.421328
C	-2.316287	0.952794	-1.673269
C	-2.967797	1.312288	0.600624
C	-3.499614	0.243485	-1.842731
H	-1.623217	1.043332	-2.503490
C	-4.126016	0.593760	0.324729
H	-2.818160	1.725338	1.593026
H	-3.730987	-0.203156	-2.806270
H	-4.865932	0.438256	1.105474
C	2.189229	-0.786517	-0.275974
C	2.626434	0.501363	-0.598570
C	2.965073	-1.575527	0.584103
C	3.802998	1.010946	-0.047824
H	2.047250	1.111165	-1.289215
C	4.146149	-1.073976	1.123876
H	2.642544	-2.583368	0.834174
C	4.563246	0.223070	0.813618
H	4.128971	2.016118	-0.302421
H	4.742384	-1.692406	1.789621
H	5.484531	0.613166	1.238151
C	-2.336294	-1.943003	2.473914
H	-3.058145	-2.069713	3.276413
O	0.967315	-3.014421	-1.275972
C	-0.790123	2.270974	-0.179631
C	-0.227984	3.073396	-1.182654
C	-0.148086	2.212510	1.064478
C	0.924386	3.783738	-0.924321
H	-0.690276	3.172023	-2.157907
C	1.007773	2.932044	1.274536
H	-0.533183	1.598708	1.869158
H	1.406819	4.429733	-1.646884
H	1.560311	2.923277	2.205310
N	1.503183	3.693761	0.285127
C	1.690219	-3.332490	-2.465577
H	1.722985	-4.422235	-2.533151
H	1.188385	-2.928200	-3.353835
H	2.715769	-2.945094	-2.418649
N	-4.402663	0.063981	-0.871705
H	2.356350	4.221926	0.457480

Pathway [Int-V·2H]$^{2+}$

[Int-III·2H]$^{2+}$-Ph,OMe,ax-a

C	-0.463949	4.166219	-0.884291
C	-0.201589	2.816933	-1.107856
C	-0.455996	1.868035	-0.109865
C	-0.997437	2.297766	1.109274
C	-1.292195	3.642078	1.317561
H	-0.244278	4.890073	-1.663885
H	0.199358	2.506803	-2.066128
H	-1.191341	1.590699	1.909550
H	-1.726920	3.954309	2.262789
P	-0.099662	0.084080	-0.403556
C	-1.575694	-1.051405	-0.343313
C	-1.564133	-2.258479	-1.049087
C	-2.727346	-0.690824	0.360256
C	-2.673596	-3.076626	-1.015327
H	-0.709848	-2.571270	-1.638450
C	-3.821759	-1.531419	0.349224
H	-2.797163	0.233792	0.920465
H	-2.735559	-4.028145	-1.527787
H	-4.749878	-1.316014	0.863707
C	0.430656	-0.297096	1.405687
C	-0.017378	-1.390052	2.153362
C	1.443282	0.502349	1.961993
C	0.508428	-1.664474	3.419702
H	-0.780317	-2.060261	1.768171
C	1.969421	0.236834	3.221406
H	1.831043	1.354505	1.405968
C	1.499739	-0.851762	3.959412
H	0.137442	-2.519319	3.979350
H	2.746320	0.879092	3.628080
H	1.907340	-1.063006	4.944386
C	-1.017042	4.581352	0.325122
H	-1.233467	5.632607	0.494194
O	-0.334558	0.201273	-2.150021
C	1.607655	-0.461798	-0.936629
C	2.518232	0.456084	-1.469259
C	2.015999	-1.786598	-0.746600
C	3.792832	0.038621	-1.789948
H	2.259091	1.494897	-1.633005
C	3.291521	-2.163755	-1.106412
H	1.358900	-2.530836	-0.309621
H	4.554747	0.692733	-2.194907
H	3.673335	-3.171249	-1.000350
N	4.136510	-1.246958	-1.607674
C	-1.568700	0.553059	-2.756300
H	-1.356069	1.192206	-3.619848
H	-2.094900	-0.345546	-3.103431
H	-2.232333	1.105186	-2.077682
N	-3.758815	-2.690673	-0.324293
H	5.080778	-1.538173	-1.854631
H	-4.574457	-3.301310	-0.318320

[Int-III·2H]$^{2+}$-Ph,OMe,ax-b

C	0.650653	4.153409	-0.691192
C	0.660430	2.775267	-0.891580
C	-0.152937	1.943809	-0.113564
C	-0.996668	2.512133	0.844600
C	-1.030137	3.893674	1.018282
H	1.298975	4.786799	-1.290003
H	1.300351	2.353414	-1.661016
H	-1.631178	1.893032	1.469000
H	-1.701080	4.323905	1.756375
P	-0.097240	0.132850	-0.407815
C	-1.739978	-0.785969	-0.340941
C	-2.156178	-1.587758	-1.406582
C	-2.570993	-0.680976	0.778834
C	-3.363775	-2.254263	-1.333364
H	-1.560671	-1.694475	-2.303787
C	-3.785439	-1.335991	0.796576
H	-2.292006	-0.108832	1.654826
H	-3.742621	-2.898843	-2.116403
H	-4.485654	-1.282623	1.620695
C	0.346073	-0.401335	1.388459
C	0.235751	-1.759806	1.724249
C	0.937317	0.454275	2.324539
C	0.671631	-2.241941	2.955457
H	-0.190496	-2.468525	1.015310
C	1.375459	-0.022186	3.562111
H	1.071384	1.508597	2.102012
H	0.568216	-3.298702	3.188177
H	1.823722	0.667105	4.273087
C	-0.199553	4.716058	0.259166
H	-0.217244	5.792354	0.406270
O	-0.290049	0.339660	-2.147228
C	1.515671	-0.647364	-0.928442
C	2.723908	-0.029078	-0.585475
C	1.552062	-1.876196	-1.596409
C	3.915998	-0.630312	-0.925810
H	2.756487	0.911219	-0.046237
C	2.769360	-2.449633	-1.896359
H	0.651477	-2.402185	-1.888193
H	4.887114	-0.206206	-0.703695
H	2.876375	-3.399970	-2.403952
C	-1.343288	1.103226	-2.711771
H	-0.959726	2.065309	-3.072039
H	-1.764060	0.548249	-3.557975
H	-2.153089	1.305996	-1.997744
N	-4.137868	-2.100489	-0.249056
H	-5.034880	-2.583755	-0.217772
C	1.240804	-1.370161	3.884283
H	1.580716	-1.741143	4.847489
N	3.904403	-1.814350	-1.561416
H	4.794120	-2.250185	-1.796477

[Int-III·2H]$^{2+}$-Ph,Ph,ax-a

C	-1.540576	2.772477	-2.167264
C	-1.184870	1.565842	-1.602266
C	-0.465524	1.551621	-0.404096
C	-0.163573	2.766271	0.216826
C	-0.575320	3.949699	-0.361724
H	-2.076559	2.866553	-3.103120
H	-1.485415	0.651901	-2.102446
H	0.388741	2.807416	1.149583
H	-0.392953	4.927295	0.066634
P	-0.005151	-0.039218	0.517276
C	-1.867109	-0.518952	0.448514
C	-2.791753	0.377610	1.009533
C	-2.366308	-1.680475	-0.146080
C	-4.159074	0.126376	0.975826
H	-2.444474	1.291620	1.489340
C	-3.740448	-1.937463	-0.187948
H	-1.700650	-2.416083	-0.587507
H	-4.849578	0.838337	1.420551
H	-4.100061	-2.848639	-0.659136
C	1.838954	0.540510	0.613121
C	2.428858	0.985753	-0.579576
C	2.653644	0.465104	1.749309
C	3.772113	1.347470	-0.640874
H	1.841504	1.057151	-1.492944
C	4.001412	0.828812	1.696430
H	2.240167	0.121332	2.690396
H	4.196174	1.688563	-1.581875
H	4.607982	0.765458	2.596472
O	0.063522	-0.221214	2.148009
C	0.573985	-1.492489	-0.497147
C	0.617833	-1.549130	-1.893353
C	1.049819	-2.584054	0.240265
C	1.129821	-2.671723	-2.509859
H	0.272876	-0.735180	-2.519153
C	1.543207	-3.688346	-0.420449
H	1.049464	-2.587754	1.325421
H	1.202495	-2.786648	-3.584005
H	1.923503	-4.569772	0.080248
C	-0.807821	-0.958436	3.015099
H	-0.192650	-1.221954	3.878902
H	-1.645684	-0.336512	3.337468
H	-1.181345	-1.870111	2.544006
N	-1.233790	3.916073	-1.531193
N	1.568860	-3.698127	-1.763509
C	4.566673	1.271423	0.503019
H	5.615488	1.553515	0.462248
C	-4.640822	-1.036004	0.370039
H	-5.708751	-1.234668	0.336759
H	-1.519354	4.797539	-1.954851
H	1.943950	-4.518370	-2.237344

[Int-III·2H]$^{2+}$-PyH^{+},OMe,ax-a

C	1.888390	0.993557	3.054643
C	1.299232	1.022218	1.811269
C	0.485462	-0.036744	1.373676
C	0.327075	-1.119842	2.245778
C	0.932555	-1.116449	3.488122
H	2.516977	1.783213	3.447031
H	1.480658	1.891099	1.185388
H	-0.265899	-1.987343	1.979960
H	0.839501	-1.922363	4.205836
P	-0.199753	0.013038	-0.490641
C	-0.884677	1.711024	-0.261779
C	-1.504997	2.085864	0.937737
C	-0.799005	2.648537	-1.298033
C	-2.043682	3.360248	1.088406
H	-1.574367	1.395541	1.772424
C	-1.306766	3.935124	-1.132475
H	-0.338208	2.376767	-2.240942
H	-2.537776	3.625680	2.018664
H	-1.216059	4.654024	-1.941867
C	-1.334204	-1.410131	-0.253596
C	-2.429969	-1.320853	0.609184
C	-1.127193	-2.586178	-0.982010
C	-3.304577	-2.396593	0.745715
H	-2.615385	-0.417156	1.181243
C	-1.987058	-3.670271	-0.821661
H	-0.303416	-2.660944	-1.686590
H	-4.159964	-2.310273	1.409774
H	-1.808841	-4.583372	-1.382674
O	-0.443481	0.020191	-2.216756
C	1.579675	-0.264831	-0.969651
C	2.210736	-1.481198	-0.688649
C	2.316711	0.756130	-1.578758
C	3.532370	-1.657601	-1.039020
H	1.692838	-2.296725	-0.196513
C	3.641957	0.540036	-1.892157
H	1.879302	1.718101	-1.817007
H	4.082653	-2.574075	-0.867108
H	4.276820	1.281308	-2.360940
C	-1.738208	0.047557	-2.798077
H	-2.054826	-0.966155	-3.072150
H	-2.492492	0.477139	-2.126314
H	-1.691949	0.663573	-3.702294
C	-3.079090	-3.576801	0.039651
H	-3.756577	-4.418369	0.154451
C	-1.937778	4.291841	0.056903
H	-2.345566	5.291276	0.180621
N	1.684985	-0.068742	3.855819
N	4.202793	-0.650309	-1.622128
H	5.180087	-0.794676	-1.870685
H	2.120434	-0.077872	4.776219

[Int-III·2H]$^{2+}$-PyH^{+},OMe,ax-b

C	2.967781	2.989854	-0.480016
C	2.250724	1.811572	-0.673151
C	0.941844	1.698400	-0.192036
C	0.349879	2.786869	0.452910
C	1.064110	3.971459	0.625520
H	3.987231	3.062161	-0.848387
H	2.717799	0.989051	-1.207250
H	-0.667989	2.732986	0.824709
H	0.589764	4.813825	1.121076
P	0.041423	0.134492	-0.516216
C	-1.839765	0.144502	-0.455780
C	-2.572187	-0.416981	-1.505480
C	-2.538270	0.696081	0.623437
C	-3.951802	-0.431798	-1.448706
H	-2.086262	-0.832420	-2.378405
C	-3.918368	0.694244	0.621976
H	-2.036157	1.128344	1.480486
H	-4.579487	-0.864644	-2.217311
H	-4.520088	1.121774	1.413825
C	0.031493	-0.443001	1.383706
C	-0.627643	-1.646225	1.691075
C	0.681845	0.213091	2.433553
C	-0.635786	-2.139804	2.974854
H	-1.141064	-2.219840	0.923706
C	0.656495	-0.311684	3.712376
H	1.228028	1.136534	2.281057
H	-1.127860	-3.058056	3.270444
H	1.142136	0.151077	4.562540
C	2.376188	4.072983	0.168431
H	2.933450	4.994684	0.310663
O	-0.011039	0.444023	-2.231875
C	1.021946	-1.375863	-0.902419
C	2.213684	-1.605726	-0.204790
C	0.592249	-2.308012	-1.851231
C	2.972534	-2.743388	-0.465892
H	2.567630	-0.897368	0.539387
C	1.336655	-3.463409	-2.083388
H	-0.319591	-2.146526	-2.414528
H	3.906285	-2.898436	0.067289
H	0.983678	-4.188652	-2.811226
C	-0.513530	1.663932	-2.750748
H	0.287544	2.409504	-2.831206
H	-0.915329	1.462563	-3.749129
H	-1.319407	2.090384	-2.136826
C	2.529905	-3.681182	-1.397608
H	3.114041	-4.576817	-1.590230
N	0.002146	-1.458620	3.945885
N	-4.575871	0.126802	-0.400749
H	-0.006713	-1.833503	4.892413
H	-5.594484	0.121057	-0.380383

[Int-III·2H]$^{2+}$-PyH^{+},OMe,ax-c

C	2.548854	-3.228431	-0.680524
C	1.456028	-2.395118	-0.790458
C	1.531781	-1.089265	-0.293734
C	2.727380	-0.654427	0.285998
C	3.799876	-1.520189	0.361367
H	2.563598	-4.250746	-1.036218
H	0.564996	-2.775418	-1.276453
H	2.848185	0.348173	0.678873
H	4.757634	-1.253317	0.790028
P	0.088247	0.055039	-0.506813
C	0.394151	1.859753	-0.268292
C	0.064265	2.762677	-1.286666
C	0.962984	2.352729	0.912915
C	0.270617	4.128906	-1.113696
H	-0.343730	2.403853	-2.224505
C	1.202564	3.715279	1.069498
H	1.229217	1.684806	1.726519
H	-0.008209	4.815999	-1.907454
H	1.660642	4.076295	1.985877
C	-0.454367	-0.142230	1.391631
C	-1.540089	0.640718	1.822977
C	0.088496	-1.039798	2.317102
C	-2.031152	0.525261	3.101762
H	-2.018123	1.354500	1.158357
C	-0.431102	-1.132720	3.595467
H	0.917088	-1.695241	2.074815
H	-2.861831	1.102342	3.488365
H	-0.052130	-1.809622	4.351372
O	0.443661	0.113989	-2.218251
C	-1.560700	-0.621497	-0.980400
C	-1.999059	-1.838862	-0.447979
C	-2.400926	0.092255	-1.840547
C	-3.250445	-2.346049	-0.789846
H	-1.372822	-2.405380	0.236050
C	-3.666568	-0.400691	-2.150926
H	-2.083843	1.037150	-2.267549
H	-3.570019	-3.301886	-0.384340
H	-4.317210	0.172243	-2.805720
C	1.703806	0.506226	-2.737164
H	2.334009	-0.373765	-2.922090
H	1.531799	1.022106	-3.687493
H	2.244748	1.189968	-2.070165
C	-4.091349	-1.623454	-1.634173
H	-5.074069	-2.011242	-1.887817
N	-1.463464	-0.354981	3.949412
H	-1.835167	-0.432988	4.893837
N	3.676829	-2.769441	-0.112876
C	0.845341	4.608573	0.061558
H	1.018439	5.673475	0.190079
H	4.477941	-3.395711	-0.047138

[Int-III·2H]$^{2+}$-PyH^{+},Ph,ax-a

C	1.067258	3.045096	-2.221882
C	0.976690	1.799695	-1.605273
C	0.257146	1.655074	-0.415148
C	-0.330012	2.779002	0.173510
C	-0.203432	4.031758	-0.422797
H	1.610507	3.142817	-3.157586
H	1.482872	0.949178	-2.052294
H	-0.881940	2.688434	1.105791
H	-0.646915	4.901588	0.053473
P	0.123700	0.041222	0.469380
C	-1.862078	0.284404	0.603507
C	-2.622874	0.117531	1.767968
C	-2.564187	0.567521	-0.580171
C	-3.998736	0.237255	1.731834
H	-2.153596	-0.101626	2.718201
C	-3.936112	0.677910	-0.582321
H	-2.045771	0.715716	-1.522967
H	-4.636864	0.125728	2.599911
H	-4.526231	0.899064	-1.463041
C	2.006725	-0.292078	0.391250
C	2.574944	-1.528729	0.066081
C	2.880392	0.756198	0.723167
C	3.960461	-1.710969	0.057977
H	1.954606	-2.383968	-0.183558
C	4.260623	0.581067	0.722836
H	2.481481	1.732117	0.991246
C	4.808252	-0.657465	0.384890
H	4.371207	-2.682629	-0.204231
H	4.909471	1.412952	0.984373
H	5.885884	-0.797684	0.378081
C	0.482630	4.163796	-1.628922
H	0.569800	5.138019	-2.102023
O	0.054953	-0.026045	2.104002
C	-0.315247	-1.489505	-0.502990
C	-0.746313	-2.595760	0.238646
C	-0.255303	-1.585105	-1.895239
C	-1.097127	-3.756851	-0.415629
H	-0.811902	-2.565644	1.321693
C	-0.632262	-2.763242	-2.507309
H	0.076705	-0.762759	-2.517270
H	-1.431083	-4.655809	0.087101
H	-0.620720	-2.914896	-3.579194
N	-1.033337	-3.802370	-1.757018
C	1.066355	-0.417172	3.042013
H	0.529858	-0.578577	3.979719
H	1.562871	-1.341837	2.741687
H	1.802204	0.378892	3.173102
N	-4.612084	0.510577	0.569433
H	-5.625586	0.602464	0.559682
H	-1.300774	-4.665549	-2.227501

[Int-III·2H]$^{2+}$-PyH^{+},Ph,ax-b

C	0.577375	-2.910716	-2.521348
C	0.215174	-1.719559	-1.895243
C	0.345716	-1.591701	-0.510227
C	0.835273	-2.666836	0.240650
C	1.179260	-3.861299	-0.388191
H	0.479038	-2.999048	-3.599753
H	-0.164829	-0.903790	-2.501385
H	0.951917	-2.579164	1.318496
H	1.548824	-4.693124	0.204956
P	-0.076482	-0.088309	0.459423
C	1.873361	0.298436	0.576056
C	2.547183	0.547759	-0.631295
C	2.646463	0.277439	1.743569
C	3.907101	0.756773	-0.653776
H	2.018091	0.577147	-1.579509
C	4.009948	0.492862	1.685885
H	2.197312	0.091801	2.710377
H	4.477302	0.950271	-1.553897
H	4.658216	0.488890	2.553673
C	-1.977998	-0.301808	0.414654
C	-2.611781	-1.460662	-0.044487
C	-2.788466	0.743557	0.886041
C	-4.005107	-1.567772	-0.048610
H	-2.030488	-2.305304	-0.401201
C	-4.176242	0.641831	0.889169
H	-2.336437	1.656525	1.269512
C	-4.791866	-0.517601	0.414874
H	-4.470913	-2.479079	-0.414853
H	-4.777437	1.467184	1.261814
H	-5.875466	-0.600313	0.410960
C	1.054015	-3.984571	-1.770890
H	1.326945	-4.914076	-2.262755
O	0.012843	-0.225940	2.090660
C	-0.262631	1.570011	-0.418668
C	0.195764	2.712661	0.242677
C	-0.909929	1.715180	-1.648207
C	0.009329	3.954120	-0.330693
H	0.692452	2.657205	1.205607
C	-1.041103	2.971273	-2.203141
H	-1.333221	0.870149	-2.177728
H	0.322264	4.883716	0.127728
H	-1.511129	3.161566	-3.159881
N	-0.584799	4.041634	-1.531097
C	-0.939099	-0.836909	2.973109
H	-0.379493	-1.046602	3.887467
H	-1.761143	-0.152903	3.193988
H	-1.328531	-1.771071	2.562582
N	4.597588	0.723268	0.501119
H	5.602996	0.879788	0.474782
H	-0.701749	4.963248	-1.949197

[Int-III·2H]$^{2+}$-PyH^{+},PyH^{+},ax-a

C	-1.235041	2.941397	-2.168301
C	-1.050299	1.705480	-1.554484
C	-0.252689	1.600986	-0.409308
C	0.315836	2.754451	0.138685
C	0.097488	3.996167	-0.454751
H	-1.836660	3.007760	-3.070385
H	-1.541578	0.830972	-1.971649
H	0.927048	2.695588	1.035795
H	0.530849	4.887816	-0.010689
P	-0.000160	-0.005888	0.460551
C	-1.951457	-0.289239	0.456228
C	-2.772189	0.718772	0.989758
C	-2.585871	-1.418044	-0.071732
C	-4.142012	0.587242	0.987753
H	-2.347419	1.623777	1.413471
C	-3.964694	-1.514930	-0.064677
H	-2.026888	-2.243374	-0.497026
H	-4.825114	1.326662	1.386792
H	-4.511765	-2.360940	-0.462161
C	1.942771	0.311221	0.583751
C	2.714062	0.138168	1.739773
C	2.629148	0.628917	-0.600606
C	4.087318	0.282877	1.695464
H	2.255844	-0.110315	2.688143
C	3.998337	0.763506	-0.609826
H	2.101796	0.776172	-1.537903
H	4.733867	0.165225	2.556411
H	4.577960	1.007548	-1.491396
C	-0.666171	4.089296	-1.616674
H	-0.824285	5.055162	-2.088511
O	0.044290	-0.132075	2.091978
C	0.362609	-1.503235	-0.533554
C	0.331160	-1.527392	-1.930202
C	0.704832	-2.661010	0.173771
C	0.636939	-2.704049	-2.611552
H	0.077826	-0.637498	-2.497804
C	1.000396	-3.836818	-0.512684
H	0.744295	-2.653968	1.260665
H	0.615262	-2.714210	-3.697822
H	1.259898	-4.732973	0.044057
C	-0.863165	-0.807841	2.973073
H	-0.267401	-1.069110	3.850351
H	-1.678923	-0.144746	3.270308
H	-1.263183	-1.720855	2.525691
C	0.966745	-3.860564	-1.906191
H	1.200267	-4.776773	-2.441427
N	4.686450	0.587978	0.534068
N	-4.695922	-0.520181	0.459134
H	5.698446	0.694075	0.517158
H	-5.710090	-0.607804	0.459145

[TS-I·2H]$^{2+}$-Ph,OMe,ax-a (ν_i = -523.12 cm^{-1})

C	1.217703	4.129264	-0.454185
C	0.784513	2.889606	-0.916237
C	0.298161	1.932949	-0.013996
C	0.243563	2.238939	1.351586
C	0.654259	3.487924	1.802915
H	1.606303	4.856678	-1.160621
H	0.835316	2.670575	-1.977764
H	-0.090643	1.504559	2.074530
H	0.600836	3.716172	2.863217
P	-0.253483	0.357099	-0.727852
C	-1.900522	-0.253133	-0.171447
C	-2.623485	-1.067818	-1.047627
C	-2.486094	0.144460	1.031021
C	-3.884581	-1.499358	-0.684889
H	-2.232565	-1.364208	-2.014215
C	-3.756825	-0.295814	1.341082
H	-1.983201	0.783853	1.743075
H	-4.500089	-2.141447	-1.301787
H	-4.277893	-0.029852	2.251987
C	0.731983	-0.853537	0.947324
C	0.015839	-1.923738	1.490256
C	1.829510	-0.357285	1.653196
C	0.346987	-2.443253	2.741091
H	-0.806918	-2.379739	0.943477
C	2.168778	-0.870926	2.902752
H	2.438501	0.439835	1.231854
H	-0.229109	-3.267925	3.152967
H	3.020979	-0.463727	3.440890
C	1.145936	4.433050	0.903063
H	1.476234	5.403861	1.261520
O	-0.703258	0.827739	-2.239148
C	0.990094	-0.824714	-1.093365
C	2.332848	-0.350597	-1.353554
C	0.708584	-2.167595	-1.548432
C	3.306587	-1.237367	-1.684830
H	2.592767	0.695871	-1.249012
C	1.736353	-2.994806	-1.870467
H	-0.299319	-2.559396	-1.579829
H	4.336977	-0.942077	-1.842574
H	1.585029	-4.027127	-2.162104
C	-1.775260	1.746953	-2.502588
H	-1.446145	2.405414	-3.308781
H	-2.656907	1.183911	-2.821844
H	-2.024738	2.349710	-1.623319
N	-4.403012	-1.103708	0.486438
H	-5.339919	-1.422299	0.733110
C	1.421830	-1.912767	3.454306
H	1.686870	-2.319906	4.426371
N	3.022023	-2.552070	-1.879154
H	3.762277	-3.183307	-2.163025

[TS-I·2H]$^{2+}$-Ph,Ph,ax-a (ν_i = -456.04 cm^{-1})

C	-0.674614	3.210633	-1.989003
C	-0.773384	1.912441	-1.526058
C	-0.311702	1.618632	-0.243241
C	0.192891	2.636280	0.568142
C	0.246209	3.920914	0.069663
H	-0.990816	3.522925	-2.976153
H	-1.211478	1.157063	-2.169364
H	0.554672	2.441942	1.571274
H	0.620004	4.769360	0.628537
P	-0.425846	-0.080652	0.434563
C	-2.226952	-0.366924	0.242692
C	-3.145584	0.610236	0.654493
C	-2.698828	-1.551349	-0.333247
C	-4.511129	0.400222	0.499197
H	-2.798765	1.538667	1.103584
C	-4.069315	-1.758571	-0.490369
H	-2.009185	-2.322047	-0.664843
H	-5.214936	1.161143	0.824100
H	-4.425620	-2.681157	-0.939608
C	1.896126	0.000282	0.389013
C	2.577271	0.668149	-0.629034
C	2.592697	-0.347004	1.546844
C	3.917128	1.027037	-0.480623
H	2.070309	0.918793	-1.560987
C	3.935229	0.004659	1.703329
H	2.095513	-0.897605	2.342141
H	4.428932	1.556405	-1.281030
H	4.462095	-0.265185	2.615795
O	-0.208531	-0.067814	2.015725
C	0.415251	-1.394871	-0.391236
C	0.628822	-1.436958	-1.807295
C	0.663573	-2.605467	0.340105
C	1.296999	-2.495065	-2.346748
H	0.306491	-0.635796	-2.459936
C	1.324375	-3.627203	-0.267922
H	0.372324	-2.705381	1.379023
H	1.528898	-2.566760	-3.402512
H	1.578012	-4.549896	0.239650
C	-1.138410	-0.605570	2.985594
H	-0.548147	-0.731546	3.893515
H	-1.948636	0.104957	3.157209
H	-1.534440	-1.569391	2.660517
N	-0.173603	4.159469	-1.184501
N	1.675740	-3.545175	-1.577646
C	4.599804	0.698389	0.691637
H	5.645066	0.971531	0.810886
C	-4.974329	-0.785636	-0.074497
H	-6.041516	-0.947807	-0.198324
H	-0.118489	5.113529	-1.539428
H	2.147918	-4.331041	-2.011881

[TS-I·2H]$^{2+}$-PyH^{+},OMe,ax-a (ν_i = -397.29 cm^{-1})

C	-3.719513	1.106176	1.356007

C	-2.425300	1.206909	0.855155
C	-1.989312	0.327190	-0.142970
C	-2.880395	-0.622047	-0.663645
C	-4.172241	-0.718298	-0.153624
H	-4.045179	1.792089	2.132354
H	-1.775063	1.980744	1.244554
H	-2.595122	-1.283352	-1.474638
H	-4.851909	-1.461058	-0.560530
P	-0.337109	0.491520	-0.854790
C	0.585513	-1.027574	-1.072586
C	1.943458	-0.879352	-1.505822
C	0.029388	-2.344311	-1.183731
C	2.702387	-1.983363	-1.767834
H	2.404465	0.096394	-1.601308
C	0.842550	-3.402178	-1.457329
H	-1.013160	-2.543581	-0.978794
H	3.744044	-1.924703	-2.059045
H	0.480823	-4.421782	-1.504202
C	0.541030	-0.820114	1.080328
C	1.848027	-0.728152	1.568397
C	-0.403783	-1.484500	1.871847
C	2.174412	-1.243160	2.803683
H	2.634100	-0.248309	0.989545
C	-0.045538	-1.990585	3.104449
H	-1.432330	-1.618361	1.549885
H	3.162757	-1.193888	3.244444
H	-0.728750	-2.499627	3.773720
C	-4.591017	0.137278	0.862633
H	-5.599117	0.058645	1.259428
O	-0.599840	1.085802	-2.348534
C	0.664812	1.871564	-0.235483
C	0.761374	2.191306	1.125399
C	1.360883	2.645473	-1.174999
C	1.534924	3.271671	1.535572
H	0.245216	1.606469	1.877740
C	2.148409	3.713631	-0.754341
H	1.293924	2.417491	-2.232658
H	1.593516	3.514086	2.592500
H	2.690653	4.298547	-1.491358
C	-1.274928	0.356716	-3.383422
H	-2.356075	0.390660	-3.223100
H	-1.027934	0.863502	-4.317377
H	-0.929024	-0.680682	-3.430464
C	2.234064	4.031252	0.598862
H	2.843474	4.869770	0.923937
N	1.221527	-1.852152	3.535402
N	2.162935	-3.220833	-1.709269
H	1.470193	-2.229174	4.447071
H	2.739406	-4.025374	-1.933785

[TS-I·2H]$^{2+}$-PyH^{+},OMe,ax-b (ν_i = -437.02 cm^{-1})

C	4.058548	-1.205969	-0.423885
C	2.833409	-0.732126	-0.883477
C	1.980421	-0.036836	-0.014770
C	2.381613	0.212503	1.301114
C	3.614316	-0.251433	1.748989
H	4.710239	-1.750965	-1.100231
H	2.555344	-0.895259	-1.921066
H	1.750115	0.763974	1.986246
H	3.920862	-0.051023	2.771294
P	0.420174	0.549265	-0.709913
C	-0.392064	1.944273	0.117818
C	-0.871321	2.963910	-0.717789
C	-0.548257	2.064382	1.505031
C	-1.500486	4.079688	-0.173258
H	-0.760043	2.891419	-1.794811
C	-1.162749	3.189896	2.042918
H	-0.219539	1.284004	2.179924
H	-1.874717	4.857025	-0.832755
H	-1.272900	3.273266	3.120028
C	-0.757052	-0.991625	0.846167
C	-2.012699	-0.716300	1.395528
C	-0.020916	-2.045842	1.398529
C	-2.478639	-1.438434	2.473102
H	-2.648713	0.066872	0.990309
C	-0.515817	-2.752438	2.474705
H	0.947021	-2.336524	0.999922
H	-3.433311	-1.266962	2.955886
H	0.005901	-3.569792	2.957519
C	4.448433	-0.969131	0.892875
H	5.407057	-1.334794	1.249551
O	0.883931	1.182820	-2.137006
C	-0.703214	-0.707577	-1.276685
C	-0.254507	-1.988909	-1.740614
C	-2.032028	-0.323535	-1.655332
C	-1.154642	-2.866179	-2.265382
H	0.774534	-2.305746	-1.628606
C	-2.878639	-1.252481	-2.183097
H	-2.397974	0.683155	-1.492204
H	-0.883491	-3.864969	-2.584773
H	-3.905971	-1.030800	-2.445197
C	1.924706	2.169350	-2.252940
H	2.882223	1.667577	-2.414638
H	1.673850	2.783308	-3.119368
H	1.984562	2.801601	-1.361924
N	-1.719029	-2.426703	2.982053
H	-2.073132	-2.954300	3.776702
N	-2.451509	-2.511011	-2.442074
H	-3.094278	-3.176490	-2.858392
C	-1.642019	4.197476	1.206997
H	-2.126310	5.071922	1.632208

[TS-I·2H]$^{2+}$-PyH^{+},Ph,ax-a (ν_i = -319.63 cm^{-1})

C	0.667367	3.281143	-2.007585

C	0.820175	1.988186	-1.513202
C	0.310438	1.667191	-0.251019
C	-0.315634	2.643906	0.529449
C	-0.442748	3.938842	0.037638
H	1.051237	3.527983	-2.993017
H	1.337176	1.241370	-2.110633
H	-0.704136	2.396259	1.512870
H	-0.921827	4.700362	0.646003
P	0.522373	0.004936	0.409458
C	-1.964688	-0.005886	0.411534
C	-2.655173	-0.436857	1.550457
C	-2.709353	0.622501	-0.594480
C	-4.012673	-0.220725	1.671798
H	-2.144181	-0.946770	2.362354
C	-4.064339	0.824201	-0.446974
H	-2.238734	0.968969	-1.512472
H	-4.604423	-0.517406	2.529869
H	-4.695463	1.311278	-1.180914
C	2.312619	-0.294787	0.236867
C	2.805026	-1.504635	-0.264958
C	3.213440	0.710677	0.618648
C	4.179871	-1.707339	-0.379479
H	2.130698	-2.297834	-0.573269
C	4.583621	0.502921	0.507837
H	2.846355	1.658930	1.004074
C	5.068060	-0.707165	0.007977
H	4.553140	-2.648311	-0.773148
H	5.273737	1.286236	0.807652
H	6.138941	-0.867163	-0.082022
C	0.038788	4.254992	-1.233169
H	-0.069481	5.265403	-1.617332
O	0.231541	-0.036694	1.979830
C	-0.310845	-1.339477	-0.422592
C	-0.524484	-2.555183	0.286962
C	-0.552620	-1.338666	-1.822899
C	-1.124312	-3.604729	-0.348209
H	-0.251606	-2.654659	1.331195
C	-1.157509	-2.422568	-2.396556
H	-0.298663	-0.490630	-2.446722
H	-1.344504	-4.545853	0.140452
H	-1.401584	-2.473969	-3.450487
N	-1.455466	-3.514197	-1.657445
C	1.168156	-0.511298	2.974215
H	0.573015	-0.635045	3.879202
H	1.603250	-1.468019	2.678654
H	1.950152	0.232596	3.136928
N	-4.674389	0.402458	0.678529
H	-5.673917	0.560122	0.780961
H	-1.887219	-4.313623	-2.111875

[Int-IV·2H]$^{2+}$-Ph,OMe,ax-a

C	-2.963293	-0.471248	-3.029465
C	-1.778358	0.072819	-2.543018
C	-1.183572	-0.474418	-1.398413
C	-1.792345	-1.547742	-0.729904
C	-2.974654	-2.083798	-1.228061
H	-3.422125	-0.047336	-3.917495
H	-1.332661	0.922115	-3.051082
H	-1.359161	-1.965331	0.174553
H	-3.442695	-2.916564	-0.711999
P	0.276926	0.322931	-0.727529
C	1.680547	-0.828856	-0.533804
C	2.935501	-0.262020	-0.280350
C	1.547977	-2.217313	-0.596742
C	4.017013	-1.095096	-0.072195
H	3.091770	0.809976	-0.251063
C	2.661987	-3.005703	-0.382909
H	0.606315	-2.705753	-0.814951
H	5.019066	-0.739907	0.132000
H	2.646113	-4.087689	-0.413998
C	-0.706613	0.235402	1.834556
C	0.136429	-0.744323	2.377118
C	-2.064795	0.201433	2.161847
C	-0.369651	-1.744374	3.203119
H	1.202044	-0.736420	2.166790
C	-2.571518	-0.797496	2.991906
H	-2.746190	0.952273	1.777402
H	0.303043	-2.494235	3.610296
H	-3.631381	-0.805824	3.230899
C	-3.558405	-1.548923	-2.376204
H	-4.483525	-1.970241	-2.758942
O	0.779630	1.455175	-1.722505
C	-0.140418	1.287788	0.874144
C	-1.126055	2.323692	0.395676
C	1.099504	1.963832	1.399934
C	-0.784778	3.616190	0.231099
H	-2.122015	2.013270	0.101448
C	1.342330	3.273684	1.207331
H	1.823683	1.377085	1.952873
H	-1.487394	4.347214	-0.153092
H	2.239939	3.751114	1.584355
C	1.434981	1.165737	-2.986019
H	1.169613	1.988578	-3.649091
H	2.513692	1.141777	-2.821677
H	1.089904	0.218149	-3.405200
N	3.842888	-2.424012	-0.123789
H	4.653352	-3.023535	0.031290
C	-1.729500	-1.779379	3.508109
H	-2.126821	-2.560168	4.150739
N	0.455827	4.097833	0.560147
H	0.639612	5.090010	0.507882

[Int-IV·2H]$^{2+}$-PyH^{+},OMe,ax-a

C	2.969260	-2.878281	-0.348603
C	1.851462	-2.117049	-0.678608
C	1.819315	-0.752814	-0.359761
C	2.923107	-0.155864	0.271373
C	4.034799	-0.924954	0.593433
H	2.988134	-3.935262	-0.596356
H	1.019031	-2.592271	-1.186672
H	2.926479	0.902774	0.508179
H	4.885615	-0.457933	1.080157
P	0.378021	0.237531	-0.784419
C	-0.359077	1.296236	0.628065
C	-1.452315	2.082034	-0.060425
C	0.680315	2.251929	1.177327
C	-1.297323	3.374848	-0.398328
H	-2.353798	1.570722	-0.378505
C	0.734097	3.541404	0.800184
H	1.406302	1.887673	1.894507
H	-2.062225	3.916745	-0.943243
H	1.492697	4.215572	1.182033
C	-0.860706	0.346738	1.716549
C	-2.223233	0.213697	2.000416
C	0.047064	-0.415088	2.465365
C	-2.639864	-0.666066	2.977786
H	-2.978182	0.787589	1.479459
C	-0.411899	-1.283200	3.431261
H	1.116742	-0.345461	2.312684
H	-3.678425	-0.817751	3.243520
H	0.235877	-1.901934	4.039035
C	4.056983	-2.286183	0.289339
H	4.927555	-2.883735	0.544327
O	0.727986	1.279847	-1.935105
C	-0.941303	-0.768697	-1.472662
C	-1.488354	-1.821056	-0.723307
C	-1.465606	-0.451543	-2.730425
C	-2.551505	-2.553159	-1.239831
H	-1.082595	-2.086948	0.248961
C	-2.532240	-1.190338	-3.236466
H	-1.047861	0.364401	-3.310734
H	-2.968866	-3.372548	-0.662356
H	-2.938247	-0.944914	-4.213241
C	2.032945	1.845877	-2.195662
H	2.737825	1.052248	-2.452206
H	1.885699	2.507803	-3.048352
H	2.379713	2.414649	-1.331427
C	-3.074638	-2.237303	-2.493882
H	-3.906049	-2.811193	-2.893196
N	-1.732361	-1.387677	3.653218
N	-0.178703	4.096584	-0.063817
H	-2.057520	-2.031297	4.372783
H	-0.152347	5.089965	-0.246870

[Int-IV·2H]$^{2+}$-PyH^{+},OMe,ax-b

C	-4.189841	-0.328237	0.311861
C	-2.980956	0.219486	-0.101009
C	-1.877311	-0.619311	-0.327240
C	-2.001718	-2.004058	-0.162133
C	-3.217390	-2.541084	0.251689
H	-5.042315	0.321673	0.484663
H	-2.904679	1.290853	-0.258911
H	-1.169194	-2.669771	-0.362475
H	-3.313022	-3.615409	0.377084
P	-0.331845	0.156403	-0.811277
C	0.925812	-1.026380	-1.307486
C	1.542518	-0.875752	-2.555519
C	1.361411	-2.022186	-0.420615
C	2.575221	-1.734775	-2.921327
H	1.229337	-0.091877	-3.238190
C	2.394277	-2.874068	-0.796549
H	0.903602	-2.140067	0.557416
H	3.050323	-1.619094	-3.890828
H	2.726918	-3.648028	-0.111406
C	0.794180	0.519426	1.702359
C	2.128144	0.336584	2.077838
C	-0.202825	-0.073875	2.490440
C	2.433307	-0.432623	3.181450
H	2.945717	0.786494	1.529782
C	0.147053	-0.835236	3.583990
H	-1.258034	0.044110	2.273043
H	3.444467	-0.616812	3.521949
H	-0.571698	-1.323987	4.229383
C	-4.306249	-1.706189	0.495860
H	-5.252272	-2.130982	0.819243
O	-0.621711	1.156254	-2.015862
C	0.422445	1.350410	0.471425
C	-0.578128	2.426233	0.830024
C	1.606240	1.964682	-0.240016
C	-0.480930	3.682295	0.359089
H	-1.406391	2.176093	1.482976
C	1.600416	3.238281	-0.674009
H	2.460905	1.342066	-0.479868
H	-1.210608	4.442588	0.614042
H	2.437925	3.656351	-1.221289
C	-1.466339	0.783753	-3.135097
H	-2.507039	0.991256	-2.879488
H	-1.144533	1.413988	-3.963702
H	-1.339897	-0.270380	-3.393611
N	1.444464	-0.996570	3.891705
N	0.553888	4.093047	-0.442783
C	2.998909	-2.732646	-2.045602
H	3.805502	-3.400208	-2.334779
H	0.621031	5.061173	-0.722971
H	1.687391	-1.559801	4.705008

[Int-IV·2H]$^{2+}$-PyH^{+},Ph,ax-a

C	-1.440672	3.038730	-1.773317
C	-0.515853	2.110689	-1.306250
C	-0.624763	1.626231	0.003703
C	-1.653560	2.071159	0.842018
C	-2.572814	3.000247	0.364137
H	-1.355068	3.418527	-2.786927
H	0.284524	1.771348	-1.958111
H	-1.740962	1.693970	1.856100
H	-3.370371	3.348817	1.013544
P	0.456307	0.303805	0.553217
C	-1.684537	-1.245205	-0.057766
C	-2.312949	-1.456741	1.176106
C	-2.480053	-0.909471	-1.158174
C	-3.679526	-1.313584	1.283421
H	-1.758537	-1.720515	2.068242
C	-3.842942	-0.773491	-1.004586
H	-2.056615	-0.744216	-2.140809
H	-4.227279	-1.456628	2.206201
H	-4.514159	-0.507405	-1.811126
C	2.164702	0.660129	0.146446
C	3.112432	-0.361198	-0.010921
C	2.559035	2.004659	0.080219
C	4.441199	-0.032553	-0.254537
H	2.827825	-1.404441	0.061610
C	3.891673	2.321001	-0.162353
H	1.836093	2.803305	0.217696
C	4.830000	1.304574	-0.333857
H	5.173915	-0.823851	-0.380425
H	4.194591	3.362177	-0.216767
H	5.869468	1.554804	-0.526047
C	-2.469574	3.479628	-0.941223
H	-3.191023	4.202869	-1.310705
O	0.241399	0.209348	2.132137
C	-0.150923	-1.334316	-0.184799
C	0.402010	-2.494359	0.621679
C	0.327079	-1.426756	-1.619230
C	1.072601	-3.510668	0.052105
H	0.233581	-2.521288	1.691964
C	1.011505	-2.486114	-2.083051
H	0.121712	-0.610191	-2.302405
H	1.431945	-4.350815	0.635914
H	1.333552	-2.545001	-3.116710
N	1.361729	-3.549993	-1.289102
C	1.318725	-0.035341	3.070450
H	0.830124	-0.160897	4.036086
H	1.863146	-0.942322	2.800716
H	1.988031	0.827204	3.091376
N	-4.398347	-0.973656	0.201526
H	-5.406843	-0.868895	0.298857
H	1.896112	-4.316368	-1.671897

[TS-II·2H]$^{2+}$-Ph,OMe,ax-a (ν_i = -241.51 cm^{-1})

C	-2.467413	-1.466929	-3.116946
C	-1.445806	-0.645337	-2.647236
C	-0.857089	-0.910672	-1.404324
C	-1.324651	-1.976281	-0.619220
C	-2.342250	-2.793549	-1.100316
H	-2.918428	-1.262391	-4.083570
H	-1.117799	0.198026	-3.247556
H	-0.904962	-2.168788	0.365432
H	-2.696507	-3.621536	-0.493304
P	0.334084	0.246691	-0.709196
C	1.905761	-0.594378	-0.317088
C	2.990511	0.228527	0.019479
C	2.052137	-1.982929	-0.251928
C	4.180418	-0.350018	0.408981
H	2.922098	1.310124	-0.024736
C	3.264318	-2.512508	0.141968
H	1.251638	-2.663409	-0.515553
H	5.063285	0.213211	0.683822
H	3.462628	-3.574777	0.209026
C	-1.004912	0.421438	1.797531
C	-0.011978	-0.287960	2.487830
C	-2.343063	0.080083	2.008620
C	-0.348208	-1.325763	3.350032
H	1.037033	-0.038592	2.347739
C	-2.680507	-0.960538	2.874450
H	-3.138305	0.622776	1.508630
H	0.436774	-1.866297	3.871679
H	-3.726722	-1.213532	3.022396
C	-2.911907	-2.541708	-2.348484
H	-3.710126	-3.179149	-2.718160
O	0.707170	1.339630	-1.824793
C	-0.618547	1.514417	0.826116
C	-1.666324	2.134978	0.016284
C	0.394951	2.468669	1.276570
C	-1.531015	3.397279	-0.462314
H	-2.537095	1.563366	-0.283298
C	0.459789	3.722780	0.766284
H	1.129862	2.170739	2.015222
H	-2.271449	3.857673	-1.105852
H	1.216296	4.437279	1.068539
C	1.524548	1.037938	-2.980168
H	1.199307	1.719723	-3.766533
H	2.572093	1.222517	-2.730750
H	1.389997	0.002059	-3.302228
N	4.276167	-1.688788	0.459255
H	5.162496	-2.101630	0.747399
C	-1.686901	-1.671156	3.541650
H	-1.951155	-2.484870	4.211288
N	-0.464154	4.173606	-0.128814
H	-0.414831	5.128038	-0.463049

[TS-II·2H]$^{2+}$-PyH^{+},OMe,ax-a (ν_i = -200.84 cm^{-1})

C	3.465284	1.762214	-1.174921

C	2.332357	0.960636	-1.069413
C	1.113210	1.518203	-0.659403
C	1.035849	2.886412	-0.367153
C	2.174144	3.681387	-0.470401
H	4.407509	1.325628	-1.493249
H	2.400689	-0.095542	-1.317011
H	0.093652	3.335930	-0.067986
H	2.111113	4.741836	-0.243822
P	-0.321189	0.415934	-0.587362
C	-1.577831	1.130836	0.490160
C	-2.927143	0.988476	0.141749
C	-1.234552	1.675706	1.735864
C	-3.921099	1.418302	1.018085
H	-3.203273	0.551176	-0.813956
C	-2.232751	2.098608	2.607675
H	-0.191784	1.775926	2.026037
H	-4.965583	1.315073	0.738264
H	-1.961322	2.529653	3.567057
C	1.074159	-1.863547	0.603080
C	1.204237	-1.181660	1.821298
C	2.175284	-2.583864	0.128198
C	2.401218	-1.205248	2.499396
H	0.385222	-0.619358	2.254223
C	3.356495	-2.579861	0.840925
H	2.136621	-3.157343	-0.789270
H	2.570283	-0.691777	3.437410
H	4.246307	-3.110495	0.526263
C	3.387472	3.120544	-0.869091
H	4.273240	3.744961	-0.945821
O	-0.964258	0.331030	-2.068568
C	-0.225223	-1.832874	-0.163251
C	-0.259552	-2.416381	-1.493791
C	-1.427945	-2.087886	0.618866
C	-1.416503	-2.894194	-2.016300
H	0.618193	-2.388478	-2.128568
C	-2.549913	-2.577734	0.031837
H	-1.459777	-1.846780	1.674976
H	-1.486177	-3.278135	-3.026873
H	-3.471599	-2.737125	0.578472
C	-1.191227	1.515426	-2.858708
H	-0.234556	1.943095	-3.170834
H	-1.755748	1.186419	-3.732009
H	-1.770308	2.254456	-2.297121
N	3.437973	-1.893519	1.990640
N	-2.560479	-2.932775	-1.280354
C	-3.575738	1.973033	2.249053
H	-4.352446	2.306807	2.931418
H	-3.401377	-3.327407	-1.685189
H	4.319139	-1.900924	2.502032

[TS-II·2H]$^{2+}$-PyH^{+},Ph,ax-a (ν_i = -239.51 cm^{-1})

C	-1.685289	2.764134	-1.835781
C	-0.672209	1.993047	-1.273095
C	-0.790095	1.540451	0.048519
C	-1.929985	1.862391	0.796674
C	-2.937316	2.635648	0.226302
H	-1.586638	3.116215	-2.858545
H	0.205603	1.747478	-1.864861
H	-2.034762	1.508253	1.817372
H	-3.817370	2.886621	0.811683
P	0.389983	0.336965	0.682946
C	-1.575640	-1.470531	-0.176713
C	-2.132275	-1.622006	1.101812
C	-2.421750	-1.098079	-1.227766
C	-3.472595	-1.378897	1.299949
H	-1.533096	-1.896838	1.962508
C	-3.756719	-0.856482	-0.980237
H	-2.066055	-0.988812	-2.244313
H	-3.962195	-1.466960	2.261250
H	-4.460920	-0.551720	-1.743791
C	2.069434	0.903261	0.318356
C	3.095972	-0.048360	0.261653
C	2.366019	2.262043	0.143218
C	4.406722	0.354415	0.022259
H	2.879237	-1.101405	0.414001
C	3.678497	2.657726	-0.097164
H	1.580956	3.011000	0.195774
C	4.696483	1.705688	-0.161409
H	5.199597	-0.386698	-0.020959
H	3.906142	3.711031	-0.233494
H	5.719192	2.019248	-0.351722
C	-2.819550	3.082245	-1.089626
H	-3.610309	3.681108	-1.532811
O	0.142833	0.436443	2.288844
C	-0.096445	-1.666242	-0.397675
C	0.504629	-2.811234	0.275510
C	0.452634	-1.419981	-1.721505
C	1.607053	-3.422320	-0.222682
H	0.082048	-3.189617	1.198242
C	1.573345	-2.056857	-2.147189
H	0.025750	-0.661270	-2.366421
H	2.077337	-4.265601	0.268585
H	2.031841	-1.846585	-3.106125
N	2.168499	-3.022322	-1.398076
C	0.850498	-0.467061	3.160015
H	0.513990	-0.229388	4.169468
H	0.606090	-1.505579	2.922190
H	1.929954	-0.303524	3.082896
N	-4.239505	-1.000748	0.263363
H	-5.228021	-0.817913	0.427483
H	2.977767	-3.511574	-1.760898

[Int-V·2H]$^{2+}$-Ph,OMe,ax-a

C	-1.501452	-2.639170	2.204882
C	-0.855029	-2.509217	0.978424
C	-0.047945	-1.394228	0.714408
C	0.080791	-0.402434	1.693166
C	-0.571236	-0.531273	2.918400
H	-2.117124	-3.513211	2.399551
H	-0.979601	-3.283457	0.224576
H	0.680671	0.485408	1.508247
H	-0.462098	0.248192	3.667773
P	0.608184	-1.177424	-0.988269
C	2.262927	-0.383859	-0.637726
C	2.741498	0.517262	-1.593937
C	3.055102	-0.655296	0.483990
C	3.970309	1.123242	-1.414616
H	2.164250	0.760474	-2.479980
C	4.278670	-0.031877	0.623645
H	2.734964	-1.344207	1.257316
H	4.403392	1.834017	-2.107025
H	4.947755	-0.192278	1.459552
C	-1.402806	2.020187	-0.056132
C	-0.220086	2.350484	-0.729382
C	-1.617141	2.518193	1.235640
C	0.743040	3.142945	-0.110697
H	-0.033042	1.960885	-1.725994
C	-0.661430	3.324869	1.844173
H	-2.535505	2.281087	1.765944
H	1.666356	3.374250	-0.634777
H	-0.840216	3.710573	2.843832
C	-1.361874	-1.649051	3.178182
H	-1.869011	-1.748623	4.134035
O	1.041649	-2.710362	-1.432315
C	-2.376526	1.098153	-0.678133
C	-3.047101	0.141026	0.099445
C	-2.625513	1.120658	-2.059279
C	-3.911574	-0.747282	-0.498605
H	-2.872616	0.058797	1.166121
C	-3.501149	0.214911	-2.614202
H	-2.150075	1.848244	-2.706975
H	-4.446420	-1.519921	0.039064
H	-3.741226	0.179305	-3.669310
C	1.935490	-3.540075	-0.679713
H	1.806010	-4.555732	-1.059179
H	2.970625	-3.221275	-0.839733
H	1.700427	-3.518736	0.389264
N	4.689875	0.831827	-0.319845
H	5.595251	1.283719	-0.201181
C	0.525422	3.630750	1.176922
H	1.276869	4.249972	1.659102
N	-4.112004	-0.688195	-1.826980
H	-4.755002	-1.352169	-2.253014

[Int-V·2H]$^{2+}$-PyH^{+},OMe,ax-a

C	4.631704	-0.590448	1.972939
C	3.315695	-0.872173	1.605598
C	2.768710	-0.332376	0.434432
C	3.565373	0.500766	-0.364210
C	4.878374	0.783759	0.001681
H	5.042302	-1.014193	2.885399
H	2.708759	-1.515377	2.239644
H	3.160378	0.934759	-1.274615
H	5.486549	1.430120	-0.625480
P	1.036203	-0.805505	0.041090
C	0.458761	0.659706	-0.911791
C	-0.206209	0.516157	-2.133478
C	0.544544	1.934915	-0.335983
C	-0.761021	1.623991	-2.775132
H	-0.294913	-0.465053	-2.592937
C	-0.012190	3.040238	-0.973581
H	1.051706	2.070825	0.617059
H	-1.268252	1.495350	-3.727809
H	0.065238	4.022400	-0.514445
C	-2.518293	0.378790	0.905491
C	-3.180294	1.342593	0.138562
C	-1.772663	0.790542	2.016572
C	-3.086094	2.672343	0.492948
H	-3.780008	1.075037	-0.723448
C	-1.711040	2.130429	2.333287
H	-1.217977	0.085850	2.624425
H	-3.569729	3.474106	-0.049905
H	-1.151044	2.524453	3.171703
C	5.413276	0.238071	1.170463
H	6.437905	0.462345	1.454939
O	1.180683	-1.974725	-1.135221
C	-2.573093	-1.059076	0.539084
C	-2.524846	-2.047571	1.528909
C	-2.634666	-1.447354	-0.803584
C	-2.509459	-3.375914	1.160390
H	-2.505343	-1.800612	2.583834
C	-2.607947	-2.788240	-1.124005
H	-2.671396	-0.722484	-1.607519
H	-2.468758	-4.195524	1.866590
H	-2.630792	-3.163589	-2.138930
C	2.144802	-1.894939	-2.190251
H	3.147542	-2.107090	-1.805049
H	1.867836	-2.657281	-2.922254
H	2.140420	-0.911626	-2.672040
N	-2.366238	3.020450	1.571004
N	-2.540427	-3.701283	-0.142215
C	-0.667230	2.888034	-2.196993
H	-1.102551	3.750838	-2.694003
H	-2.518553	-4.687670	-0.397593
H	-2.308354	4.007167	1.818234

[Int-V·2H]$^{2+}$-PyH^{+},Ph,ax-a

C	-1.305517	-1.215327	2.674934
C	-0.343384	-1.120204	1.668476
C	-0.622146	-1.569893	0.374348
C	-1.889533	-2.108484	0.104695
C	-2.843718	-2.218380	1.111741
H	-1.072860	-0.860232	3.675489
H	0.626602	-0.693049	1.904763
H	-2.134164	-2.446545	-0.900432
H	-3.817829	-2.645543	0.888570
P	0.538055	-1.443058	-1.043205
C	-1.840403	1.634121	-0.406035
C	-2.145607	1.088232	-1.658450
C	-2.770085	1.510577	0.631415
C	-3.350839	0.445496	-1.842739
H	-1.450869	1.135210	-2.488261
C	-3.963190	0.858511	0.398540
H	-2.590222	1.927480	1.615141
H	-3.652610	-0.008210	-2.778052
H	-4.731399	0.726791	1.149461
C	2.108785	-0.922984	-0.250196
C	2.655969	0.308418	-0.622707
C	2.794614	-1.723937	0.673445
C	3.852637	0.752727	-0.058700
H	2.147851	0.924223	-1.362531
C	3.994085	-1.287371	1.228204
H	2.386405	-2.689495	0.962017
C	4.521157	-0.044558	0.867459
H	4.265659	1.714758	-0.350852
H	4.518983	-1.913781	1.944583
H	5.456818	0.295453	1.303444
C	-2.553787	-1.768630	2.401183
H	-3.301138	-1.846135	3.186372
O	0.774059	-3.093995	-1.232284
C	-0.545277	2.325107	-0.180398
C	0.054724	3.071091	-1.201667
C	0.096160	2.239698	1.060169
C	1.259759	3.699364	-0.965079
H	-0.409060	3.190556	-2.173744
C	1.304592	2.876993	1.246561
H	-0.322173	1.668748	1.879651
H	1.779783	4.296976	-1.702869
H	1.864615	2.843889	2.172150
N	1.842126	3.581885	0.238665
C	1.528922	-3.482009	-2.380831
H	1.493147	-4.572652	-2.427963
H	1.096380	-3.063661	-3.298634
H	2.574144	-3.160615	-2.291182
N	-4.215550	0.355456	-0.819722
H	-5.100579	-0.125038	-0.972673
H	2.735690	4.045972	0.393079

Final Products

BiPy

C	0.742260	-0.000031	0.000014
C	1.468254	-1.131421	0.382854
C	1.468203	1.131379	-0.382860
C	2.857619	-1.080506	0.367319
H	0.966866	-2.038218	0.707588
C	2.857595	1.080517	-0.367358
H	0.966792	2.038224	-0.707412
H	3.436609	-1.950335	0.667936
H	3.436545	1.950412	-0.667872
C	-0.742257	0.000004	0.000020
C	-1.468226	1.131416	0.382812
C	-1.468229	-1.131400	-0.382850
C	-2.857602	1.080492	0.367389
H	-0.966836	2.038214	0.707504
C	-2.857614	-1.080498	-0.367389
H	-0.966825	-2.038243	-0.707435
H	-3.436570	1.950393	0.667846
H	-3.436595	-1.950382	-0.667873
N	3.557715	0.000030	-0.000006
N	-3.557715	-0.000001	0.000007

Phosph-Ph,Ph,OMe

C	3.771818	-0.142717	0.391612
C	2.652682	0.636088	0.100662
C	1.457717	0.034663	-0.315628
C	1.414002	-1.357887	-0.459973
C	2.537438	-2.134038	-0.178772
H	4.688279	0.336911	0.725373
H	2.712326	1.716003	0.207607
H	0.499141	-1.847603	-0.785133
H	2.486022	-3.213919	-0.290383
P	0.028417	1.080765	-0.803060
C	-1.377118	0.034285	-0.248482
C	-2.314621	-0.384138	-1.197072
C	-1.542632	-0.342133	1.091589
C	-3.396037	-1.182769	-0.818584
H	-2.202718	-0.087842	-2.238193
C	-2.627234	-1.126366	1.472160
H	-0.819665	-0.022012	1.838357
H	-4.116219	-1.508715	-1.564262
H	-2.750568	-1.412258	2.513486
C	3.717866	-1.529308	0.251796
H	4.591511	-2.135254	0.476798
O	0.154111	2.184700	0.450337
C	-0.685166	3.335487	0.349898
H	-1.742998	3.060781	0.446265
H	-0.411247	3.997060	1.174761
H	-0.529238	3.857349	-0.602553
C	-3.553117	-1.551487	0.515382
H	-4.397359	-2.167651	0.813548

Phosph-Py,Ph,OMe

C	-2.504691	-1.326628	1.322246
C	-1.375389	-0.652571	0.866448
C	-1.415922	0.070957	-0.334647
C	-2.609542	0.100891	-1.067253
C	-3.741914	-0.574302	-0.611123
H	-2.461411	-1.883492	2.254412
H	-0.459762	-0.694603	1.450277
H	-2.656130	0.652291	-2.003941
H	-4.660015	-0.545394	-1.191515
P	-0.008295	1.030908	-1.024680
C	-3.689384	-1.287985	0.584149
H	-4.568756	-1.817634	0.940979
O	0.079504	2.391989	-0.075556
C	1.428874	0.043032	-0.425671
C	1.500342	-1.334744	-0.655468
C	2.549097	0.658473	0.137618
C	2.655888	-2.021522	-0.300957
H	0.671678	-1.880808	-1.098540
C	3.656928	-0.118765	0.463505
H	2.570725	1.727310	0.329883
H	2.724362	-3.093676	-0.469262
H	4.531816	0.344356	0.913726
C	-0.098165	2.364880	1.344322
H	0.512322	1.587066	1.815051
H	0.216396	3.343602	1.713706
H	-1.152018	2.202683	1.592734
N	3.726065	-1.438789	0.255447

Phosph-PyH$^+$,Ph,OMe

C	-2.401593	-1.529429	1.151700
C	-1.277379	-0.860544	0.710831
C	-1.380755	0.038117	-0.356674
C	-2.632958	0.235494	-0.948832
C	-3.733717	-0.451573	-0.475057
H	-2.401923	-2.236276	1.972169
H	-0.334111	-1.049270	1.210858
H	-2.762865	0.919082	-1.781592
H	-4.732098	-0.352895	-0.882086
P	0.033463	1.046797	-1.045734
O	-0.019123	2.376322	-0.064264
C	1.479540	0.097186	-0.425740
C	1.628020	-1.246110	-0.797369
C	2.511918	0.728582	0.275791
C	2.774996	-1.952716	-0.444488
H	0.844577	-1.751411	-1.359375
C	3.659794	0.018763	0.628399
H	2.427665	1.776843	0.550573
H	2.874499	-2.995930	-0.731890
H	4.451913	0.518180	1.179716
C	-0.253446	2.304916	1.349341
H	0.307634	1.488907	1.815279
H	0.078754	3.257764	1.766296
H	-1.323144	2.173868	1.542238
C	3.792718	-1.322065	0.272234
H	4.688041	-1.873334	0.546544
N	-3.581511	-1.305990	0.549118
H	-4.400163	-1.809859	0.886730

PhPy

C	0.746892	-0.000017	0.000090
C	1.478546	-1.123931	0.399142
C	1.478457	1.123914	-0.399087
C	2.867638	-1.074693	0.380863
H	0.979493	-2.026304	0.739778
C	2.867553	1.074739	-0.380995
H	0.979309	2.026428	-0.739249
H	3.445721	-1.941297	0.693129
H	3.445576	1.941368	-0.693302
C	-0.738259	0.000020	0.000146
C	-1.451232	-1.145733	-0.377114
C	-1.451329	1.145739	0.377251
C	-2.844270	-1.144676	-0.379042
H	-0.915145	-2.038290	-0.689515
C	-2.844351	1.144626	0.378932
H	-0.915307	2.038272	0.689860
H	-3.382401	-2.038855	-0.682105
H	-3.382568	2.038764	0.681966
N	3.570162	0.000034	-0.000099
C	-3.545281	-0.000035	-0.000126
H	-4.631993	-0.000031	-0.000225

[BiPy·2H]$^{2+}$

C	-0.742470	0.000173	0.000390
C	-1.451131	1.140021	-0.395240
C	-1.451090	-1.139745	0.395730
C	-2.830050	1.115065	-0.388953
H	-0.943721	2.039420	-0.725094
C	-2.830044	-1.115072	0.388674
H	-0.943656	-2.039070	0.725765
H	-3.447654	1.953067	-0.686023
H	-3.447594	-1.953261	0.685329
C	0.742469	0.000134	0.000315
C	1.451324	1.139913	0.395724
C	1.450890	-1.139858	-0.395245
C	2.830266	1.114947	0.388653
H	0.944117	2.039319	0.725878
C	2.829832	-1.115185	-0.388998
H	0.943256	-2.039170	-0.724980
H	3.448016	1.952991	0.685311
H	3.447245	-1.953371	-0.685949
N	3.469529	-0.000169	-0.000386
N	-3.469528	-0.000094	-0.000311
H	-4.488195	-0.000240	-0.000779
H	4.488196	-0.000213	-0.000871

[BiPy·H]$^{+}$

C	0.786862	0.000222	-0.000088
C	1.506229	-1.133188	-0.385637
C	1.506651	1.133416	0.385572
C	2.895812	-1.080324	-0.371994
H	1.004330	-2.038748	-0.712411
C	2.896174	1.080059	0.372038
H	1.005060	2.039154	0.712288
H	3.475354	-1.948184	-0.675848
H	3.476074	1.947739	0.675701
C	-0.695261	0.000300	0.000190
C	-1.411303	1.144132	-0.378182
C	-1.410962	-1.143807	0.378367
C	-2.788979	1.120561	-0.370754
H	-0.904559	2.048046	-0.696257
C	-2.788639	-1.120771	0.370809
H	-0.903766	-2.047476	0.696448
H	-3.406202	1.963274	-0.655328
H	-3.405601	-1.963796	0.655018
N	3.592794	-0.000231	-0.000137
N	-3.431476	-0.000261	-0.000153
H	-4.449426	-0.000162	0.000502

[PhPy·H]$^+$

C	0.697948	0.000024	0.000082
C	1.421526	1.143789	-0.374714
C	1.421543	-1.143721	0.374936
C	2.797979	1.121314	-0.366235
H	0.918579	2.049047	-0.694630
C	2.797984	-1.121303	0.366165
H	0.918613	-2.048992	0.694849
H	3.413957	1.965560	-0.649241
H	3.413990	-1.965531	0.649160
C	-0.781209	0.000014	0.000064
C	-1.490098	1.153929	0.361308
C	-1.490021	-1.153954	-0.361197
C	-2.881922	1.150257	0.365833
H	-0.955822	2.050608	0.663621
C	-2.881833	-1.150301	-0.365937
H	-0.955683	-2.050622	-0.663441
H	-3.421036	2.046716	0.658775
H	-3.420882	-2.046781	-0.658926
N	3.443698	0.000005	-0.000076
H	4.461177	-0.000177	-0.000613
C	-3.580519	-0.000020	-0.000110
H	-4.667046	-0.000023	-0.000182

MeO-Py Couplings

[TS-I·2H]$^{2+}$-Ph,OMe,ax-MeO-PyH$^+$

(ν_i = -316.16 cm^{-1})

C	1.442186	3.567193	1.422495
C	0.909501	2.287138	1.299626
C	0.646652	1.753942	0.029161
C	0.927517	2.517694	-1.111496
C	1.437637	3.804593	-0.978281
H	1.650221	3.965913	2.410887
H	0.710093	1.712673	2.198157
H	0.767428	2.112542	-2.102459
H	1.642084	4.391571	-1.868779
P	-0.018163	0.067769	-0.055242
C	-1.494770	-0.169317	-1.130411
C	-2.295450	-1.294243	-0.917031
C	-1.880573	0.773109	-2.083996
C	-3.425777	-1.476203	-1.688990
H	-2.068799	-2.031762	-0.155282
C	-3.031380	0.559671	-2.814618
H	-1.313169	1.673698	-2.273386
H	-4.085886	-2.328951	-1.594447
H	-3.398058	1.245011	-3.568017
C	1.698694	4.330577	0.286128
H	2.105545	5.333021	0.384676
C	-0.803660	-0.179849	1.580190
C	-1.936749	0.579163	1.907565
C	-0.297964	-1.097231	2.505308
C	-2.552786	0.420426	3.143044
H	-2.337369	1.303399	1.201295

C	-0.920260	-1.254579	3.744233
H	0.580876	-1.693447	2.279269
H	-3.428790	1.013528	3.389299
H	-0.520806	-1.969815	4.457481
C	-2.044724	-0.498841	4.063366
H	-2.527438	-0.623472	5.028647
N	-3.753453	-0.552468	-2.603890
H	-4.595723	-0.697112	-3.159736
C	1.245688	-1.217238	-0.232789
C	2.546525	-0.925653	0.272032
C	0.948301	-2.585872	-0.502955
C	3.493622	-1.911076	0.317452
C	1.940484	-3.518866	-0.439029
H	2.817724	0.069979	0.603188
H	-0.040896	-2.904167	-0.806027
H	4.505179	-1.737890	0.663951
H	1.782410	-4.563977	-0.675112
N	3.192061	-3.174296	-0.048754
H	3.909333	-3.890373	0.003487
O	0.969779	-0.310530	-1.973497
C	2.214571	0.013618	-2.527689
H	2.803898	0.696790	-1.896252
H	2.814882	-0.895490	-2.695033
H	2.067519	0.504460	-3.500583

[TS-I·2H]$^{2+}$-PyH^{+},OMe,ax-MeOPyH^{+}

(ν_i = -310.68 cm^{-1})

C	1.318639	3.588703	1.483515
C	0.646535	2.382586	1.300134
C	0.928188	1.597823	0.177299
C	1.885212	2.015591	-0.752964
C	2.563881	3.212977	-0.553097
H	1.093468	4.200201	2.352229
H	-0.083018	2.062643	2.039021
H	2.095163	1.416684	-1.634699
H	3.311458	3.532873	-1.272855
P	0.054093	0.046168	-0.138825
C	0.209039	-0.844466	1.510150
C	-0.677569	-1.888487	1.799291
C	1.195291	-0.530005	2.450828
C	-0.570444	-2.570990	2.994311
H	-1.456348	-2.194679	1.110573
C	1.268137	-1.239075	3.633619
H	1.924815	0.252871	2.280282
H	-1.221968	-3.385928	3.282953
H	2.005440	-1.050010	4.403310
C	2.277551	4.002350	0.560939
H	2.804015	4.940755	0.710337
C	0.975960	-1.099465	-1.210715
C	2.137593	-1.683252	-0.685405
C	0.588999	-1.394086	-2.523687
C	2.898448	-2.549728	-1.463873
H	2.474649	-1.462427	0.321889
C	1.344734	-2.279473	-3.287488
H	-0.288175	-0.928140	-2.952673
H	3.802384	-2.985536	-1.048926

H	1.030444	-2.508391	-4.301588
C	2.498985	-2.856865	-2.763016
H	3.088878	-3.540872	-3.366576
N	0.388589	-2.224706	3.867003
H	0.453066	-2.735276	4.746978
C	-1.740865	0.126761	-0.388345
C	-2.468517	-0.971232	-0.953078
C	-2.510191	1.093849	0.331568
C	-3.829818	-0.947494	-0.969743
C	-3.873837	1.056260	0.274813
H	-1.956434	-1.813890	-1.401839
H	-2.041223	1.889326	0.896602
H	-4.425369	-1.730172	-1.423439
H	-4.500124	1.790550	0.766938
N	-4.515003	0.067533	-0.386792
H	-5.528998	0.054927	-0.402168
O	-0.815131	0.936184	-1.843747
C	-1.125739	2.295297	-2.025266
H	-0.933299	2.906531	-1.131724
H	-0.510902	2.691861	-2.843713
H	-2.184660	2.408851	-2.298776

Molecular Coordinates Used in the COSMO-RS Study

EtOH (in gas phase)

C	1.221003	-0.221581	-0.000002
H	1.288465	-0.858986	0.887113
H	2.070778	0.469551	0.000405
H	1.288835	-0.858403	-0.887504
C	-0.085445	0.547513	-0.000001
H	-0.143619	1.192112	0.889449
H	-0.143625	1.192114	-0.889450
O	-1.148091	-0.395809	0.000002
H	-1.989455	0.074490	-0.000008

EtOH (optimized with SMD in EtOH)

C	1.225396	-0.221402	0.000002
H	1.305368	-0.856258	0.889898
H	2.068666	0.478274	0.000352
H	1.305682	-0.855759	-0.890220
C	-0.080173	0.544623	-0.000004
H	-0.147658	1.185829	0.888786
H	-0.147652	1.185820	-0.888801
O	-1.157913	-0.396258	-0.000007
H	-1.992442	0.092832	0.000053

[Int-III·2H]$^{2+}$-PyH^{+},OMe,ax-a (in gas phase)

C	-0.457074	1.802509	3.288322
C	-0.624563	1.391601	1.984295
C	0.140467	0.340651	1.442786
C	1.103346	-0.229930	2.290379
C	1.250387	0.200847	3.595256
H	-1.037754	2.589608	3.755240
H	-1.394689	1.882128	1.395795
H	1.738727	-1.042369	1.953263
H	1.963742	-0.223599	4.292501

P	-0.087173	-0.162822	-0.524056
C	-1.913166	-0.152159	-0.357717
C	-2.557493	-0.688908	0.766880
C	-2.695007	0.366913	-1.399116
C	-3.945286	-0.717671	0.840779
H	-1.989604	-1.095763	1.597744
C	-4.084438	0.370561	-1.306101
H	-2.221422	0.745770	-2.298410
H	-4.429089	-1.161379	1.705159
H	-4.675220	0.784131	-2.117206
C	0.824964	-1.730382	-0.322190
C	0.354815	-2.747538	0.514854
C	1.994765	-1.933816	-1.063869
C	1.052213	-3.948068	0.615115
H	-0.563537	-2.625617	1.080241
C	2.706911	-3.123949	-0.936224
H	2.334642	-1.181850	-1.771148
H	0.667074	-4.742034	1.247102
H	3.615646	-3.272286	-1.511044
O	-0.071997	-0.195034	-2.222498
C	0.865611	1.420029	-0.821351
C	2.246498	1.496419	-0.593136
C	0.207354	2.553456	-1.320212
C	2.930133	2.652660	-0.903292
H	2.804747	0.654609	-0.197107
C	0.925122	3.695298	-1.601307
H	-0.857725	2.545139	-1.521988
H	4.000727	2.767769	-0.780731
H	0.481928	4.598423	-2.004383
C	-0.524921	-1.306656	-2.999211
H	0.307609	-1.985102	-3.204714
H	-1.321649	-1.859985	-2.489625
H	-0.911642	-0.908881	-3.939333
C	2.235709	-4.132370	-0.098246
H	2.780299	-5.067408	-0.013878
C	-4.712059	-0.177928	-0.191218
H	-5.795533	-0.193431	-0.128402
N	0.468936	1.193941	4.059319
N	2.258005	3.711978	-1.395744
H	2.777649	4.553354	-1.631897
H	0.574315	1.490526	5.025772

[Int-III·H]$^+$-PyH$^+$,OMe,ax-b (in gas phase)

C	-1.871722	-2.975711	-2.181909
C	-1.551009	-1.666926	-1.825519
C	-0.362195	-1.434651	-1.136758
C	0.458591	-2.529359	-0.861258
C	0.057200	-3.791643	-1.290717
H	-2.800677	-3.185739	-2.706203
H	-2.222170	-0.858057	-2.091923
H	1.397939	-2.421818	-0.326342
H	0.689511	-4.657338	-1.108477
P	0.070704	0.261747	-0.560291
C	-1.230728	1.499598	-0.145787
C	-2.149938	1.876373	-1.132845
C	-1.325808	2.092378	1.120150

C	-3.152648	2.801076	-0.852432
H	-2.067474	1.459943	-2.130734
C	-2.304710	3.043286	1.389198
H	-0.638408	1.819574	1.915212
H	-3.864765	3.070153	-1.626358
H	-2.348277	3.508510	2.369265
C	1.819284	0.669754	-0.216956
C	2.181931	1.653347	0.706306
C	2.813480	0.010397	-0.947112
C	3.525177	1.960776	0.910985
H	1.425135	2.199153	1.261285
C	4.156532	0.302447	-0.722107
H	2.541266	-0.713399	-1.710300
H	3.796733	2.739340	1.617409
H	4.921786	-0.219391	-1.288471
O	0.158722	0.698717	-2.203494
C	-0.165293	-0.577895	1.304140
C	-1.458431	-0.991863	1.684338
C	0.879886	-0.934601	2.171692
C	-1.673182	-1.708182	2.835788
H	-2.317945	-0.756682	1.063189
C	0.637396	-1.654533	3.323312
H	1.905990	-0.656876	1.953894
H	-2.646690	-2.051875	3.164488
H	1.411222	-1.955054	4.020137
C	0.656879	1.952327	-2.643621
H	1.752393	1.946933	-2.667002
H	0.277555	2.112211	-3.655499
H	0.320142	2.779492	-2.004888
C	4.514529	1.276916	0.207421
H	5.561149	1.514066	0.371587
C	-3.228487	3.391776	0.405718
H	-3.999896	4.125407	0.618705
N	-1.091915	-4.027179	-1.926037
N	-0.621988	-2.022830	3.627007
H	-0.787929	-2.554952	4.474392

[Int-IV·2H]$^{2+}$-PyH^{+},OMe,ax-b (in gas phase)

C	-3.869463	1.661507	0.297159
C	-2.685414	1.252908	-0.304356
C	-2.021153	0.105076	0.166985
C	-2.573856	-0.642522	1.216475
C	-3.760624	-0.222745	1.811136
H	-4.386856	2.540908	-0.072771
H	-2.296359	1.806954	-1.153875
H	-2.103969	-1.559253	1.556908
H	-4.193233	-0.807350	2.616617
P	-0.505907	-0.385327	-0.654800
C	0.165957	-1.918384	-0.016604
C	0.496788	-2.939806	-0.916370
C	0.447206	-2.068679	1.351181
C	1.078534	-4.113686	-0.445104
H	0.311766	-2.820671	-1.979409
C	1.029488	-3.243715	1.810994
H	0.202569	-1.282717	2.061514
H	1.325724	-4.908268	-1.141534

H	1.232987	-3.368323	2.869806
C	1.353091	1.204455	0.764243
C	2.699864	1.066437	1.122352
C	0.465686	1.708235	1.730849
C	3.121197	1.411139	2.389580
H	3.433900	0.715364	0.407028
C	0.925394	2.045454	2.985381
H	-0.586804	1.856754	1.515420
H	4.150071	1.330442	2.720412
H	0.291568	2.446981	3.767227
C	-4.401964	0.929182	1.359895
H	-5.331249	1.247038	1.822242
O	-0.779194	-0.518597	-2.213609
C	0.892003	0.914227	-0.669940
C	0.424957	2.211902	-1.294950
C	1.969725	0.291373	-1.527660
C	0.802270	2.593043	-2.529001
H	-0.216818	2.870425	-0.720724
C	2.263621	0.746795	-2.758963
H	2.469106	-0.604557	-1.173495
H	0.456374	3.524427	-2.962804
H	3.006961	0.260223	-3.380156
C	-1.961686	-1.172391	-2.744380
H	-2.841703	-0.556981	-2.549522
H	-1.785126	-1.254344	-3.815152
H	-2.085001	-2.164473	-2.303297
N	2.230490	1.885678	3.281466
N	1.663083	1.854330	-3.297948
C	1.340847	-4.266914	0.914192
H	1.788781	-5.186051	1.278376
H	1.951349	2.195677	-4.202747
H	2.558297	2.149074	4.207624

[Int-IV·H]$^{+}$-Py,OMe,ax-b (in gas phase)

C	-4.103376	-0.797506	0.458300
C	-2.971731	-0.101775	0.050500
C	-1.794909	-0.802550	-0.261698
C	-1.773060	-2.199799	-0.189104
C	-2.911499	-2.887259	0.221583
H	-5.012335	-0.255160	0.698354
H	-3.005088	0.980683	-0.034577
H	-0.882327	-2.757088	-0.458631
H	-2.892541	-3.970894	0.277515
P	-0.360574	0.160128	-0.753197
C	1.011703	-0.872363	-1.279411
C	1.606915	-0.618809	-2.521839
C	1.555342	-1.846403	-0.427376
C	2.718174	-1.355515	-2.920589
H	1.216804	0.159610	-3.170128
C	2.666025	-2.575816	-0.835009
H	1.129812	-2.030055	0.554925
H	3.175182	-1.159871	-3.885325
H	3.083855	-3.328357	-0.174020
C	0.819494	0.570288	1.685748
C	2.175866	0.545530	2.001439
C	-0.029558	-0.227793	2.459565

C	2.618680	-0.285982	3.029100
H	2.895017	1.162305	1.475547
C	0.513615	-1.023857	3.463966
H	-1.102715	-0.249013	2.297955
H	3.674974	-0.320463	3.283628
H	-0.132269	-1.654290	4.070014
C	-4.070664	-2.189055	0.552005
H	-4.955581	-2.730323	0.872029
O	-0.799287	1.098429	-1.970597
C	0.267874	1.412245	0.530259
C	-0.847922	2.323956	0.983849
C	1.308565	2.213859	-0.216333
C	-0.970515	3.586875	0.543951
H	-1.546749	1.960266	1.727851
C	1.087602	3.474210	-0.623764
H	2.244674	1.739423	-0.486836
H	-1.767266	4.235679	0.889784
H	1.828014	4.026873	-1.190668
C	-1.606522	0.609579	-3.061204
H	-2.634879	0.459146	-2.725665
H	-1.568540	1.387614	-3.822360
H	-1.202677	-0.325556	-3.459403
N	1.817013	-1.073836	3.746113
N	-0.072679	4.152895	-0.332093
C	3.243859	-2.334954	-2.081024
H	4.111105	-2.907850	-2.394335
H	-0.147670	5.131919	-0.558523

[Int-V·2H]$^{2+}$-PyH^{+},OMe,ax-a (in gas phase)

C	-3.200766	-3.544044	-1.202714
C	-2.088208	-2.744408	-0.953752
C	-2.232636	-1.502786	-0.319376
C	-3.513801	-1.067809	0.050474
C	-4.624068	-1.865419	-0.202912
H	-3.081413	-4.503204	-1.696717
H	-1.102563	-3.085651	-1.263165
H	-3.649396	-0.102113	0.530334
H	-5.613123	-1.522293	0.084238
P	-0.707964	-0.560432	0.002097
C	-1.338908	1.167993	0.103720
C	-1.289464	1.935067	1.272958
C	-1.795216	1.771687	-1.078264
C	-1.695664	3.271334	1.266480
H	-0.941031	1.487958	2.200029
C	-2.191560	3.107289	-1.090076
H	-1.869123	1.186680	-1.993770
H	-1.689262	3.842618	2.191092
H	-2.570584	3.551045	-2.006522
C	2.499404	0.868426	-0.279536
C	2.270234	1.665005	0.844749
C	2.073884	1.317202	-1.535891
C	1.606557	2.867905	0.696090
H	2.591441	1.359314	1.833983
C	1.401368	2.517392	-1.630677
H	2.210041	0.717360	-2.428642
H	1.381468	3.531799	1.521003

H	1.006312	2.911144	-2.558900
C	-4.467704	-3.103981	-0.826267
H	-5.337244	-3.722924	-1.024713
O	-0.300619	-0.882942	1.593180
C	3.177038	-0.448920	-0.134074
C	4.284036	-0.771208	-0.928341
C	2.707286	-1.377438	0.804707
C	4.901677	-1.995657	-0.765744
H	4.684077	-0.074119	-1.656828
C	3.354487	-2.590929	0.925994
H	1.817307	-1.183680	1.403490
H	5.767878	-2.311159	-1.335459
H	3.047224	-3.364005	1.620444
C	-1.279860	-1.225746	2.587283
H	-1.715483	-2.203753	2.367149
H	-0.753173	-1.259155	3.542451
H	-2.079871	-0.480797	2.635307
N	1.199890	3.254791	-0.522994
N	4.422442	-2.859503	0.148716
C	-2.137894	3.864312	0.084077
H	-2.477837	4.896035	0.083931
H	4.888812	-3.757660	0.257717
H	0.632307	4.097967	-0.596849

[Int-V·H]$^{+}$-Py,OMe,ax-a (in gas phase)

C	5.281576	0.228471	-1.253566
C	3.984705	0.675649	-1.010072
C	3.081321	-0.110786	-0.284168
C	3.499907	-1.362436	0.188920
C	4.793448	-1.810956	-0.055894
H	5.971932	0.846154	-1.819977
H	3.670781	1.643934	-1.394022
H	2.811020	-1.994476	0.742914
H	5.107247	-2.782506	0.313922
P	1.422176	0.603171	0.018009
C	0.392208	-0.908021	0.229455
C	-0.449298	-1.076474	1.333159
C	0.350064	-1.858936	-0.799474
C	-1.305497	-2.173815	1.416049
H	-0.424934	-0.353749	2.145029
C	-0.502831	-2.955597	-0.716608
H	1.004088	-1.757143	-1.663332
H	-1.946162	-2.295574	2.284768
H	-0.513165	-3.691477	-1.515620
C	-3.120775	0.442751	-0.363768
C	-4.101747	0.267399	0.615956
C	-3.015055	-0.518664	-1.368942
C	-4.923348	-0.852784	0.541525
H	-4.252937	0.994960	1.407914
C	-3.881042	-1.608338	-1.341048
H	-2.242634	-0.464670	-2.129488
H	-5.703023	-1.010864	1.281813
H	-3.807374	-2.382913	-2.099545
C	5.685571	-1.015372	-0.775390
H	6.694156	-1.369296	-0.966987
O	1.494837	1.212084	1.571787

C	-2.195881	1.591608	-0.323763
C	-1.749893	2.207496	-1.505427
C	-1.708585	2.080778	0.897087
C	-0.844795	3.240066	-1.443139
H	-2.113600	1.884683	-2.473851
C	-0.796177	3.110106	0.915065
H	-1.996749	1.622559	1.835084
H	-0.455958	3.747971	-2.316784
H	-0.346420	3.494050	1.821073
C	2.233540	0.566451	2.611938
H	3.307564	0.629253	2.413704
H	2.000150	1.098436	3.536383
H	1.945814	-0.485660	2.714132
N	-4.819868	-1.782018	-0.411228
N	-0.398443	3.666018	-0.244757
C	-1.335800	-3.114843	0.390838
H	-2.003928	-3.968303	0.454121
H	0.301287	4.399866	-0.216189

[Int-V]-Py,OMe,ax-a (in gas phase)

C	0.367932	-1.574268	2.773782
C	-0.156578	-0.562910	1.969906
C	-0.460917	-0.816843	0.630716
C	-0.233833	-2.095098	0.110608
C	0.286769	-3.105146	0.912659
H	0.601460	-1.367493	3.815176
H	-0.319676	0.431536	2.373996
H	-0.449883	-2.302748	-0.935472
H	0.472620	-4.087690	0.489065
P	-1.103844	0.467721	-0.509935
C	-2.905196	0.078050	-0.447389
C	-3.573097	-0.195275	-1.643052
C	-3.623808	0.065636	0.754404
C	-4.936751	-0.493425	-1.641550
H	-3.025493	-0.172471	-2.583103
C	-4.984563	-0.218755	0.757208
H	-3.109726	0.279265	1.688422
H	-5.446281	-0.709448	-2.576466
H	-5.535462	-0.226039	1.693728
C	2.696868	-0.248876	-0.696060
C	2.194659	-0.708812	-1.916647
C	3.369681	-1.176384	0.101725
C	2.381797	-2.040510	-2.269386
H	1.626008	-0.054946	-2.570145
C	3.497165	-2.488624	-0.341353
H	3.800376	-0.889131	1.055694
H	1.989642	-2.414312	-3.212728
H	4.012610	-3.222781	0.273503
C	0.592245	-2.844756	2.247830
H	1.007269	-3.629443	2.874405
O	-1.006981	1.751426	0.548594
C	2.501185	1.156051	-0.260856
C	2.367527	1.488546	1.088482
C	2.420294	2.204623	-1.181877
C	2.149570	2.814837	1.444666
H	2.385177	0.722163	1.856059

C	2.205338	3.498965	-0.721410
H	2.539045	2.026621	-2.246166
H	2.024996	3.084049	2.491033
H	2.142514	4.325096	-1.426323
C	-1.315591	3.032836	0.020986
H	-2.398044	3.141869	-0.125662
H	-0.966843	3.768340	0.748148
H	-0.799319	3.204527	-0.932318
N	3.017779	-2.932597	-1.505473
N	2.064323	3.817893	0.568107
C	-5.641973	-0.503370	-0.441959
H	-6.704530	-0.730212	-0.437610

[Int-III]-Py,OMe,ax-b (in gas phase)

C	0.893724	4.035952	-0.634811
C	0.959420	2.646832	-0.708775
C	-0.139576	1.869850	-0.334457
C	-1.312727	2.499799	0.083575
C	-1.382300	3.890274	0.141109
H	1.757286	4.630023	-0.919906
H	1.865906	2.169267	-1.070452
H	-2.183011	1.913805	0.364664
H	-2.303033	4.368920	0.462115
P	-0.019175	0.041731	-0.465139
C	-1.600847	-0.949317	-0.433393
C	-1.894418	-1.864868	-1.444548
C	-2.537847	-0.816606	0.593255
C	-3.073591	-2.602757	-1.373151
H	-1.227371	-1.992478	-2.288480
C	-3.707939	-1.570527	0.548895
H	-2.367537	-0.155606	1.436599
H	-3.303547	-3.337569	-2.141262
H	-4.456351	-1.460132	1.330042
C	0.180183	-0.220031	1.461712
C	0.280883	-1.532183	1.942872
C	0.278083	0.785918	2.422524
C	0.457597	-1.770222	3.298742
H	0.225981	-2.380589	1.263201
C	0.457349	0.449284	3.767476
H	0.225278	1.836427	2.153988
H	0.534400	-2.788881	3.672978
H	0.534000	1.233775	4.518268
C	-0.276739	4.661372	-0.209311
H	-0.329180	5.745022	-0.158273
O	-0.110962	0.148664	-2.225096
C	1.643082	-0.723412	-0.744886
C	2.723287	-0.344365	0.058980
C	1.848765	-1.679971	-1.743738
C	3.985051	-0.897360	-0.141316
H	2.588377	0.383876	0.852916
C	3.100618	-2.265262	-1.913689
H	1.035087	-1.956635	-2.402266
H	4.815319	-0.576942	0.481285
H	3.238335	-3.021421	-2.681295
C	-1.121721	0.863012	-2.892474
H	-0.896794	1.937852	-2.921996

H	-1.174270	0.485967	-3.919583
H	-2.112615	0.732414	-2.430936
C	4.174352	-1.870170	-1.119460
H	5.153957	-2.317243	-1.262804
N	0.545483	-0.800392	4.218277
N	-3.981632	-2.461978	-0.405667

[TS-I·2H]$^{2+}$-PyH^{+},OMe,ax-b (in gas phase)

C	-4.046648	-1.196231	-0.504226
C	-2.749231	-0.928981	-0.929477
C	-1.676128	-1.047206	-0.031503
C	-1.913099	-1.482120	1.277244
C	-3.211306	-1.763215	1.690369
H	-4.872002	-1.103865	-1.202851
H	-2.574604	-0.666205	-1.969700
H	-1.098583	-1.623201	1.976756
H	-3.387751	-2.114950	2.701791
P	-0.032475	-0.724148	-0.690079
C	1.396996	-1.395396	0.186347
C	2.401723	-1.960409	-0.617082
C	1.545490	-1.411009	1.580753
C	3.532266	-2.523717	-0.033010
H	2.302684	-1.967911	-1.698324
C	2.668485	-1.991853	2.157260
H	0.801174	-0.962071	2.227382
H	4.303011	-2.955031	-0.663527
H	2.766801	-2.013323	3.237925
C	0.045845	1.268258	0.916477
C	1.224924	1.774081	1.481978
C	-1.164861	1.743298	1.442970
C	1.186557	2.667721	2.531300
H	2.201093	1.462440	1.116810
C	-1.178998	2.641836	2.490475
H	-2.122347	1.406583	1.053499
H	2.065165	3.075286	3.018618
H	-2.082739	3.030670	2.946171
C	-4.278698	-1.608687	0.806982
H	-5.289581	-1.830525	1.134201
O	-0.032537	-1.501942	-2.107616
C	0.243224	0.937305	-1.314420
C	-0.814031	1.751186	-1.820173
C	1.572485	1.332194	-1.650495
C	-0.529805	2.922263	-2.460749
H	-1.852436	1.474290	-1.688056
C	1.794660	2.514713	-2.297426
H	2.422830	0.706514	-1.404543
H	-1.297359	3.580915	-2.849476
H	2.785626	2.860097	-2.567888
C	-0.340303	-2.904829	-2.254615
H	-1.394779	-3.082313	-2.030323
H	-0.133499	-3.145275	-3.296280
H	0.290160	-3.510268	-1.597517
N	-0.009942	3.073862	3.008063
H	-0.030694	3.728049	3.784785
N	0.756336	3.300184	-2.672823
H	0.942322	4.155480	-3.184621

C	3.663700	-2.546859	1.353082
H	4.538698	-3.000004	1.808231

[TS-I·H]$^{+}$-Py,OMe,ax-a (in gas phase)

C	-3.857004	-1.811078	-0.564265
C	-2.621609	-1.312053	-0.967103
C	-1.577615	-1.178367	-0.041130
C	-1.783371	-1.571665	1.285024
C	-3.009709	-2.096160	1.676435
H	-4.661846	-1.900486	-1.287097
H	-2.466098	-1.040669	-2.007365
H	-1.006337	-1.449342	2.028873
H	-3.155142	-2.405904	2.706395
P	-0.001673	-0.527720	-0.668623
C	1.569060	-1.189405	-0.039007
C	2.610641	-1.338238	-0.965460
C	1.773294	-1.576396	1.289314
C	3.841897	-1.846339	-0.561314
H	2.456429	-1.071145	-2.006991
C	2.995235	-2.109967	1.682182
H	0.998839	-1.441954	2.033755
H	4.644862	-1.947387	-1.284698
H	3.139272	-2.414660	2.713844
C	0.002719	1.069365	0.968292
C	1.190856	1.467227	1.576287
C	-1.184149	1.470359	1.576783
C	1.141924	2.190017	2.767550
H	2.161767	1.225969	1.150158
C	-1.132685	2.193083	2.768012
H	-2.155944	1.231631	1.151304
H	2.061353	2.495160	3.262293
H	-2.051084	2.500646	3.263170
C	-4.050293	-2.209316	0.756040
H	-5.009870	-2.609604	1.068263
O	-0.003283	-1.210287	-2.176018
C	0.005290	1.164856	-1.166473
C	-1.210399	1.849147	-1.515521
C	1.227731	1.837242	-1.515144
C	-1.169506	3.151981	-1.897217
H	-2.171544	1.356051	-1.441645
C	1.199766	3.140414	-1.896895
H	2.183887	1.334456	-1.441571
H	-2.060230	3.722717	-2.130304
H	2.096103	3.702323	-2.129935
C	-0.010904	-2.617035	-2.426515
H	-0.911511	-3.083909	-2.014701
H	-0.001227	-2.735537	-3.510523
H	0.874558	-3.097194	-1.997399
N	0.005216	2.551480	3.365596
N	0.018383	3.801737	-2.040249
H	0.023130	4.765483	-2.345620
C	4.033363	-2.238533	0.761044
H	4.989603	-2.645904	1.074348

[TS-II·2H]$^{2+}$-PyH^{+},OMe,ax-a (in gas phase)

C	3.965345	0.096175	-1.292585

C	2.605846	-0.136332	-1.112509
C	1.760176	0.904347	-0.700442
C	2.291281	2.181974	-0.468422
C	3.652688	2.407035	-0.645870
H	4.616987	-0.706707	-1.622741
H	2.200255	-1.126517	-1.310942
H	1.647249	2.999551	-0.157062
H	4.061974	3.397031	-0.471641
P	-0.003773	0.546228	-0.568189
C	-0.747001	1.672194	0.622784
C	-2.043842	2.155772	0.396294
C	-0.104558	1.953742	1.840508
C	-2.678381	2.929768	1.365105
H	-2.544552	1.950109	-0.545721
C	-0.747947	2.721076	2.805153
H	0.909444	1.604075	2.021710
H	-3.672548	3.322690	1.176526
H	-0.240347	2.956543	3.735433
C	-0.082172	-2.167525	0.626107
C	0.091417	-1.640842	1.919805
C	0.703951	-3.272279	0.262602
C	1.019095	-2.189068	2.773067
H	-0.480251	-0.786802	2.266527
C	1.623457	-3.792201	1.148738
H	0.591226	-3.760851	-0.697279
H	1.195940	-1.822947	3.777359
H	2.248639	-4.648271	0.923251
C	4.487386	1.367472	-1.055902
H	5.547915	1.550828	-1.197371
O	-0.716493	0.819143	-1.994052
C	-1.114727	-1.610351	-0.305858
C	-1.181525	-2.076472	-1.666377
C	-2.383946	-1.228289	0.264803
C	-2.327098	-1.964414	-2.390064
H	-0.297358	-2.438919	-2.177568
C	-3.500733	-1.145851	-0.509903
H	-2.477044	-0.981538	1.315220
H	-2.392060	-2.260052	-3.430093
H	-4.462458	-0.843609	-0.112638
C	-0.445866	2.011444	-2.763862
H	0.602608	2.027952	-3.070917
H	-1.090626	1.954613	-3.639939
H	-0.684387	2.904886	-2.179511
N	1.760947	-3.242333	2.369308
N	-3.465565	-1.484234	-1.823692
C	-2.034611	3.208835	2.568623
H	-2.529021	3.816813	3.319650
H	-4.315765	-1.442807	-2.372465
H	2.435650	-3.643931	3.015385

[TS-II·H]$^+$-Py,OMe,ax-a (in gas phase)

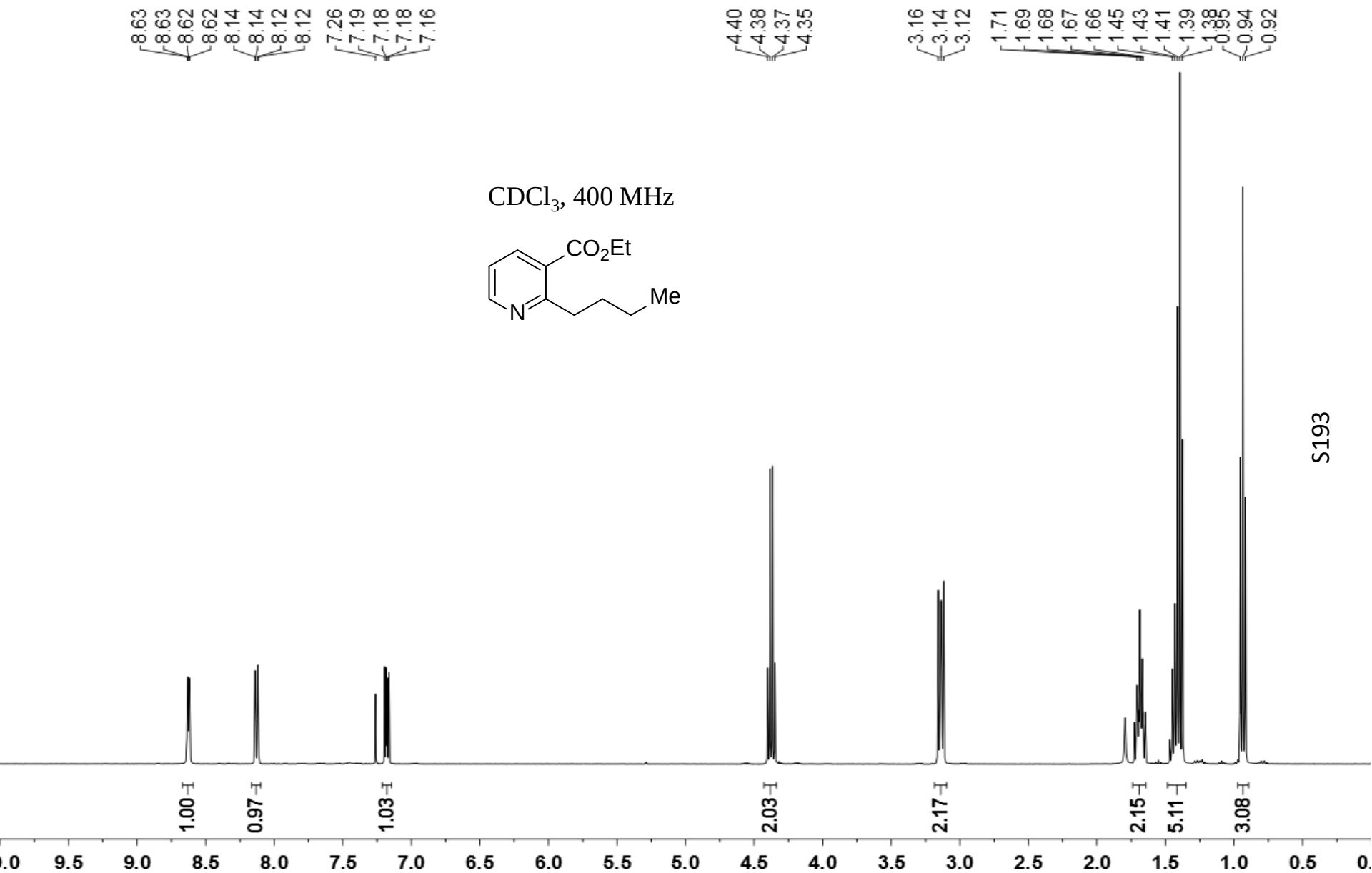
C	3.932411	-1.211160	1.306256
C	2.640801	-1.266481	0.794197
C	2.140731	-0.209122	0.019838
C	2.949766	0.904199	-0.234931
C	4.239838	0.958556	0.286558

H	4.316265	-2.033669	1.901762
H	2.022298	-2.140337	0.989158
H	2.579022	1.726334	-0.839846
H	4.864318	1.823863	0.087194
P	0.452954	-0.391801	-0.616605
C	-0.094103	1.208592	-1.252881
C	-0.714799	1.293964	-2.505483
C	-0.071112	2.333367	-0.414476
C	-1.273060	2.498614	-2.927001
H	-0.759518	0.421982	-3.152242
C	-0.632152	3.532017	-0.840329
H	0.382161	2.276988	0.572388
H	-1.740386	2.562941	-3.904938
H	-0.605072	4.398880	-0.187386
C	-1.490996	-0.108417	1.543691
C	-2.531004	0.817638	1.523245
C	-0.473398	0.088271	2.483341
C	-2.492360	1.896564	2.407512
H	-3.372875	0.720842	0.846894
C	-0.530792	1.194653	3.321411
H	0.378098	-0.582666	2.550198
H	-3.290357	2.634513	2.398542
H	0.255365	1.369282	4.051332
C	4.730112	-0.094867	1.055763
H	5.736669	-0.047511	1.459859
O	0.527230	-1.402506	-1.891890
C	-1.453932	-1.266834	0.590737
C	-1.085842	-2.563986	1.111712
C	-2.377194	-1.311136	-0.518653
C	-1.407741	-3.702837	0.448497
H	-0.539637	-2.640462	2.044398
C	-2.653484	-2.481043	-1.150221
H	-2.799427	-0.396331	-0.917209
H	-1.131292	-4.688024	0.804438
H	-3.297805	-2.538546	-2.019157
C	1.577407	-1.298257	-2.867531
H	2.535517	-1.576535	-2.419963
H	1.321774	-1.996356	-3.664980
H	1.638499	-0.281400	-3.268429
N	-1.514154	2.099772	3.287140
N	-2.148046	-3.660534	-0.695965
C	-1.230580	3.617016	-2.097238
H	-1.665865	4.554972	-2.428058
H	-2.395598	-4.522237	-1.162093

[TS-I]-Py,OMe,ax-a (in gas phase)

C	-4.172155	0.481785	-0.359814
C	-2.872821	0.340384	-0.836408
C	-1.916512	-0.349044	-0.079374
C	-2.288745	-0.934044	1.132452
C	-3.591834	-0.797760	1.601262
H	-4.903447	1.028621	-0.947084
H	-2.605950	0.758296	-1.802905
H	-1.572512	-1.494868	1.720205
H	-3.870545	-1.249934	2.548112
P	-0.263886	-0.490397	-0.801466

C	0.789864	-1.751282	-0.025685
C	1.480530	-2.608257	-0.893248
C	0.965953	-1.893123	1.356346
C	2.323540	-3.593351	-0.387094
H	1.372229	-2.494558	-1.967221
C	1.798647	-2.887611	1.857390
H	0.493341	-1.204841	2.046731
H	2.862252	-4.241620	-1.071439
H	1.928974	-2.982956	2.930982
C	0.594478	1.164094	0.864544
C	1.863827	1.131483	1.433554
C	-0.394257	1.830254	1.588454
C	2.076059	1.696253	2.687702
H	2.699143	0.683839	0.897181
C	-0.088837	2.368705	2.836857
H	-1.403950	1.949288	1.200540
H	3.063976	1.667622	3.144417
H	-0.856769	2.878388	3.416755
C	-4.530891	-0.080966	0.863340
H	-5.544451	0.031232	1.236782
O	-0.583427	-1.131284	-2.270101
C	0.576816	1.038385	-1.083015
C	-0.109952	2.225398	-1.552005
C	1.934479	0.937519	-1.582071
C	0.636690	3.268164	-2.052838
H	-1.171415	2.366261	-1.383693
C	2.546324	2.065337	-2.086553
H	2.498091	0.013758	-1.493355
H	0.123810	4.196164	-2.304164
H	3.595707	2.001441	-2.374356
C	-1.415213	-2.274712	-2.457739
H	-1.100769	-3.107357	-1.818004
H	-2.460468	-2.028465	-2.245809
H	-1.310106	-2.559459	-3.505582
N	1.120488	2.301558	3.401358
N	1.957935	3.251713	-2.303900
C	2.478110	-3.739155	0.988647
H	3.135002	-4.508253	1.384279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CO2Et
Me
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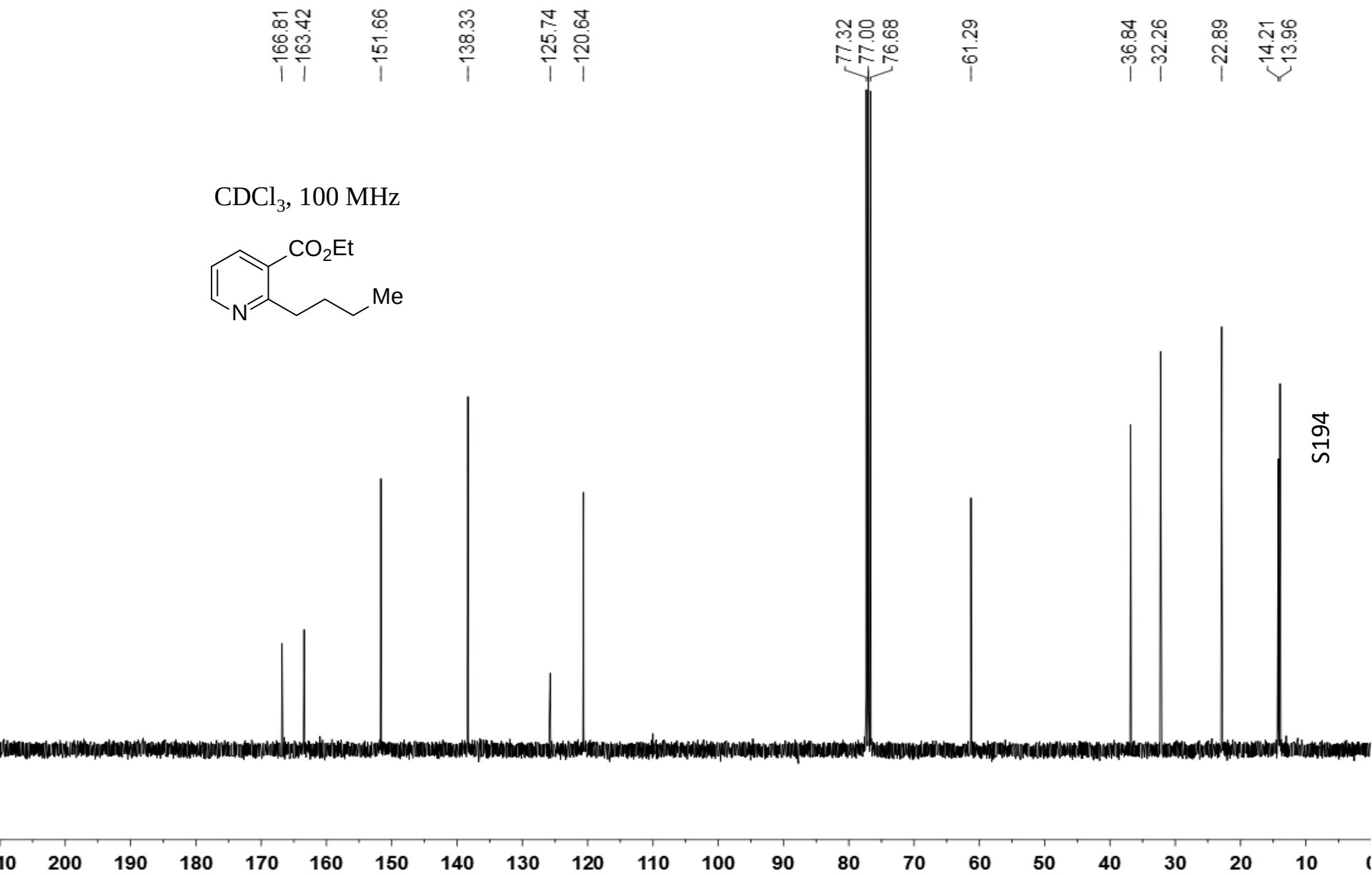
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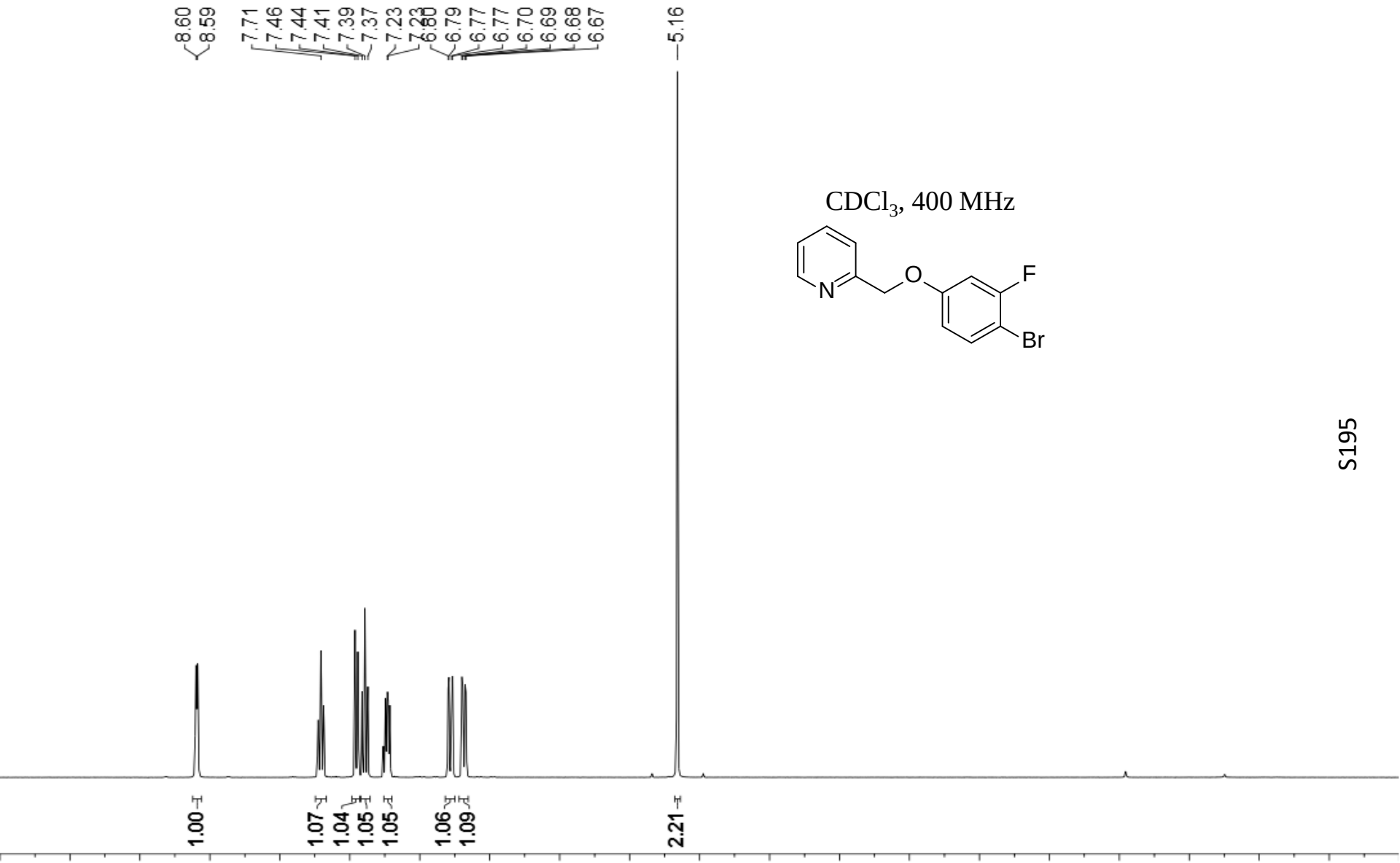
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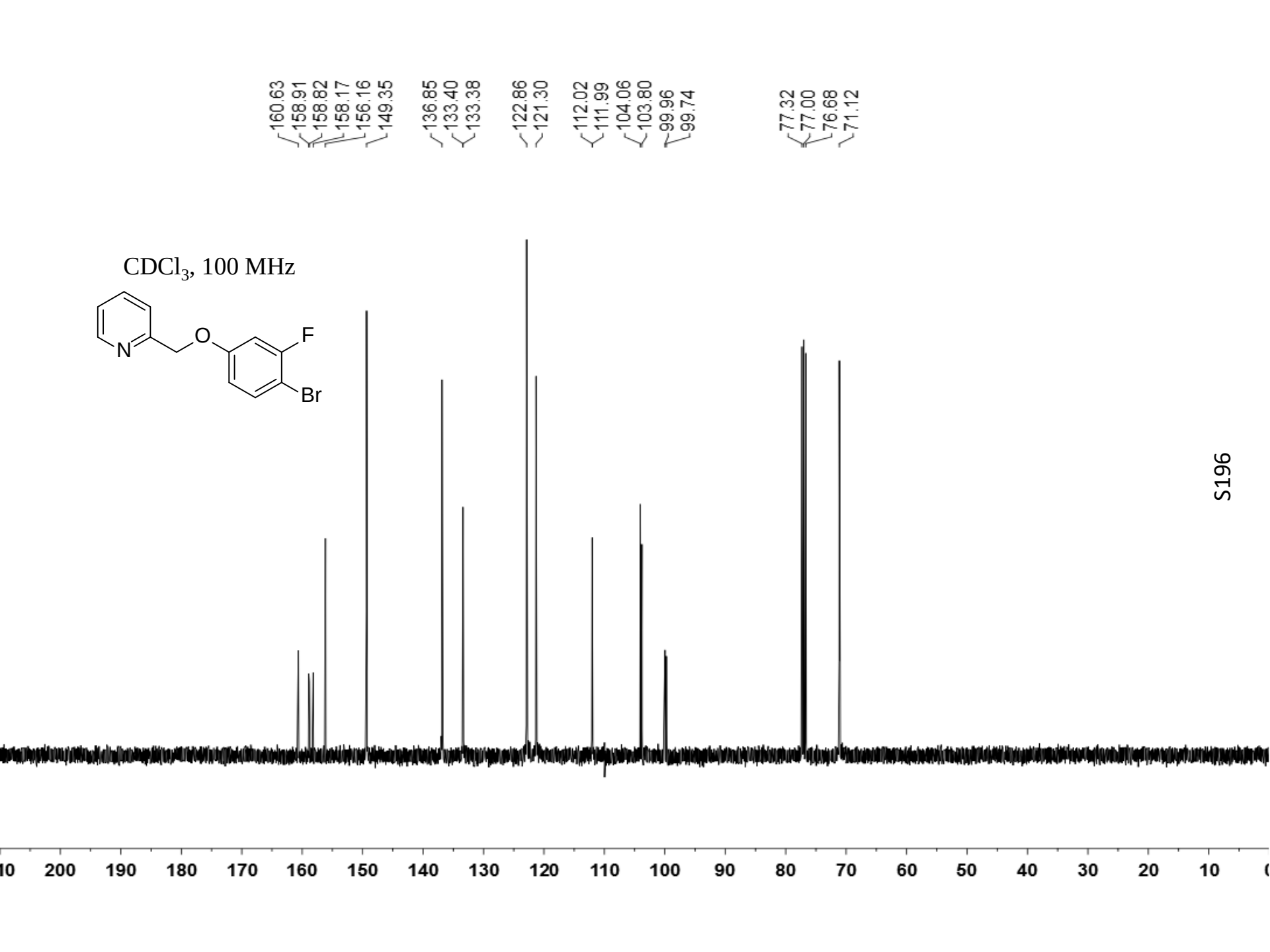
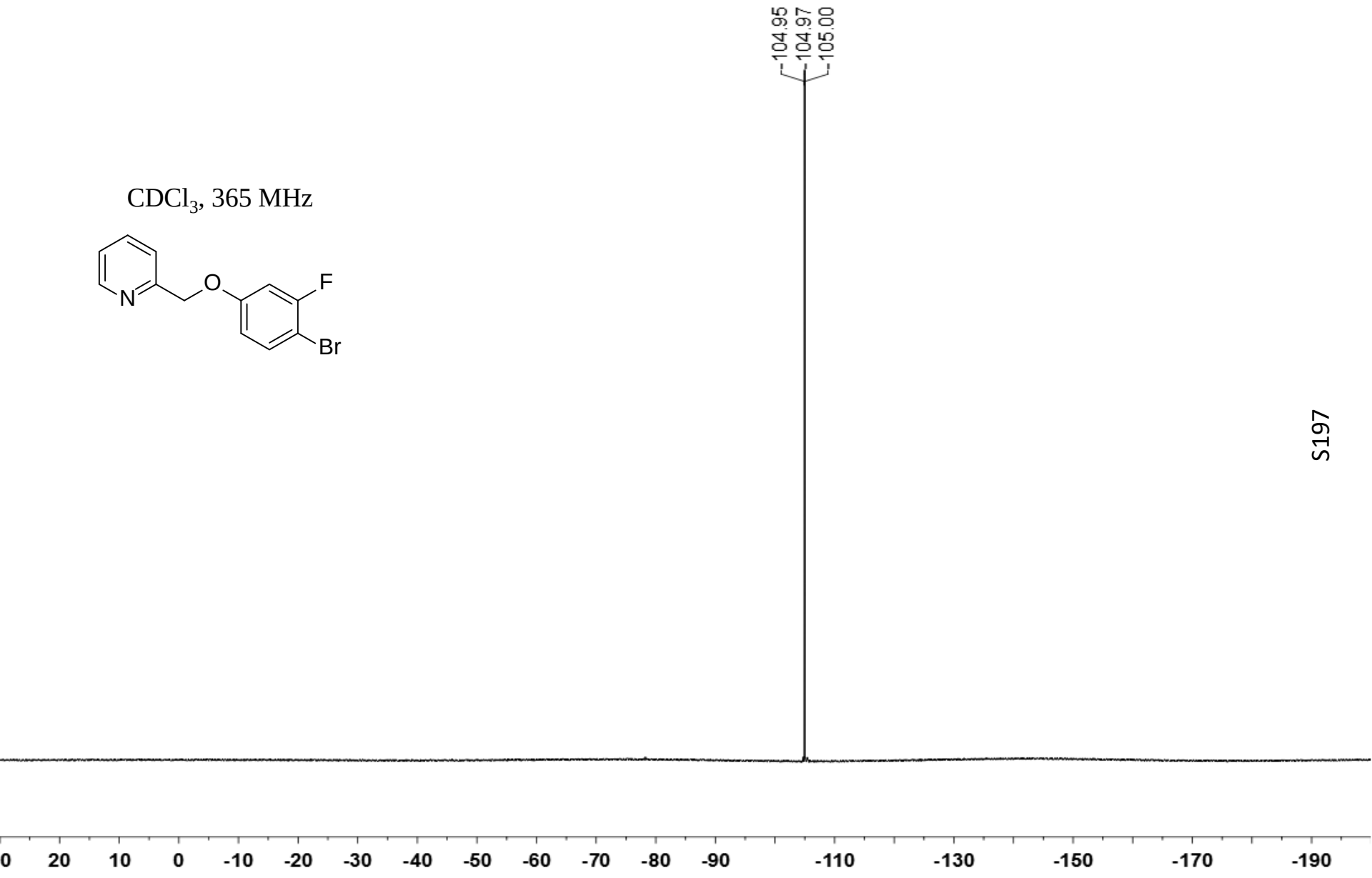
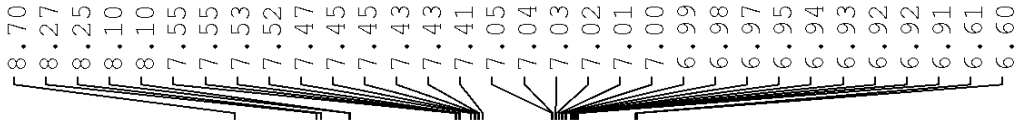
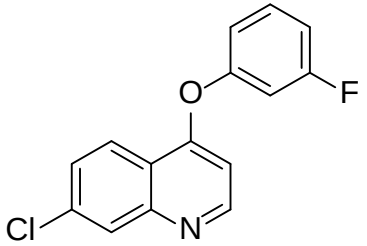
3.5
3.0
2.5
2.0
1.5
1.0
0.5


160.63
158.91
158.82
158.17
156.16
149.35
136.85
133.40
133.38
122.86
121.30
112.02
111.99
104.06
103.80
99.96
99.74
77.32
77.00
76.68
71.12
CDCl3, 100 MHz
N
O
F
Br
S196
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

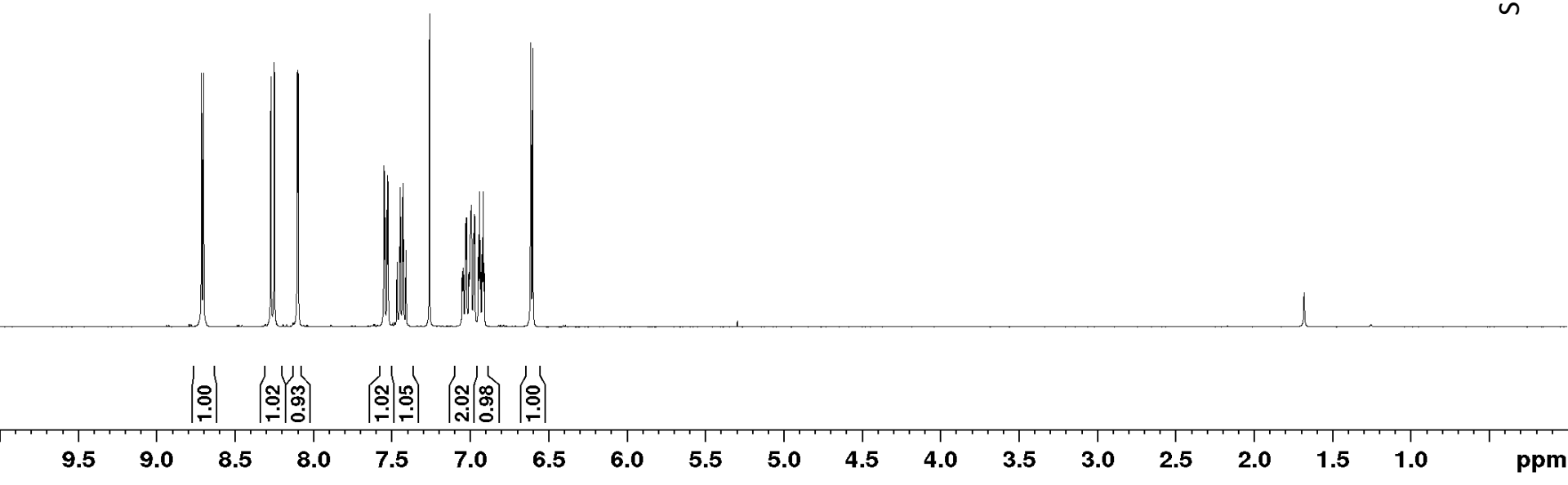

104.95
104.97
105.00
CDCl3, 365 MHz
N
O
F
Br
S197
0
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-110
-130
-150
-170
-190

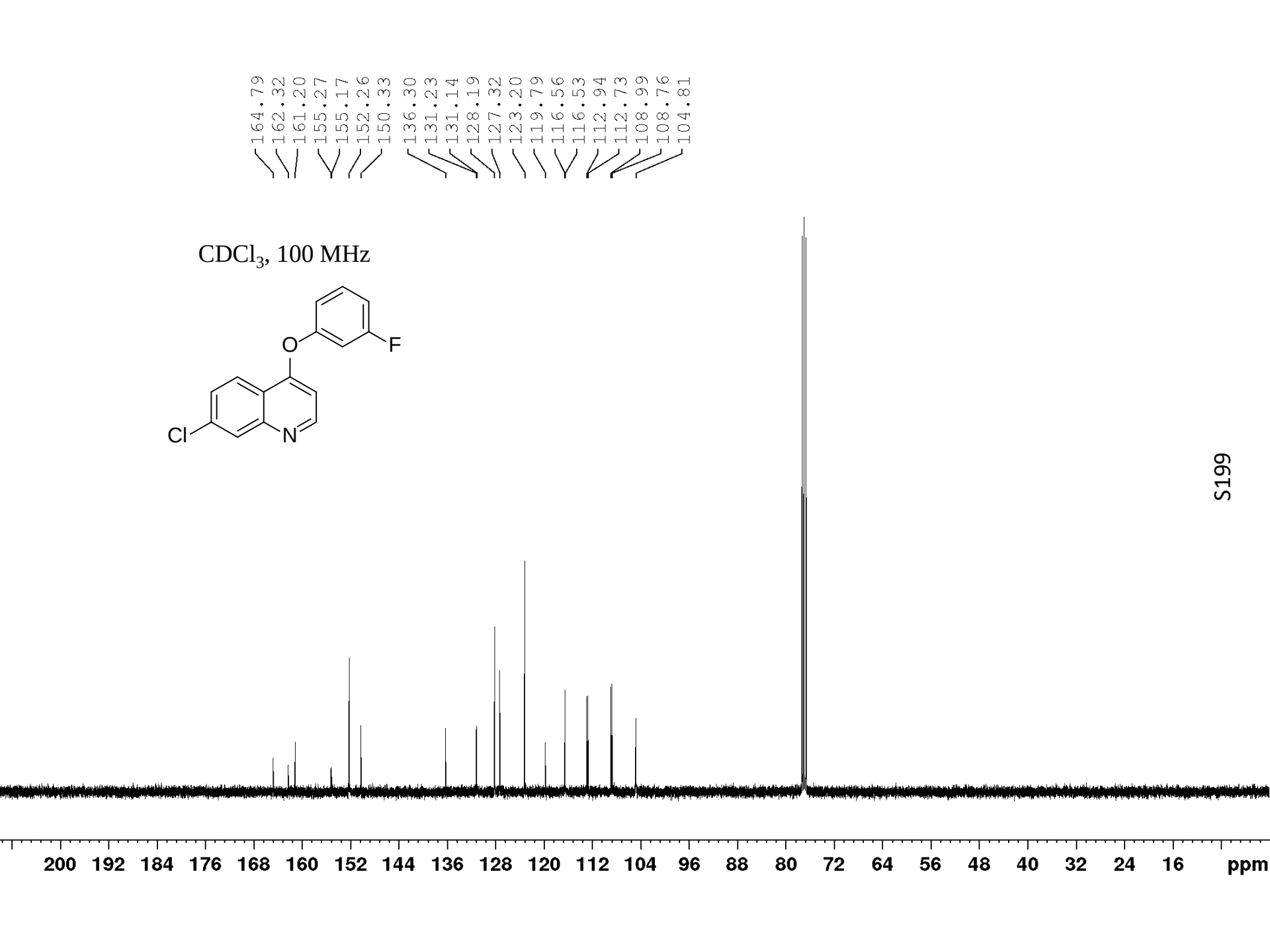


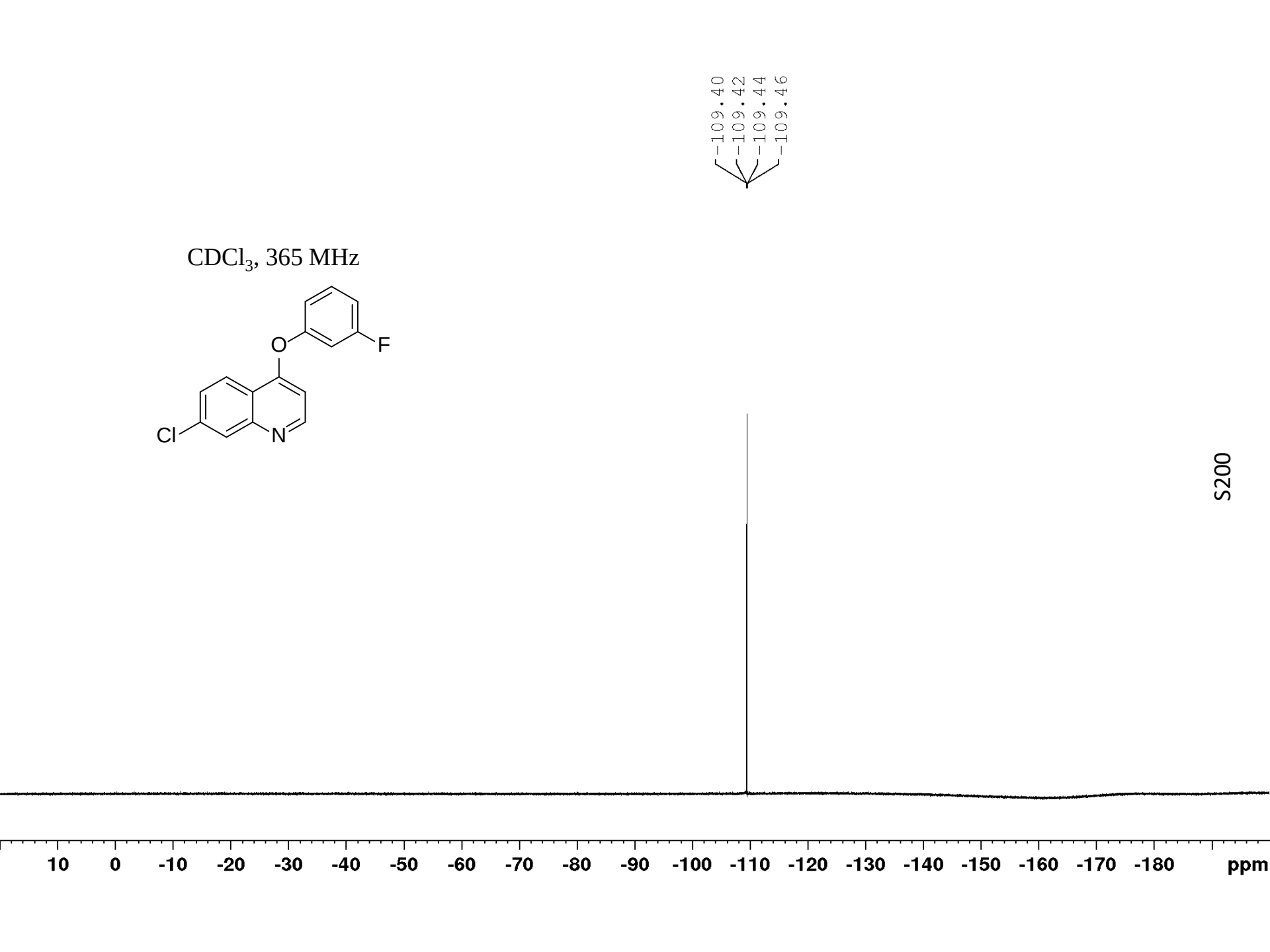
$CDCl_3$, 400 MHz

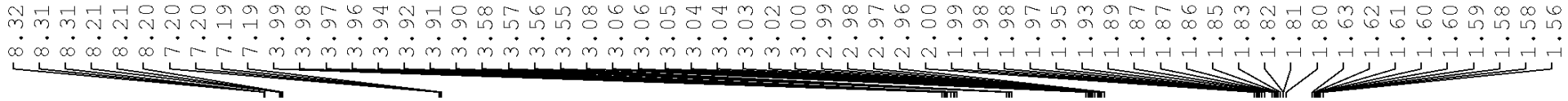


S198

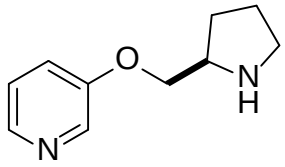


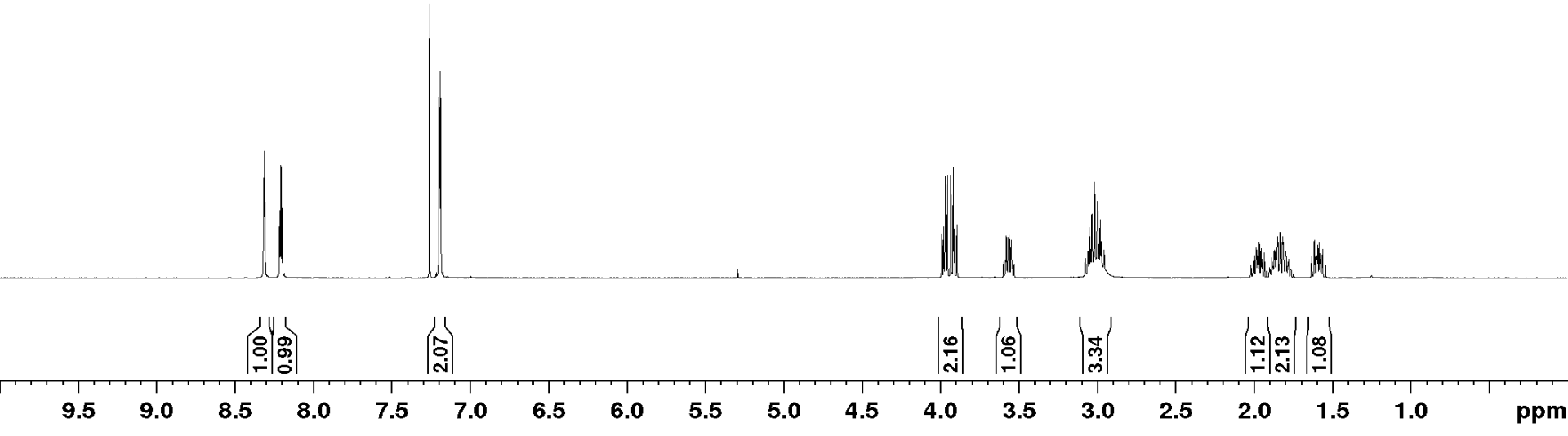

164.79
162.32
161.20
155.27
155.17
152.26
150.33
136.30
131.23
131.14
128.19
127.32
123.20
119.79
116.56
116.53
112.94
112.73
108.99
108.76
104.81
CDCl3, 100 MHz
O
F
Cl
N
S199
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 ppm


-109.40
-109.42
-109.44
-109.46
CDCl3, 365 MHz
O
F
Cl
N
S200
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
ppm



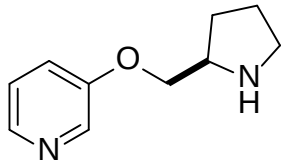
$CDCl_3$, 400 MHz





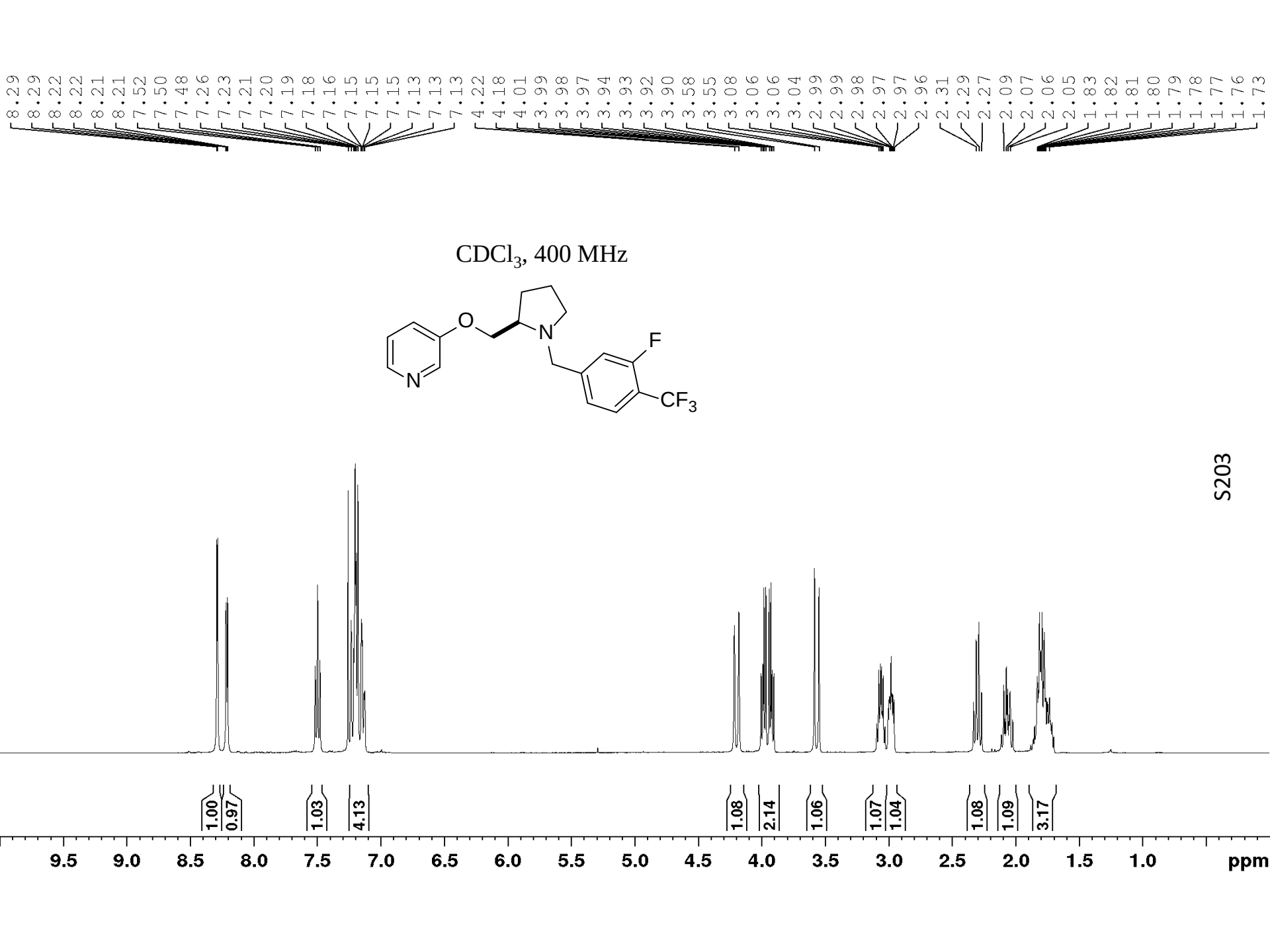
154.85
142.23
138.01
123.74
121.07
70.73
57.26
46.31
27.71
24.98

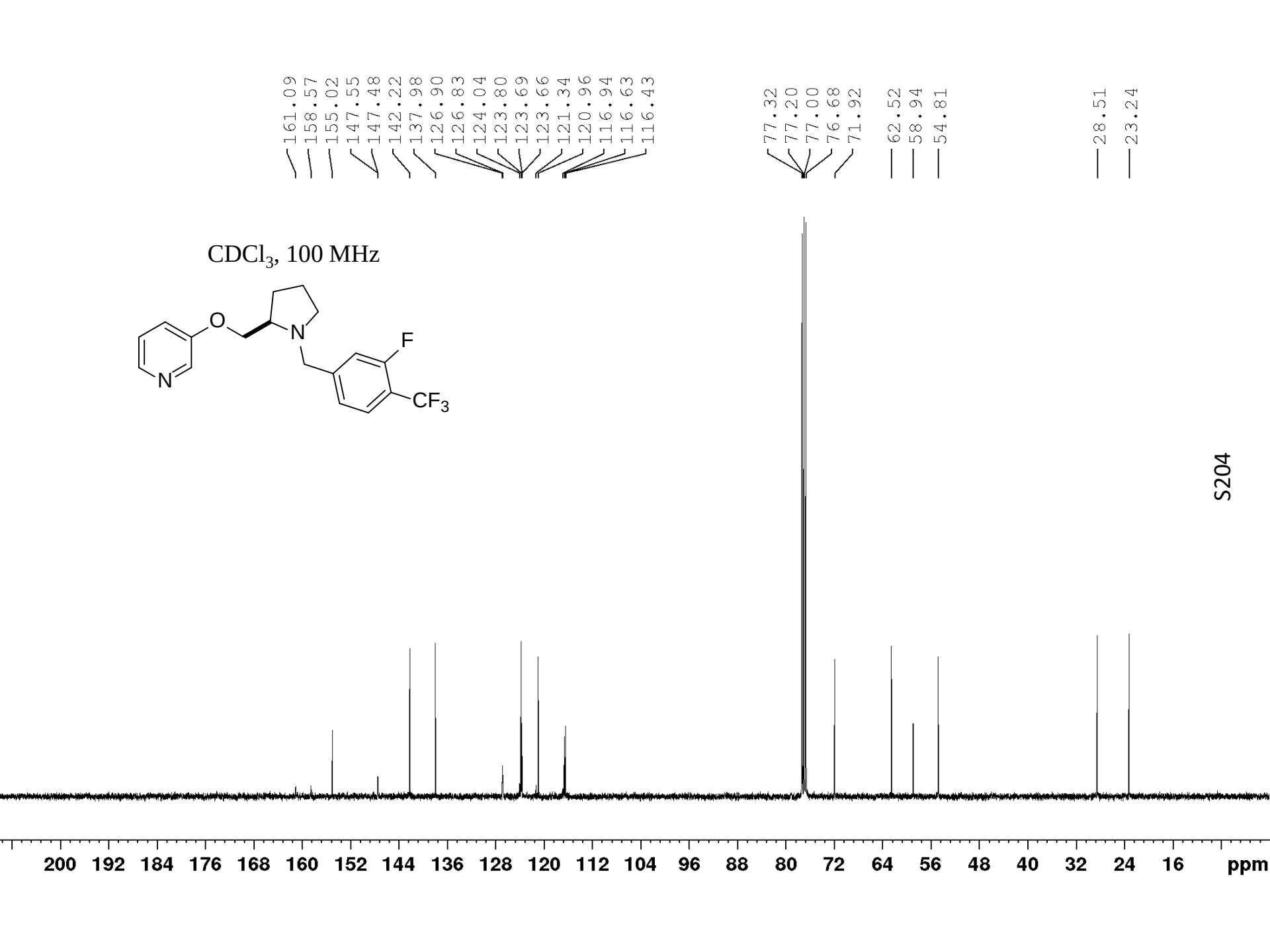
$CDCl_3$, 100 MHz

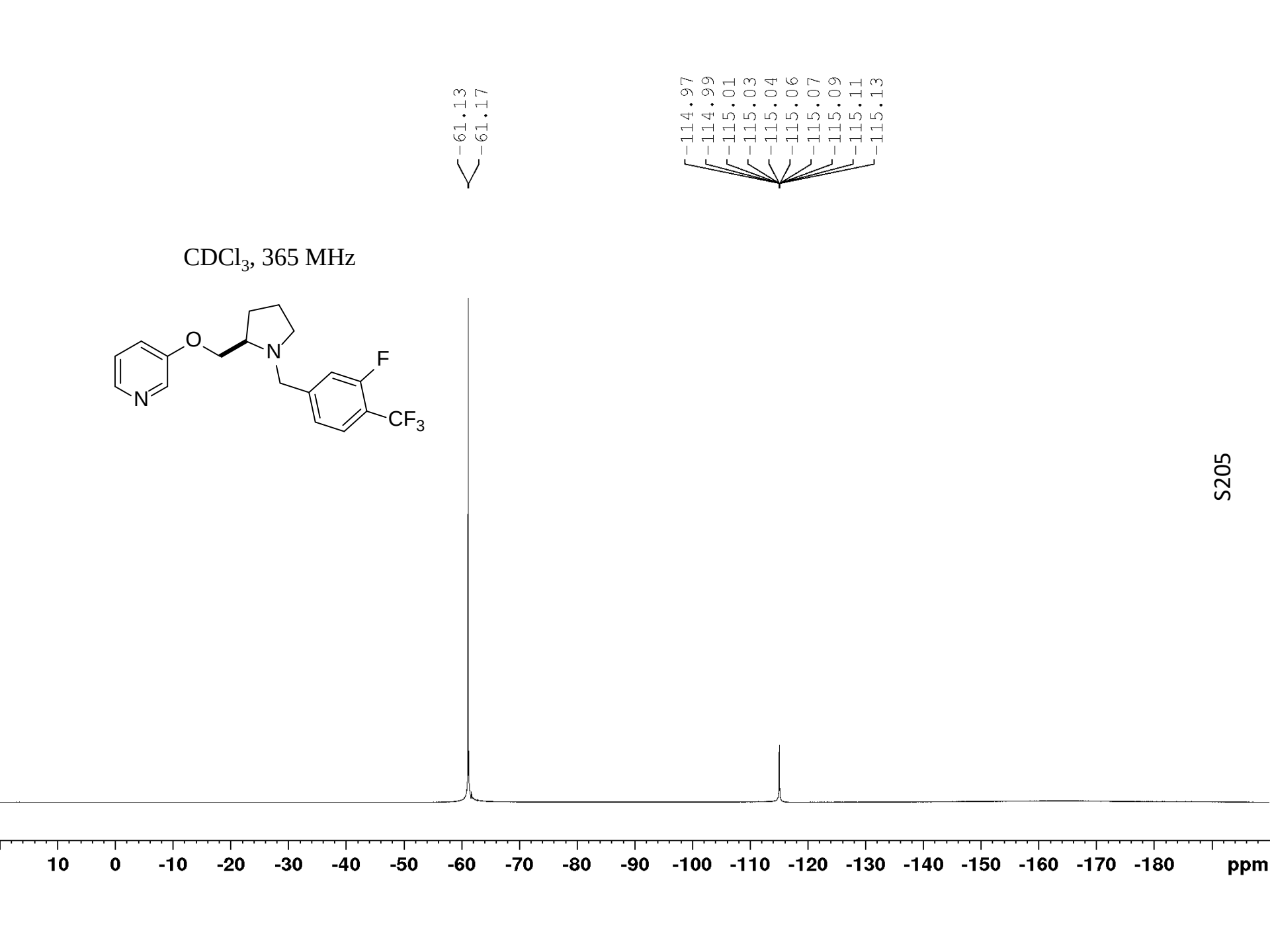


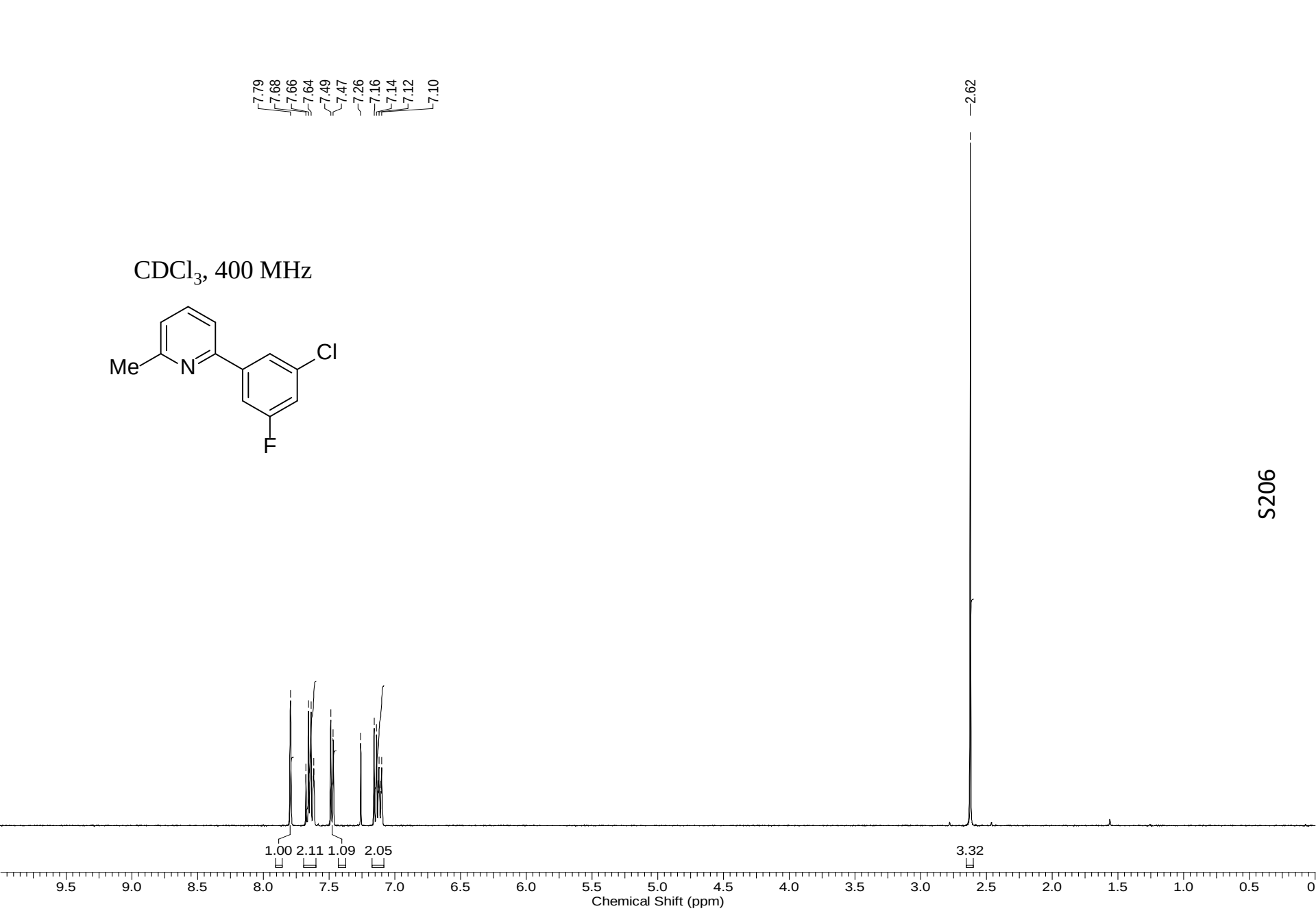
S202

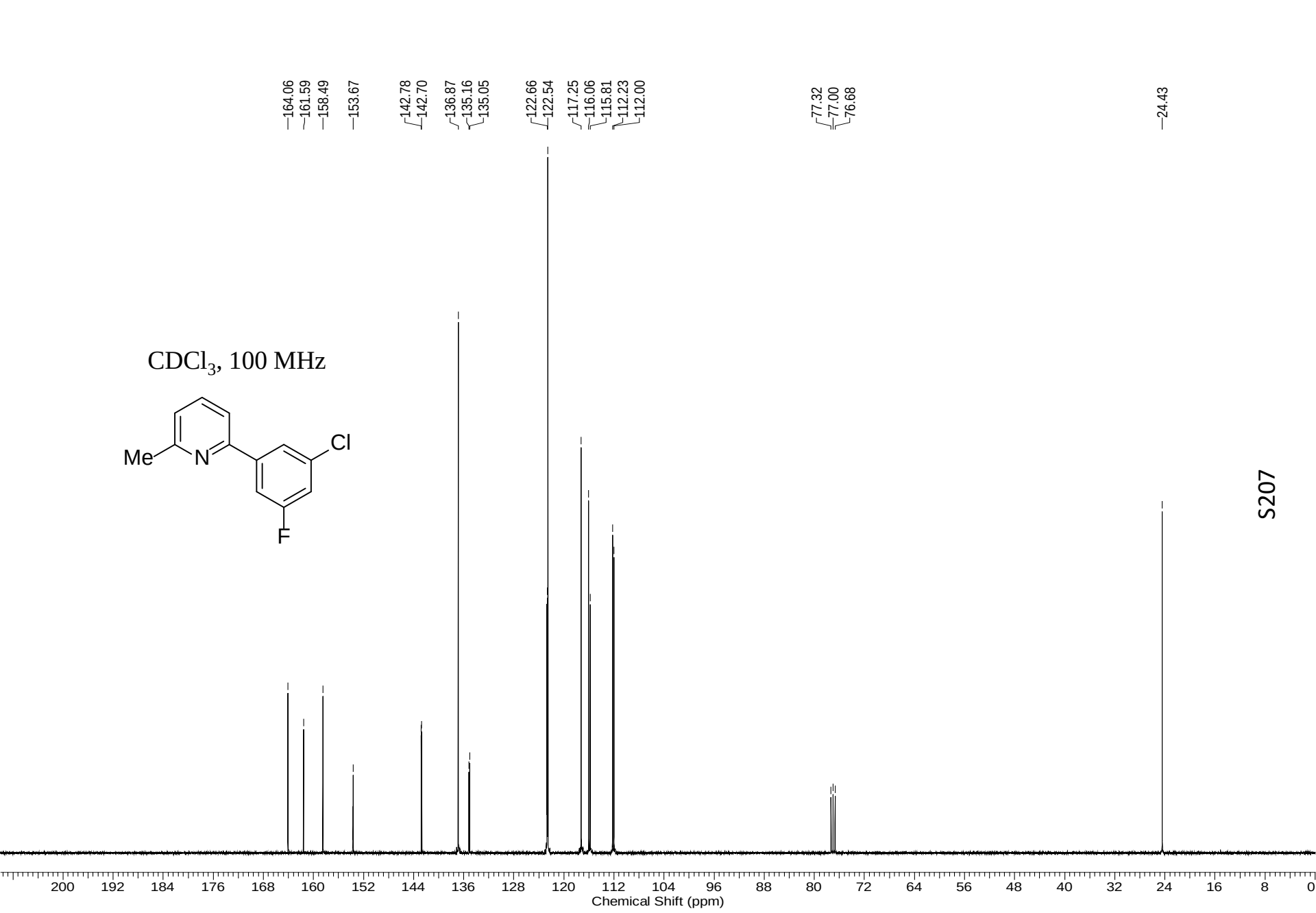
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 ppm

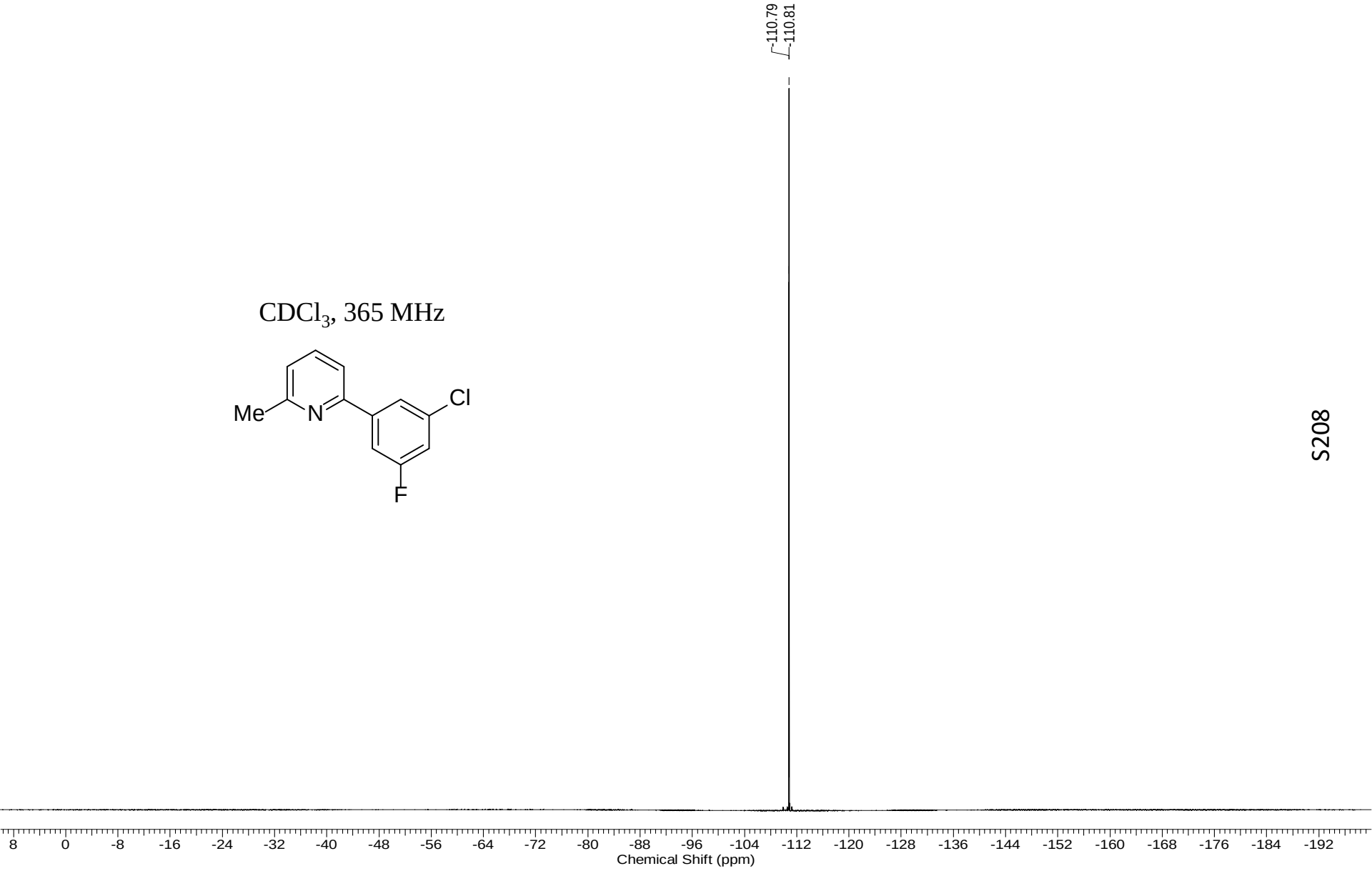

8.29
8.29
8.22
8.22
8.21
8.21
7.52
7.50
7.48
7.26
7.23
7.21
7.20
7.19
7.18
7.16
7.15
7.15
7.15
7.13
7.13
7.13
4.22
4.18
4.01
3.99
3.98
3.97
3.94
3.93
3.92
3.90
3.58
3.55
3.08
3.06
3.06
3.04
2.99
2.99
2.98
2.97
2.97
2.96
2.31
2.29
2.27
2.09
2.07
2.06
2.05
1.83
1.82
1.81
1.80
1.79
1.78
1.77
1.76
1.73
CDCl3, 400 MHz
O
N
N
F
CF3
S203
1.00
0.97
1.03
4.13
1.08
2.14
1.06
1.07
1.04
1.08
1.09
3.17
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

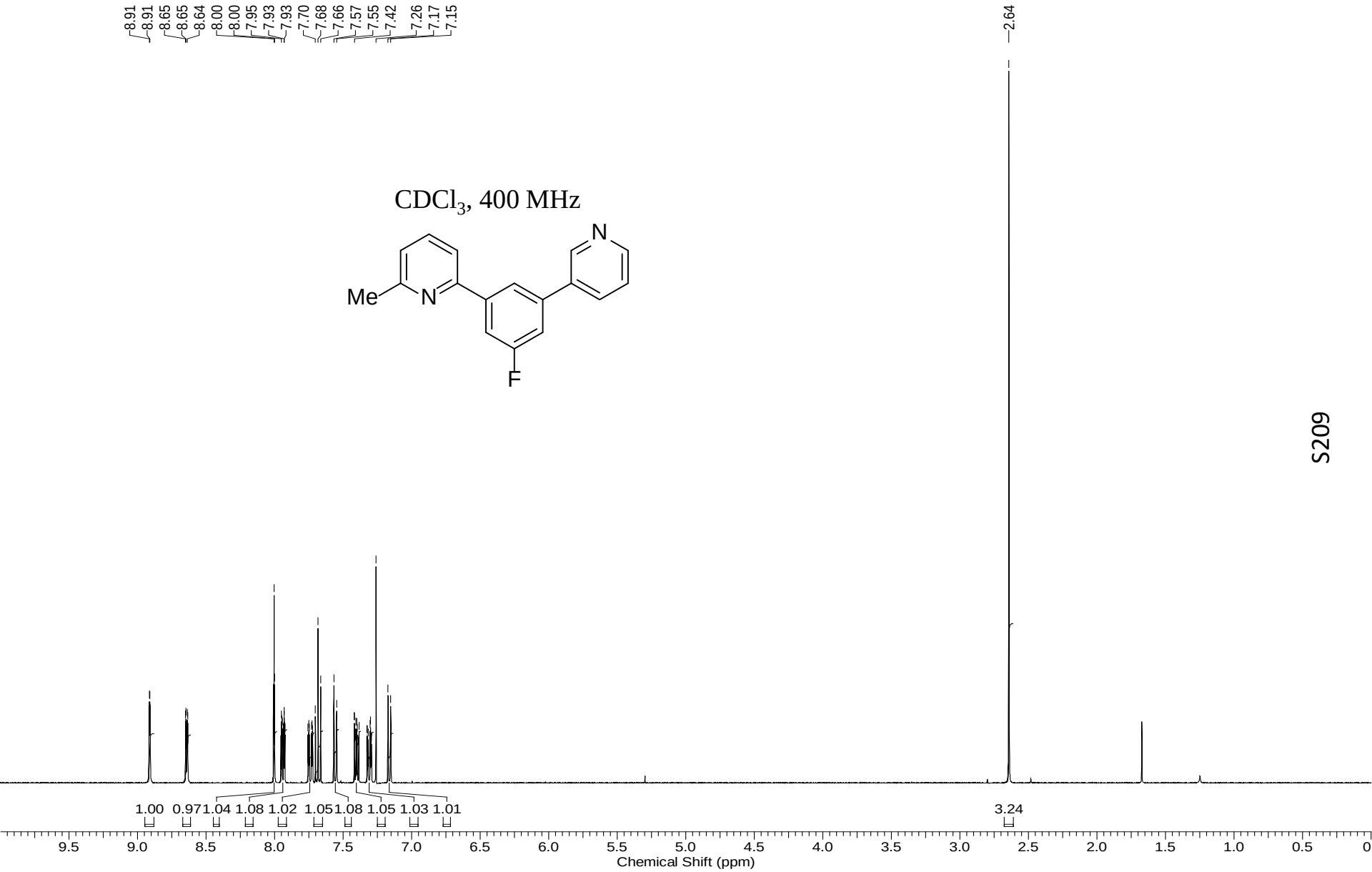

161.09
158.57
155.02
147.55
147.48
142.22
137.98
126.90
126.83
124.04
123.80
123.69
123.66
121.34
120.96
116.94
116.63
116.43
77.32
77.20
77.00
76.68
71.92
62.52
58.94
54.81
28.51
23.24
CDCl3, 100 MHz
O
N
N
F
CF3
S204
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 ppm

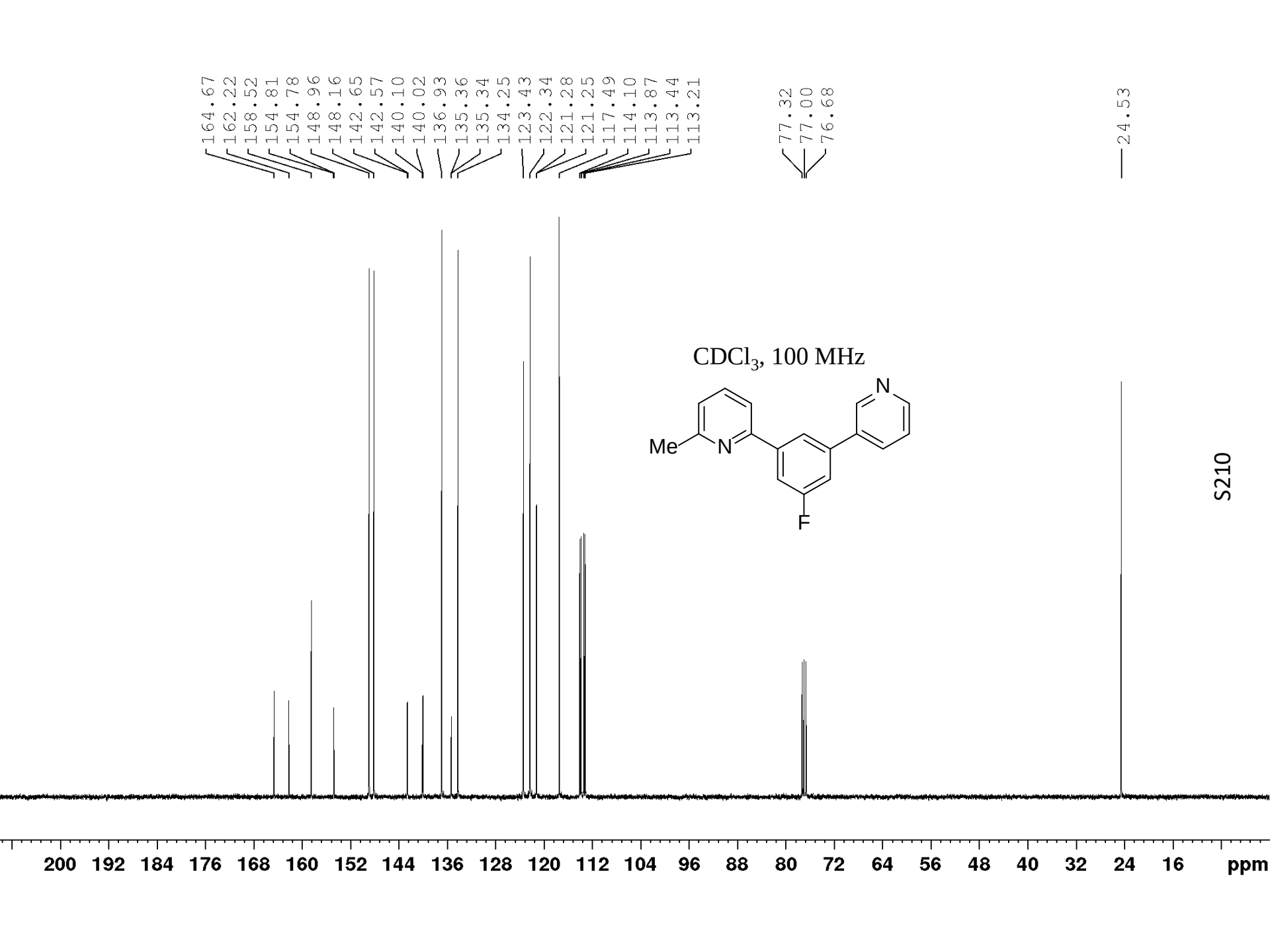

-61.13
-61.17
-114.97
-114.99
-115.01
-115.03
-115.04
-115.06
-115.07
-115.09
-115.11
-115.13
CDCl3, 365 MHz
O
N
N
F
CF3
S205
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
ppm


7.79
7.68
7.66
7.64
7.49
7.47
7.26
7.16
7.14
7.12
7.10
2.62
CDCl3, 400 MHz
Me
N
Cl
F
1.00
2.11
1.09
2.05
3.32
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

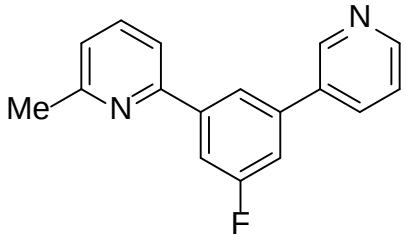

164.06
161.59
158.49
153.67
142.78
142.70
136.87
135.16
135.05
122.66
122.54
117.25
116.06
115.81
112.23
112.00
77.32
77.00
76.68
24.43
CDCl3, 100 MHz
Me
N
Cl
F
S207
200
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)


-110.79
-110.81
CDCl3, 365 MHz
Me
N
Cl
F
8
0
-8
-16
-24
-32
-40
-48
-56
-64
-72
-80
-88
-96
-104
-112
-120
-128
-136
-144
-152
-160
-168
-176
-184
-192
Chemical Shift (ppm)


8.91
8.91
8.65
8.65
8.64
8.00
8.00
7.95
7.93
7.93
7.70
7.68
7.66
7.57
7.55
7.42
7.26
7.17
7.15
2.64
CDCl3, 400 MHz
N
Me
N
F
S209
1.00 0.97 1.04 1.08 1.02 1.05 1.08 1.05 1.03 1.01
3.24
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
Chemical Shift (ppm)


164.67
162.22
158.52
154.81
154.78
148.96
148.16
142.65
142.57
140.10
140.02
136.93
135.36
135.34
134.25
123.43
122.34
121.28
121.25
117.49
114.10
113.87
113.44
113.21
77.32
77.00
76.68
24.53
CDCl3, 100 MHz
Me
N
N
F
S210
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

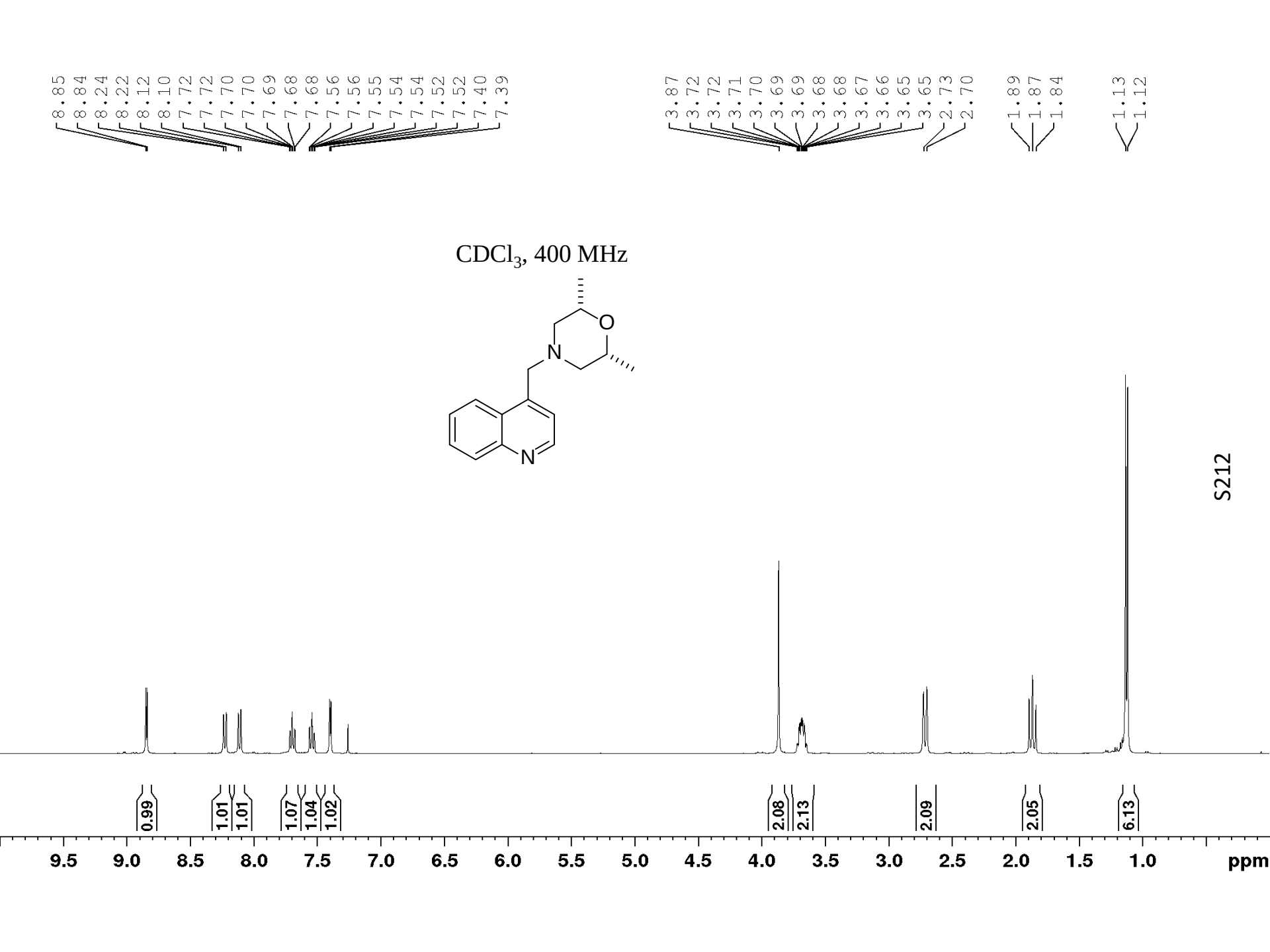
$CDCl_3$, 365 MHz

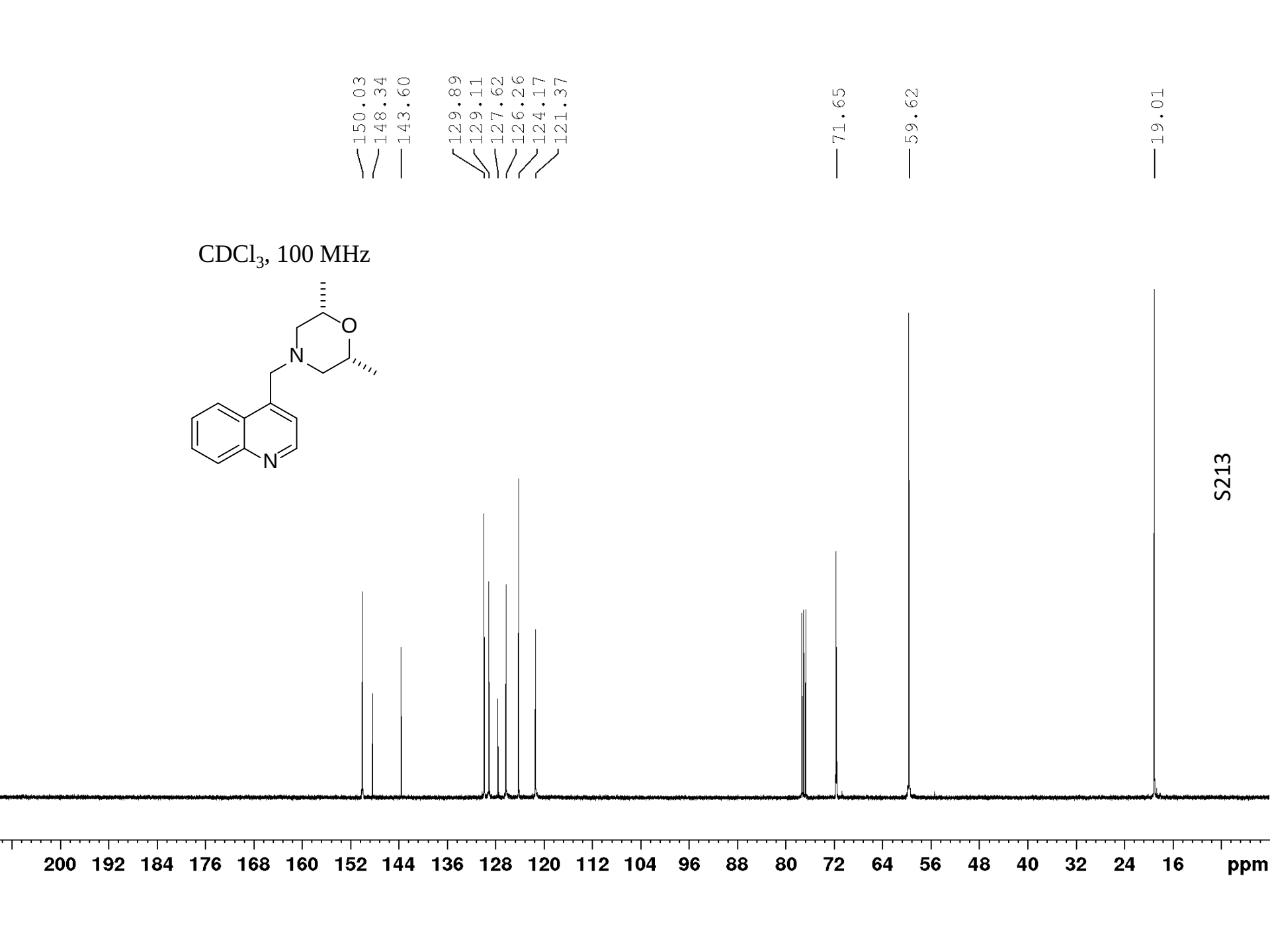


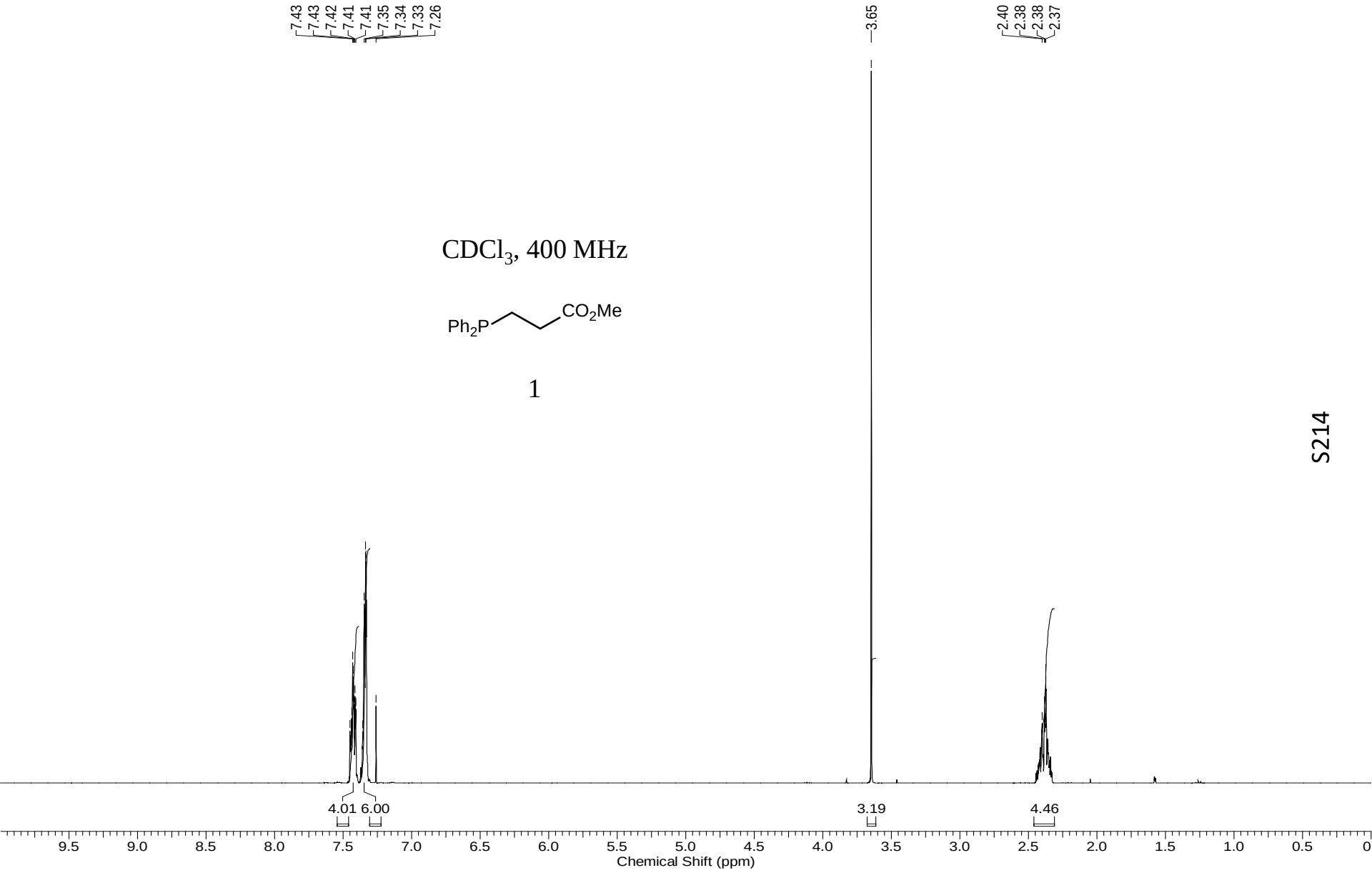
-112.31
-112.34

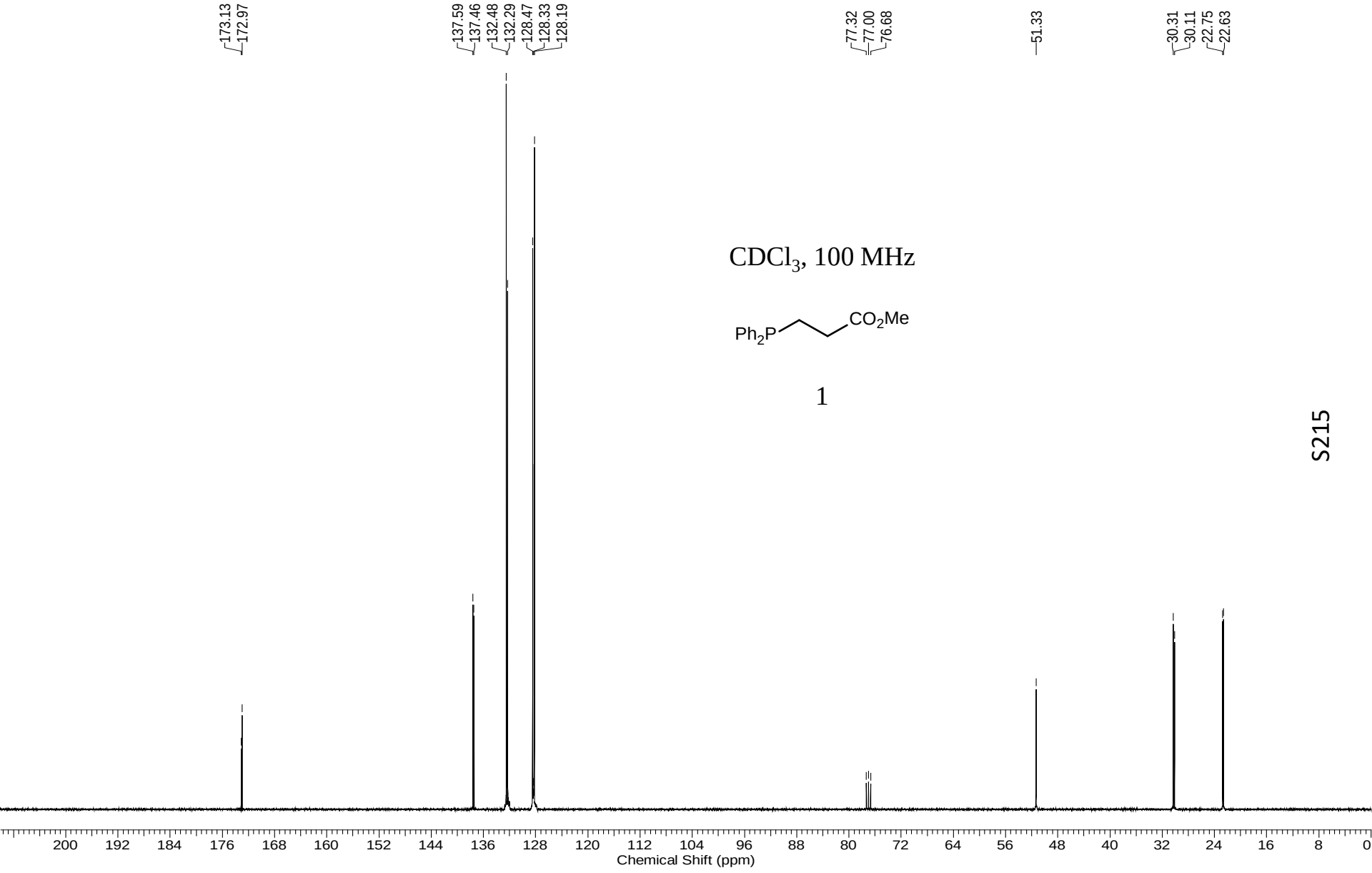
8 0 -8 -16 -24 -32 -40 -48 -56 -64 -72 -80 -88 -96 -104 -112 -120 -128 -136 -144 -152 -160 -168 -176 -184 -192

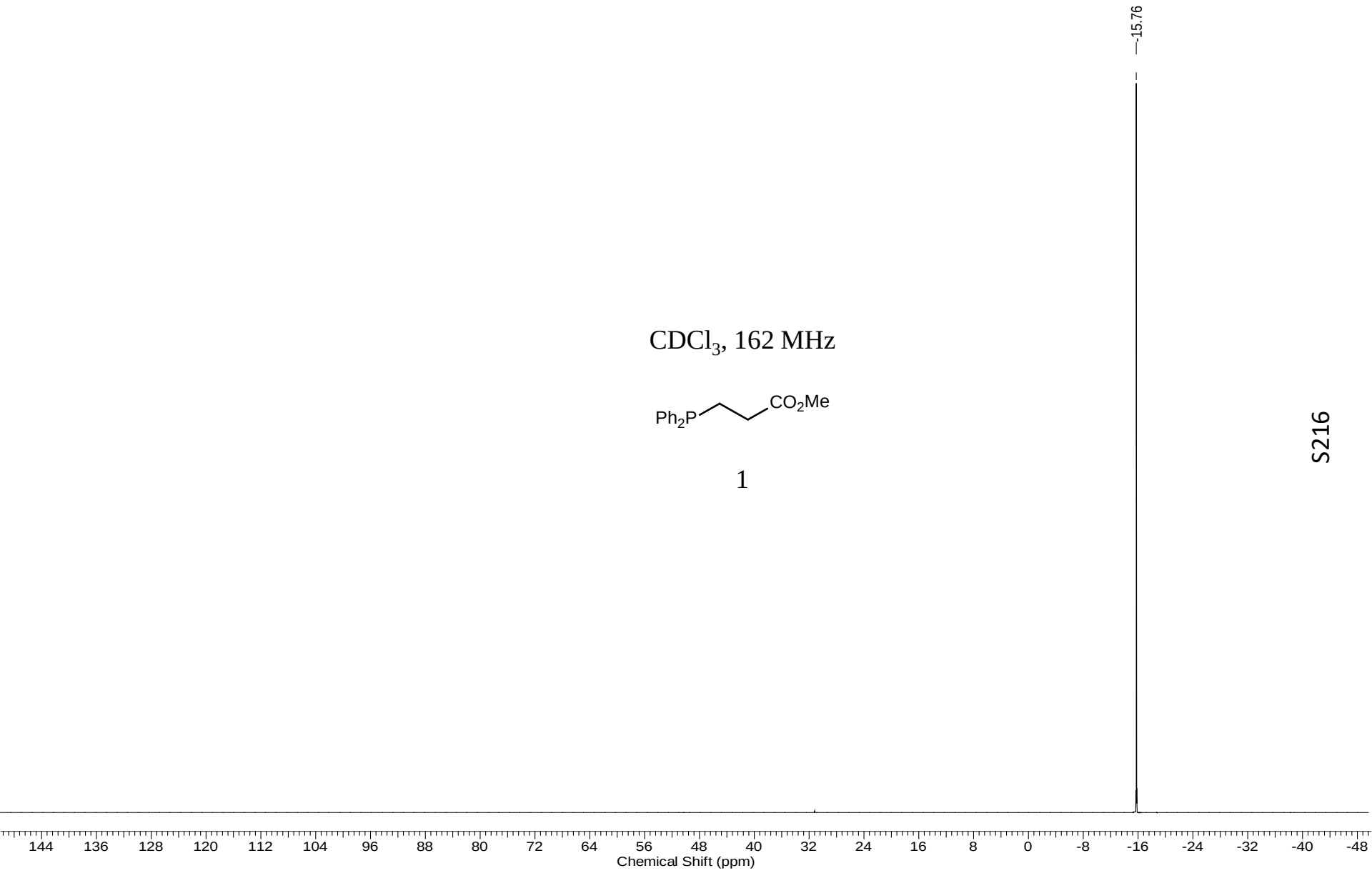
Chemical Shift (ppm)

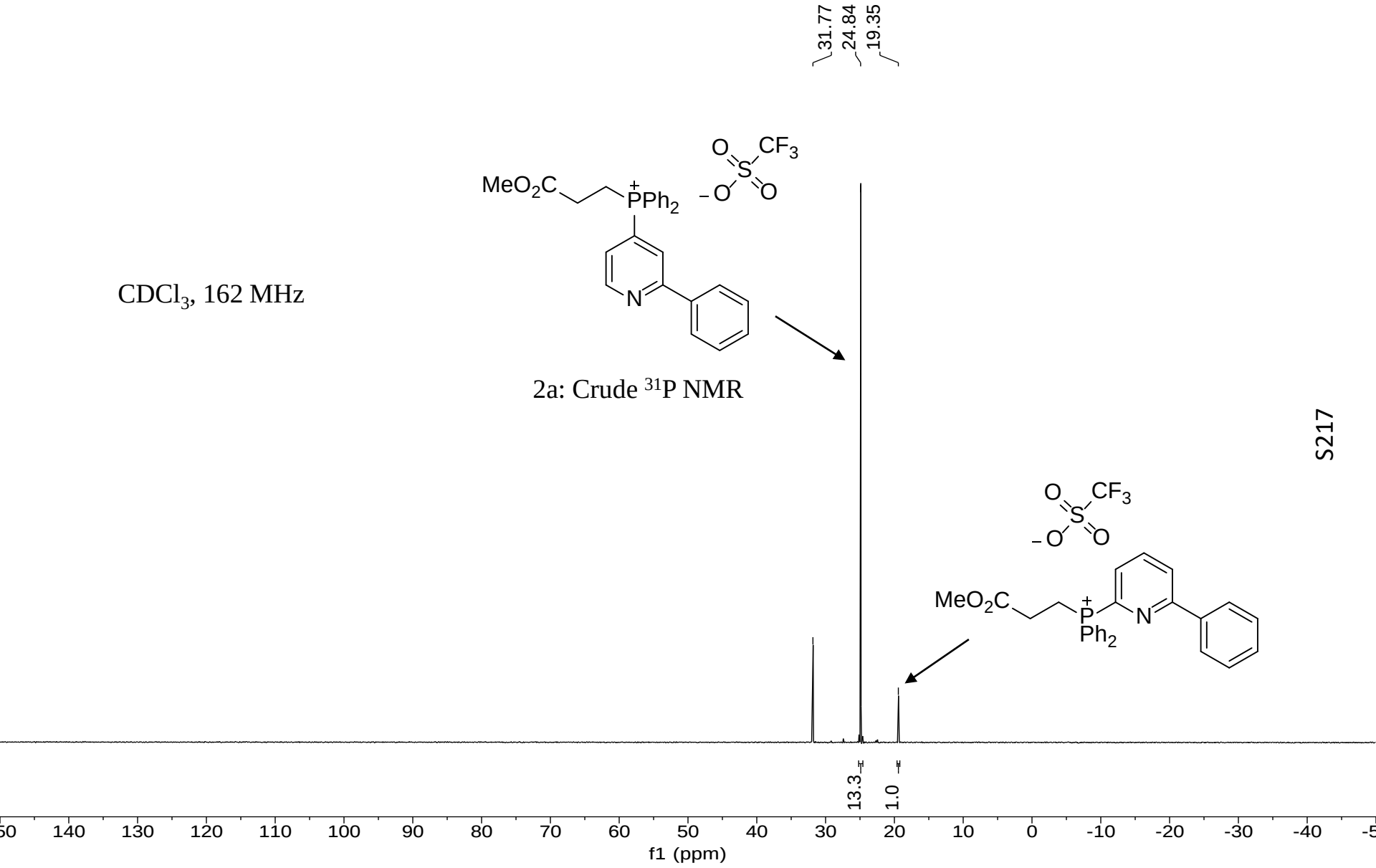

8.85
8.84
8.24
8.22
8.12
8.10
7.72
7.72
7.70
7.70
7.69
7.68
7.68
7.56
7.56
7.55
7.54
7.54
7.52
7.52
7.40
7.39
3.87
3.72
3.72
3.71
3.70
3.69
3.69
3.68
3.68
3.67
3.66
3.65
3.65
2.73
2.70
1.89
1.87
1.84
1.13
1.12
CDCl3, 400 MHz
O
N
N
S212
0.99
1.01
1.01
1.07
1.04
1.02
2.08
2.13
2.09
2.05
6.13
9.5
9.0
8.5
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


150.03
148.34
143.60
129.89
129.11
127.62
126.26
124.17
121.37
71.65
59.62
19.01
CDCl3, 100 MHz
O
N
N
S213
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

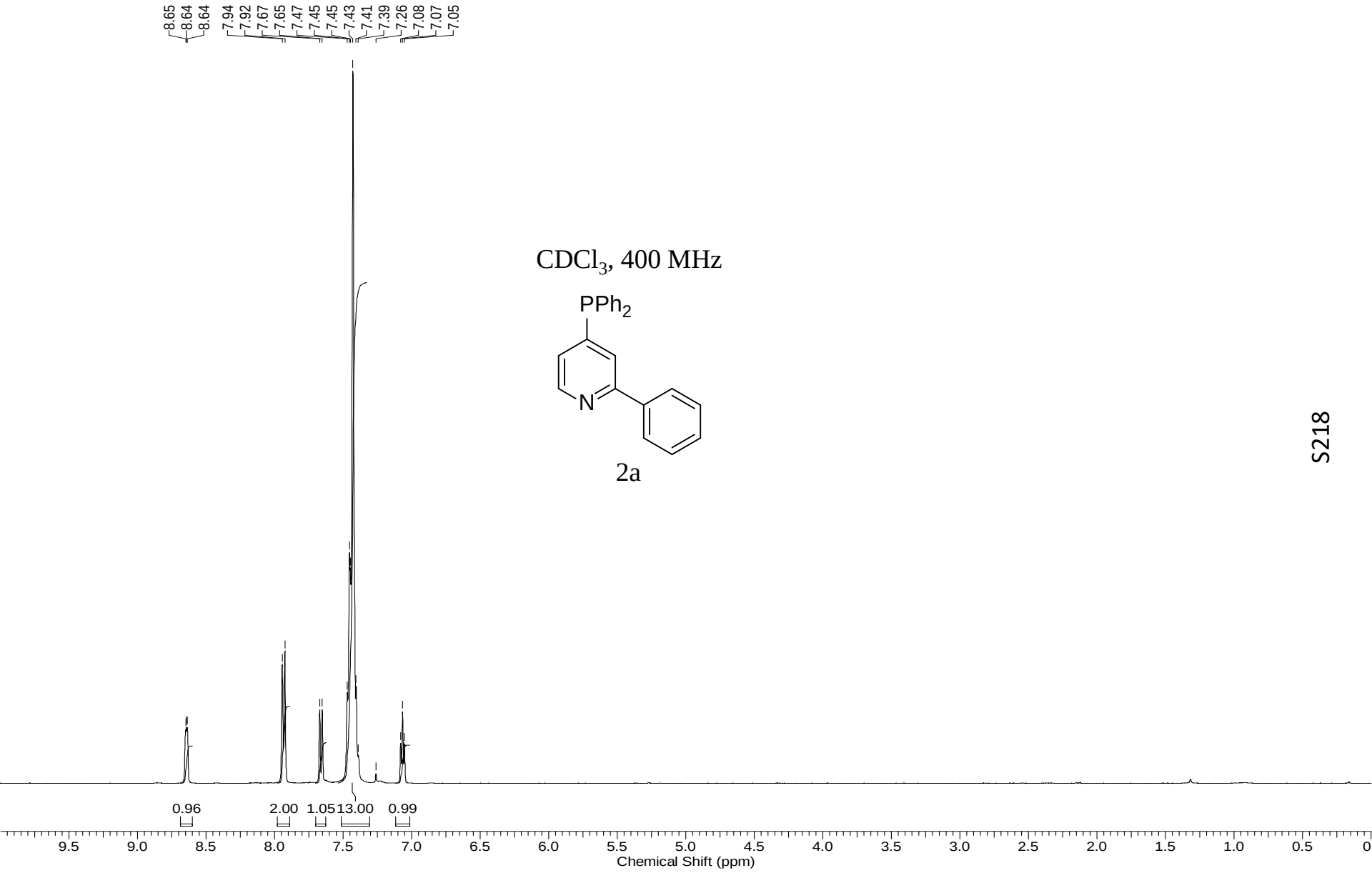

7.43
7.43
7.42
7.41
7.41
7.35
7.34
7.33
7.26
3.65
2.40
2.38
2.38
2.37
CDCl3, 400 MHz
Ph2P
CO2Me
1
S214
4.01
6.00
3.19
4.46
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

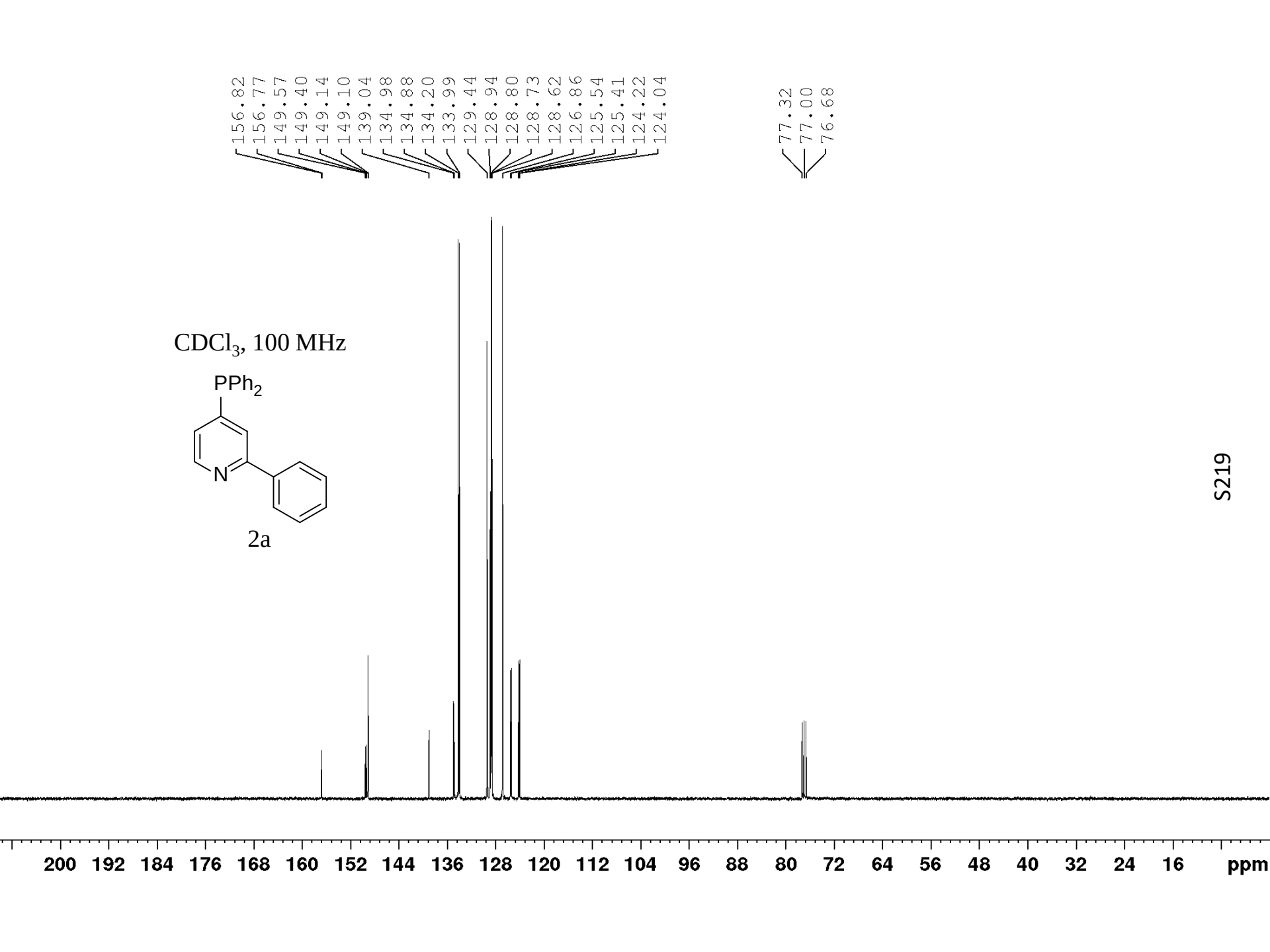

173.13
172.97
137.59
137.46
132.48
132.29
128.47
128.33
128.19
77.32
77.00
76.68
51.33
30.31
30.11
22.75
22.63
CDCl3, 100 MHz
Ph2P
CO2Me
1
S215
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 0
Chemical Shift (ppm)

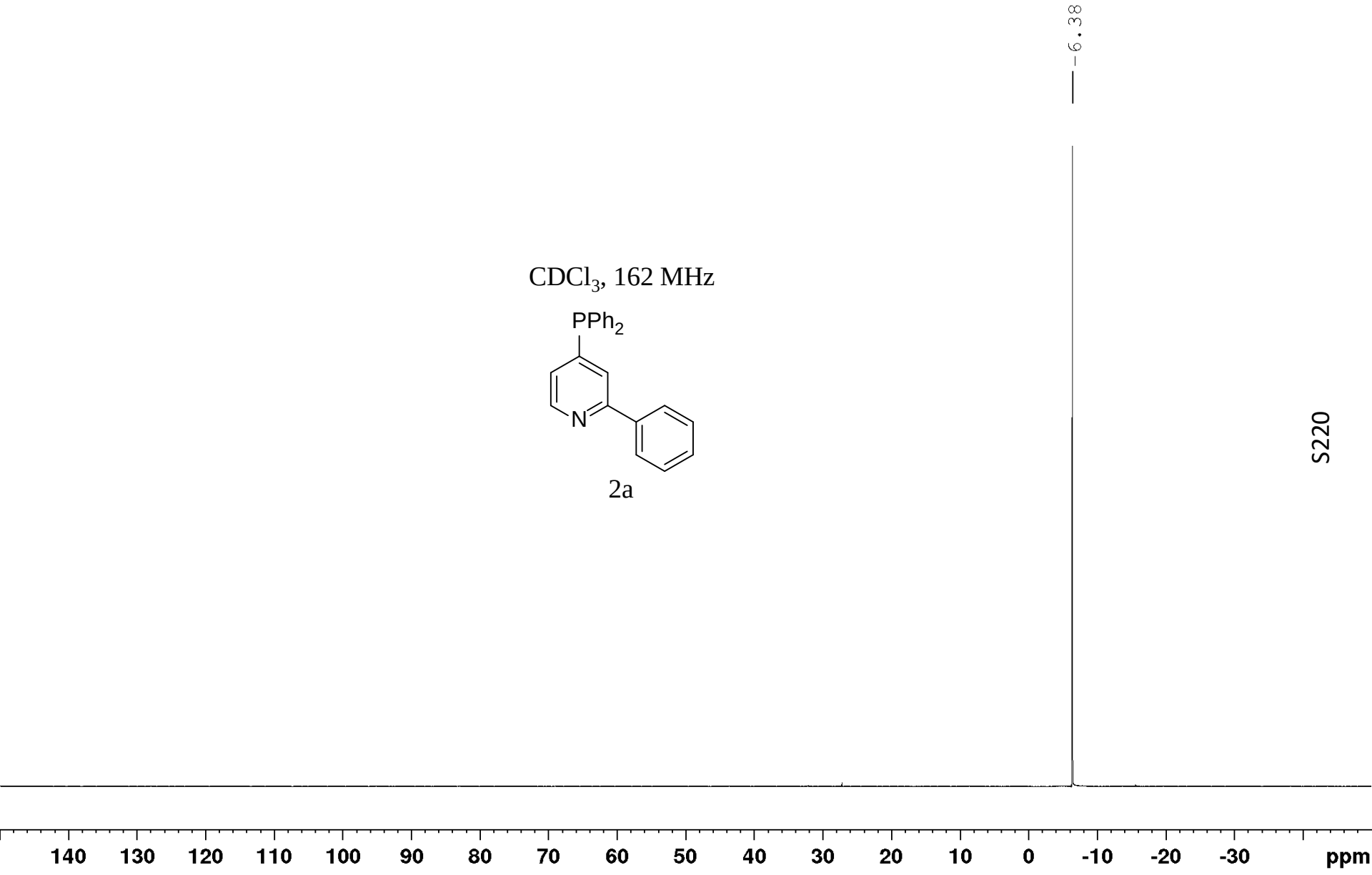

-15.76
CDCl3, 162 MHz
Ph2P
CO2Me
1
144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 0 -8 -16 -24 -32 -40 -48
Chemical Shift (ppm)

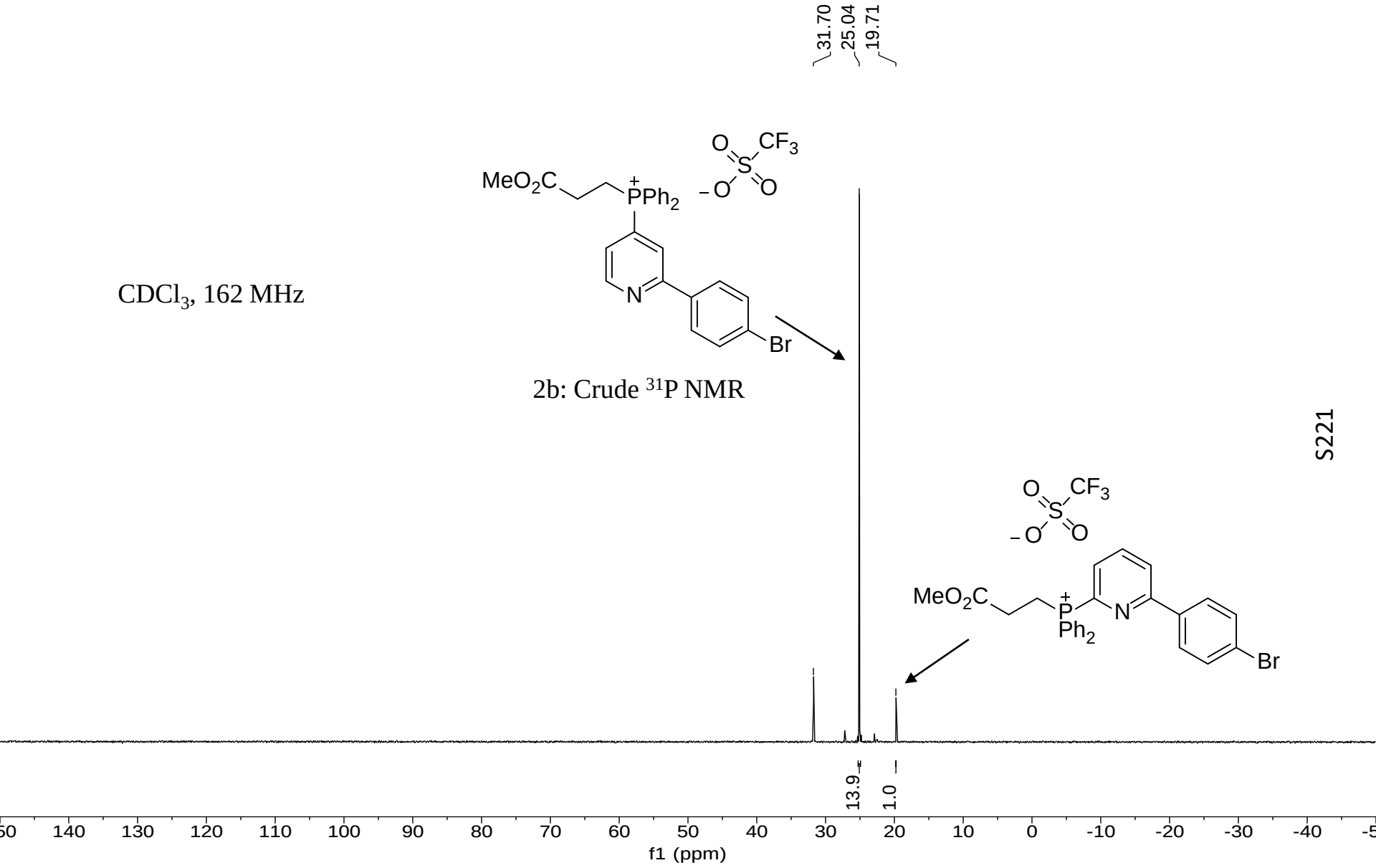


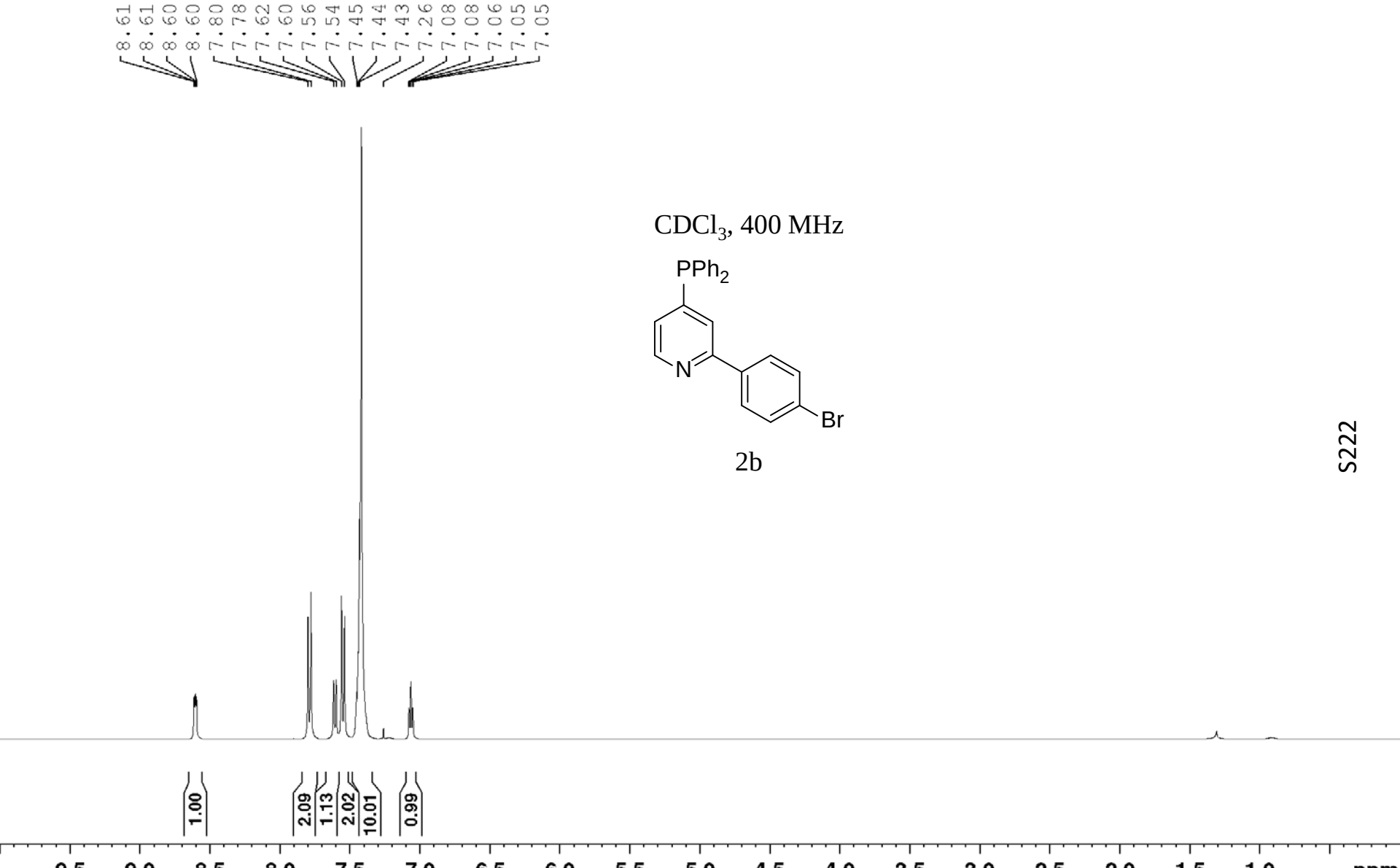
2a: Crude ^{31}P NMR

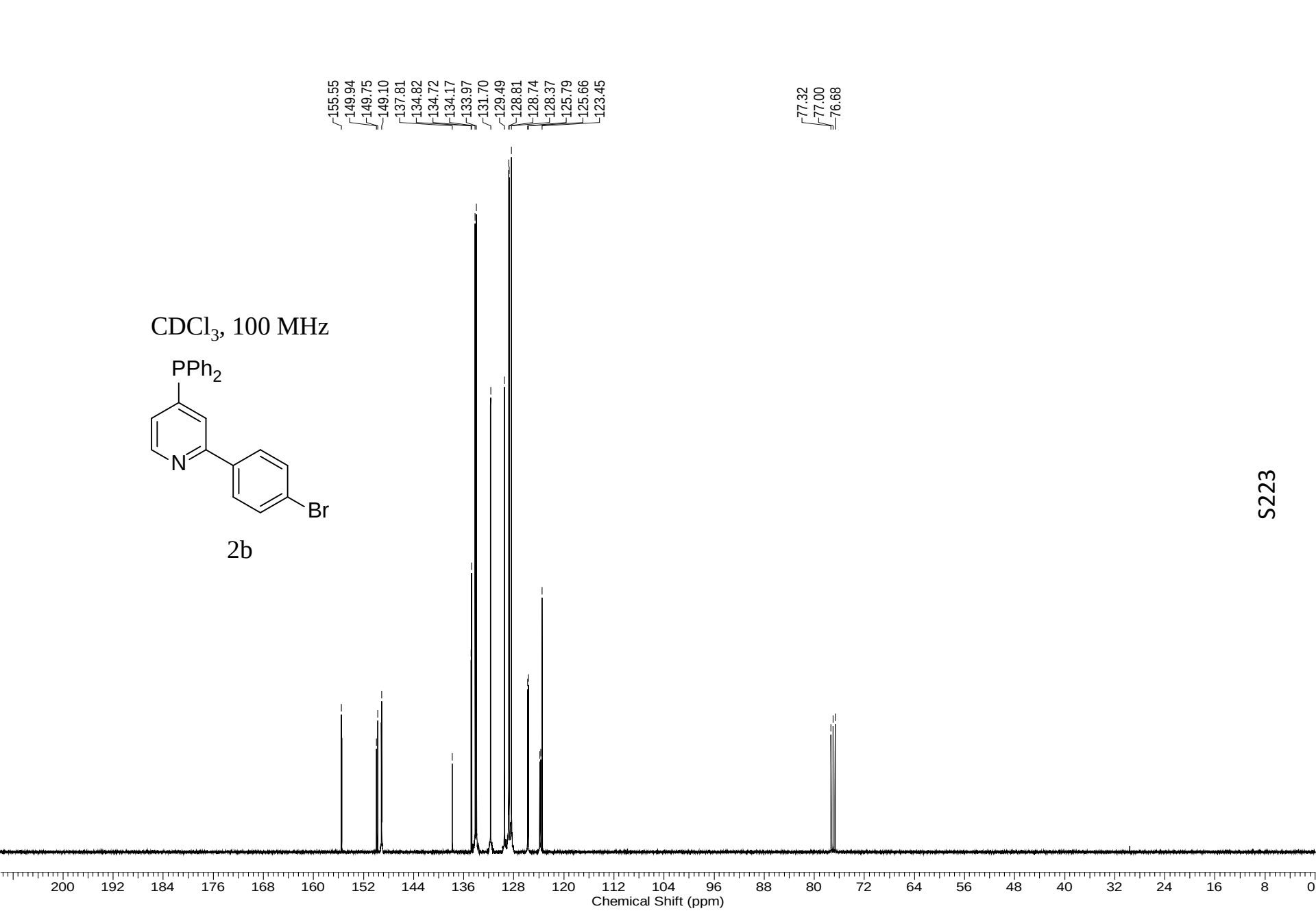

8.65
8.64
8.64
7.94
7.92
7.67
7.65
7.47
7.45
7.45
7.43
7.41
7.39
7.26
7.08
7.07
7.05
CDCl3, 400 MHz
PPh2
N
2a
0.96
2.00
1.05
13.00
0.99
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

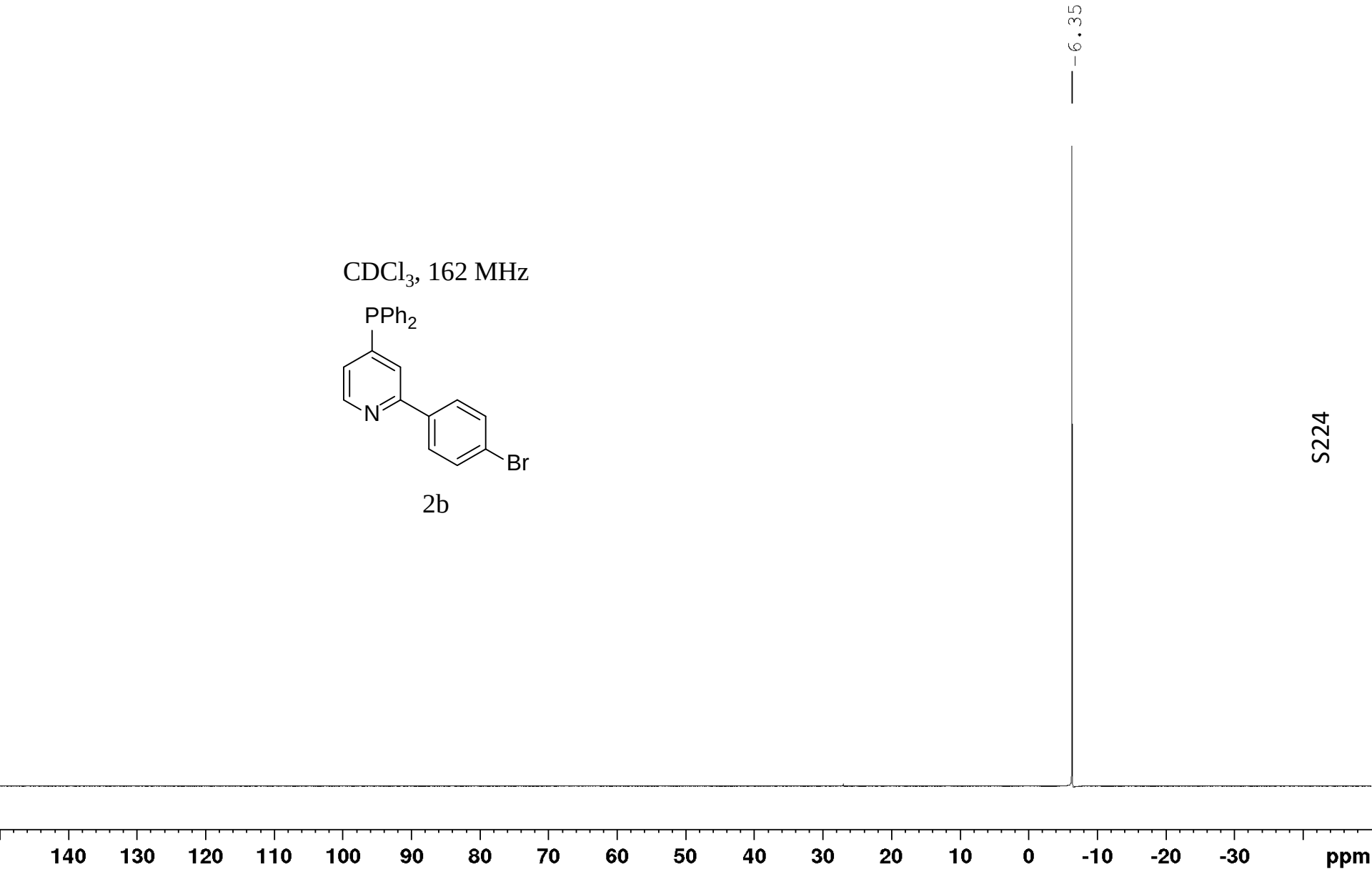

156.82
156.77
149.57
149.40
149.14
149.10
139.04
134.98
134.88
134.20
133.99
129.44
128.94
128.80
128.73
128.62
126.86
125.54
125.41
124.22
124.04
77.32
77.00
76.68
CDCl3, 100 MHz
PPh2
N
2a
S219
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 ppm

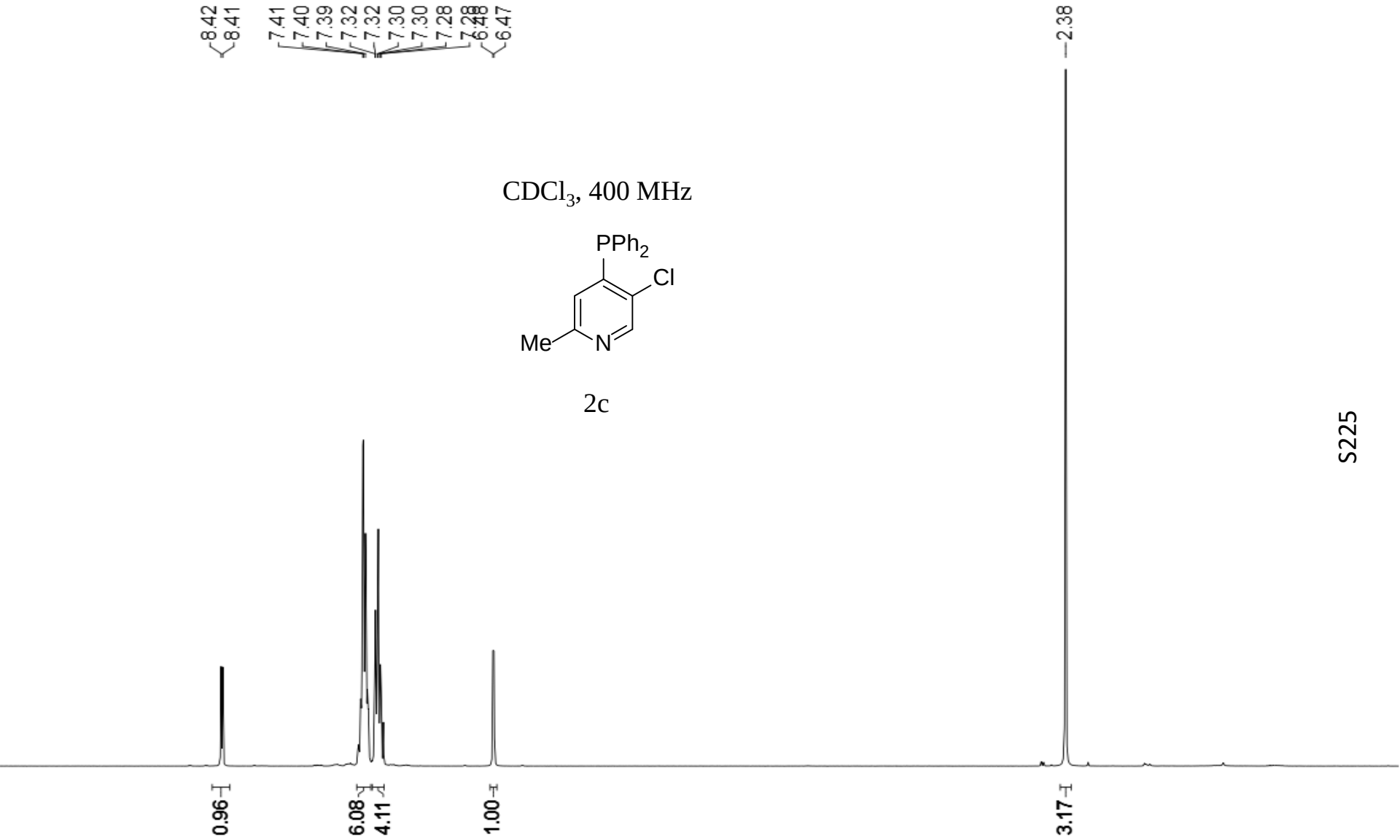

-6.38
CDCl3, 162 MHz
PPh2
N
2a
S220
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
ppm

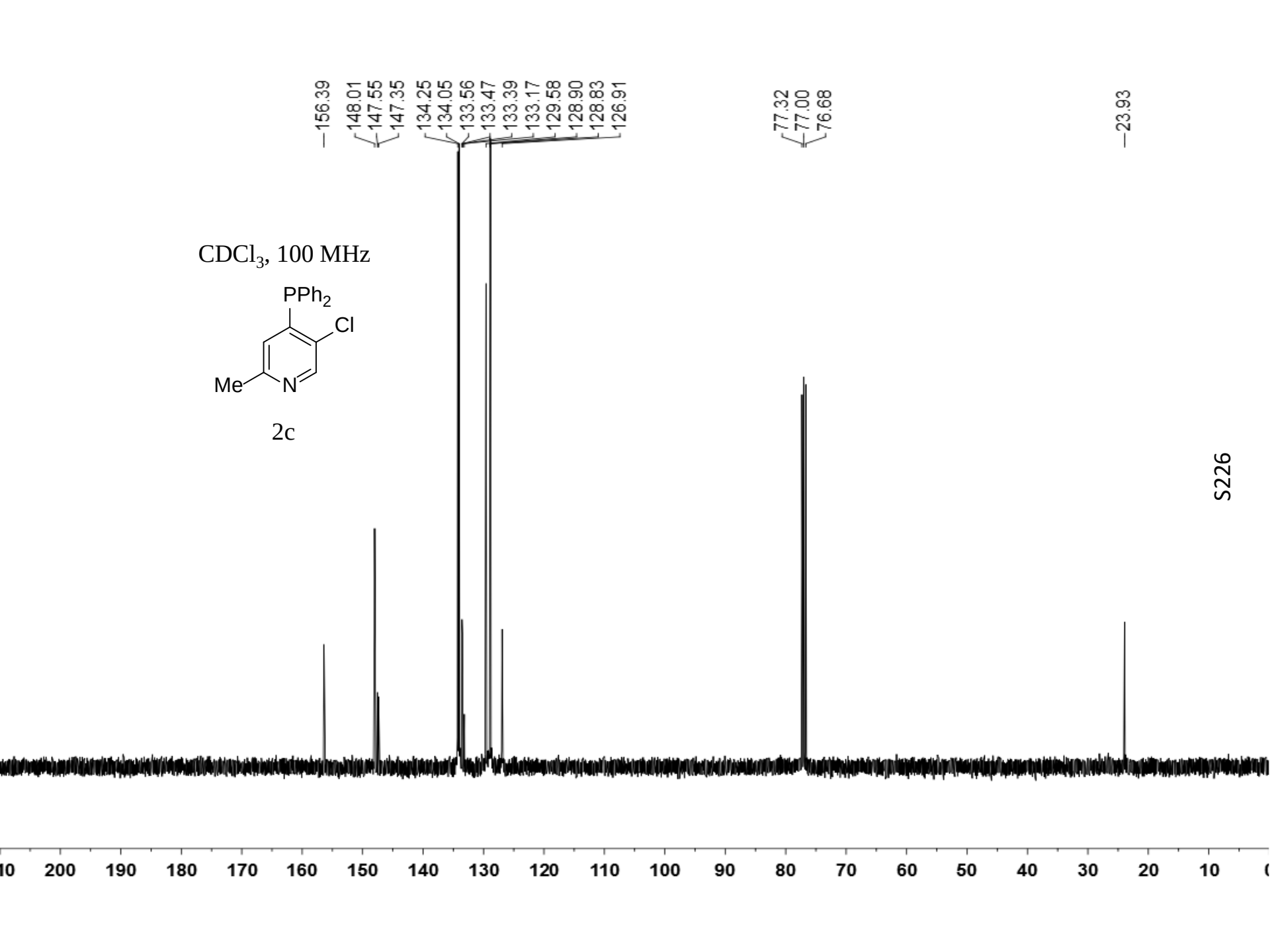

31.70
25.04
19.71
CDCl3, 162 MHz
MeO2C
PPh2
O
CF3
S
O
O
N
Br
2b: Crude 31P NMR
S221
MeO2C
P
Ph2
N
Br
13.9
1.0
f1 (ppm)

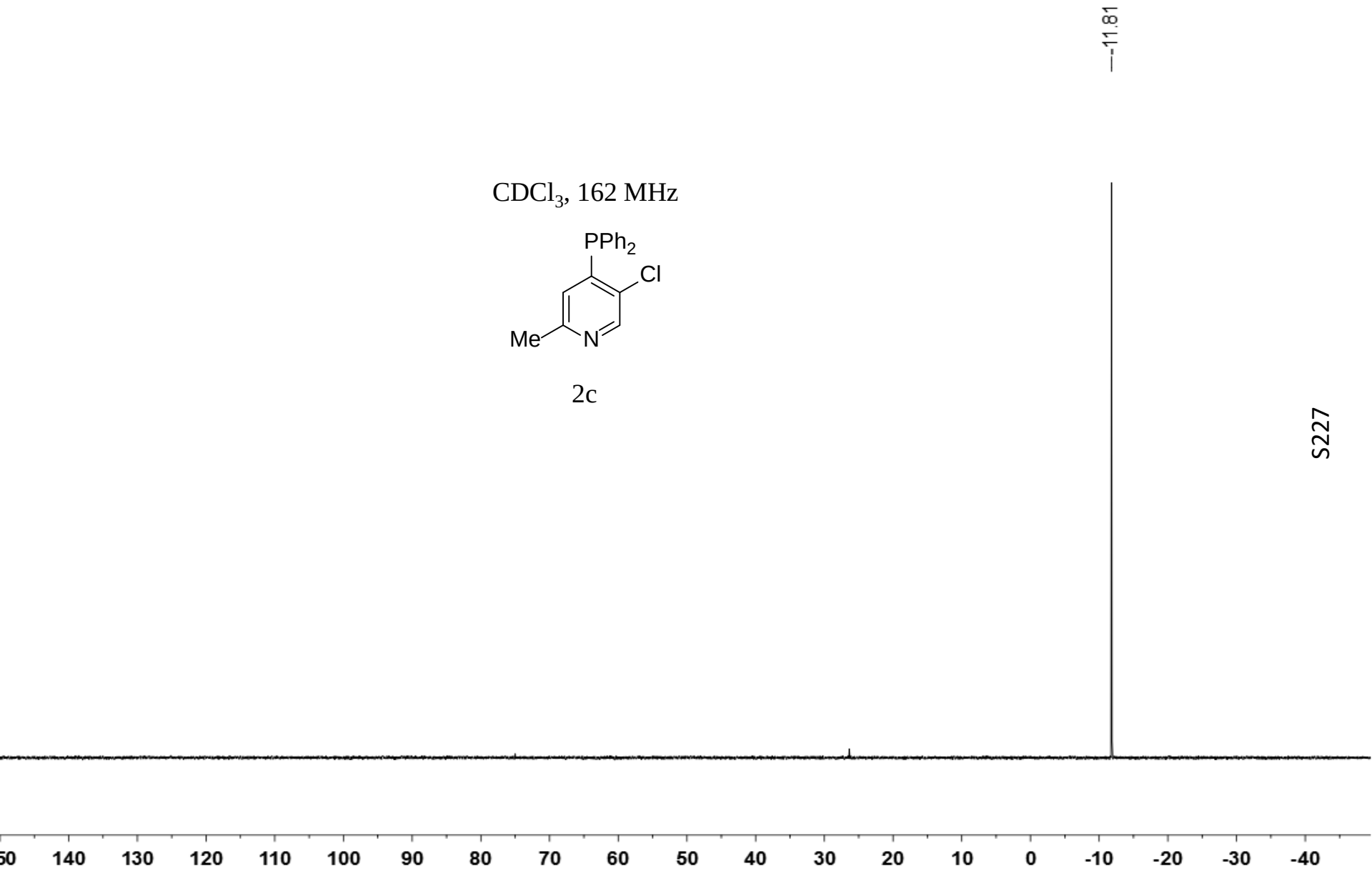

8.61
8.61
8.60
8.60
7.80
7.78
7.62
7.60
7.56
7.54
7.45
7.44
7.43
7.26
7.08
7.08
7.06
7.05
7.05
CDCl3, 400 MHz
PPh2
N
Br
2b
1.00
2.09
1.13
2.02
10.01
0.99
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

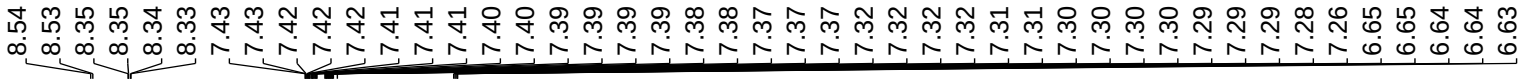

155.55
149.94
149.75
149.10
137.81
134.82
134.72
134.17
133.97
131.70
129.49
128.81
128.74
128.37
125.79
125.66
123.45
77.32
77.00
76.68
CDCl3, 100 MHz
PPh2
N
Br
2b
200
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)


-6.35
CDCl3, 162 MHz
PPh2
N
Br
2b
S224
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
ppm

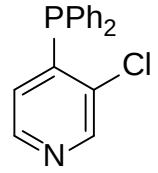

8.42
8.41
7.41
7.40
7.39
7.32
7.32
7.30
7.30
7.28
6.47
2.38
CDCl3, 400 MHz
PPh2
Cl
Me
N
2c
0.96
6.08
4.11
1.00
3.17
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5


156.39
148.01
147.55
147.35
134.25
134.05
133.56
133.47
133.39
133.17
129.58
128.90
128.83
126.91
77.32
77.00
76.68
23.93
CDCl3, 100 MHz
PPh2
Cl
Me
N
2c
S226
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

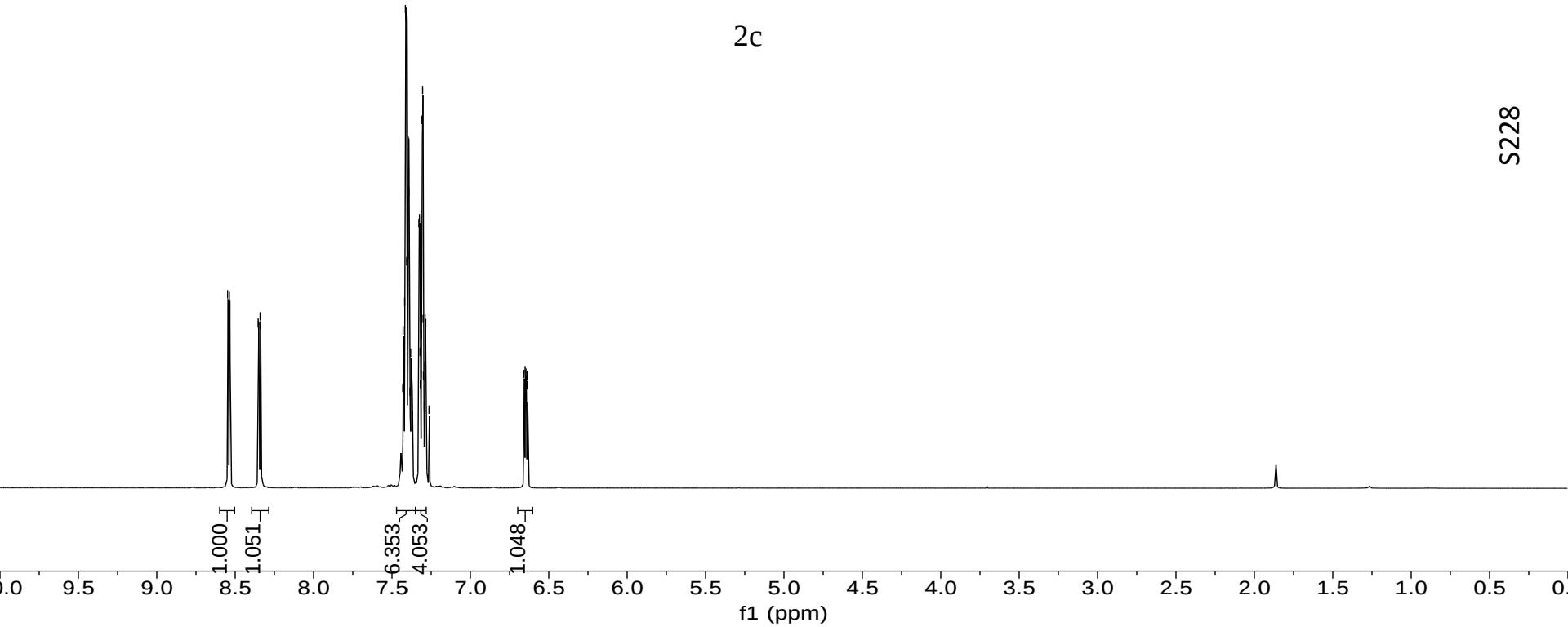

-11.81
CDCl3, 162 MHz
PPh2
Cl
Me
N
2c
S227
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40

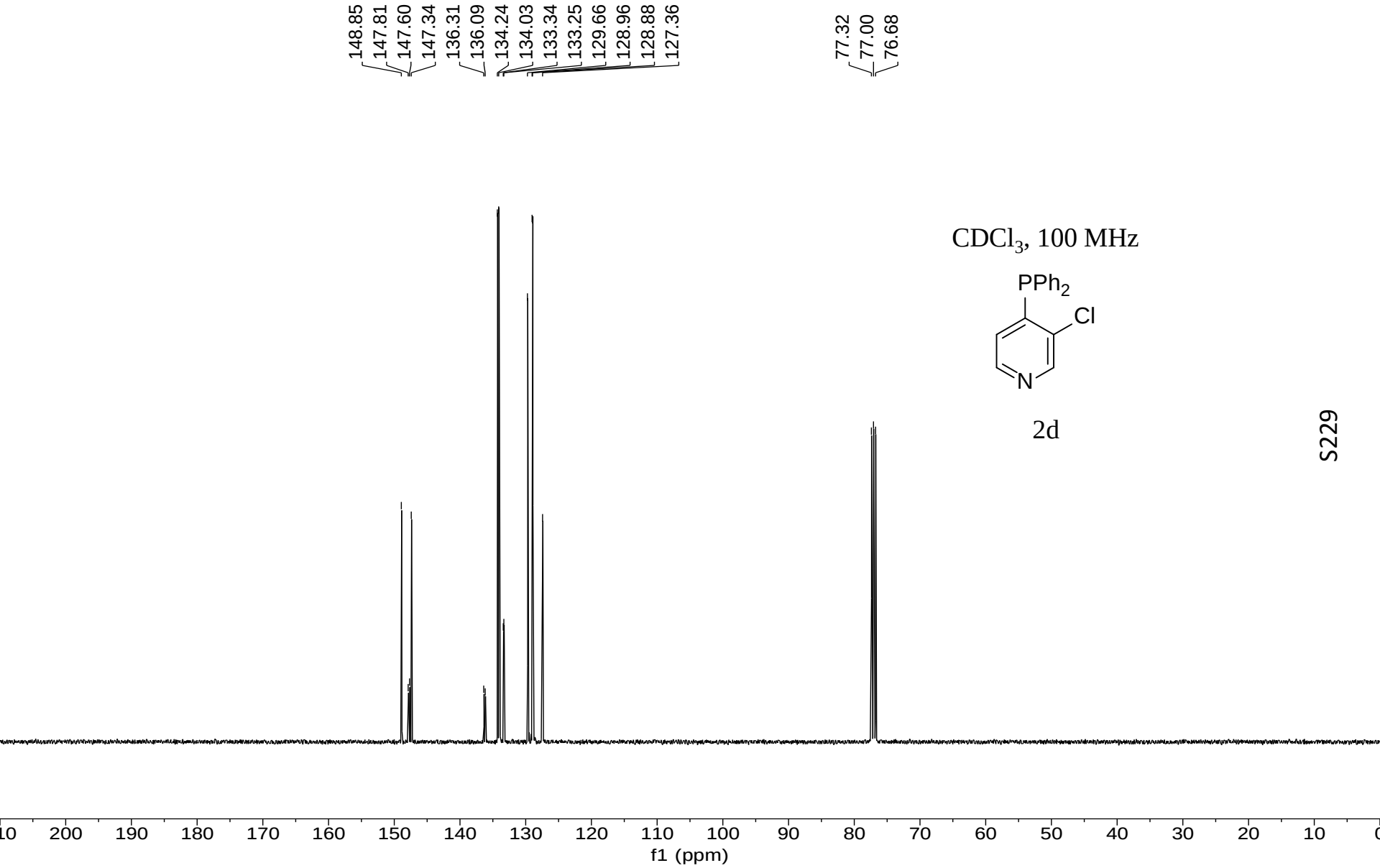


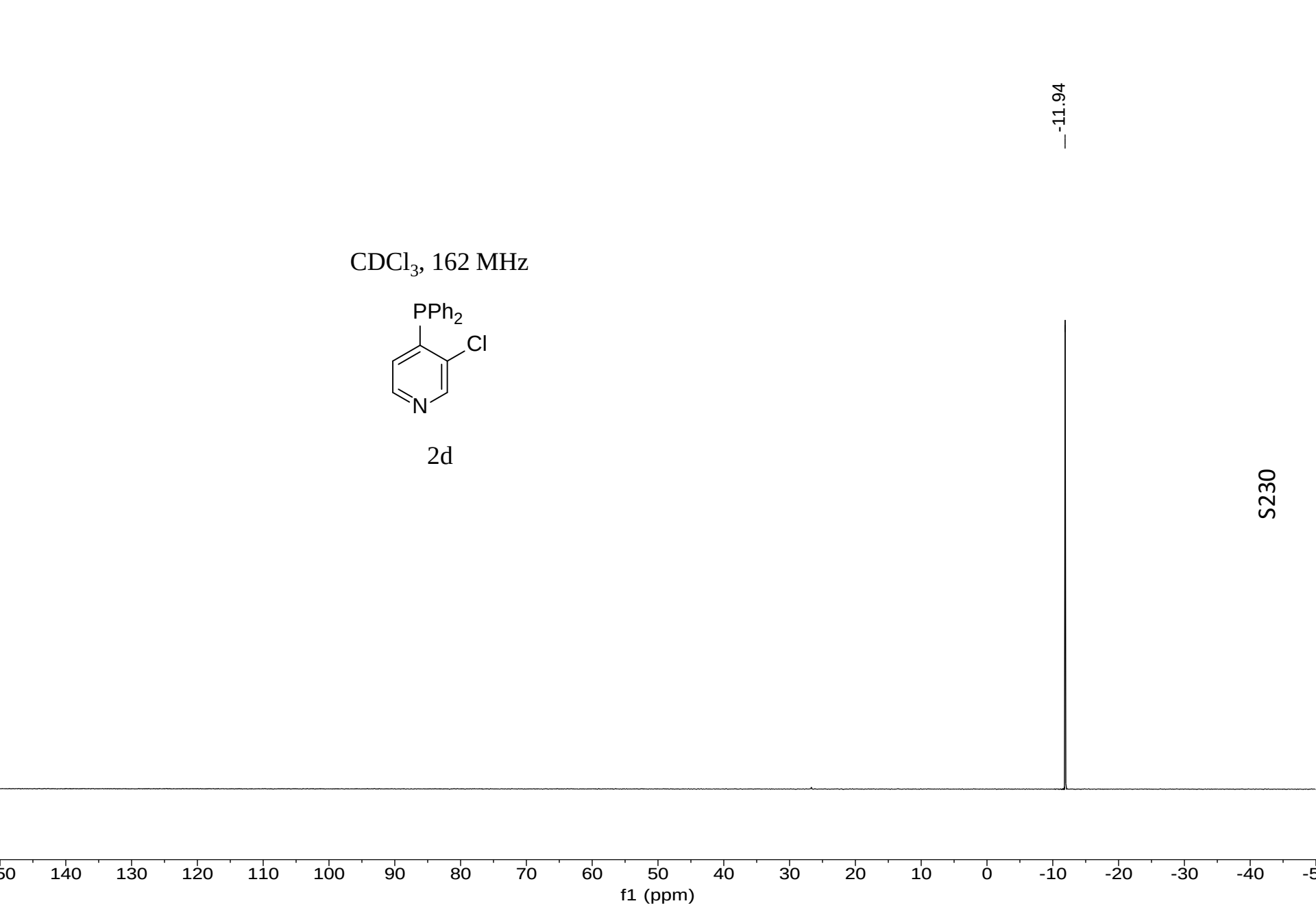
$CDCl_3$, 400 MHz

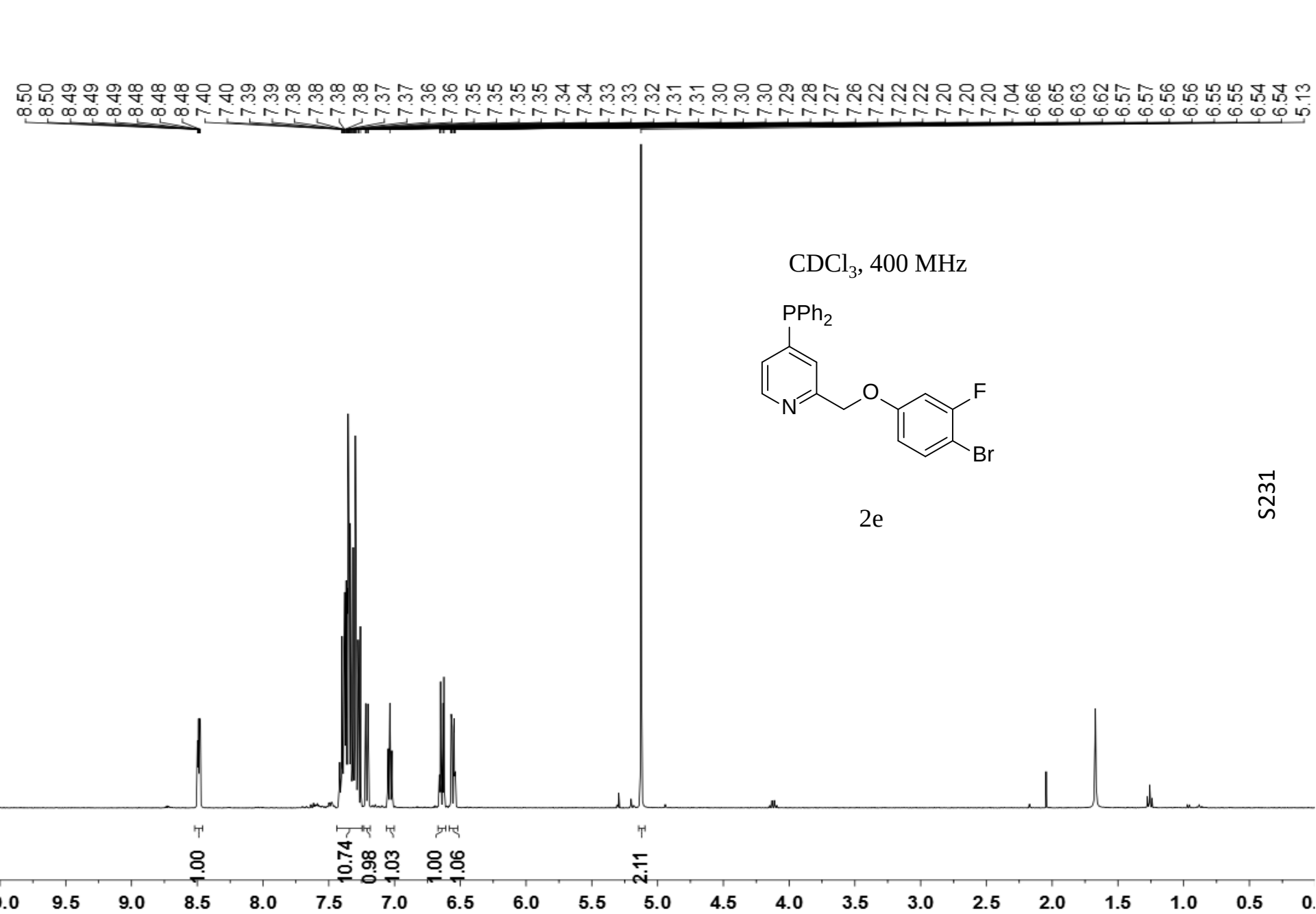


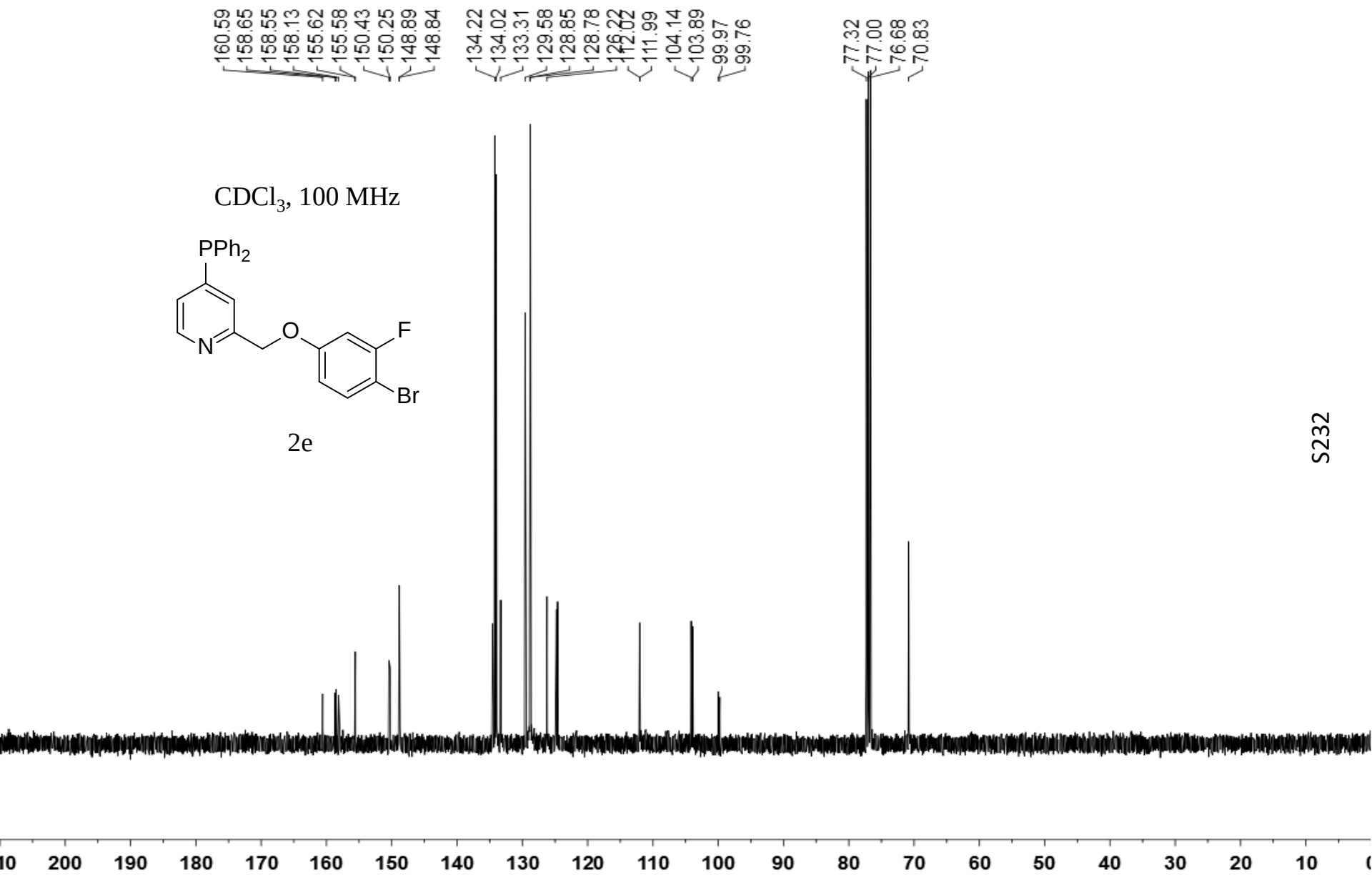
2c

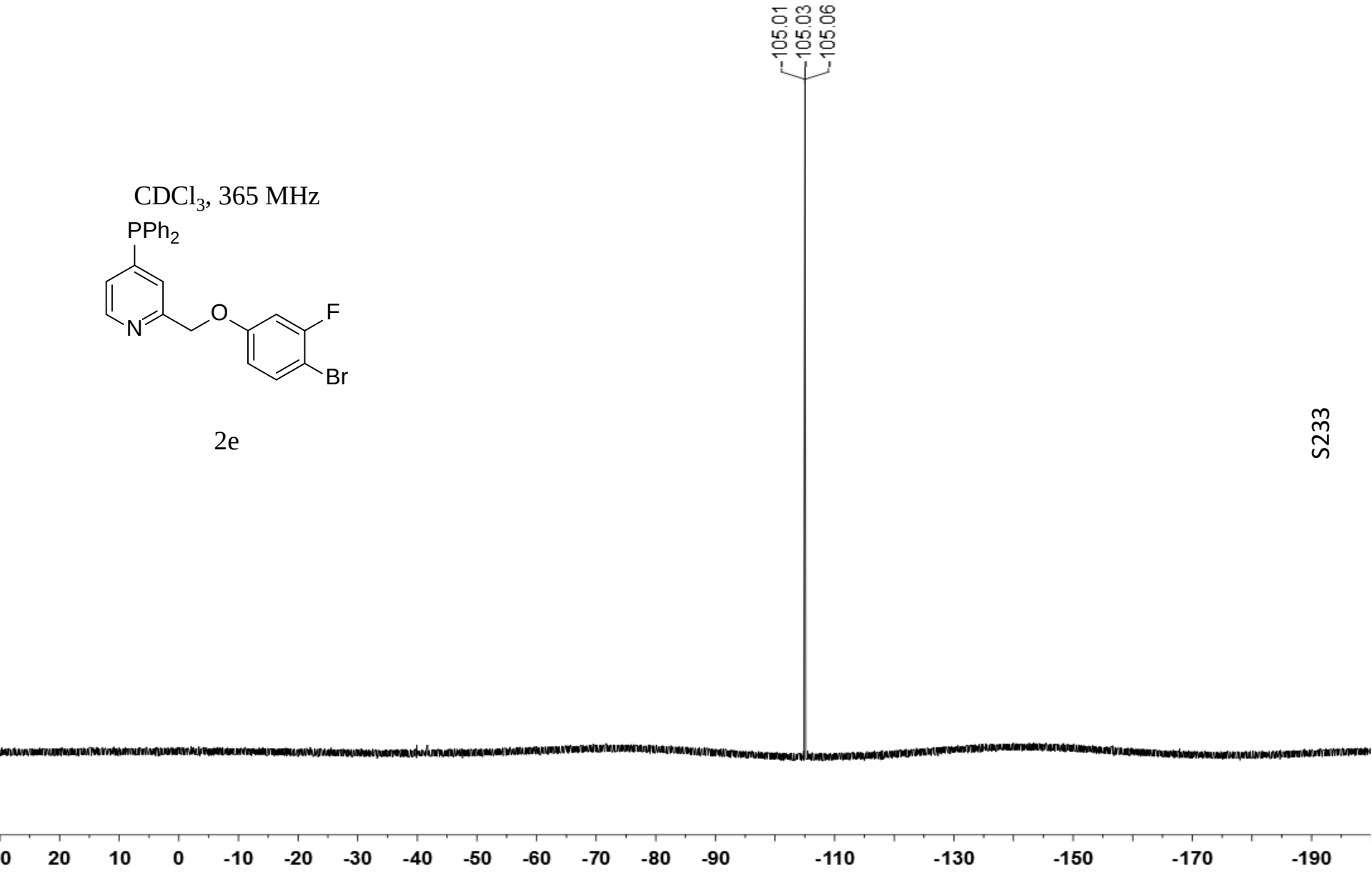


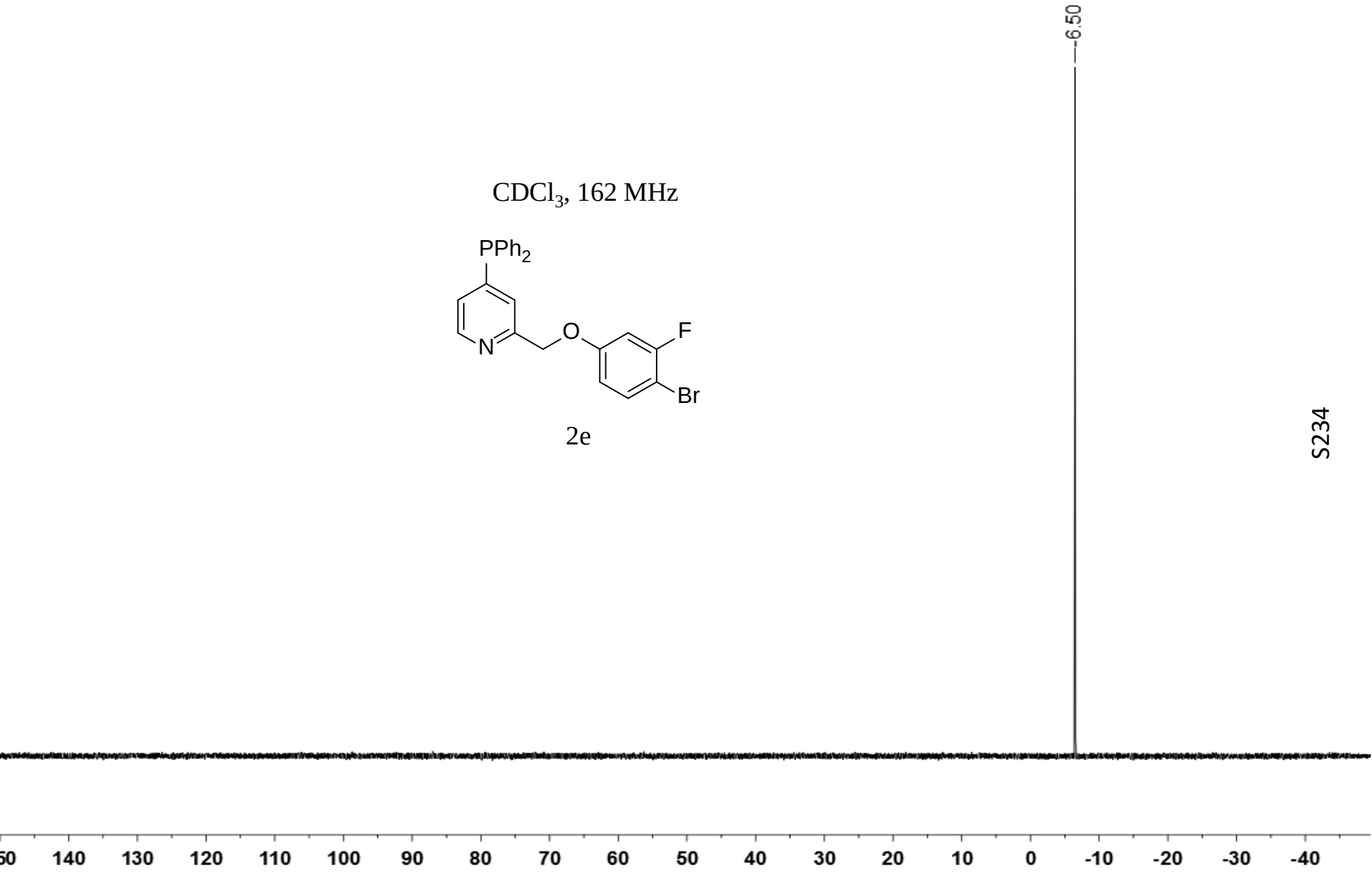

148.85
147.81
147.60
147.34
136.31
136.09
134.24
134.03
133.34
133.25
129.66
128.96
128.88
127.36
77.32
77.00
76.68
CDCl3, 100 MHz
PPh2
Cl
N
2d
f1 (ppm)

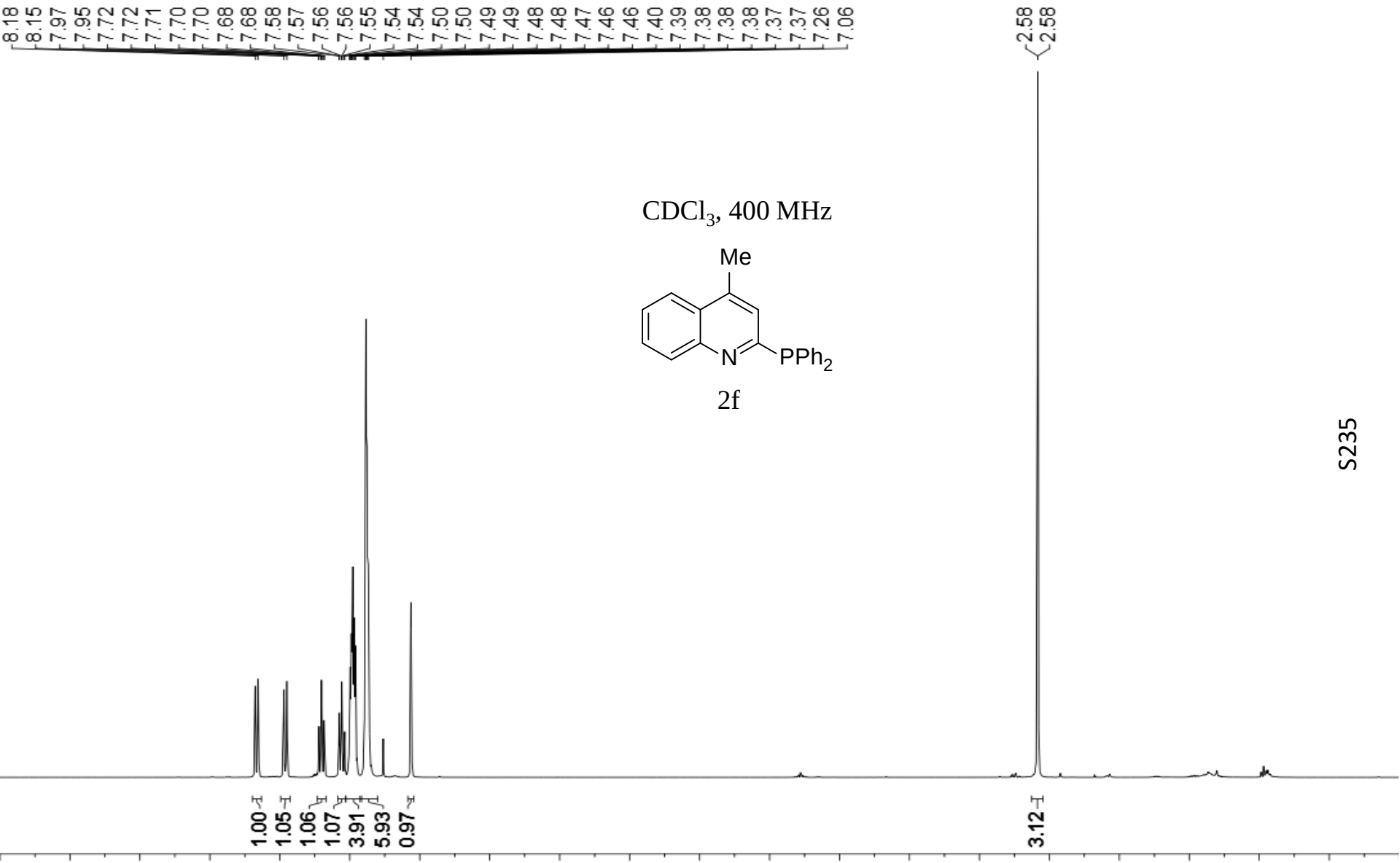

-11.94
CDCl3, 162 MHz
PPh2
Cl
N
2d
S230
f1 (ppm)

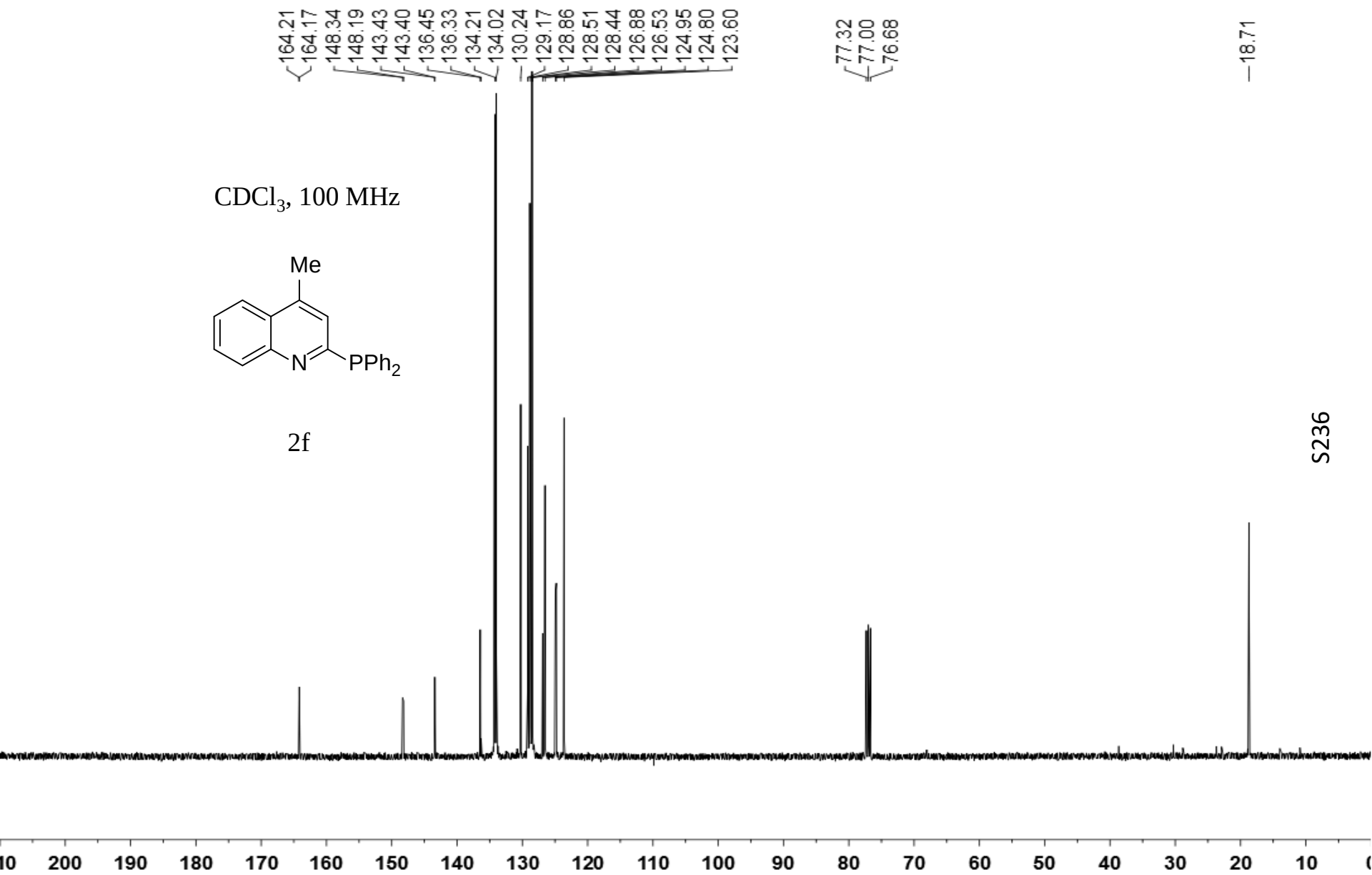

8.50 8.50 8.49 8.49 8.49 8.48 8.48 8.48 8.40 7.40 7.39 7.39 7.38 7.38 7.38 7.38 7.37 7.37 7.36 7.36 7.35 7.35 7.35 7.35 7.34 7.34 7.33 7.33 7.32 7.31 7.31 7.30 7.30 7.30 7.29 7.28 7.27 7.26 7.22 7.22 7.22 7.20 7.20 7.20 7.04 6.66 6.65 6.63 6.62 6.57 6.57 6.56 6.56 6.55 6.55 6.54 6.54 5.13
CDCl3, 400 MHz
PPh2
N
O
F
Br
2e
S231
1.00
10.74
0.98
1.03
1.00
1.06
2.11
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5


160.59
158.65
158.55
158.13
155.62
155.58
150.43
150.25
148.89
148.84
134.22
134.02
133.31
129.58
128.85
128.78
126.22
112.02
111.99
104.14
103.89
99.97
99.76
77.32
77.00
76.68
70.83
CDCl3, 100 MHz
PPh2
N
O
F
Br
2e
S232
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

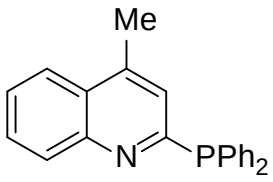

105.01
105.03
105.06
CDCl3, 365 MHz
PPh2
N
O
F
Br
2e
S233
0
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-110
-130
-150
-170
-190


-6.50
CDCl3, 162 MHz
PPh2
N
O
F
Br
2e
S234
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40

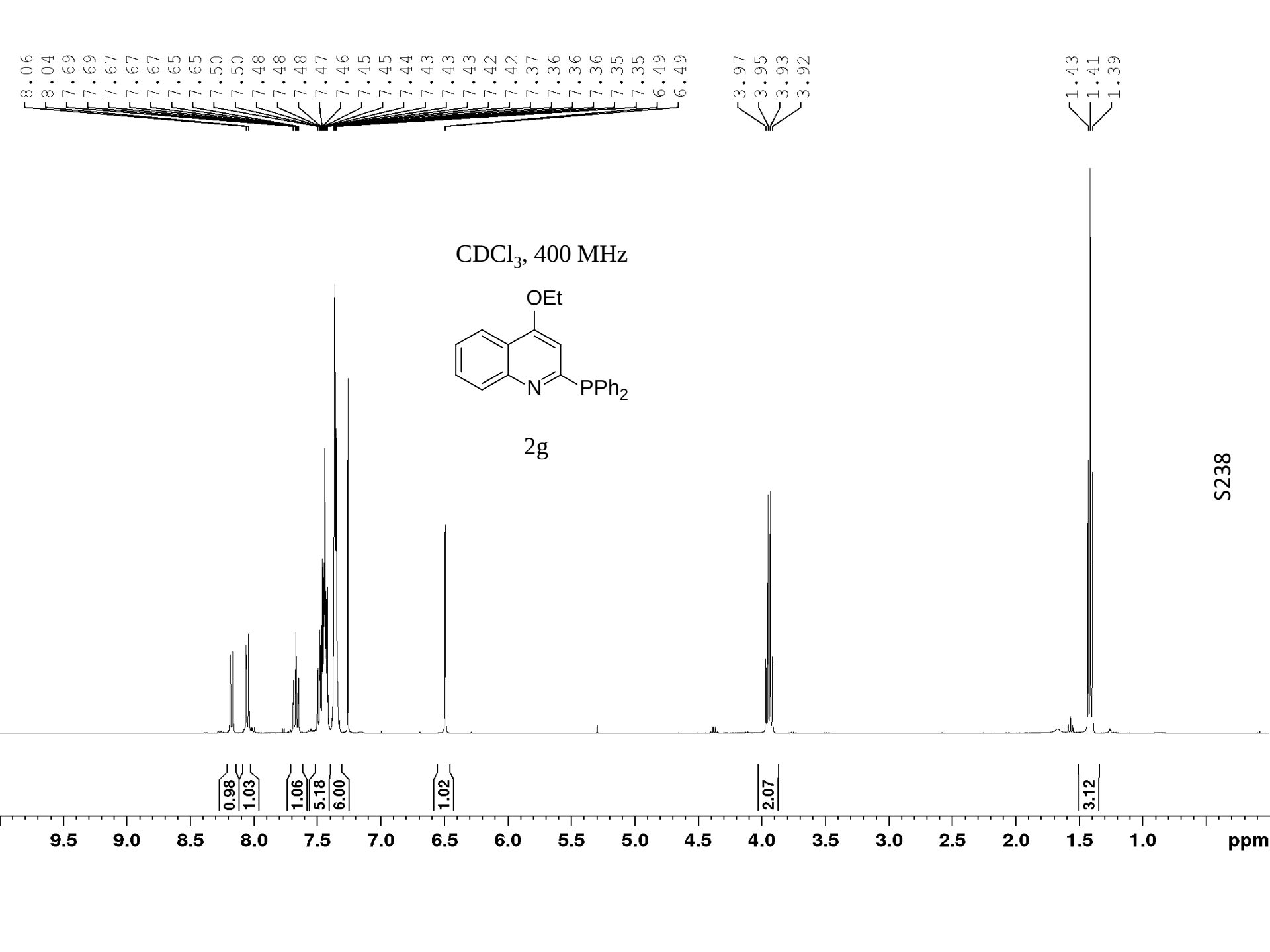

8.18
8.15
7.97
7.95
7.72
7.72
7.71
7.70
7.70
7.68
7.68
7.58
7.57
7.56
7.56
7.55
7.54
7.54
7.50
7.50
7.49
7.49
7.48
7.48
7.47
7.46
7.46
7.40
7.39
7.38
7.38
7.38
7.37
7.37
7.26
7.06
2.58
2.58
CDCl3, 400 MHz
Me
N
PPh2
2f
1.00
1.05
1.06
1.07
3.91
5.93
0.97
3.12
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

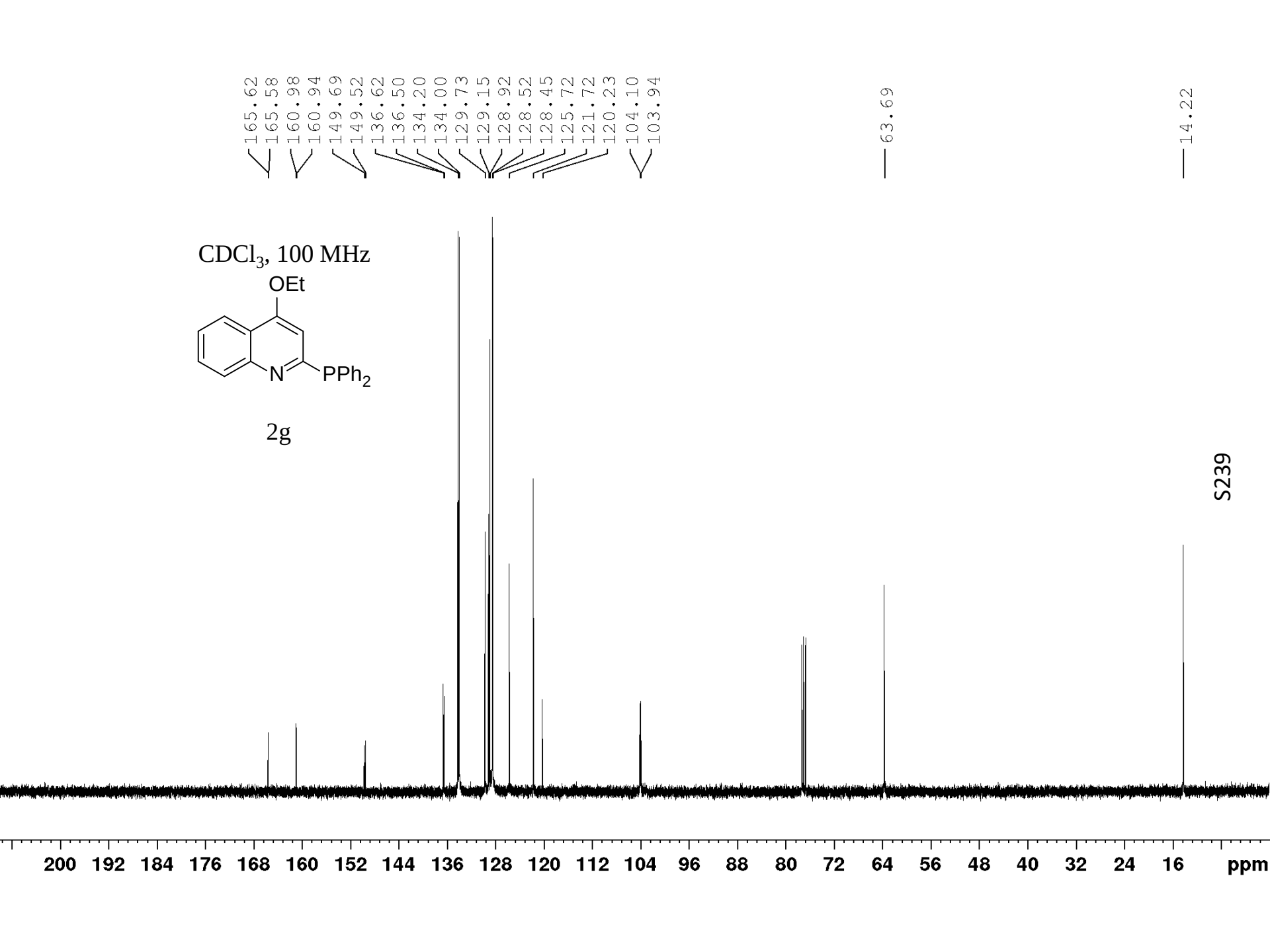

164.21
164.17
148.34
148.19
143.43
143.40
136.45
136.33
134.21
134.02
130.24
129.17
128.86
128.51
128.44
126.88
126.53
124.95
124.80
123.60
77.32
77.00
76.68
18.71
CDCl3, 100 MHz
Me
N
PPh2
2f
S236
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

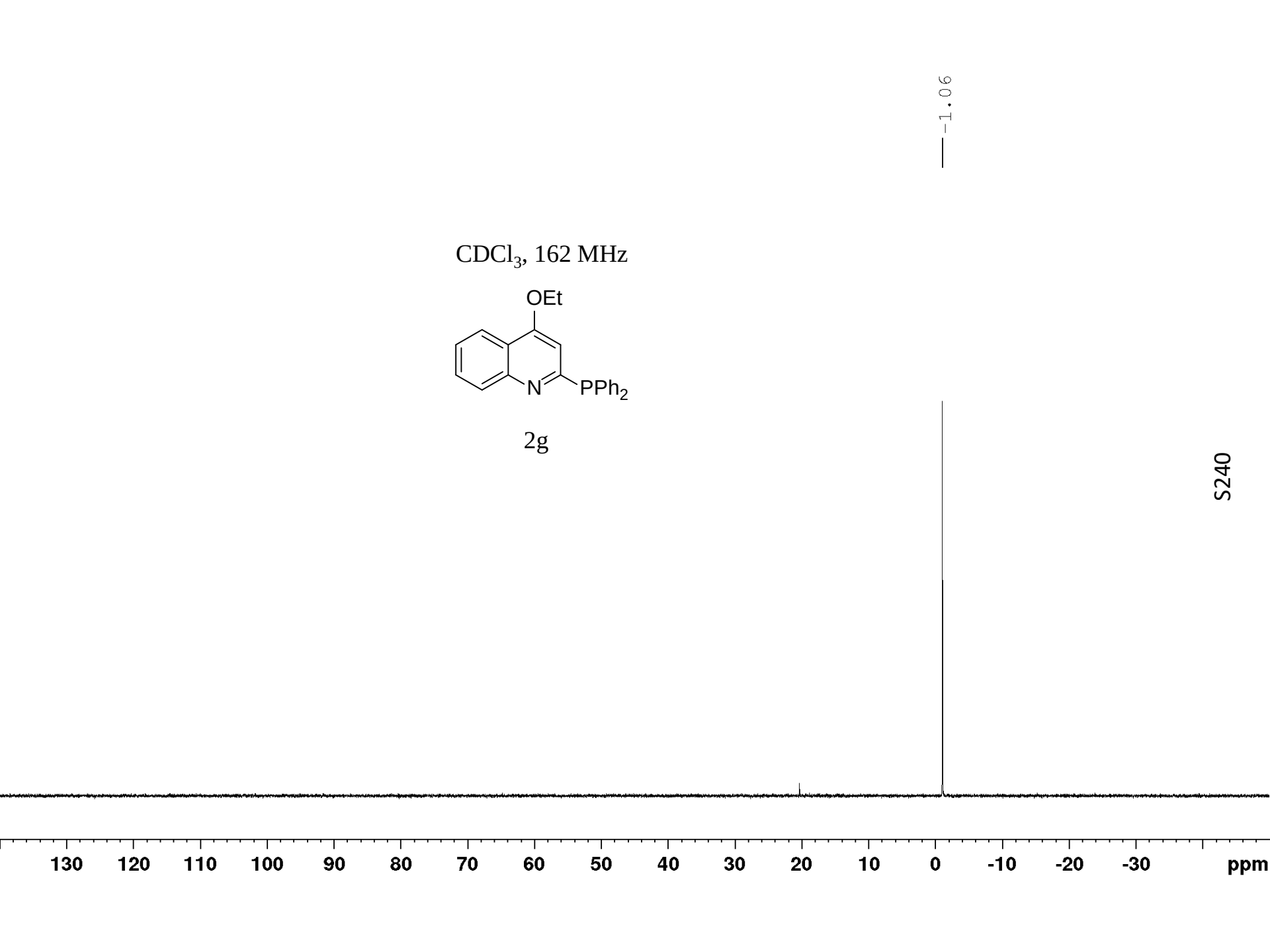
$CDCl_3$, 162 MHz

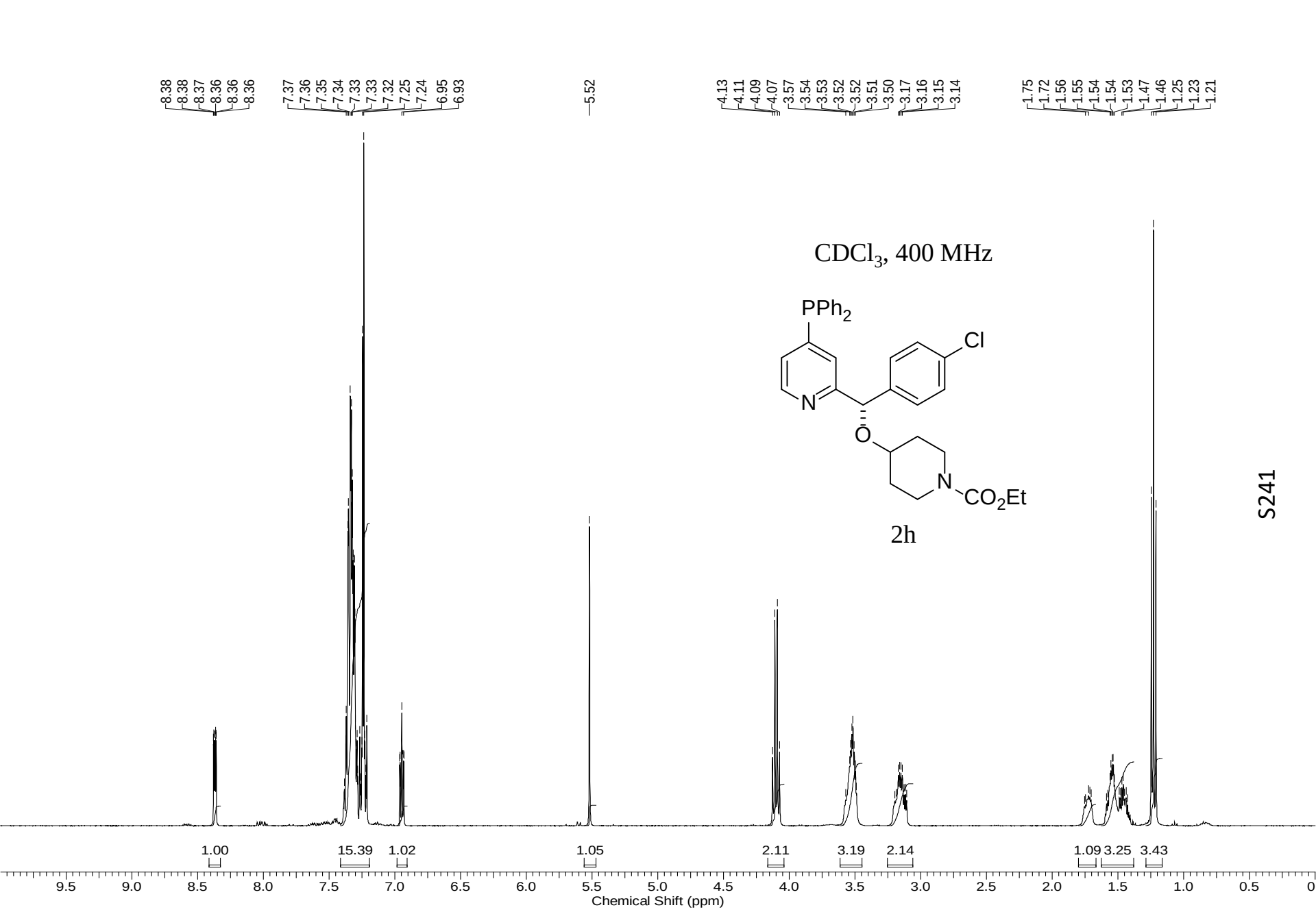


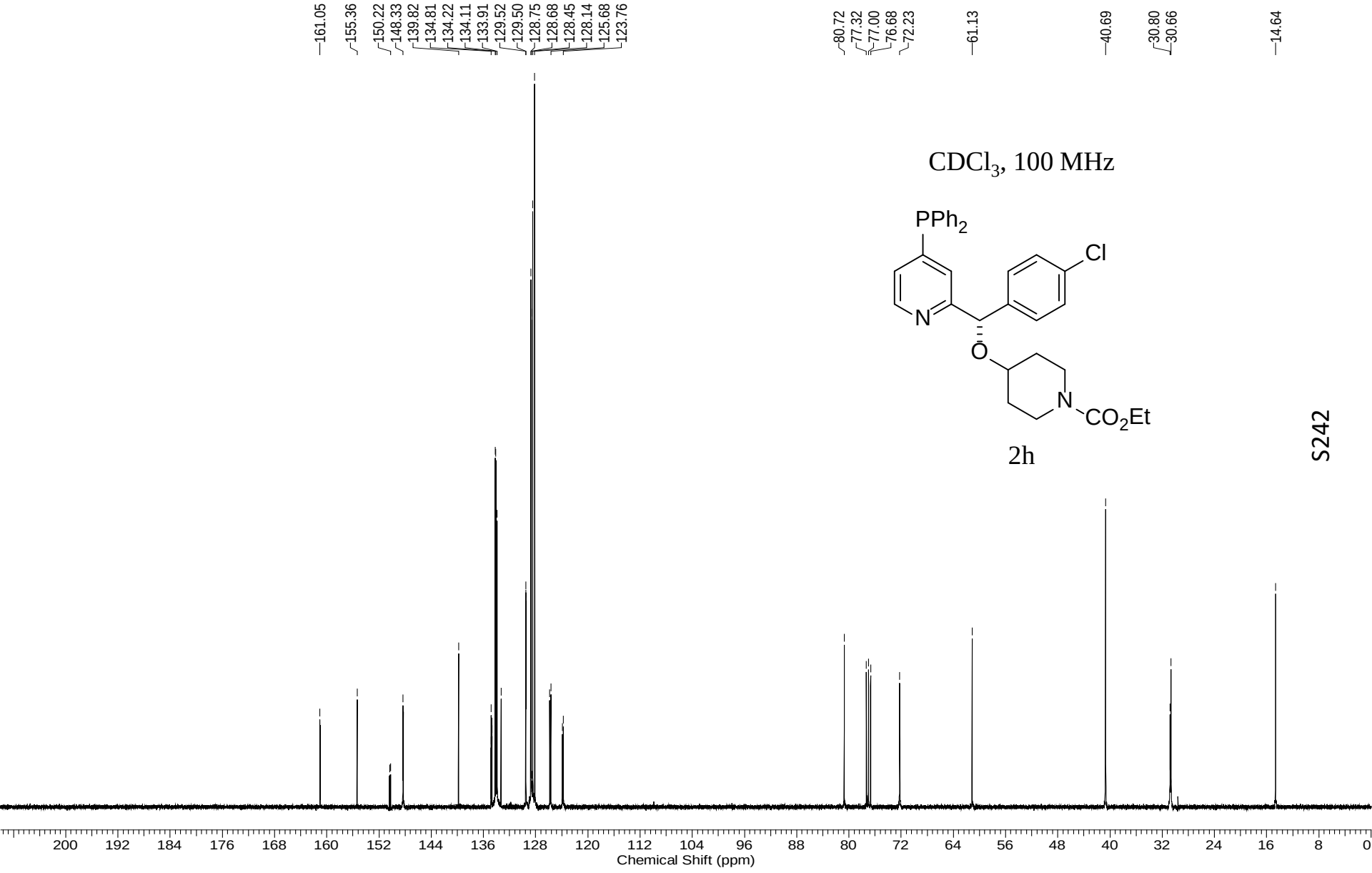
2f


8.06
8.04
7.69
7.69
7.67
7.67
7.67
7.65
7.65
7.50
7.50
7.48
7.48
7.48
7.47
7.46
7.45
7.45
7.44
7.43
7.43
7.43
7.42
7.42
7.37
7.36
7.36
7.36
7.35
7.35
6.49
6.49
3.97
3.95
3.93
3.92
1.43
1.41
1.39
CDCl3, 400 MHz
OEt
N
PPh2
2g
S238
0.98
1.03
1.06
5.18
6.00
1.02
2.07
3.12
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

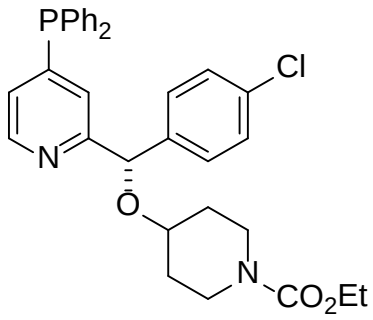

165.62
165.58
160.98
160.94
149.69
149.52
136.62
136.50
134.20
134.00
129.73
129.15
128.92
128.52
128.45
125.72
121.72
120.23
104.10
103.94
63.69
14.22
CDCl3, 100 MHz
OEt
N
PPh2
2g
S239
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 ppm


-1.06
CDCl3, 162 MHz
OEt
N
PPh2
2g
S240
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
ppm


8.38
8.38
8.37
8.36
8.36
8.36
7.37
7.36
7.35
7.34
7.33
7.33
7.32
7.25
7.24
6.95
6.93
5.52
4.13
4.11
4.09
4.07
3.57
3.54
3.53
3.52
3.52
3.51
3.50
3.17
3.16
3.15
3.14
1.75
1.72
1.56
1.55
1.54
1.54
1.53
1.47
1.46
1.25
1.23
1.21
CDCl3, 400 MHz
PPh2
Cl
N
O
N
CO2Et
2h
S241
1.00
15.39
1.02
1.05
2.11
3.19
2.14
1.09
3.25
3.43
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)


161.05
155.36
150.22
148.33
139.82
134.81
134.22
134.11
133.91
129.52
129.50
128.75
128.68
128.45
128.14
125.68
123.76
80.72
77.32
77.00
76.68
72.23
61.13
40.69
30.80
30.66
14.64
CDCl3, 100 MHz
PPh2
Cl
N
O
N
CO2Et
2h
S242
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
Chemical Shift (ppm)

$CDCl_3$, 162 MHz



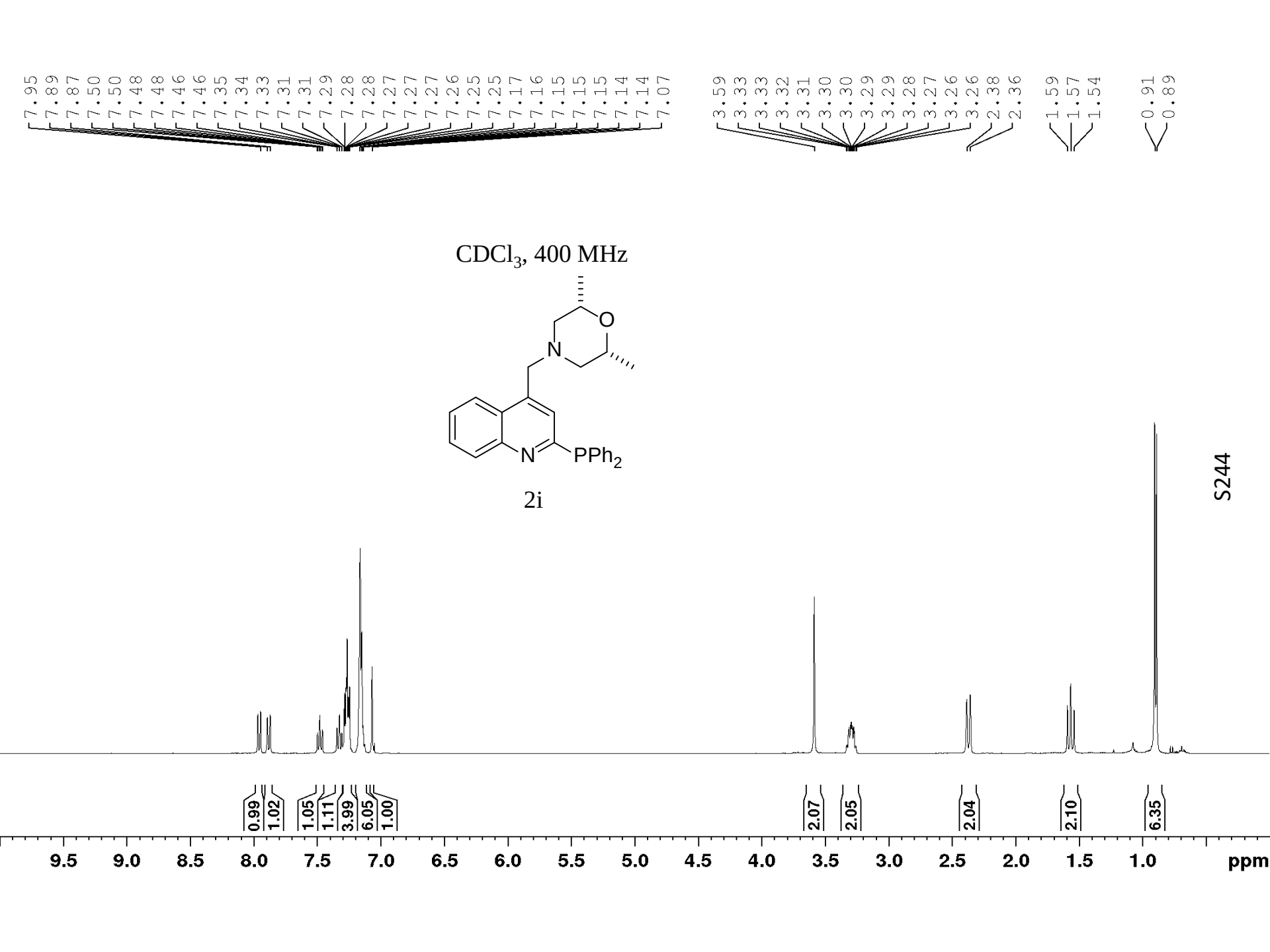
2h

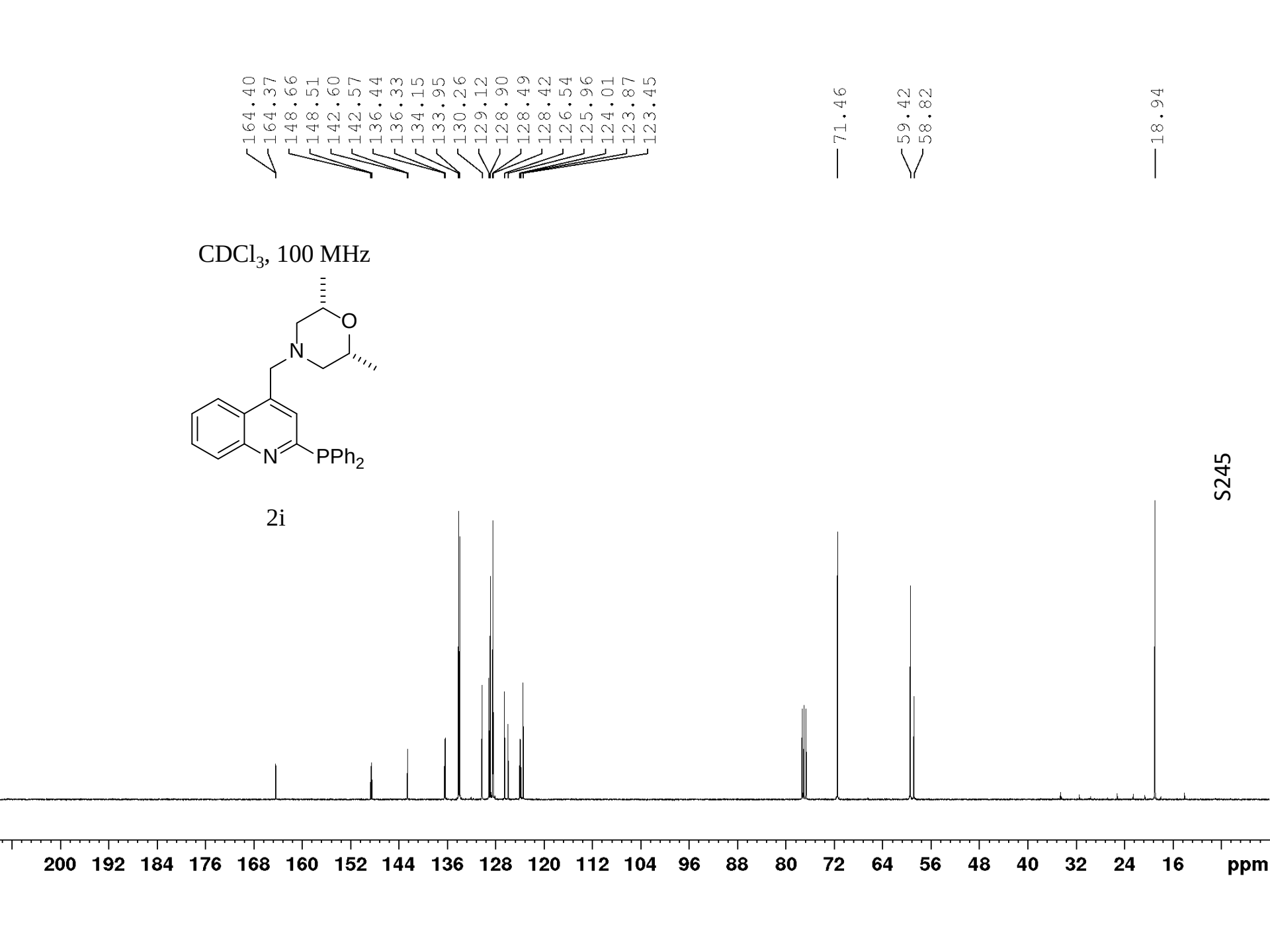
-6.35

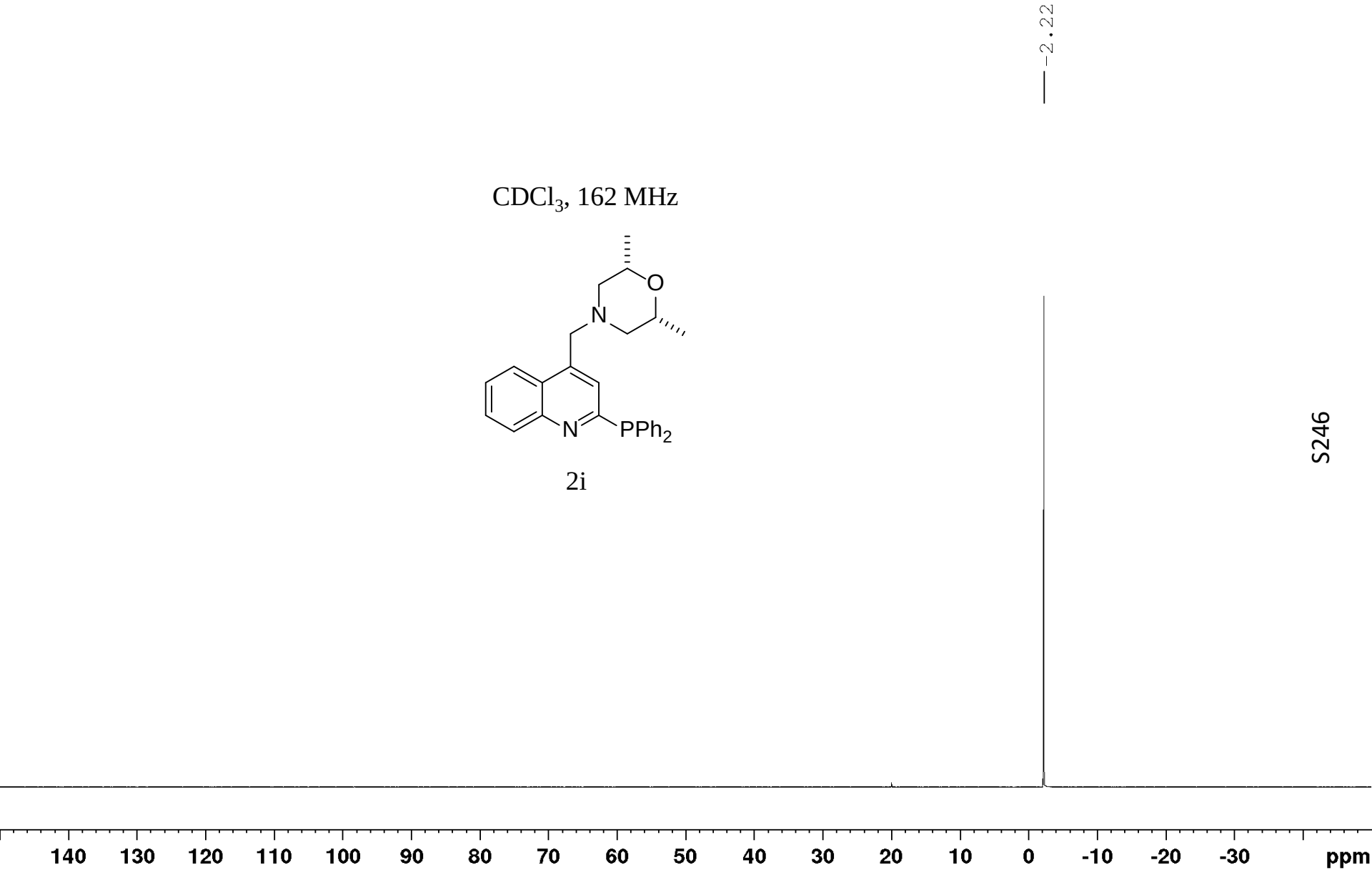
S243

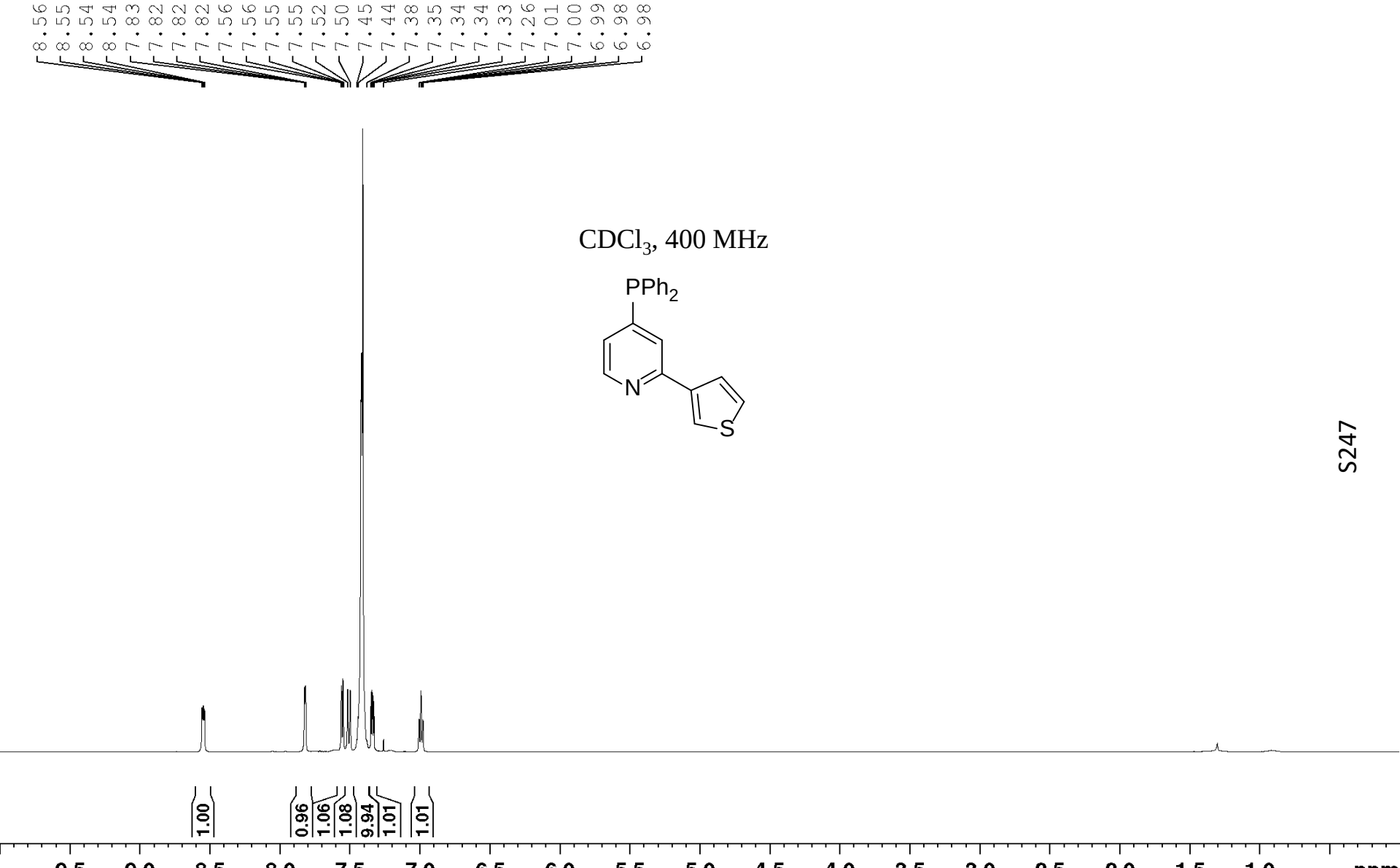
144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 0 -8 -16 -24 -32 -40 -48

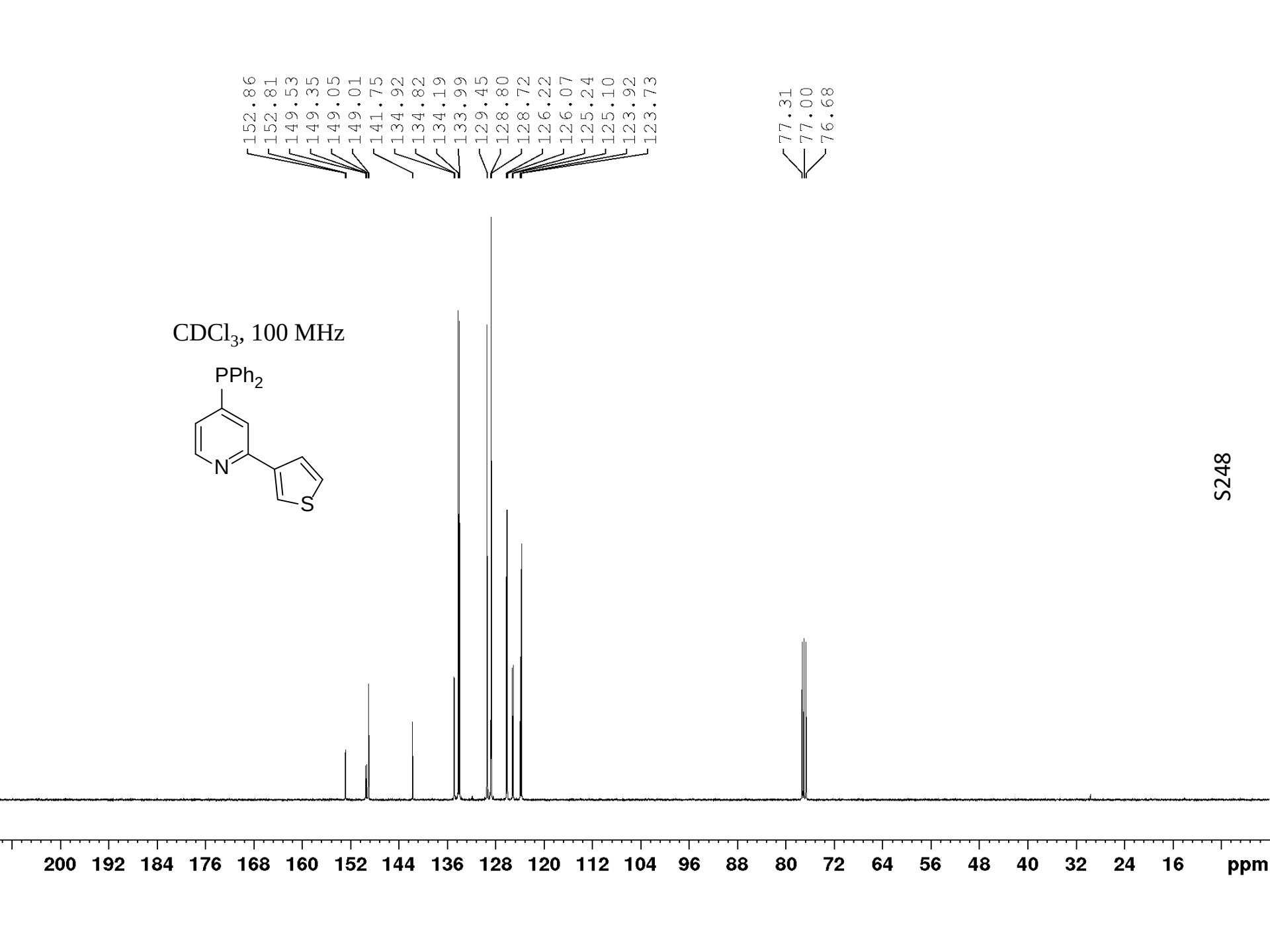
Chemical Shift (ppm)

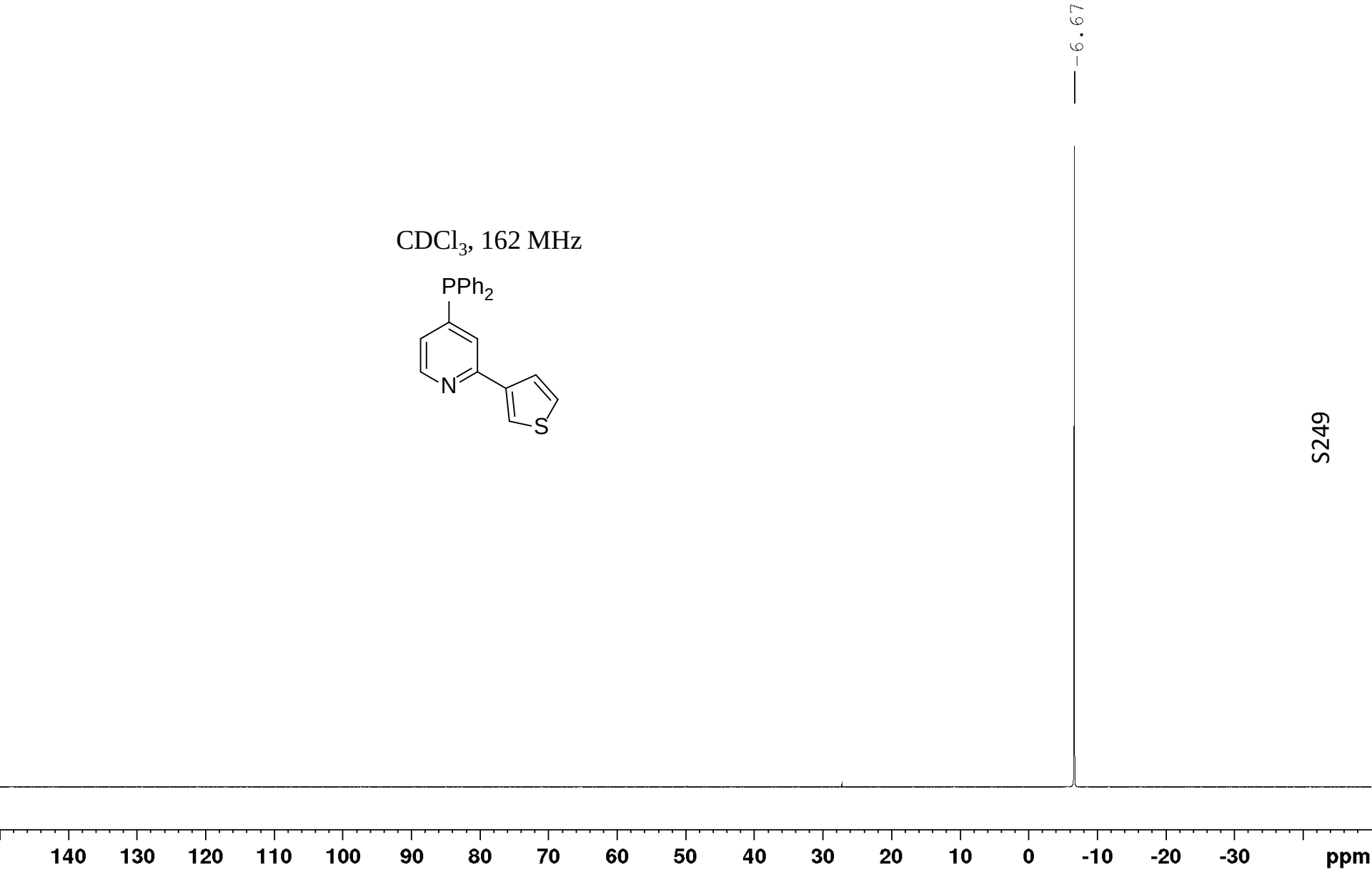

7.95
7.89
7.87
7.50
7.50
7.48
7.48
7.46
7.46
7.35
7.34
7.33
7.31
7.31
7.29
7.28
7.28
7.27
7.27
7.27
7.26
7.25
7.25
7.17
7.16
7.15
7.15
7.15
7.14
7.14
7.07
3.59
3.33
3.33
3.32
3.31
3.30
3.30
3.29
3.29
3.28
3.27
3.26
3.26
2.38
2.36
1.59
1.57
1.54
0.91
0.89
CDCl3, 400 MHz
O
N
N
PPh2
2i
S244
0.99
1.02
1.05
1.11
3.99
6.05
1.00
2.07
2.05
2.04
2.10
6.35
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

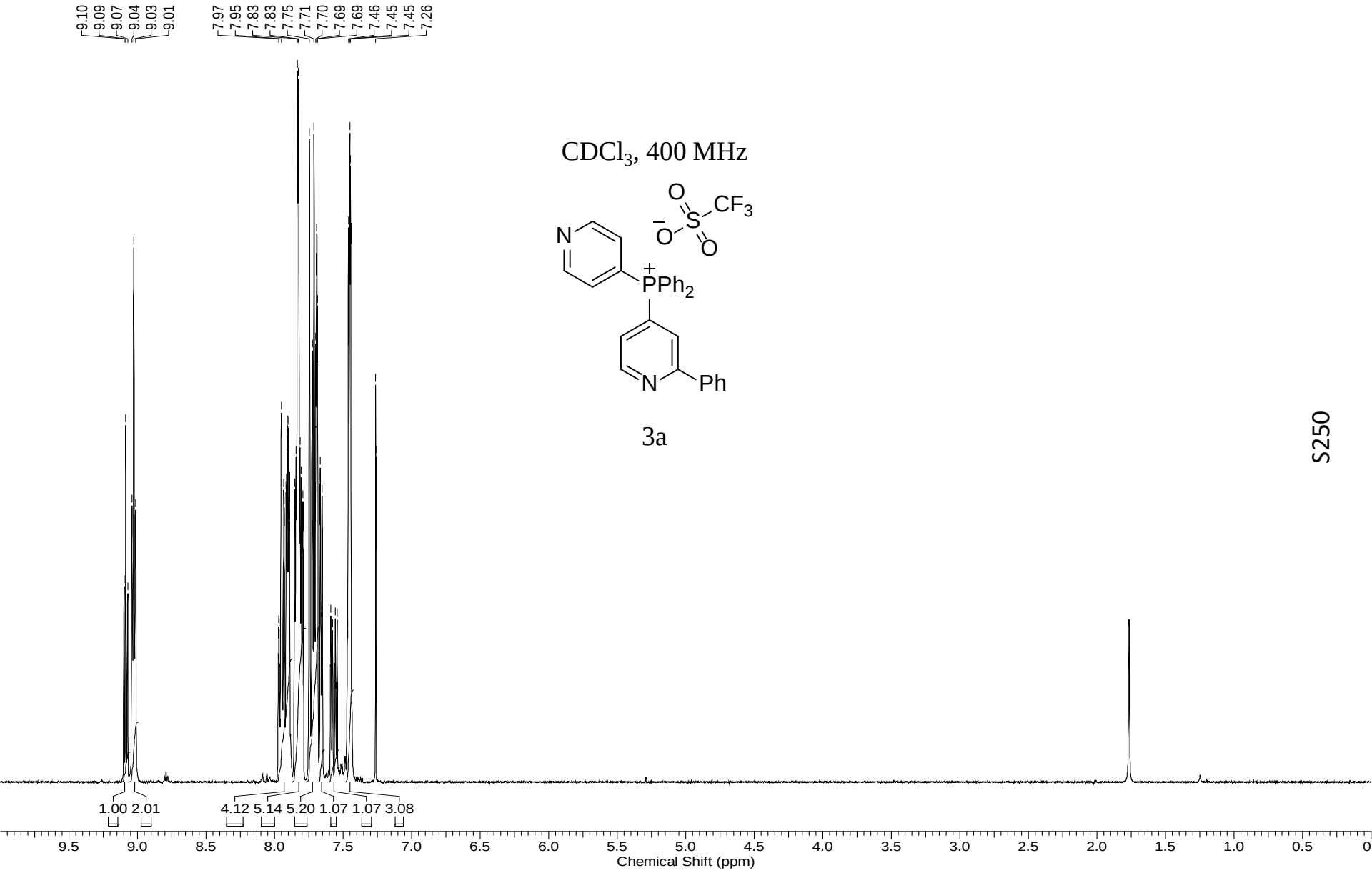

164.40
164.37
148.66
148.51
142.60
142.57
136.44
136.33
134.15
133.95
130.26
129.12
128.90
128.49
128.42
126.54
125.96
124.01
123.87
123.45
71.46
59.42
58.82
18.94
CDCl3, 100 MHz
O
N
N
PPh2
2i
S245
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 ppm

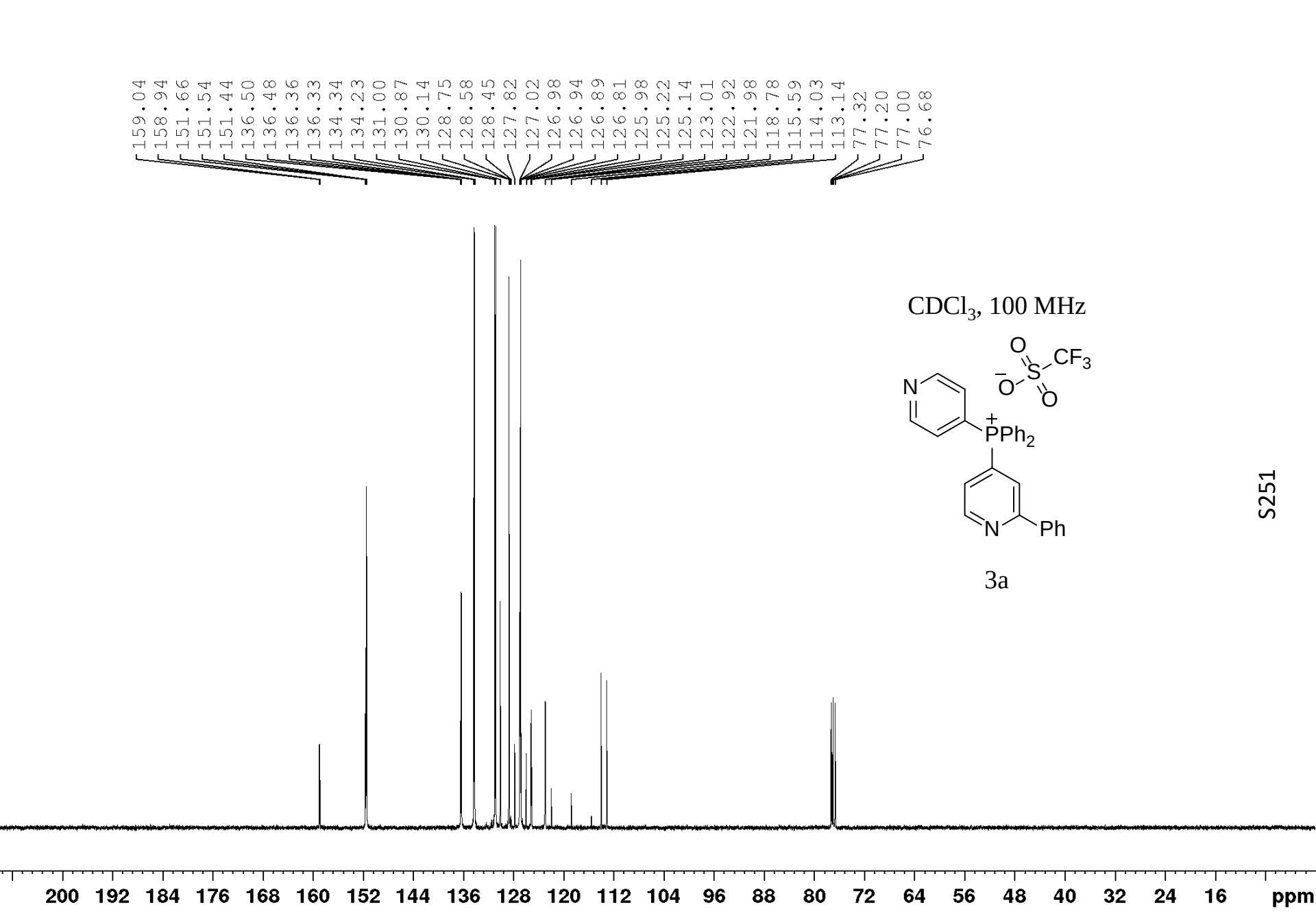

-2.22
CDCl3, 162 MHz
O
N
N
PPh2
2i
S246
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
ppm

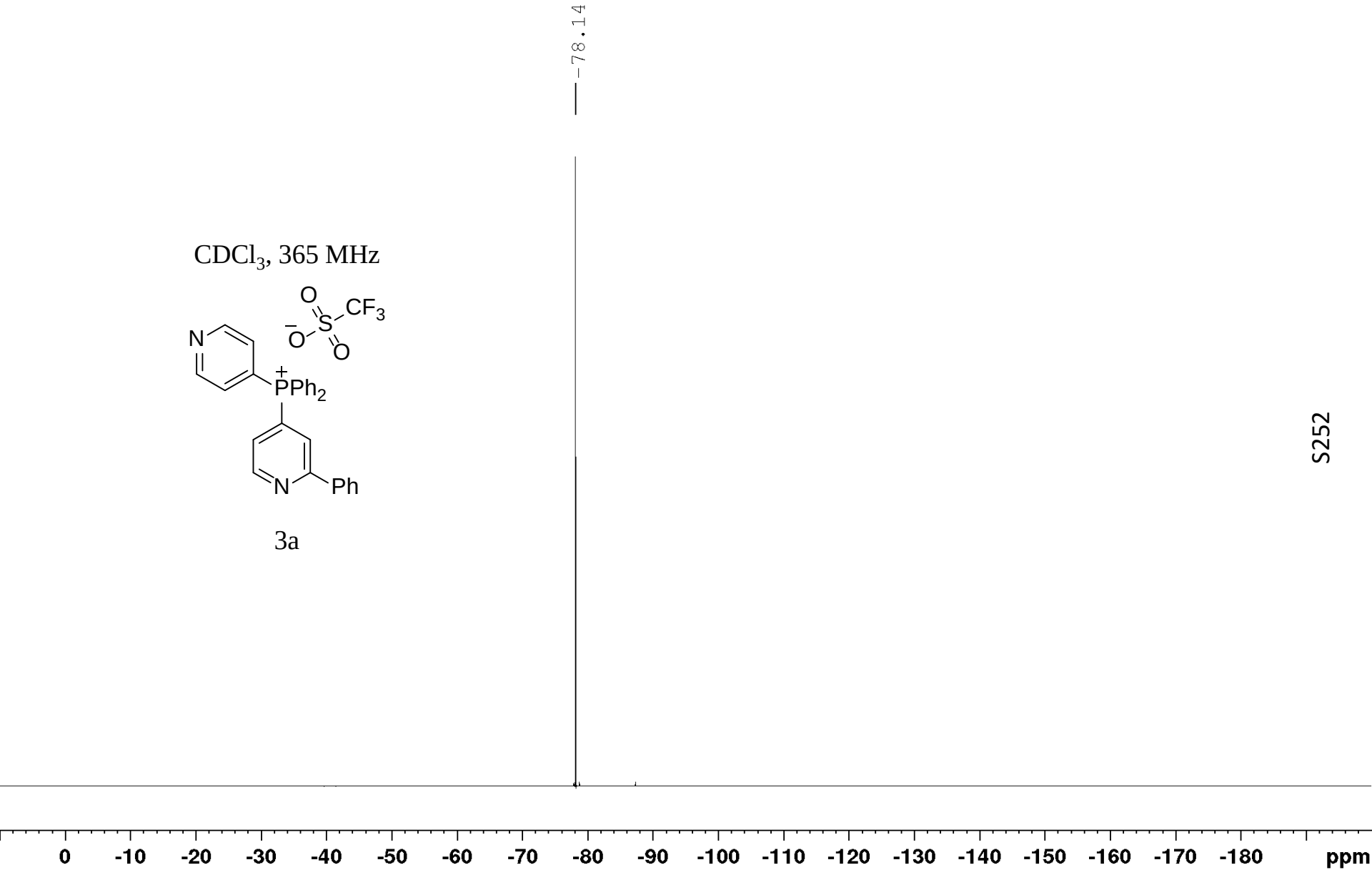

8.56
8.55
8.54
8.54
7.83
7.82
7.82
7.82
7.56
7.56
7.55
7.55
7.52
7.50
7.45
7.44
7.38
7.35
7.34
7.34
7.33
7.26
7.01
7.00
6.99
6.98
6.98
CDCl3, 400 MHz
PPh2
N
S
1.00
0.96
1.06
1.08
9.94
1.01
1.01
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

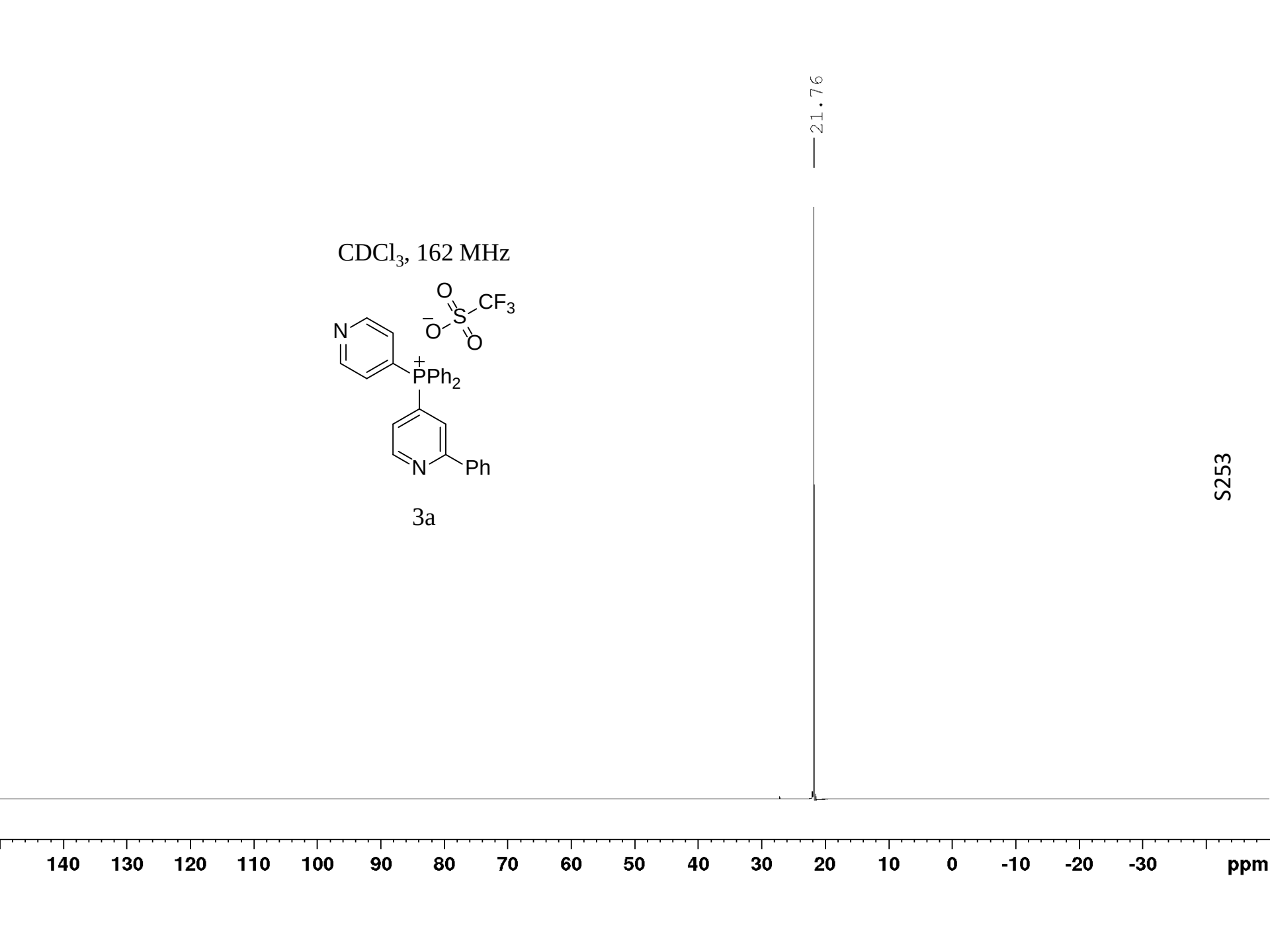

152.86
152.81
149.53
149.35
149.05
149.01
141.75
134.92
134.82
134.19
133.99
129.45
128.80
128.72
126.22
126.07
125.24
125.10
123.92
123.73
77.31
77.00
76.68
CDCl3, 100 MHz
PPh2
N
S
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 ppm

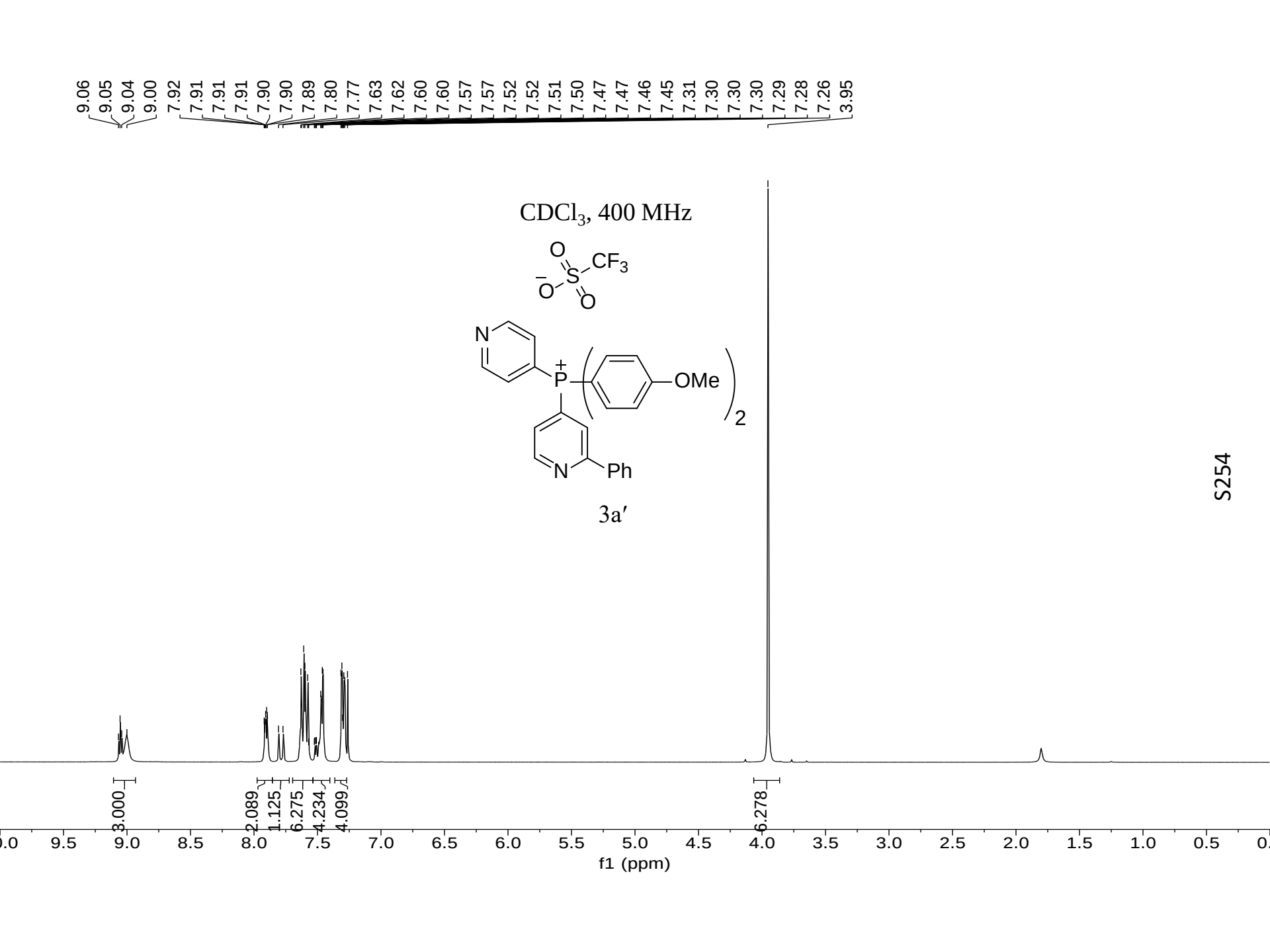

-6.67
CDCl3, 162 MHz
PPh2
N
S
S249
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
ppm

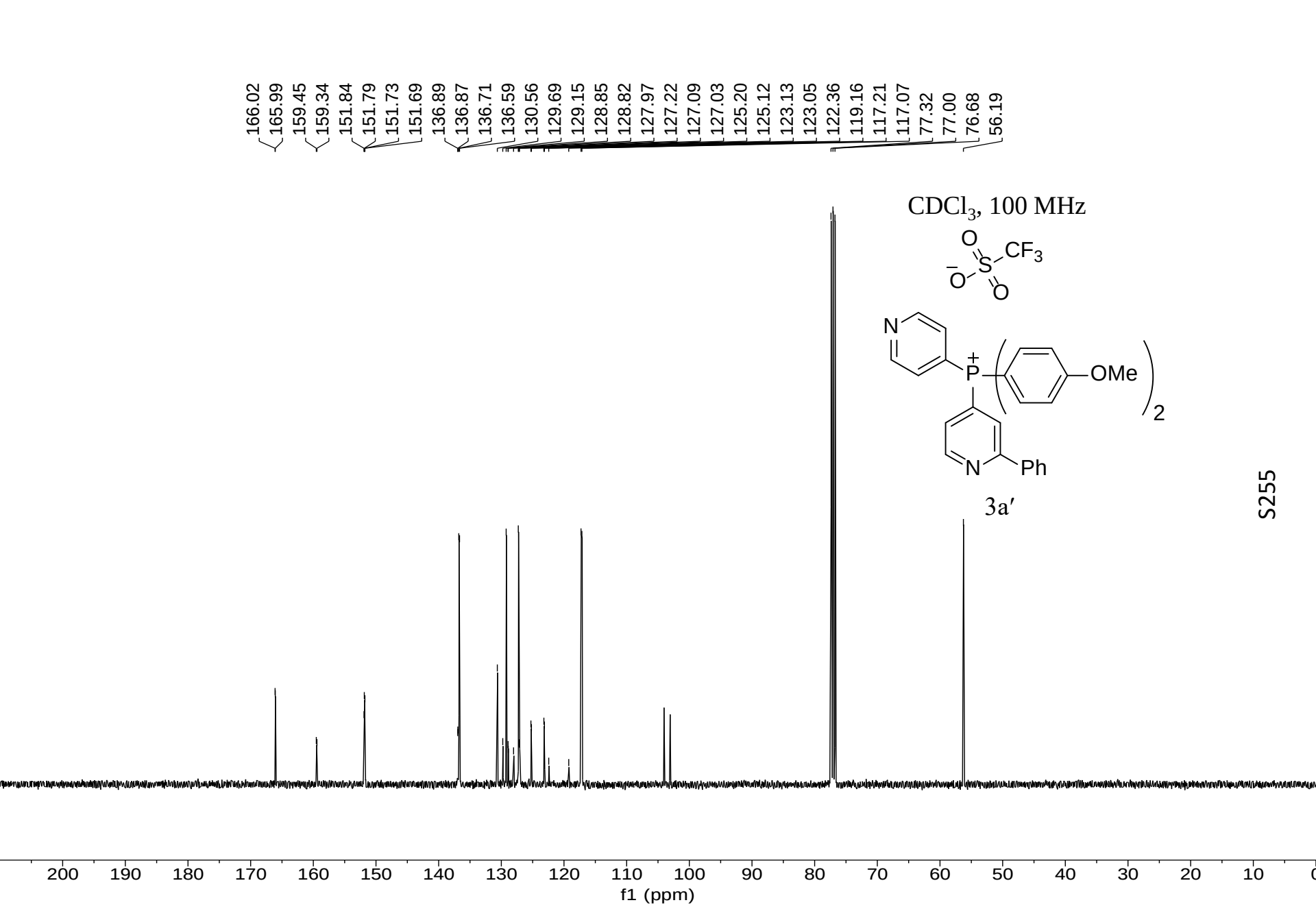

9.10
9.09
9.07
9.04
9.03
9.01
7.97
7.95
7.83
7.83
7.75
7.71
7.70
7.69
7.69
7.46
7.45
7.45
7.26
CDCl3, 400 MHz
O
CF3
S
O
O
N
PPh2
N
Ph
3a
1.00 2.01
4.12 5.14 5.20 1.07 1.07 3.08
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

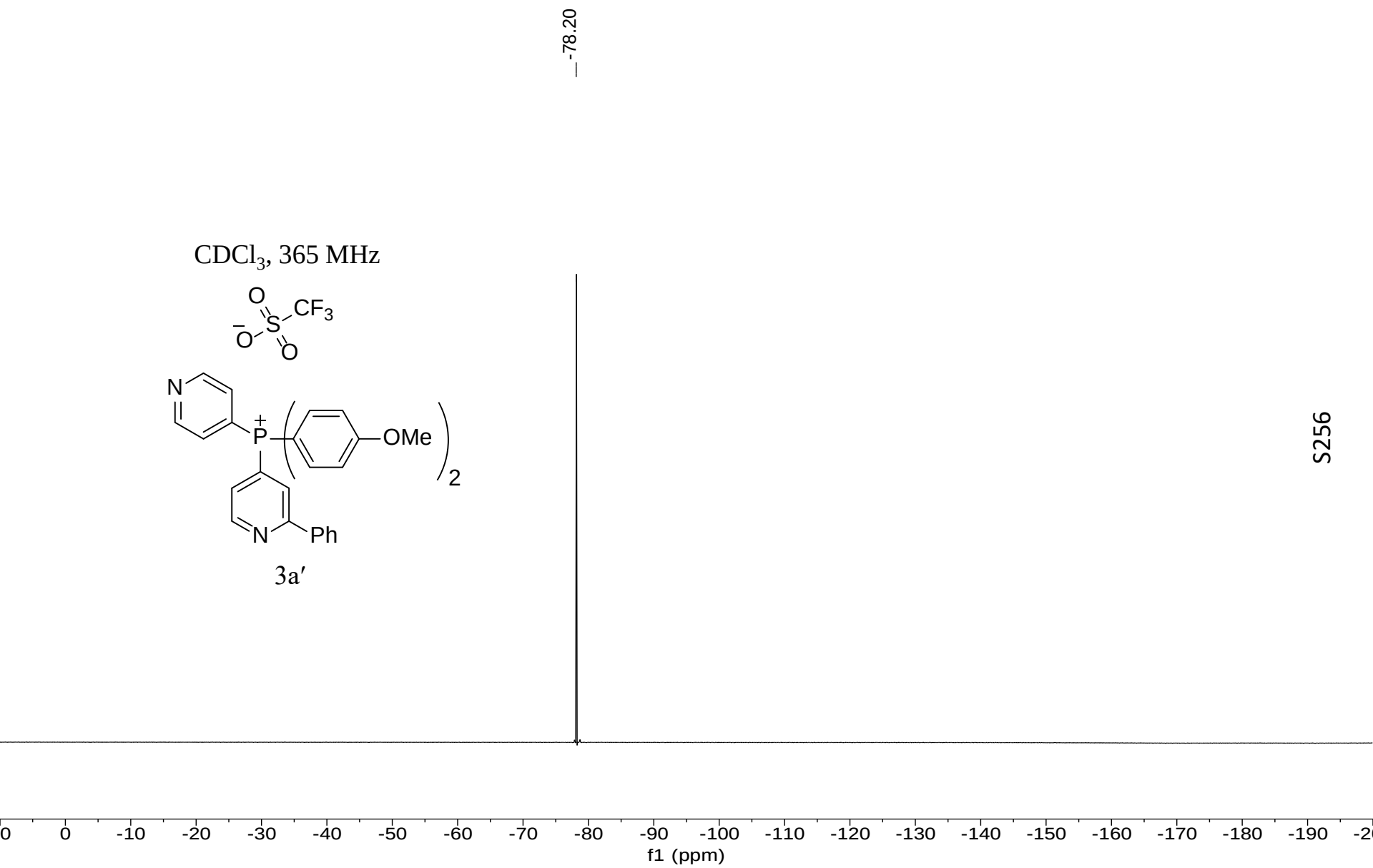

159.04
158.94
151.66
151.54
151.44
136.50
136.48
136.36
136.33
134.34
134.23
131.00
130.87
130.14
128.75
128.58
128.45
127.82
127.02
126.98
126.94
126.89
126.81
125.98
125.22
125.14
123.01
122.92
121.98
118.78
115.59
114.03
113.14
77.32
77.20
77.00
76.68
CDCl3, 100 MHz
O
CF3
S
O
O
N
PPh2
N
Ph
3a
S251
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

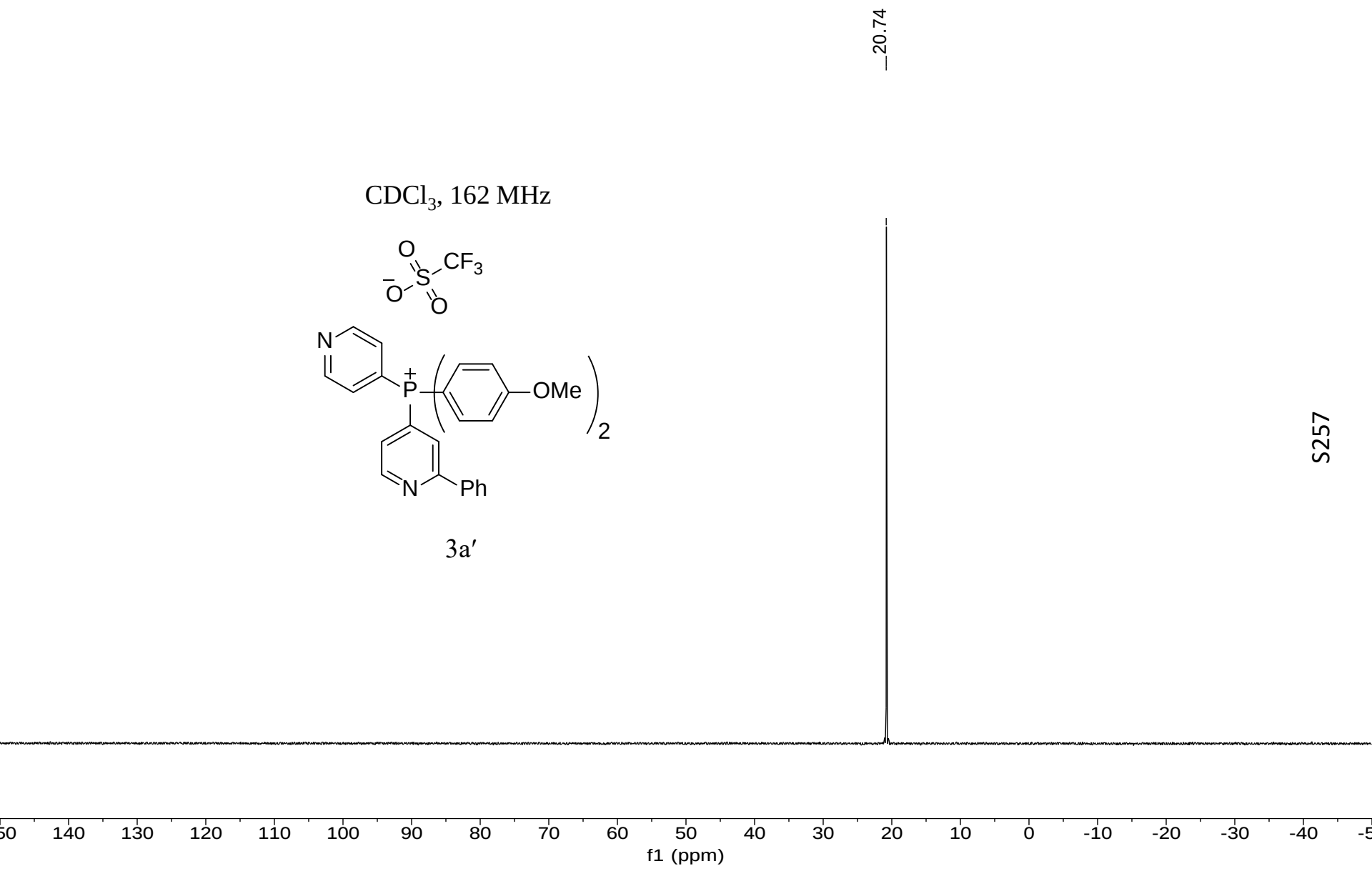

-78.14
CDCl3, 365 MHz
O
CF3
S
O
O
N
PPh2
N
Ph
3a
S252
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
ppm

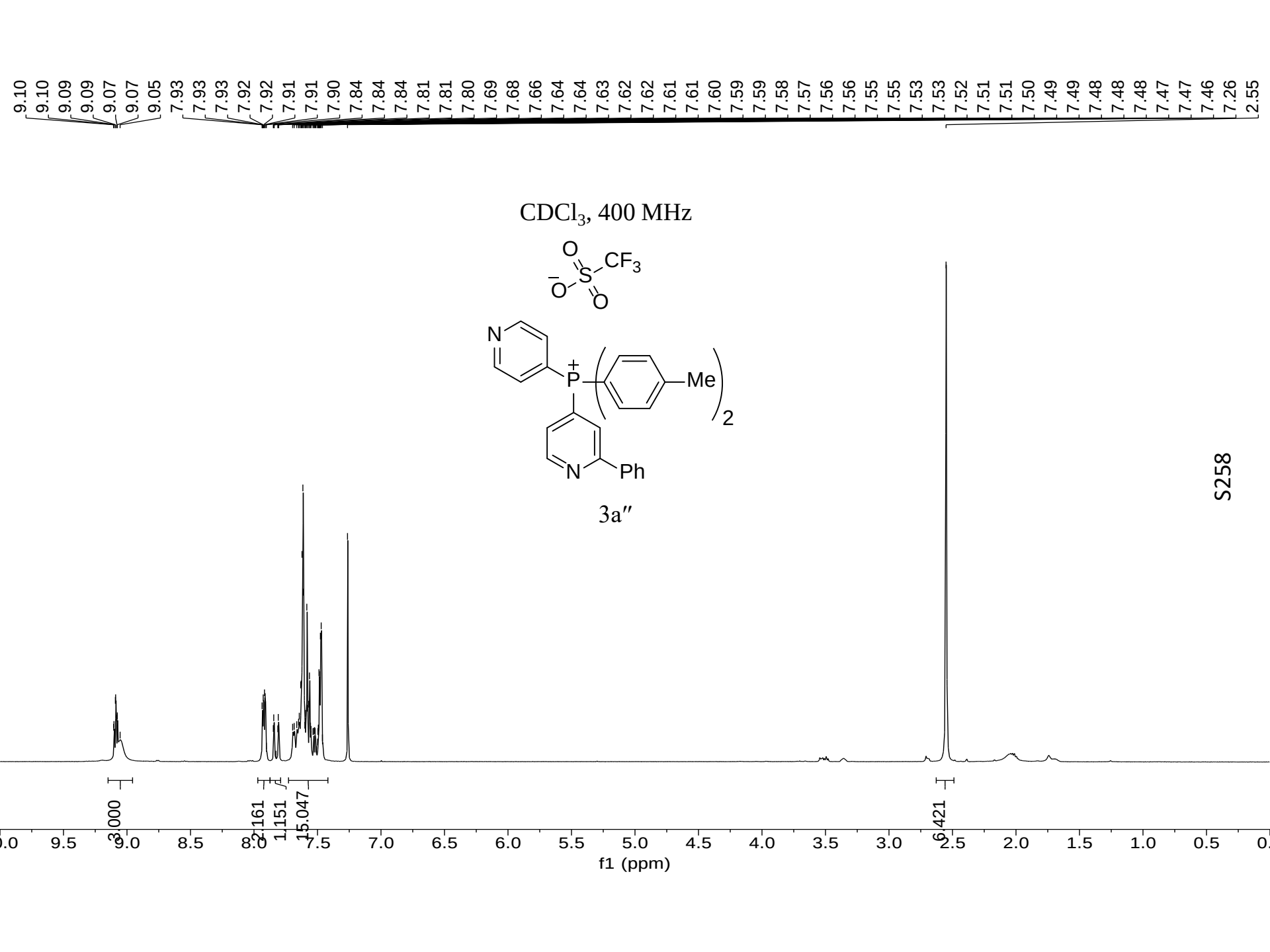

21.76
CDCl3, 162 MHz
O
CF3
S
O
O
N
PPh2
N
Ph
3a
S253
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
ppm

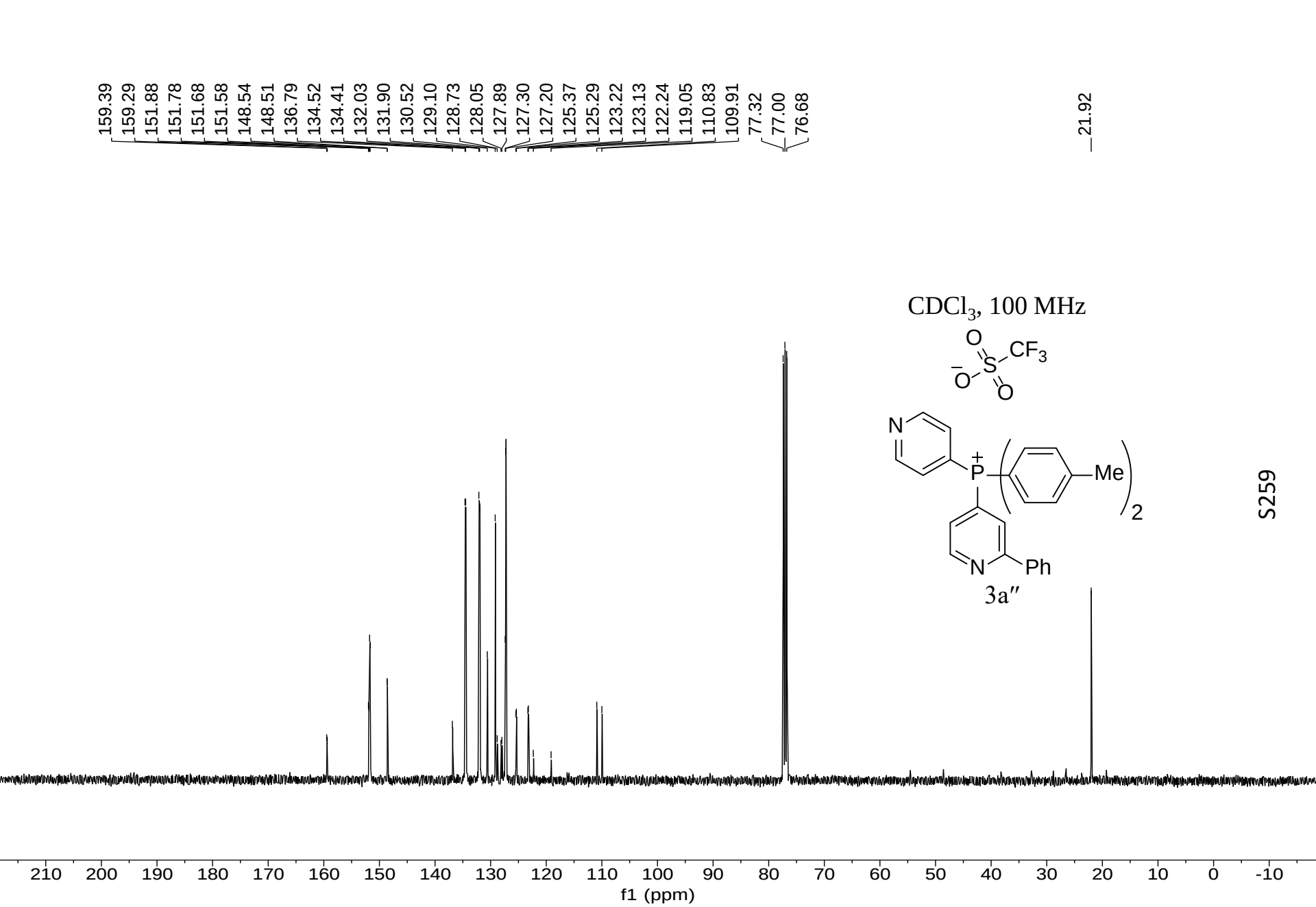

9.06 9.05 9.04 9.00 7.92 7.91 7.91 7.91 7.90 7.90 7.89 7.80 7.77 7.63 7.62 7.60 7.60 7.57 7.57 7.52 7.52 7.51 7.50 7.47 7.47 7.46 7.45 7.31 7.30 7.30 7.30 7.29 7.28 7.26 3.95
CDCl3, 400 MHz
O
S
CF3
O
O
N
P
OMe
2
N
Ph
3a′
S254
3.000
2.089
1.125
6.275
4.234
4.099
6.278
f1 (ppm)

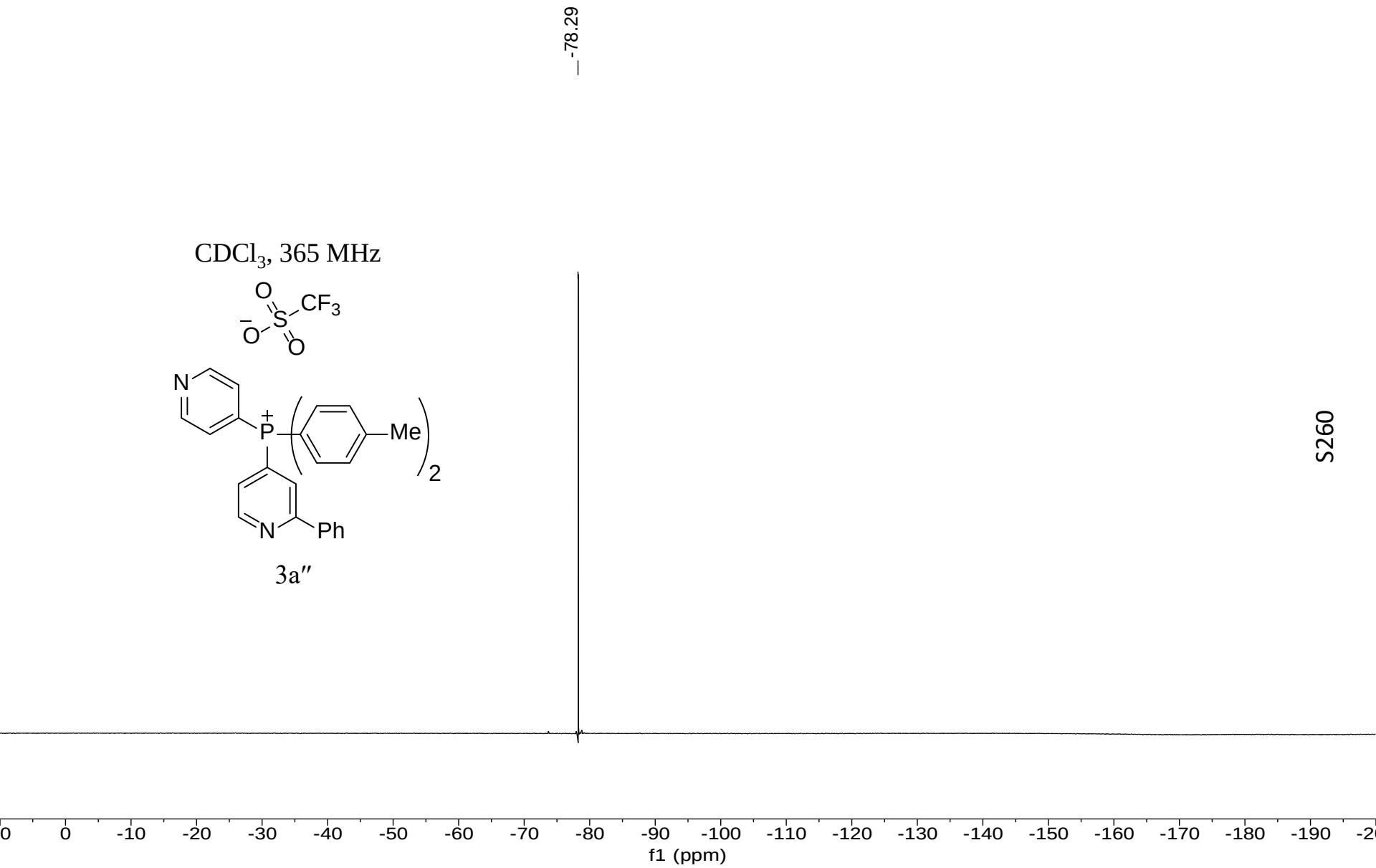

166.02
165.99
159.45
159.34
151.84
151.79
151.73
151.69
136.89
136.87
136.71
136.59
130.56
129.69
129.15
128.85
128.82
127.97
127.22
127.09
127.03
125.20
125.12
123.13
123.05
122.36
119.16
117.21
117.07
77.32
77.00
76.68
56.19
CDCl3, 100 MHz
O
CF3
S
O
O
N
P
OMe
2
N
Ph
3a′
S255
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

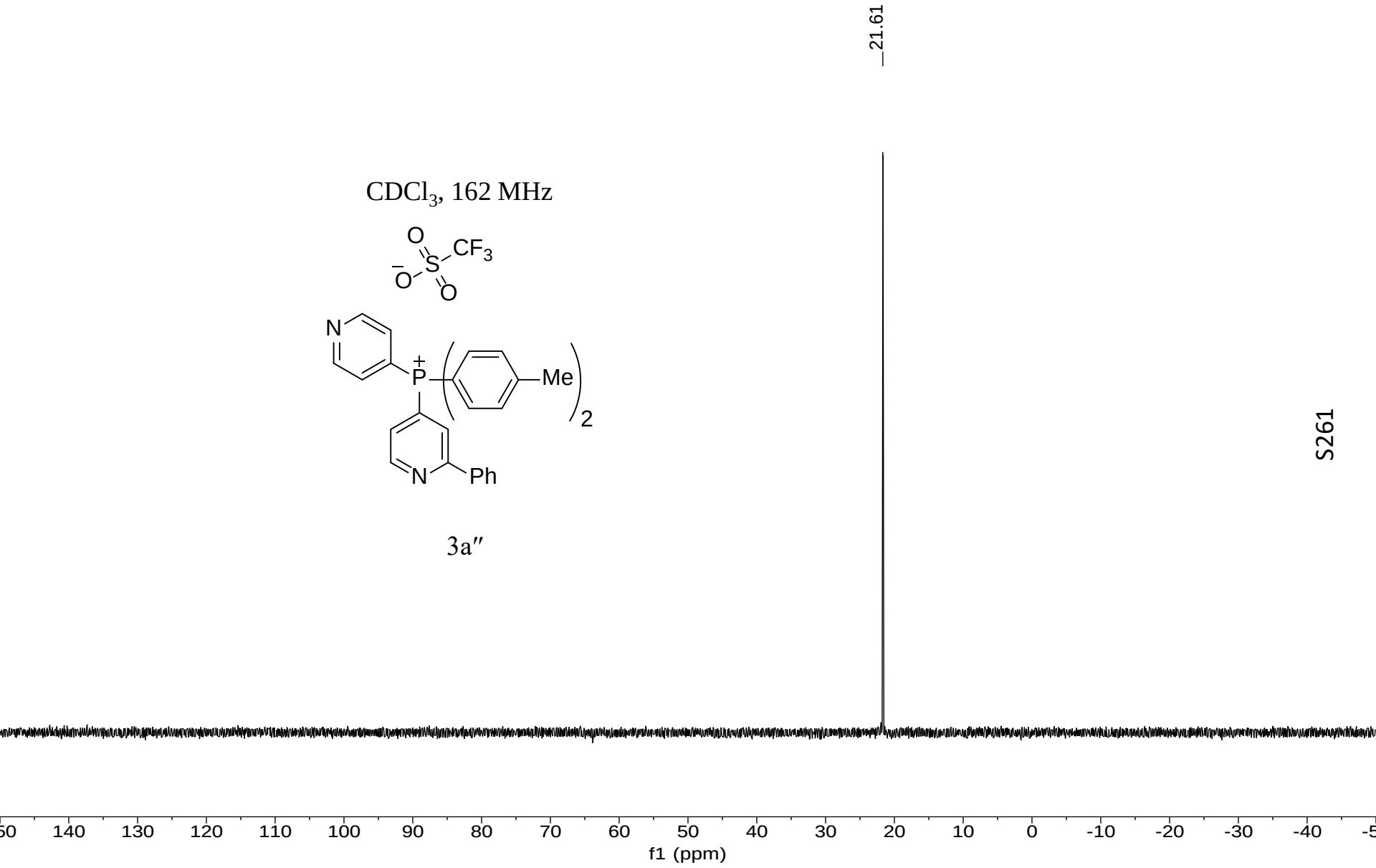

-78.20
CDCl3, 365 MHz
O
CF3
S
O
O
N
P
OMe
2
N
Ph
3a′
S256
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)

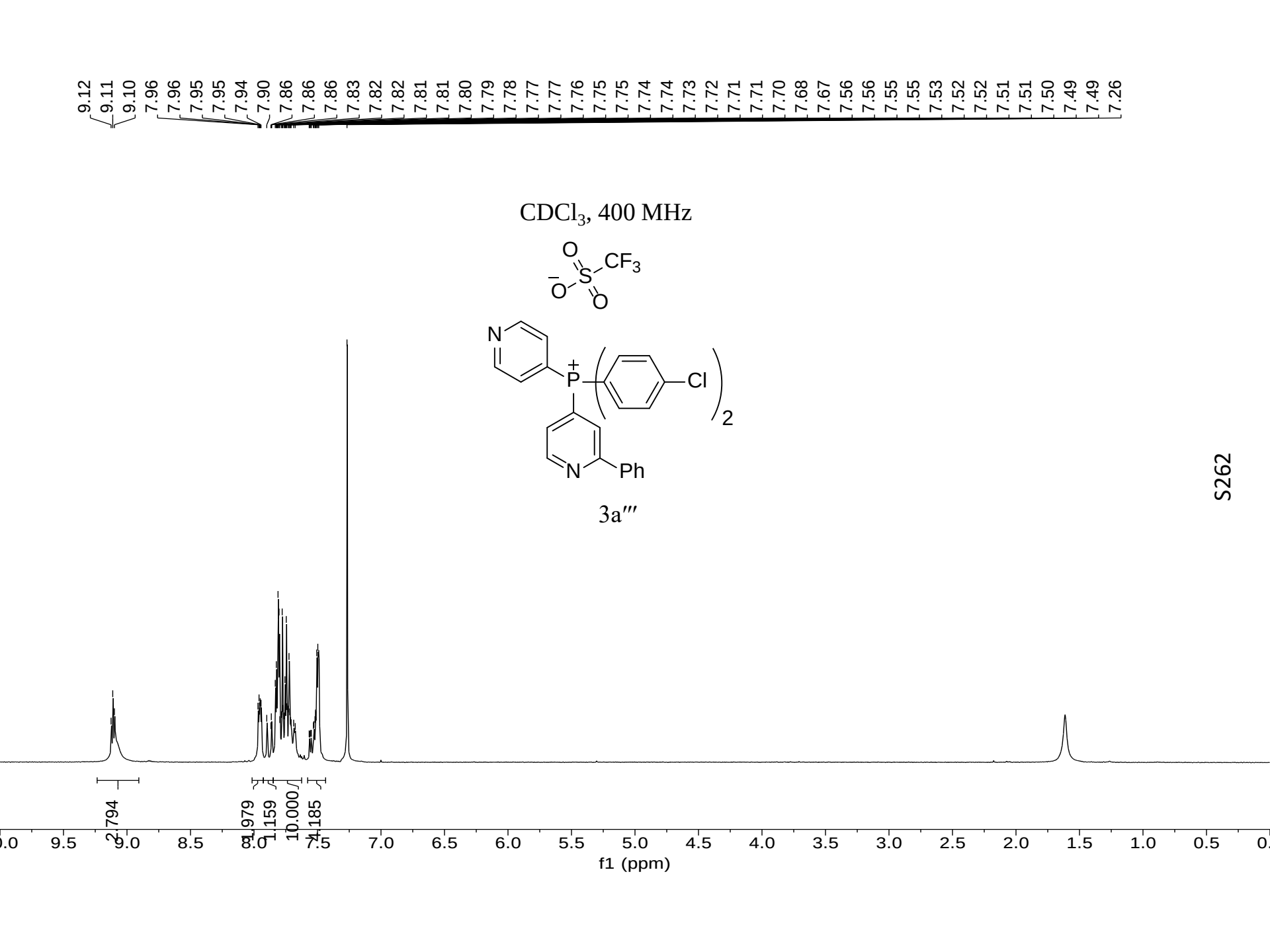

20.74
CDCl3, 162 MHz
O
CF3
S
O
O
N
P
OMe
2
N
Ph
3a′
S257
f1 (ppm)

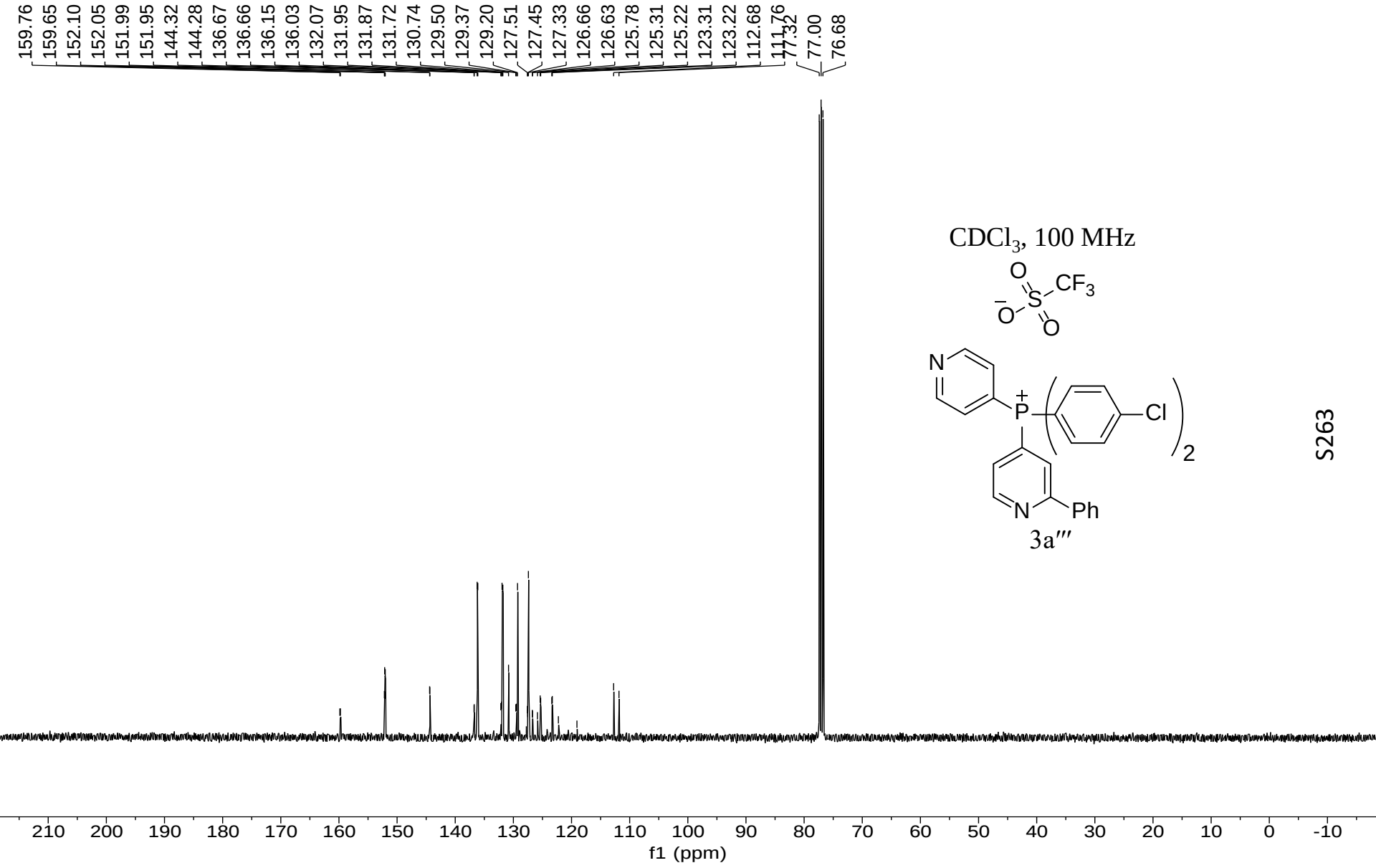

9.10 9.10 9.09 9.09 9.07 9.07 9.05 7.93 7.93 7.93 7.92 7.92 7.91 7.91 7.90 7.84 7.84 7.84 7.81 7.81 7.80 7.69 7.68 7.66 7.64 7.64 7.63 7.62 7.62 7.61 7.61 7.60 7.59 7.59 7.58 7.57 7.56 7.56 7.55 7.55 7.53 7.53 7.52 7.51 7.51 7.50 7.49 7.49 7.48 7.48 7.48 7.47 7.47 7.46 7.26 2.55
CDCl3, 400 MHz
O
CF3
S
O
O
N
P
Me
2
N
Ph
3a″
S258
3.000
2.161
1.151
15.047
6.421
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

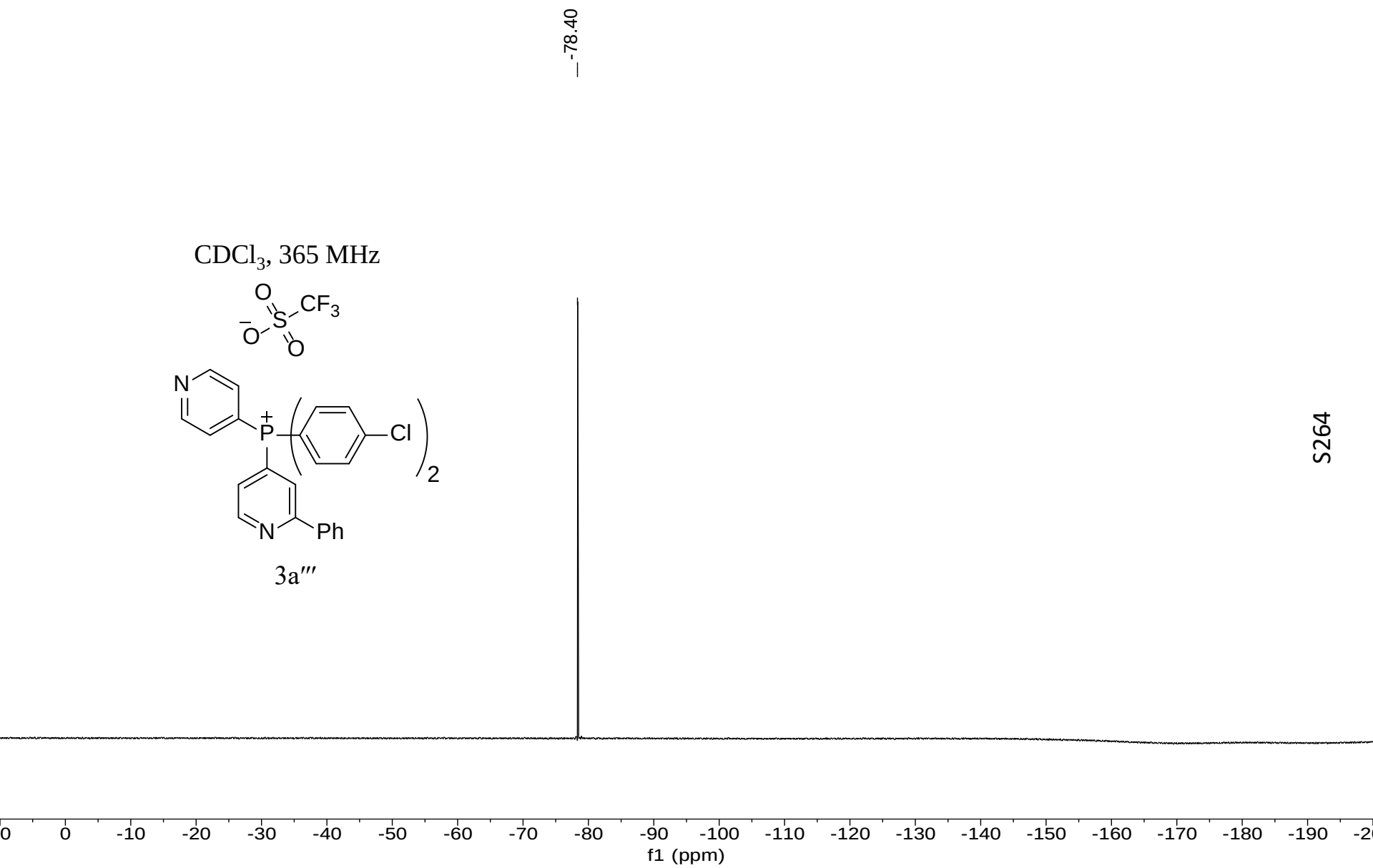

159.39
159.29
151.88
151.78
151.68
151.58
148.54
148.51
136.79
134.52
134.41
132.03
131.90
130.52
129.10
128.73
128.05
127.89
127.30
127.20
125.37
125.29
123.22
123.13
122.24
119.05
110.83
109.91
77.32
77.00
76.68
21.92
CDCl3, 100 MHz
O
CF3
S
O
O
N
P
Me
2
N
Ph
3a″
S259
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

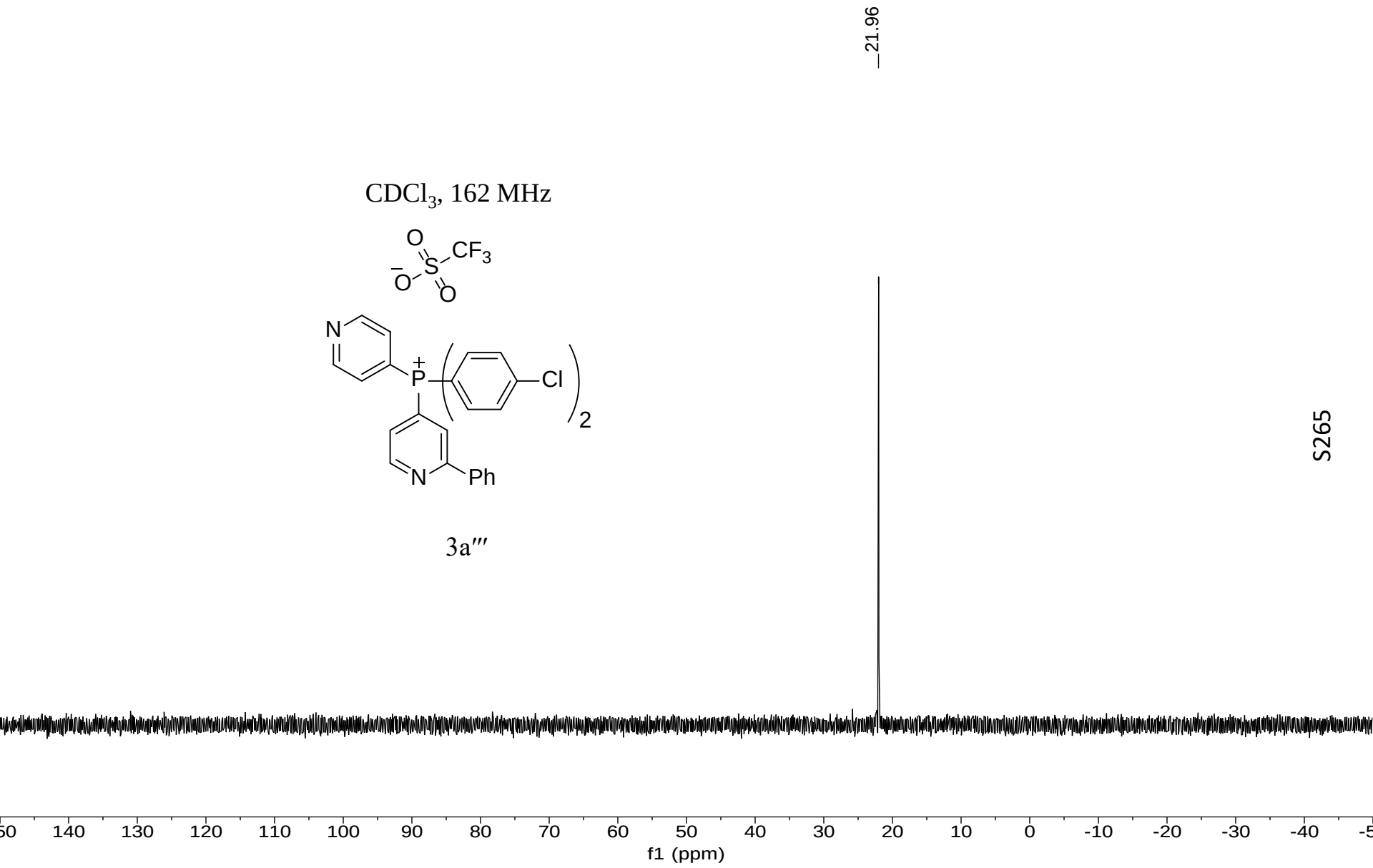

-78.29
CDCl3, 365 MHz
O
CF3
S
O
O
N
P
Me
2
N
Ph
3a″
S260
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)

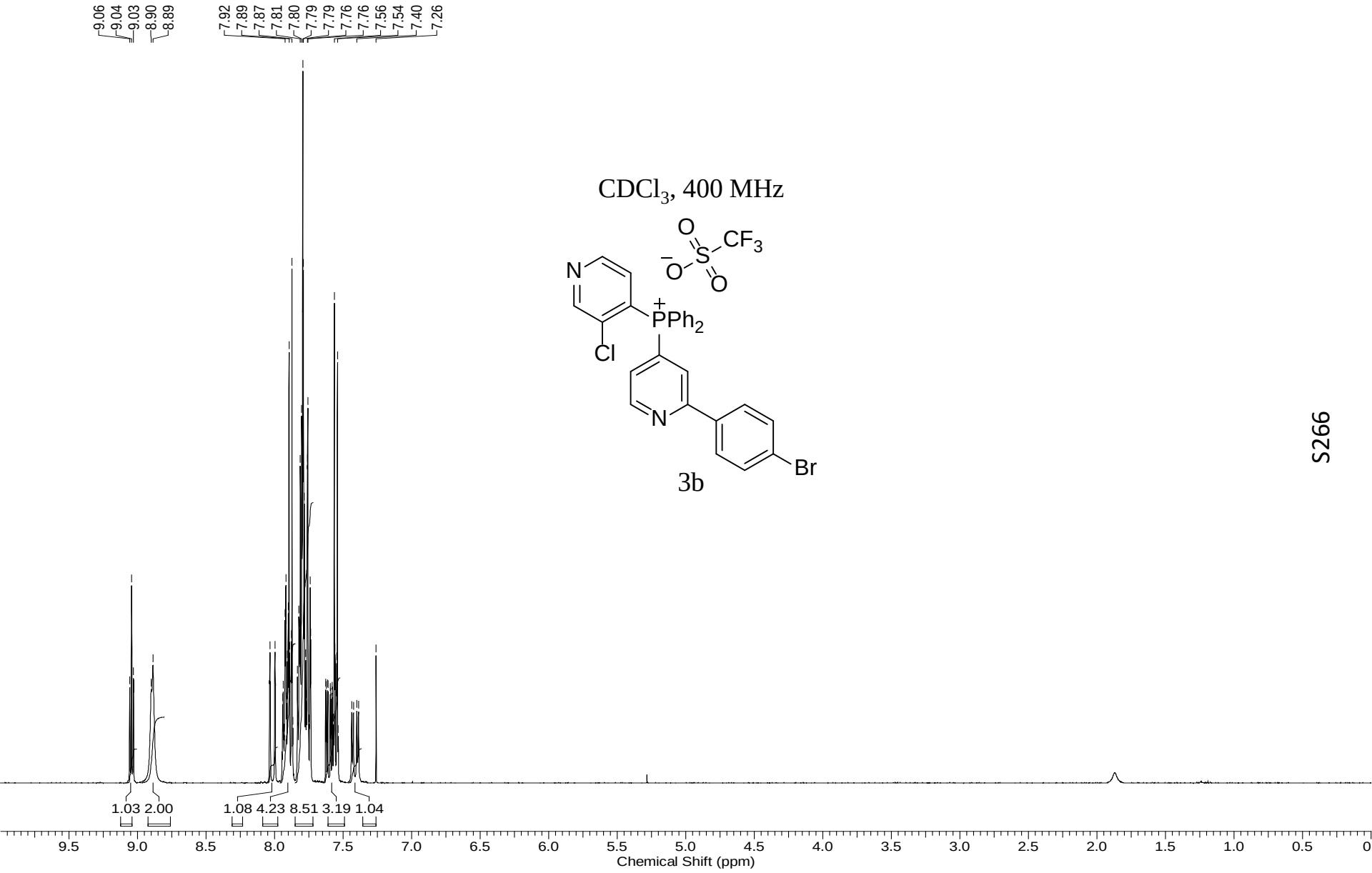

21.61
CDCl3, 162 MHz
O
CF3
S
O
O
N
P
Me
2
N
Ph
3a″
S261
f1 (ppm)

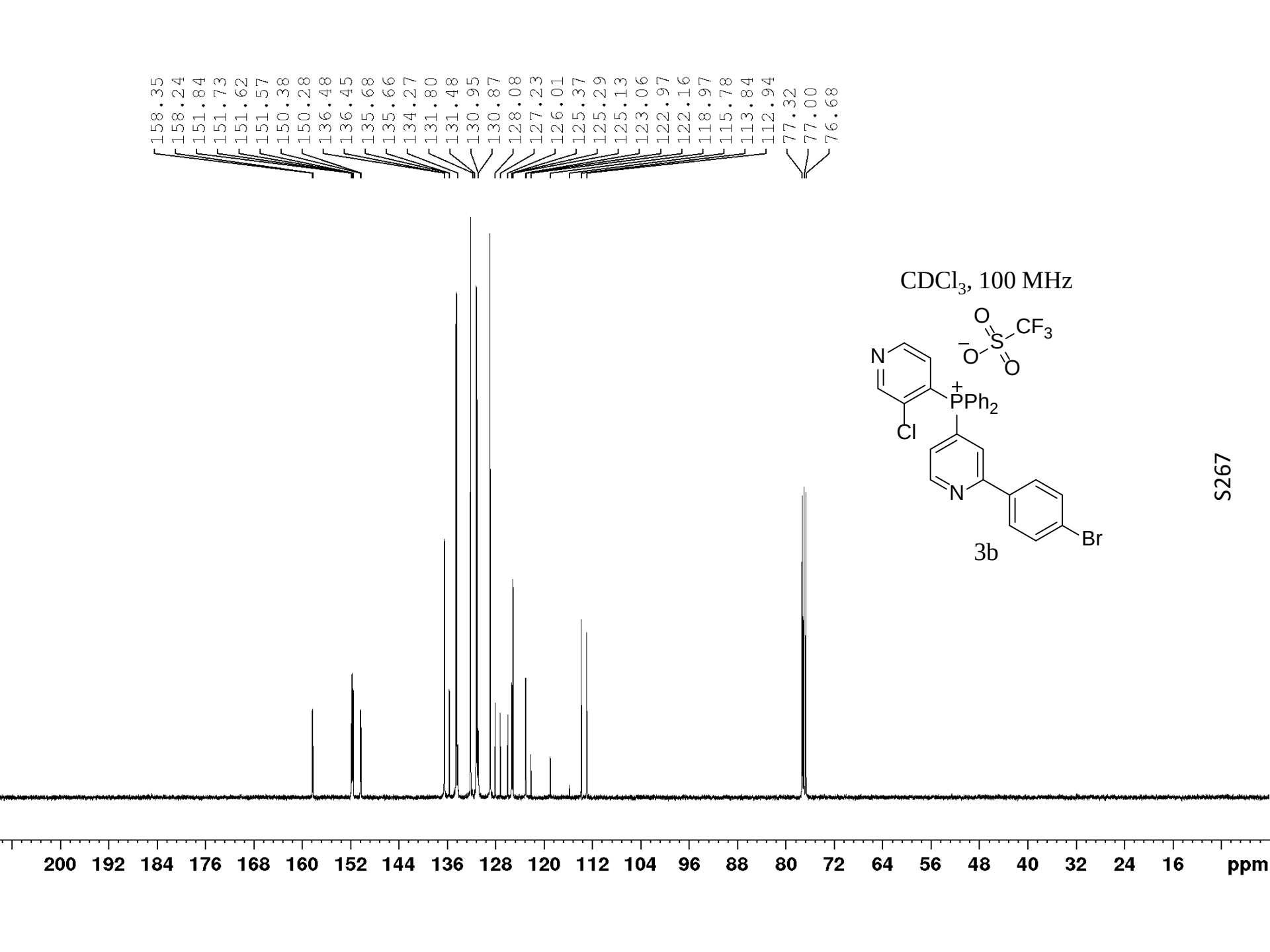

9.12
9.11
9.10
7.96
7.96
7.95
7.95
7.94
7.90
7.86
7.86
7.86
7.83
7.82
7.82
7.81
7.81
7.80
7.79
7.78
7.77
7.77
7.76
7.75
7.75
7.74
7.74
7.73
7.72
7.71
7.71
7.70
7.68
7.67
7.56
7.56
7.55
7.55
7.53
7.52
7.52
7.51
7.51
7.50
7.49
7.49
7.26
CDCl3, 400 MHz
O
CF3
S
O
O
N
P
Cl
2
N
Ph
3a‴
S262
2.794
1.979
1.159
10.000
4.185
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

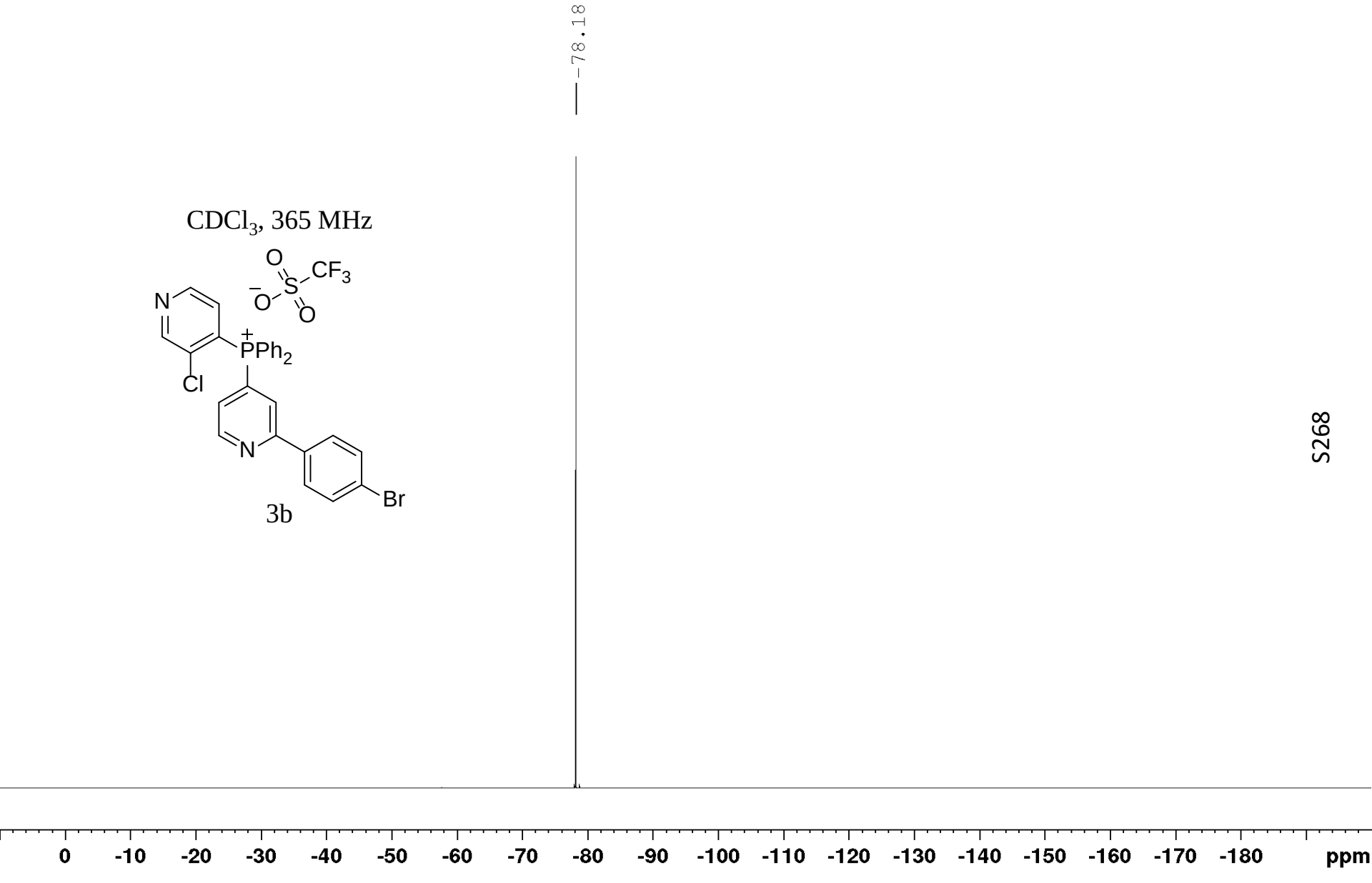

159.76
159.65
152.10
152.05
151.99
151.95
144.32
144.28
136.67
136.66
136.15
136.03
132.07
131.95
131.87
131.72
130.74
129.50
129.37
129.20
127.51
127.45
127.33
126.66
126.63
125.78
125.31
125.22
123.31
123.22
112.68
111.76
77.32
77.00
76.68
CDCl3, 100 MHz
O
CF3
S
O
O
N
P
Cl
2
N
Ph
3a'''
S263
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

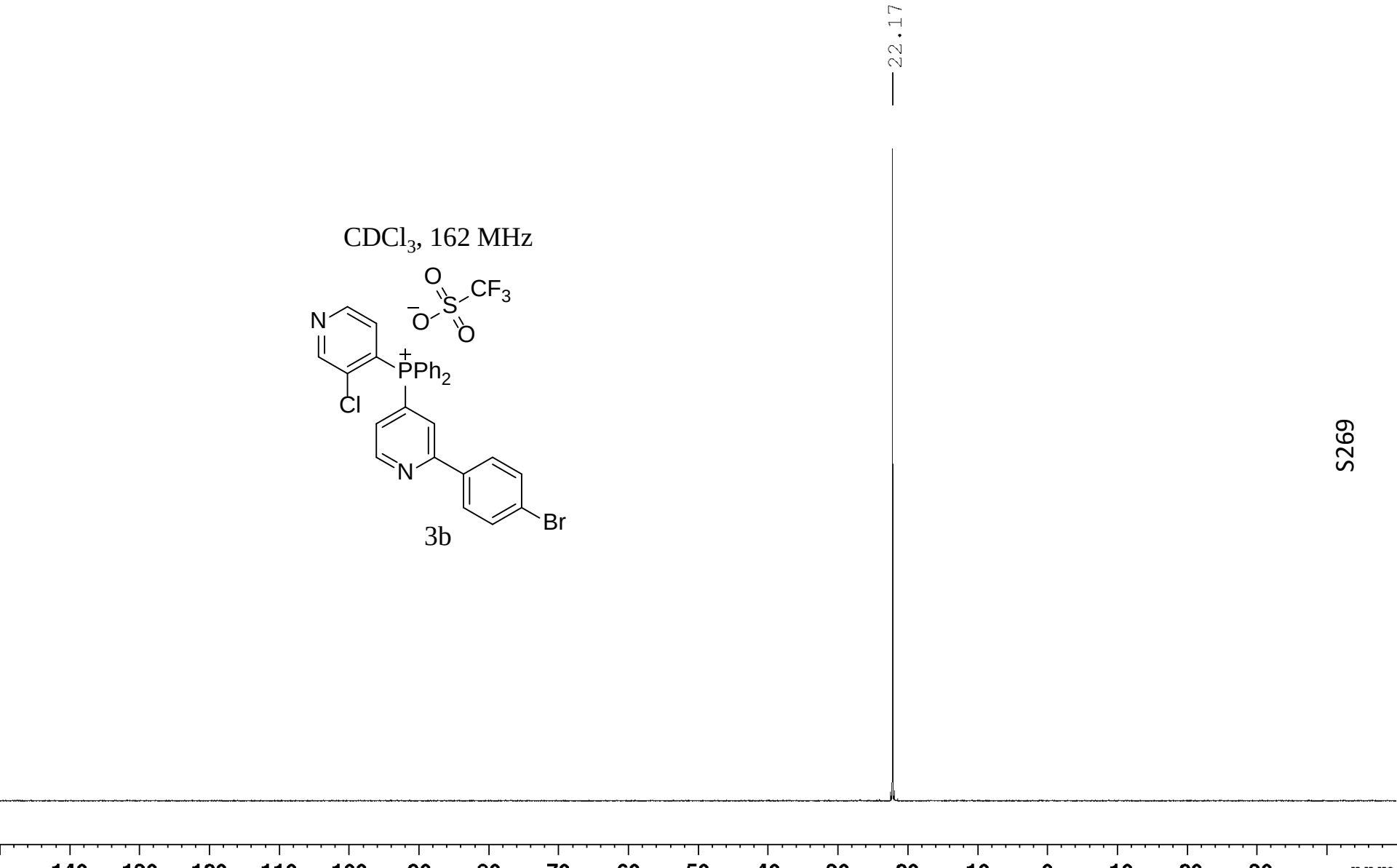

-78.40
CDCl3, 365 MHz
O
CF3
O
S
O
N
P
Cl
2
N
Ph
3a‴
S264
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)

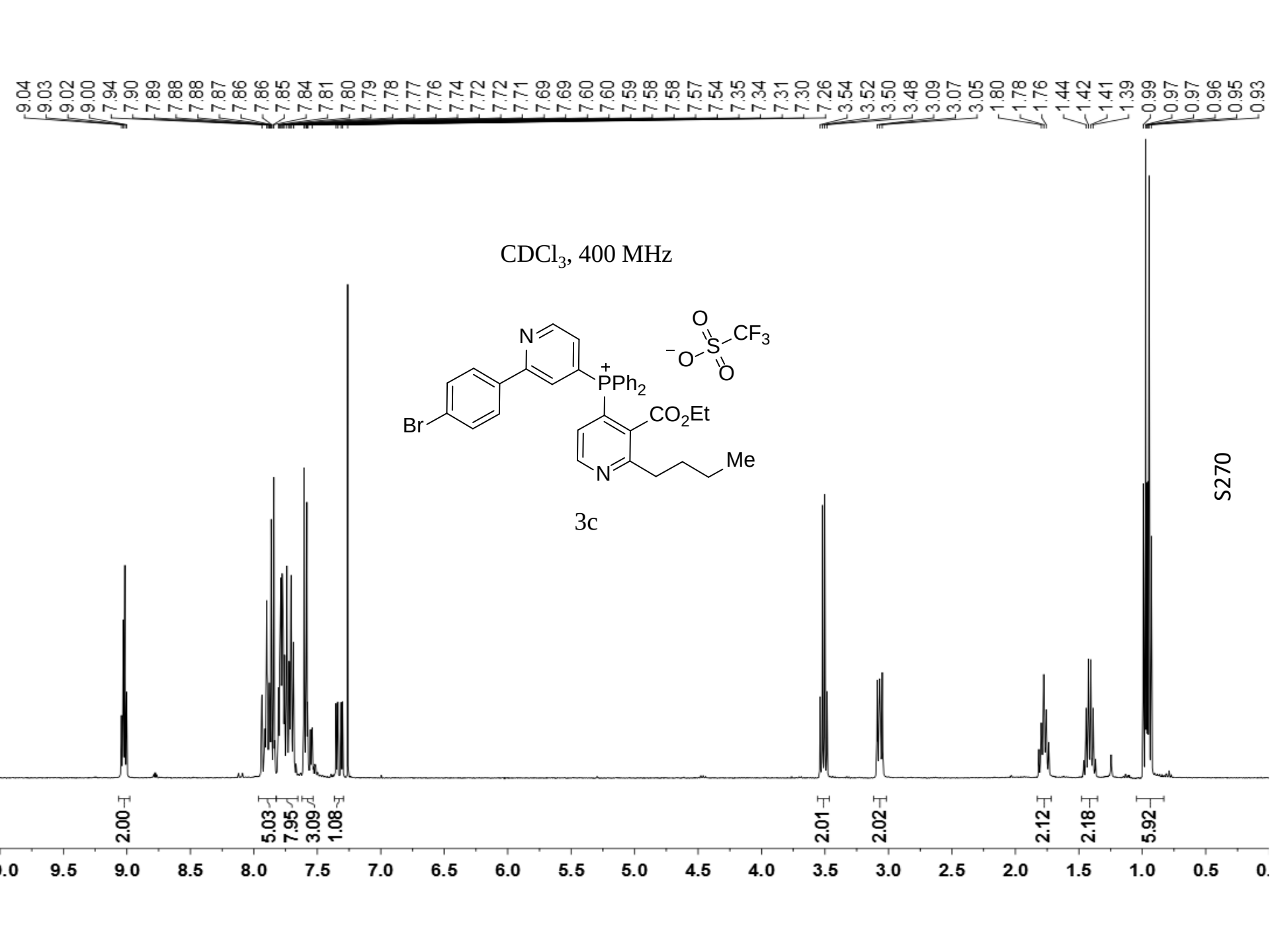

21.96
CDCl3, 162 MHz
O
CF3
S
O
O
N
P
Cl
2
N
Ph
3a‴
S265
f1 (ppm)

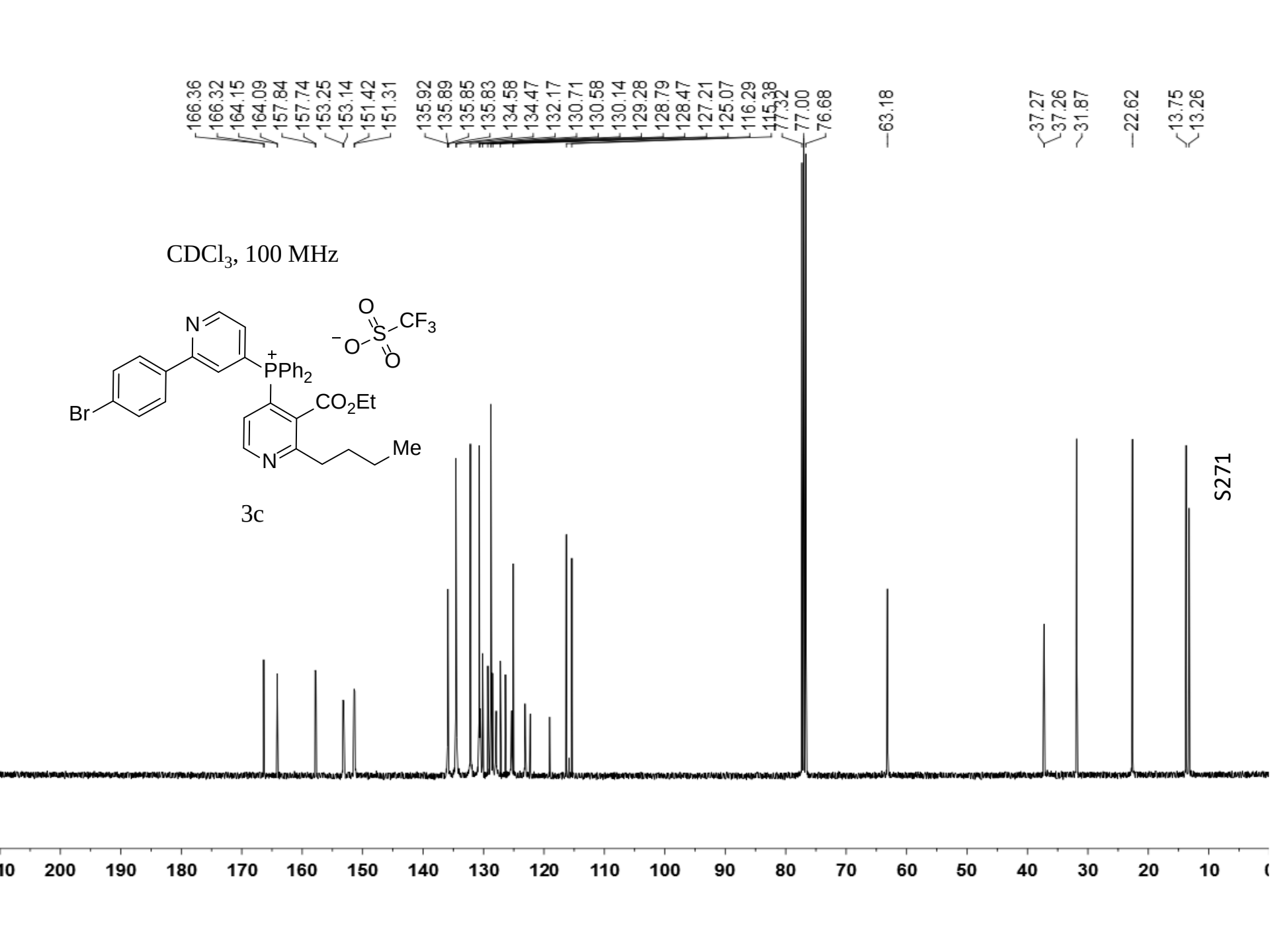

9.06
9.04
9.03
8.90
8.89
7.92
7.89
7.87
7.81
7.80
7.79
7.79
7.76
7.76
7.56
7.54
7.40
7.26
CDCl3, 400 MHz
O
CF3
S
O
O
N
PPh2
Cl
N
Br
3b
1.03 2.00
1.08 4.23 8.51 3.19 1.04
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)


158.35
158.24
151.84
151.73
151.62
151.57
150.38
150.28
136.48
136.45
135.68
135.66
134.27
131.80
131.48
130.95
130.87
128.08
127.23
126.01
125.37
125.29
125.13
123.06
122.97
122.16
118.97
115.78
113.84
112.94
77.32
77.00
76.68
CDCl3, 100 MHz
O
S
CF3
O
O
N
PPh2
Cl
N
Br
3b
S267
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

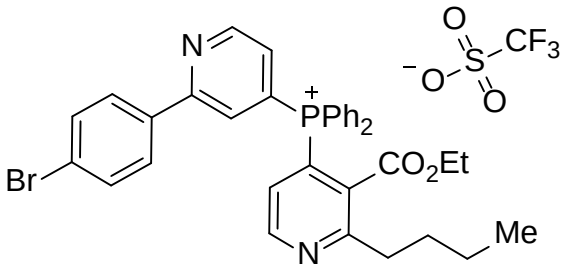

-78.18
CDCl3, 365 MHz
O
S
CF3
O
O
N
PPh2
Cl
N
Br
3b
S268
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
ppm


22.17
CDCl3, 162 MHz
O
CF3
S
O
O
N
PPh2
Cl
N
Br
3b
S269
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
ppm

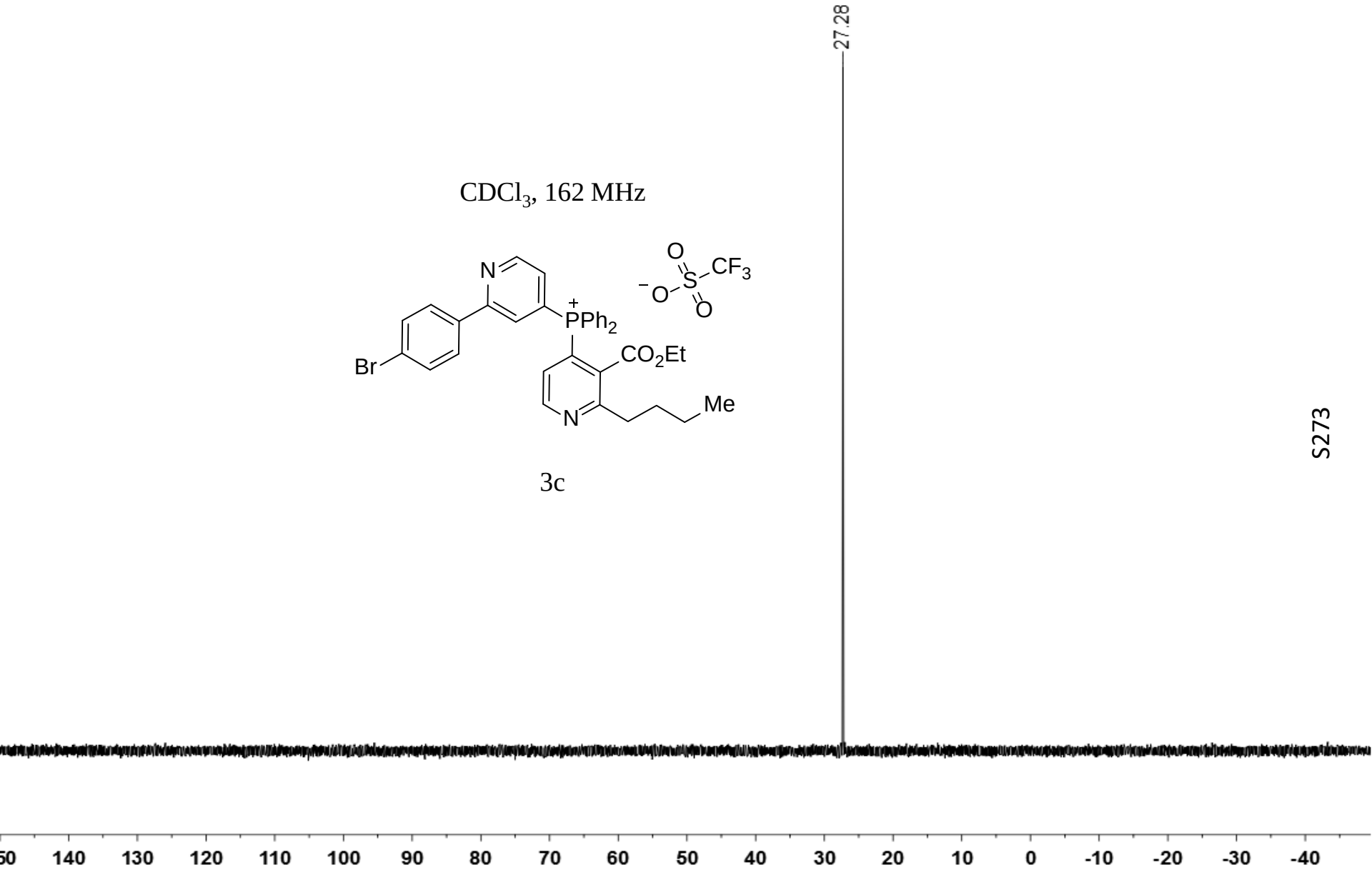

9.04 9.03 9.02 9.00 7.94 7.90 7.89 7.88 7.88 7.87 7.86 7.86 7.85 7.84 7.81 7.80 7.79 7.78 7.77 7.76 7.74 7.72 7.72 7.71 7.69 7.69 7.60 7.60 7.59 7.58 7.58 7.57 7.54 7.35 7.34 7.31 7.30 7.26 3.54 3.52 3.50 3.48 3.09 3.07 3.05 1.80 1.78 1.76 1.44 1.42 1.41 1.39 0.99 0.97 0.97 0.96 0.95 0.93
CDCl3, 400 MHz
N
PPh2
Br
CO2Et
Me
N
O
S
CF3
O
O
3c
S270
2.00
5.03
7.95
3.09
1.08
2.01
2.02
2.12
2.18
5.92
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

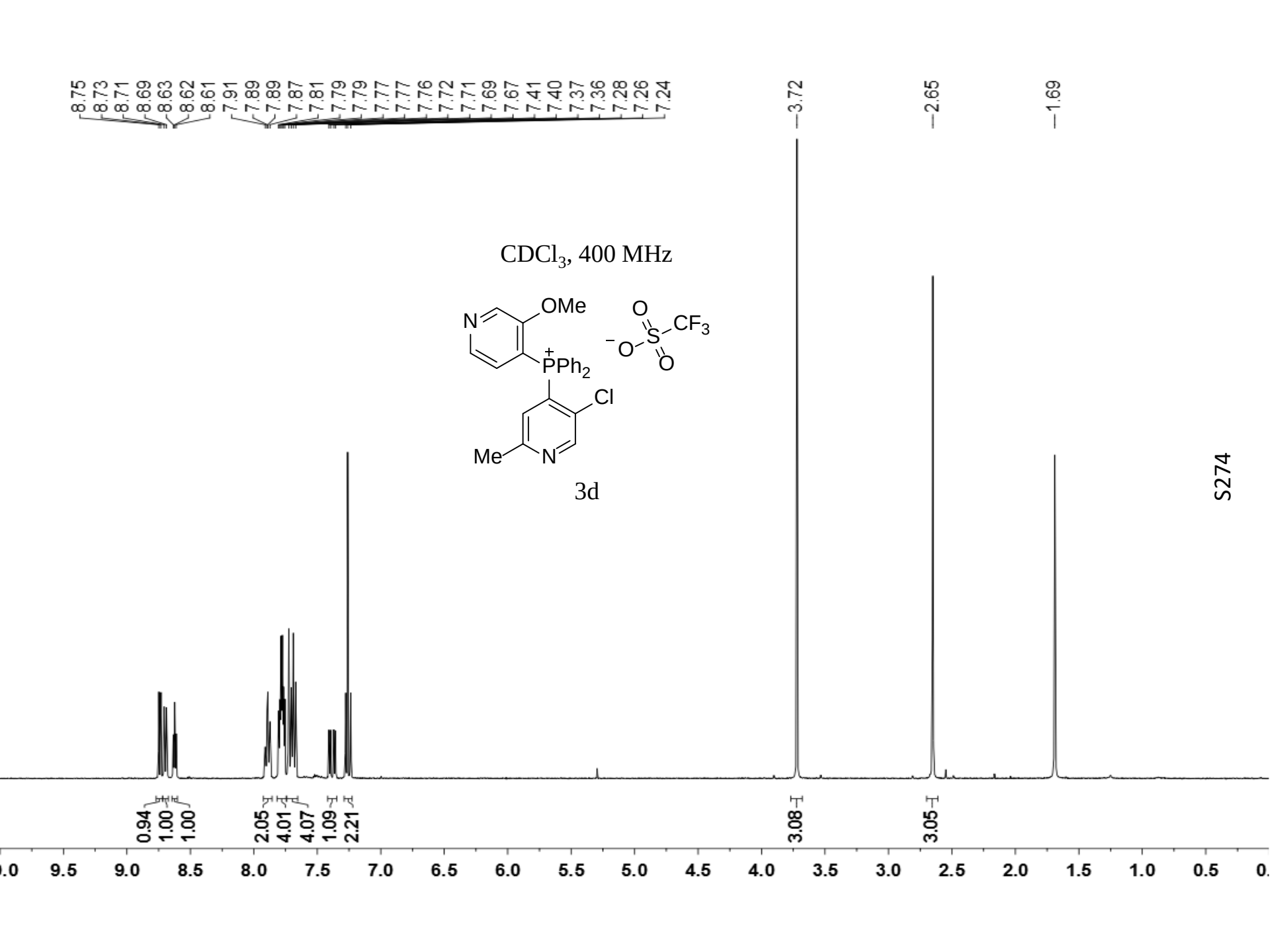

166.36
166.32
164.15
164.09
157.84
157.74
153.25
153.14
151.42
151.31
135.92
135.89
135.85
135.83
134.58
134.47
132.17
130.71
130.58
130.14
129.28
128.79
128.47
127.21
125.07
116.29
115.38
77.32
77.00
76.68
63.18
37.27
37.26
31.87
22.62
13.75
13.26
CDCl3, 100 MHz
N
O
S
CF3
O
O
PPh2
Br
CO2Et
N
Me
3c
S271
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

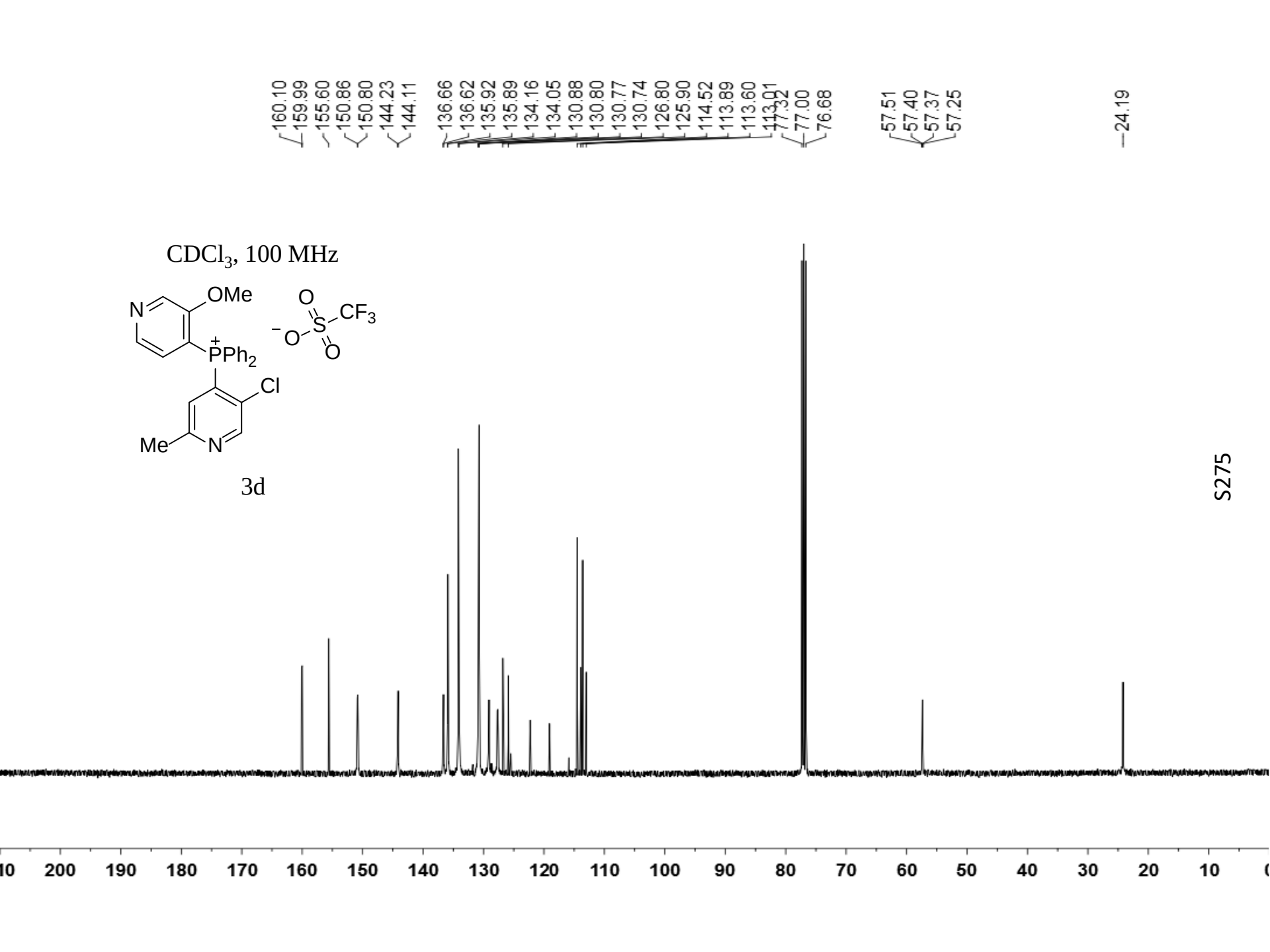
$CDCl_3$, 365 MHz

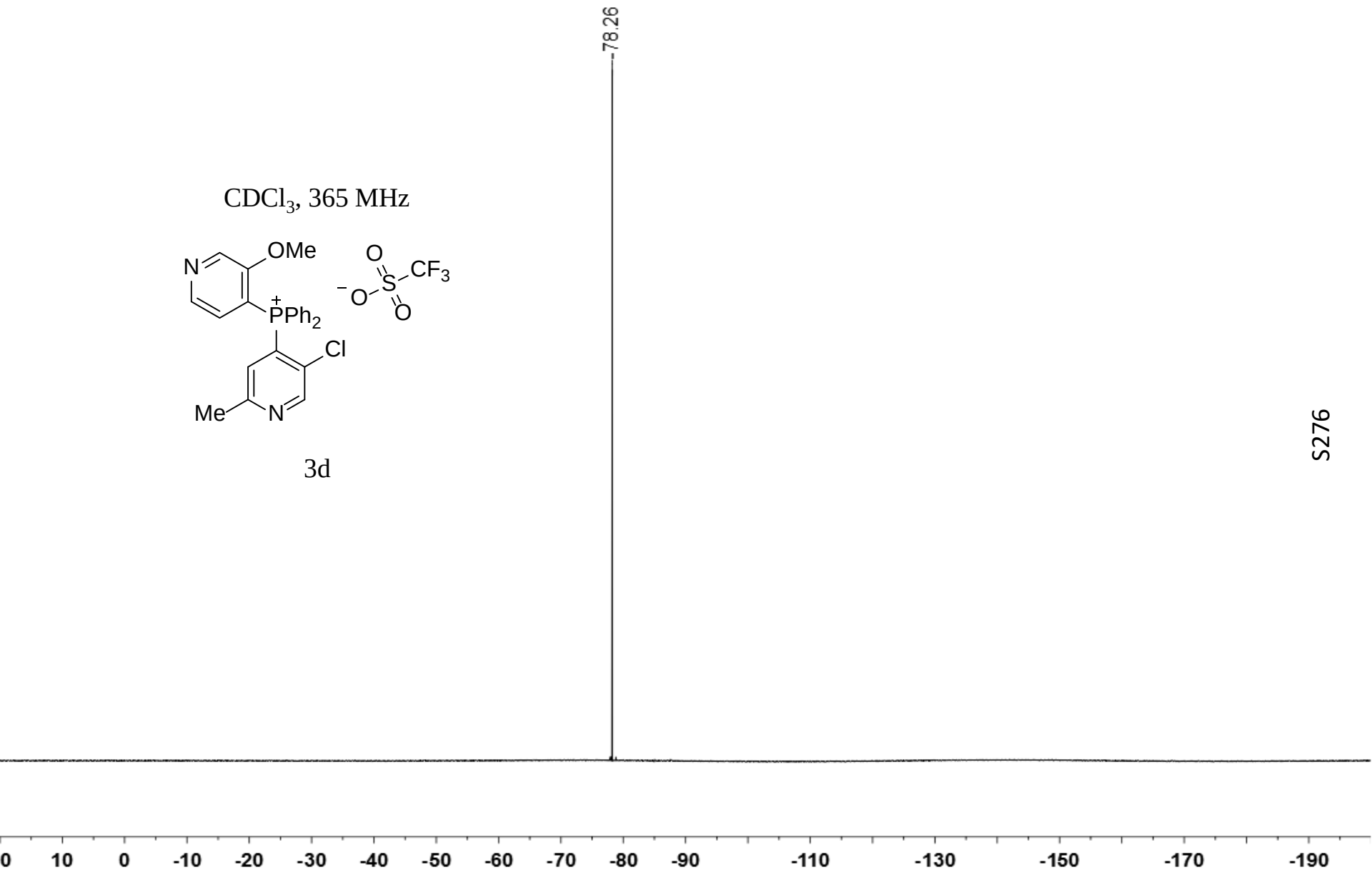


3c


27.28
CDCl3, 162 MHz
N
PPh2
O
S
CF3
O
O
Br
CO2Et
Me
N
3c
S273
50
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40

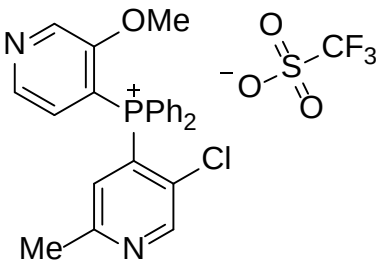

8.75
8.73
8.71
8.69
8.63
8.62
8.61
7.91
7.89
7.89
7.87
7.81
7.79
7.79
7.77
7.77
7.76
7.72
7.71
7.69
7.67
7.41
7.40
7.37
7.36
7.28
7.26
7.24
3.72
2.65
1.69
CDCl3, 400 MHz
OMe
N
PPh2
Cl
Me
N
O
S
CF3
O
O
O
3d
S274
0.94
1.00
1.00
2.05
4.01
4.07
1.09
2.21
3.08
3.05
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5


160.10
159.99
155.60
150.86
150.80
144.23
144.11
136.66
136.62
135.92
135.89
134.16
134.05
130.88
130.80
130.77
130.74
126.80
125.90
114.52
113.89
113.60
113.01
77.32
77.00
76.68
57.51
57.40
57.37
57.25
24.19
CDCl3, 100 MHz
OMe
N
PPh2
Cl
Me
N
O
CF3
O
S
O
O
3d
S275
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

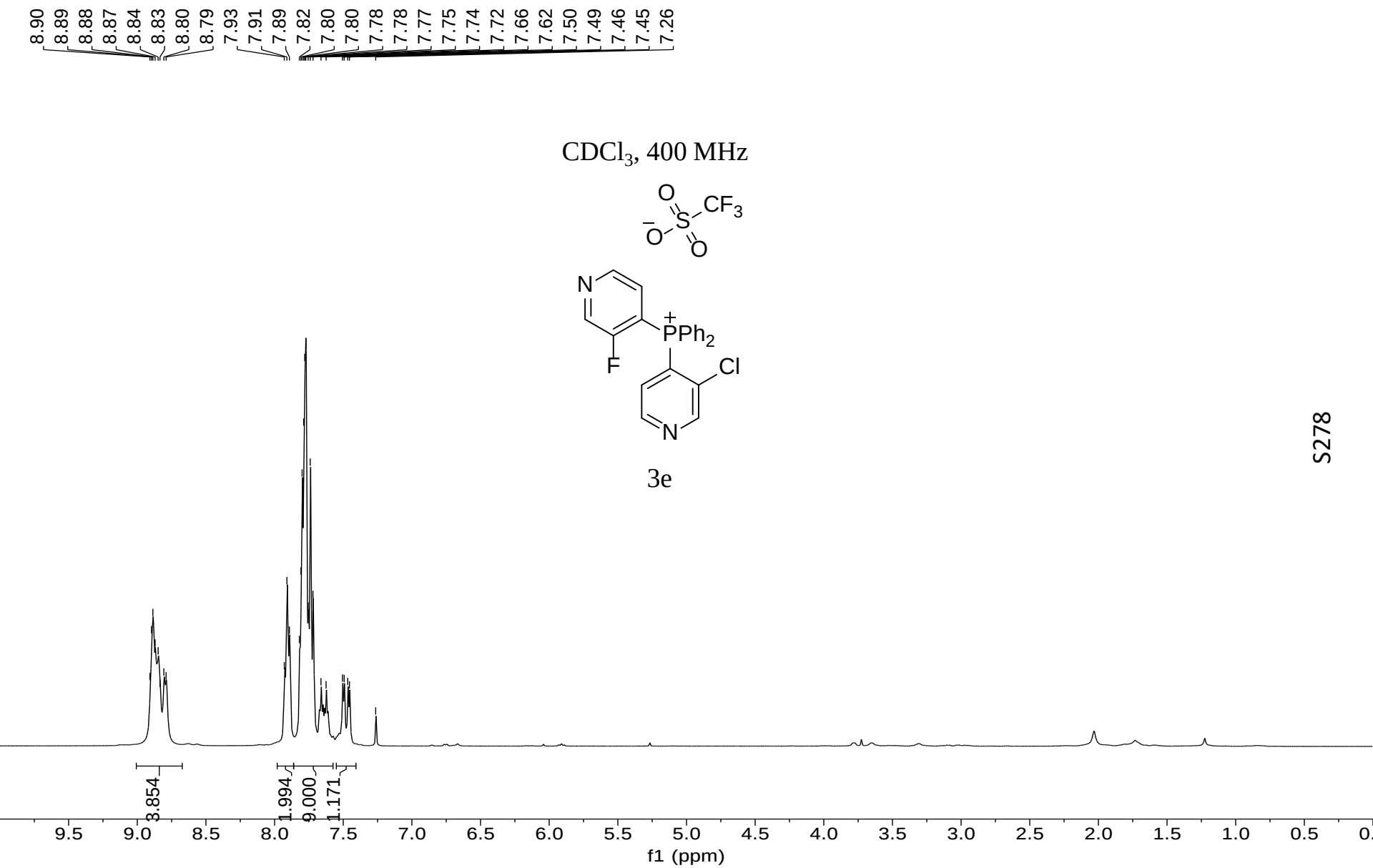

-78.26
CDCl3, 365 MHz
OMe
N
PPh2
Cl
Me
N
O
S
CF3
O
O
O
3d
S276
0
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-110
-130
-150
-170
-190

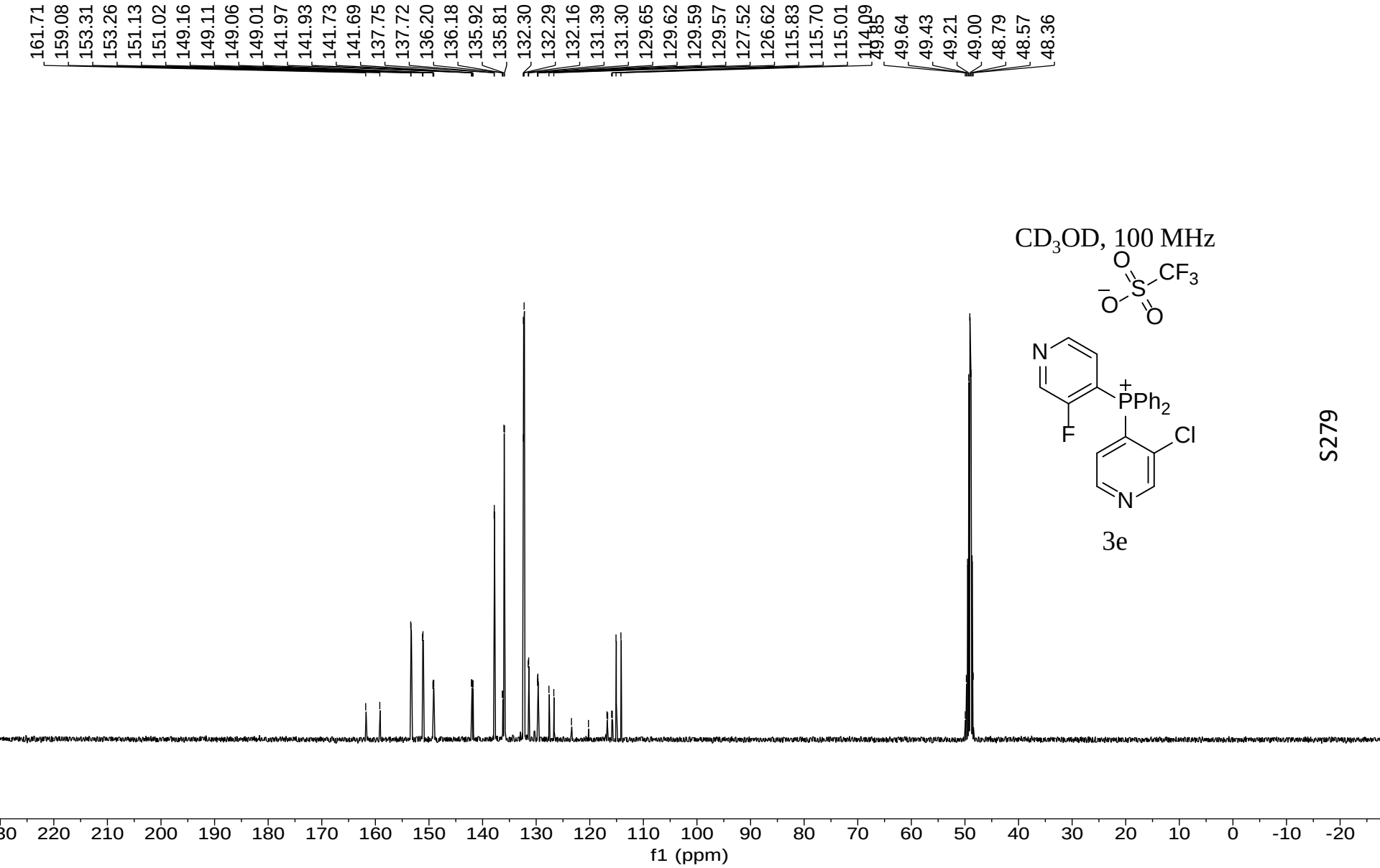
21.15

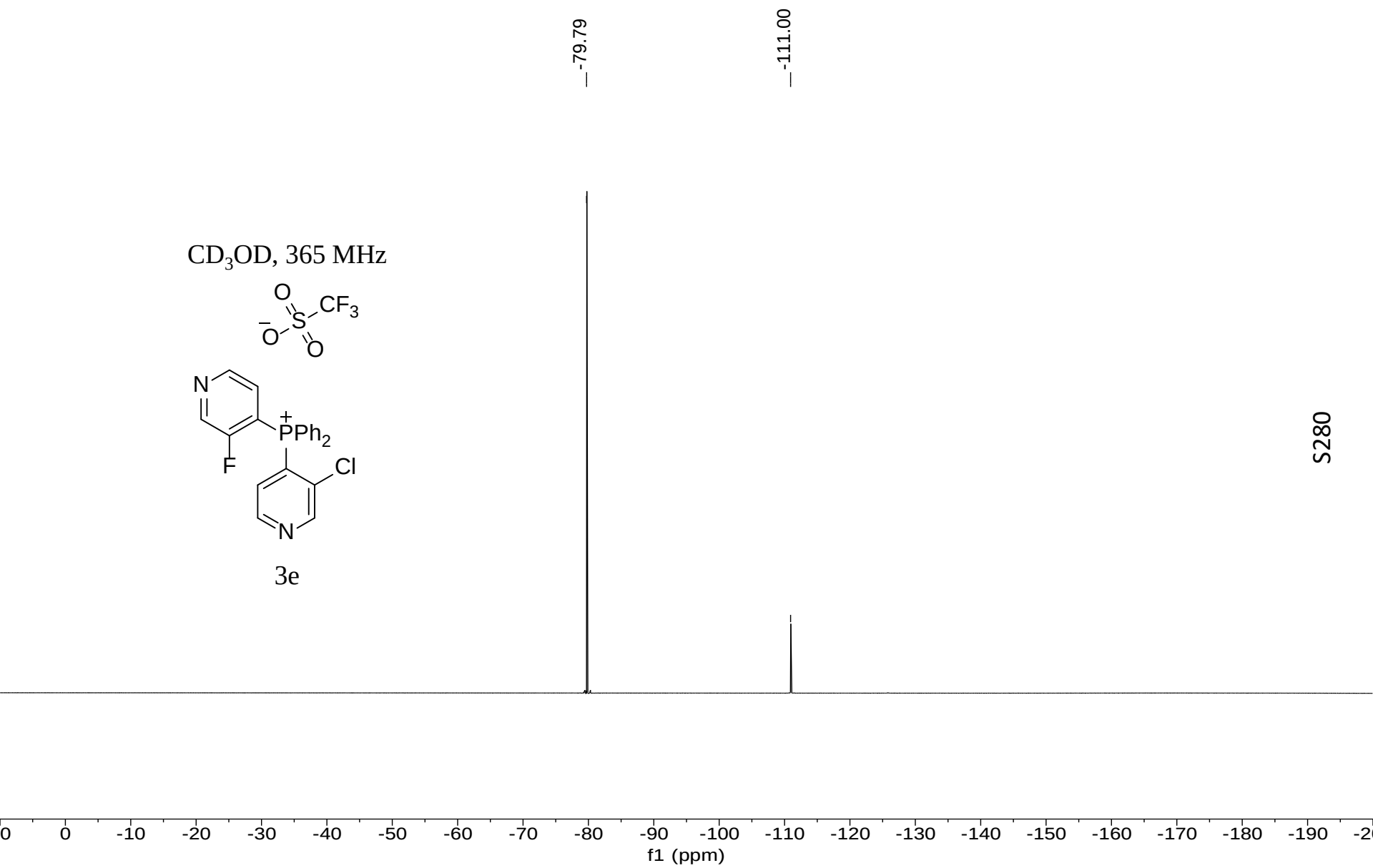
$CDCl_3$, 162 MHz



3d

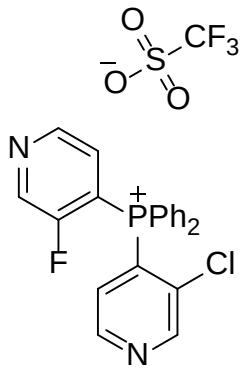

8.90
8.89
8.88
8.87
8.84
8.83
8.80
8.79
7.93
7.91
7.89
7.82
7.80
7.80
7.78
7.78
7.77
7.75
7.74
7.72
7.66
7.62
7.50
7.49
7.46
7.45
7.26
CDCl3, 400 MHz
O
CF3
S
O
O
N
PPh2
F
Cl
N
3e
3.854
1.994
9.000
1.171
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


161.71
159.08
153.31
153.26
151.13
151.02
149.16
149.11
149.06
149.01
141.97
141.93
141.73
141.69
137.75
137.72
136.20
136.18
135.92
135.81
132.30
132.29
132.16
131.39
131.30
129.65
129.62
129.59
129.57
127.52
126.62
115.83
115.70
115.01
114.09
49.85
49.64
49.43
49.21
49.00
48.79
48.57
48.36
CD3OD, 100 MHz
O
CF3
S
O
O
N
PPh2
F
Cl
N
3e
S279
f1 (ppm)


-79.79
-111.00
CD3OD, 365 MHz
O
S
CF3
O
O
N
PPh2
F
Cl
N
3e
S280
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)

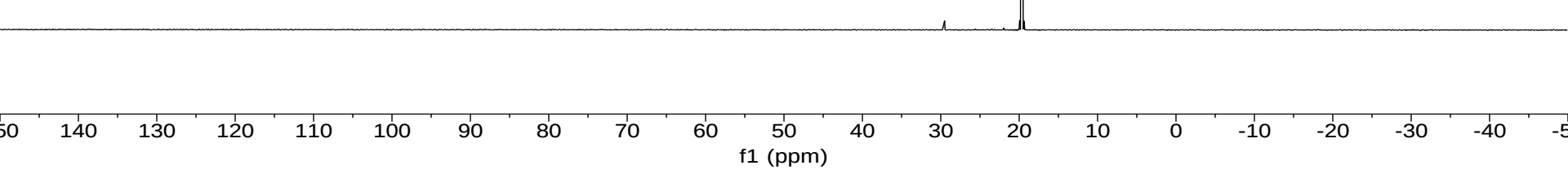
19.63
19.61

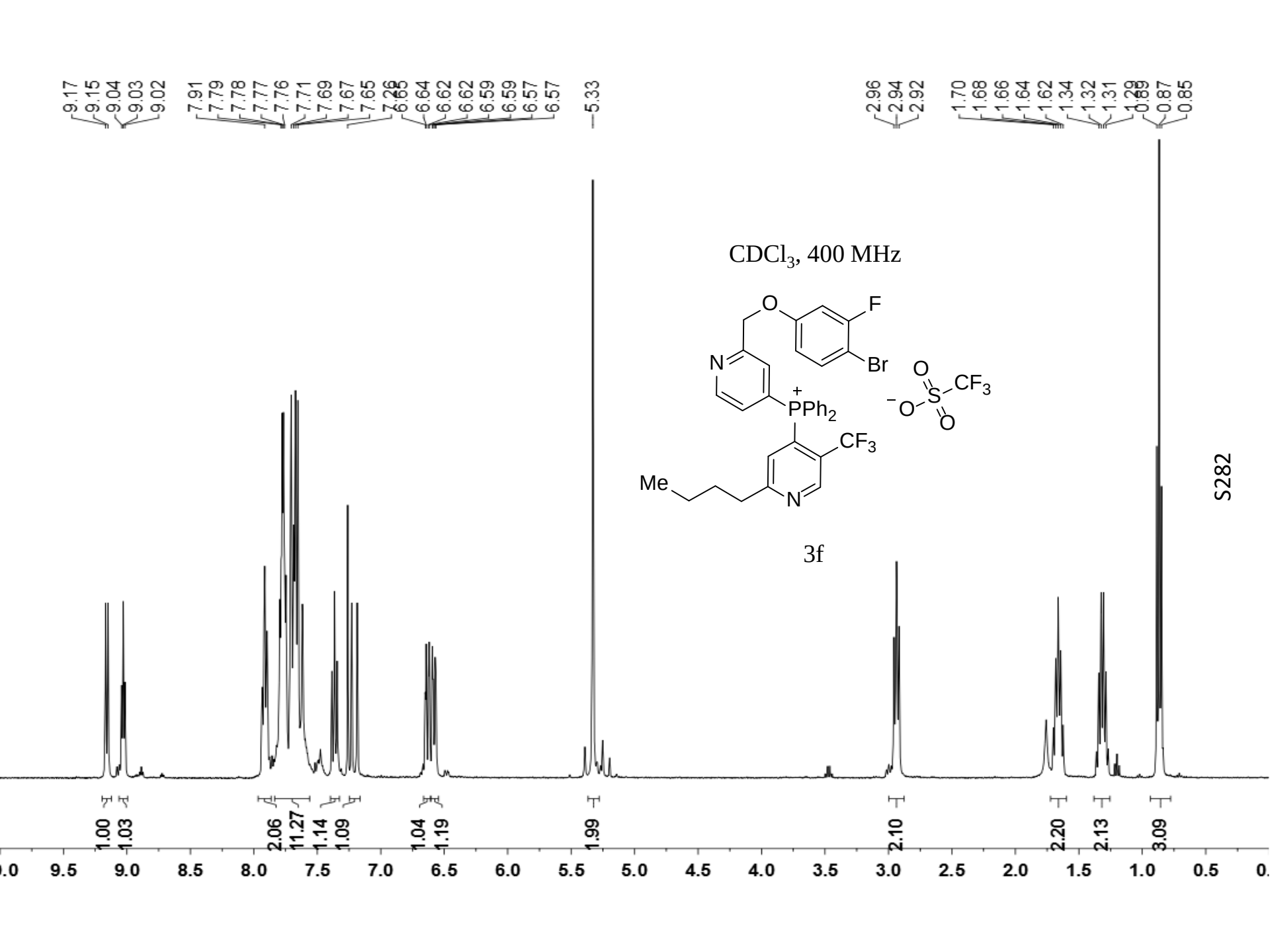
CD_3OD, 162 MHz

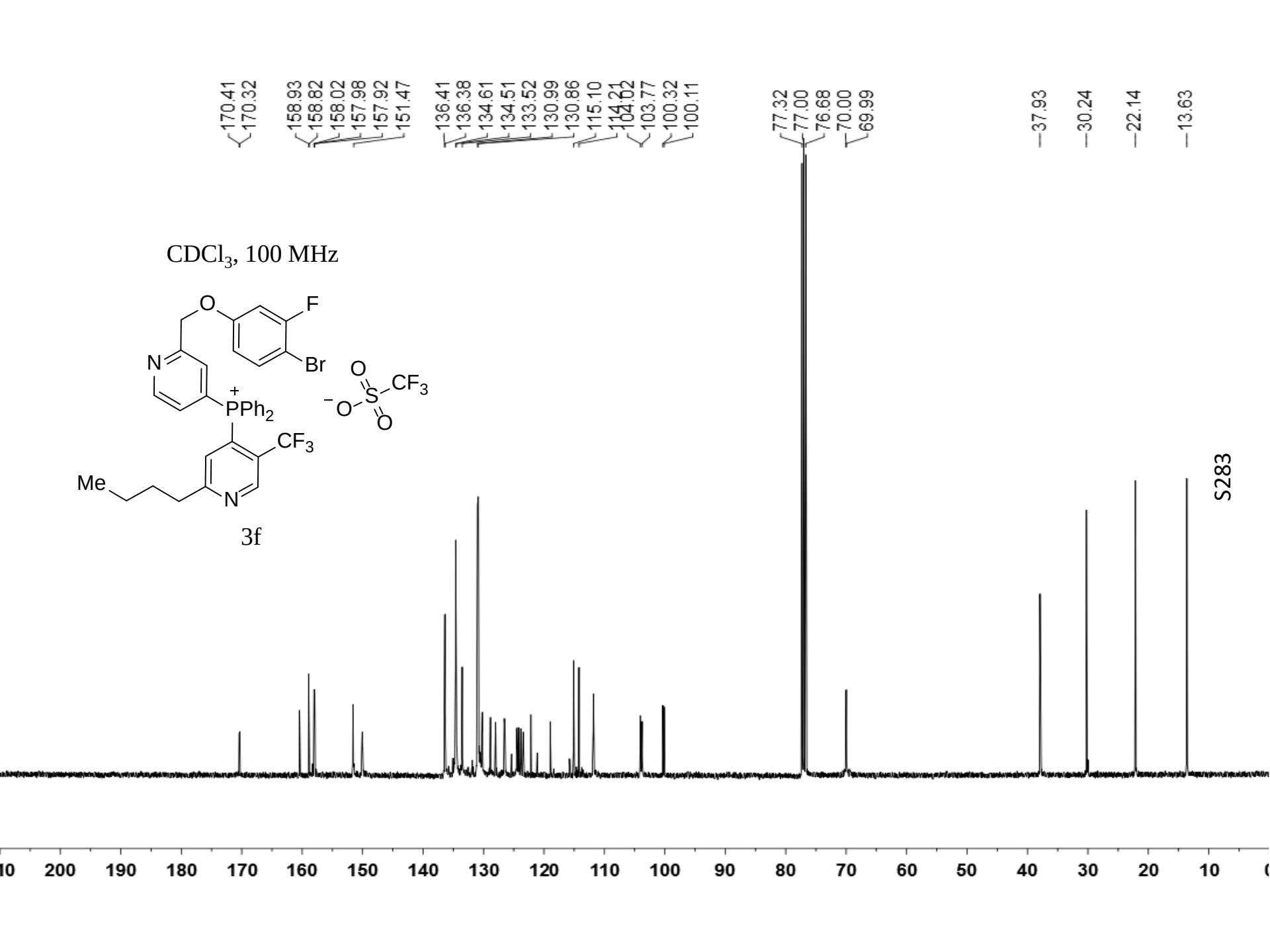


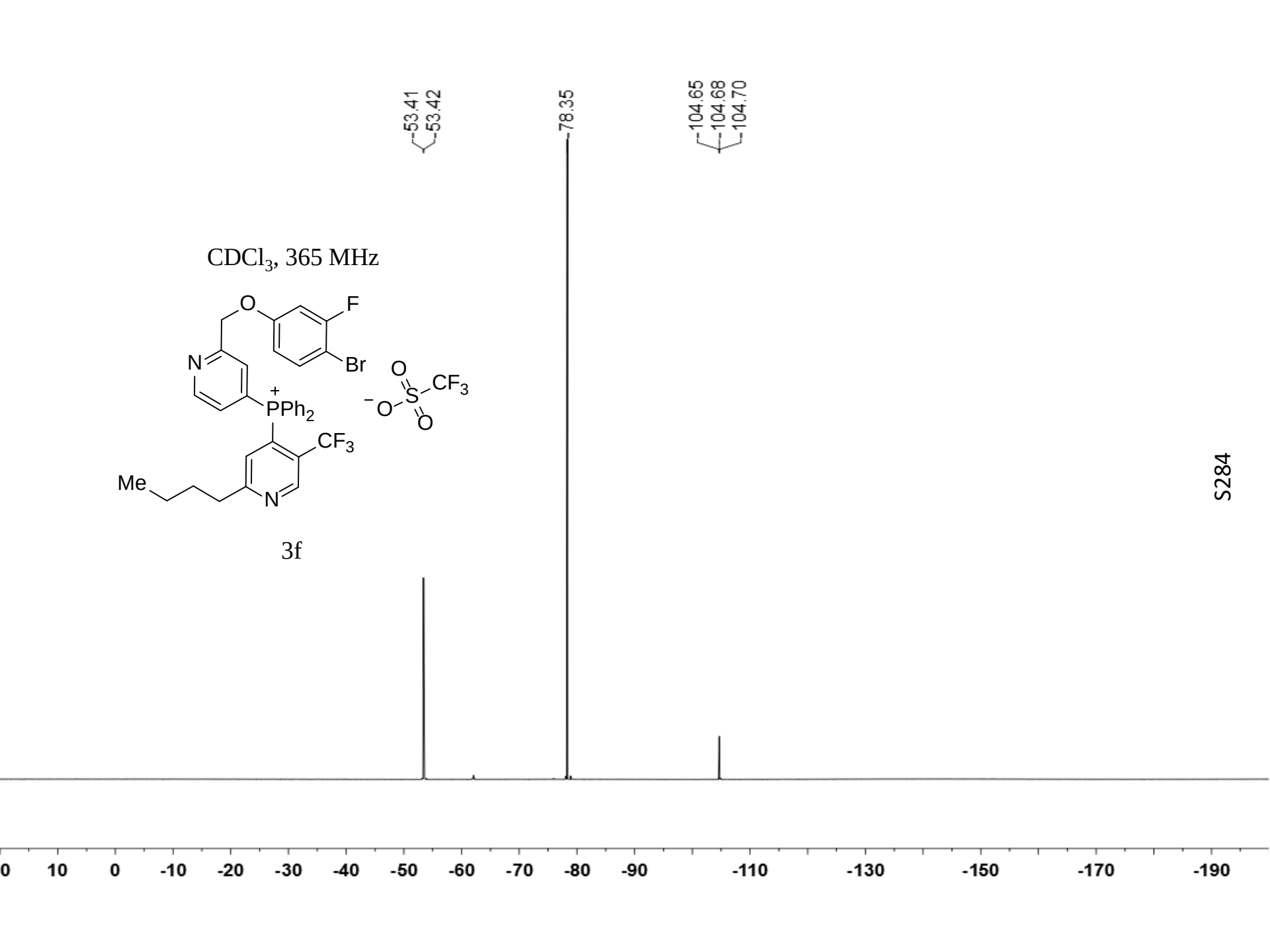
3e

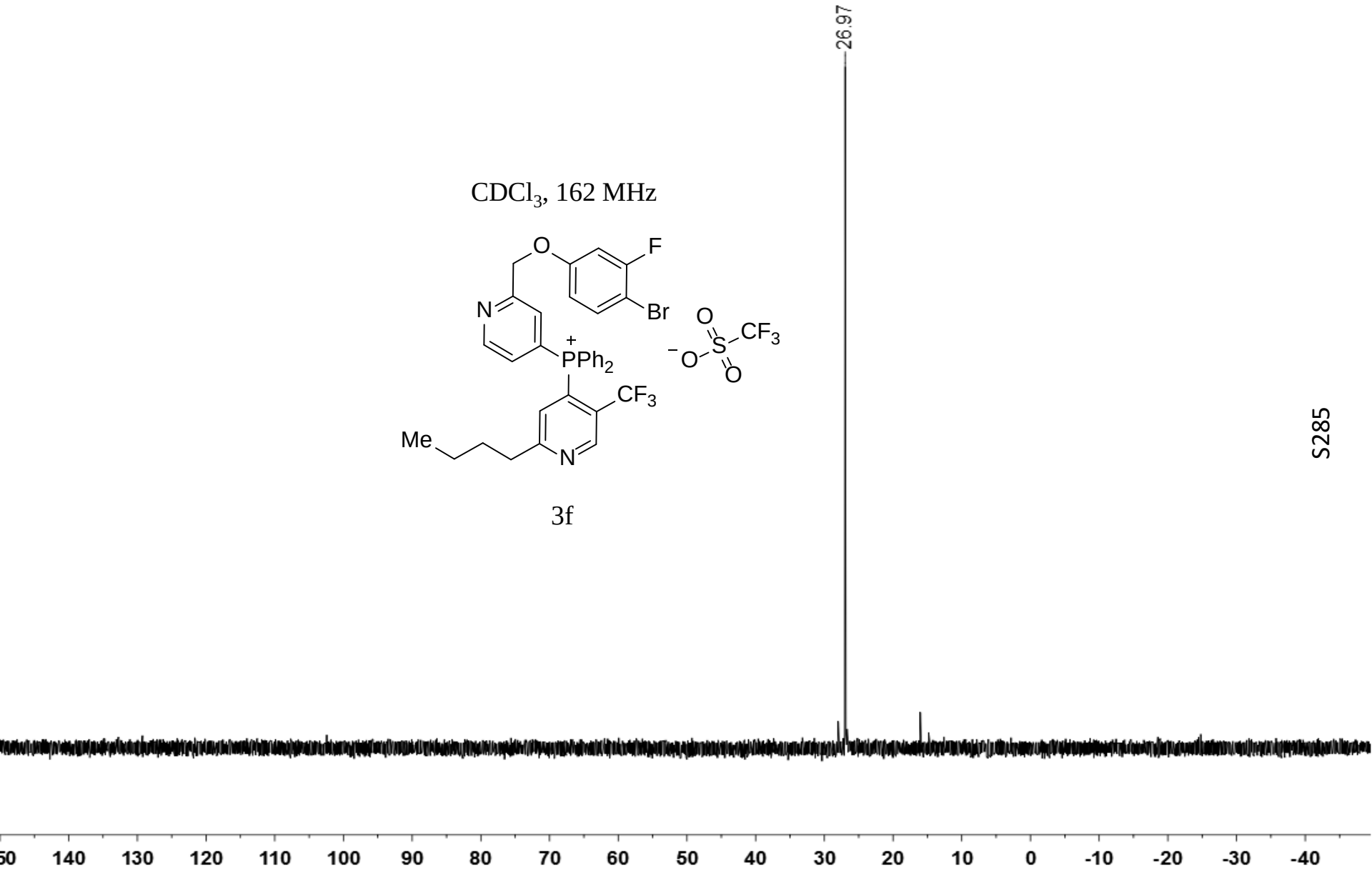
S281



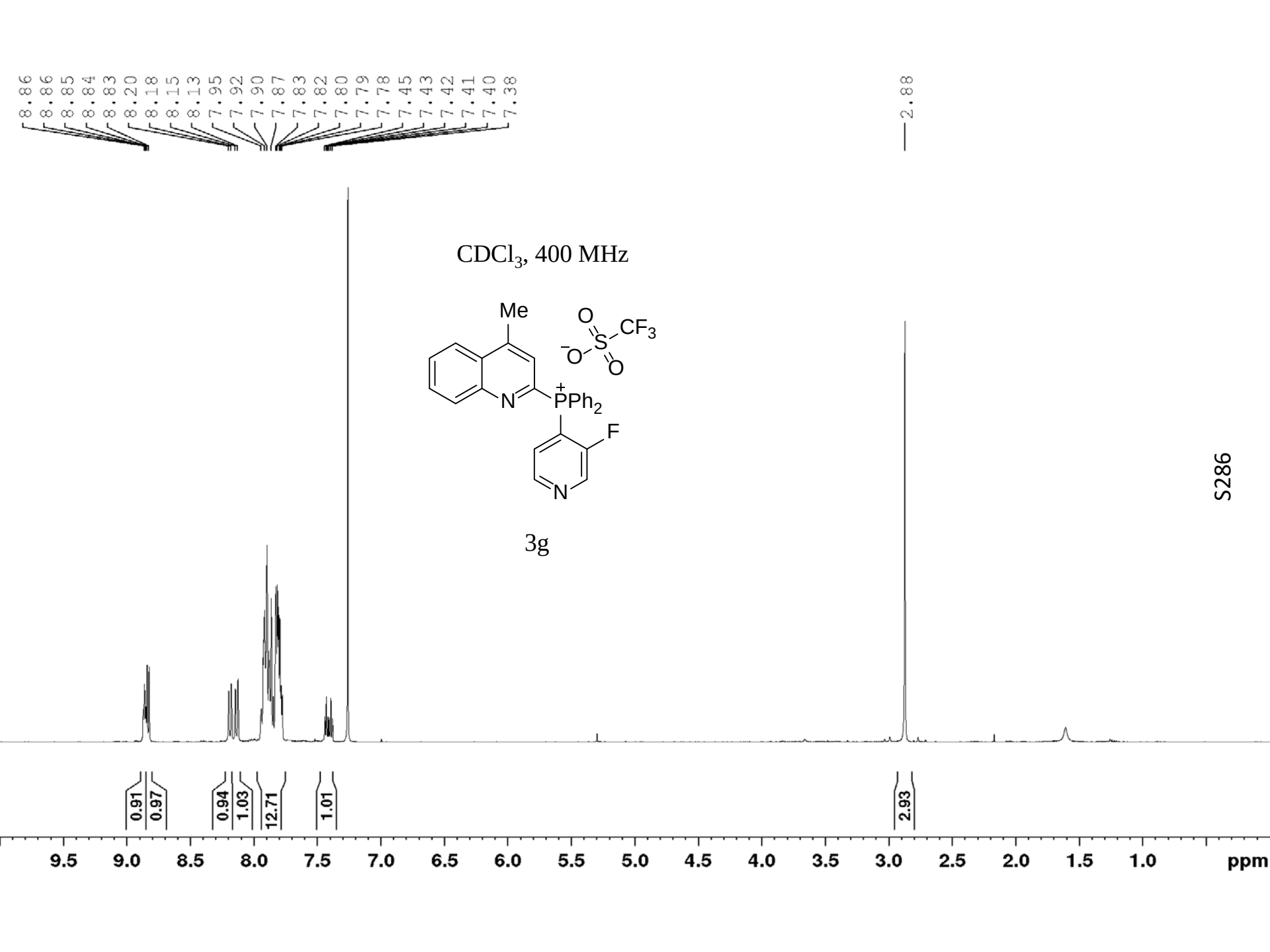

9.17
9.15
9.04
9.03
9.02
7.91
7.79
7.78
7.77
7.76
7.71
7.69
7.67
7.65
6.64
6.62
6.62
6.59
6.59
6.57
6.57
5.33
2.96
2.94
2.92
1.70
1.68
1.66
1.64
1.62
1.34
1.32
1.31
0.89
0.87
0.85
CDCl3, 400 MHz
O
F
Br
N
PPh2
CF3
Me
N
O
S
CF3
O
O
3f
S282
1.00
1.03
2.06
11.27
1.14
1.09
1.04
1.19
1.99
2.10
2.20
2.13
3.09
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5


170.41
170.32
158.93
158.82
158.02
157.98
157.92
151.47
136.41
136.38
134.61
134.51
133.52
130.99
130.86
115.10
114.21
104.02
103.77
100.32
100.11
77.32
77.00
76.68
70.00
69.99
37.93
30.24
22.14
13.63
CDCl3, 100 MHz
O
F
N
Br
O
CF3
S
O
O
PPh2
CF3
Me
N
3f
S283
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10


-53.41
-53.42
-78.35
-104.65
-104.68
-104.70
CDCl3, 365 MHz
O
F
N
Br
O
CF3
+
PPh2
O
S
CF3
Me
N
3f
S284
0
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-110
-130
-150
-170
-190


26.97
CDCl3, 162 MHz
O
F
N
Br
O
CF3
+
PPh2
O
S
CF3
Me
N
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40

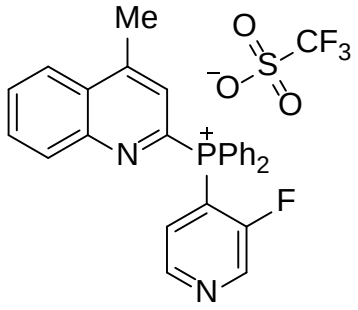
3f


8.86
8.86
8.85
8.84
8.83
8.20
8.18
8.15
8.13
7.95
7.92
7.90
7.87
7.83
7.82
7.80
7.79
7.78
7.45
7.43
7.42
7.41
7.40
7.38
2.88
CDCl3, 400 MHz
Me
O
S
CF3
O
O
N
PPh2
F
N
3g
S286
0.91
0.97
0.94
1.03
12.71
1.01
2.93
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

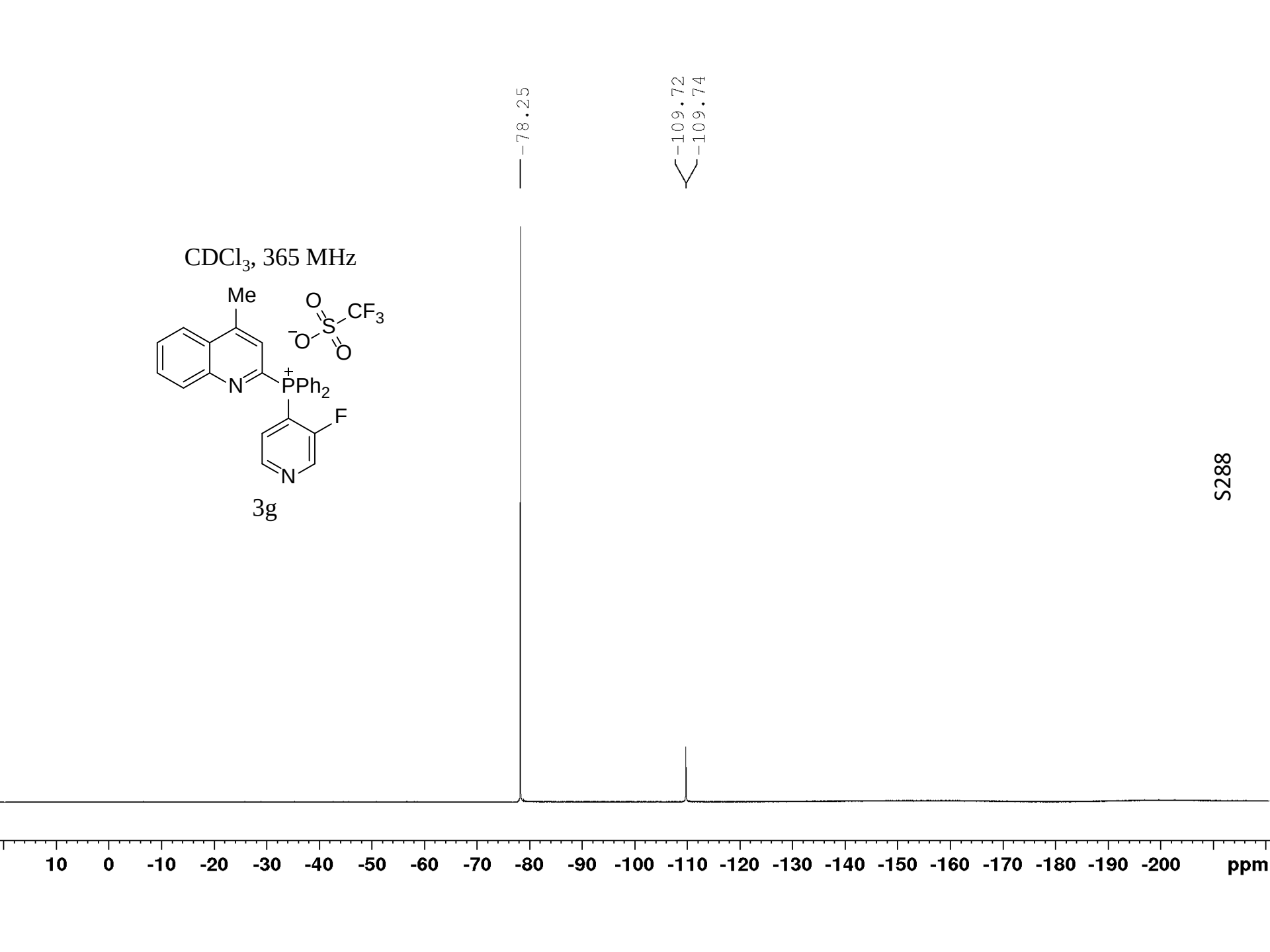
160.07
157.43
149.10
148.99
148.40
148.16
147.94
147.88
147.84
147.78
142.92
141.72
139.88
139.84
139.64
139.60
136.19
136.16
134.42
134.31
131.66
130.85
130.72
130.51
130.45
128.94
128.91
128.47
128.41
124.76
124.48
124.37
124.36
122.21
119.01
116.75
116.62
115.91
115.77
114.90
114.02

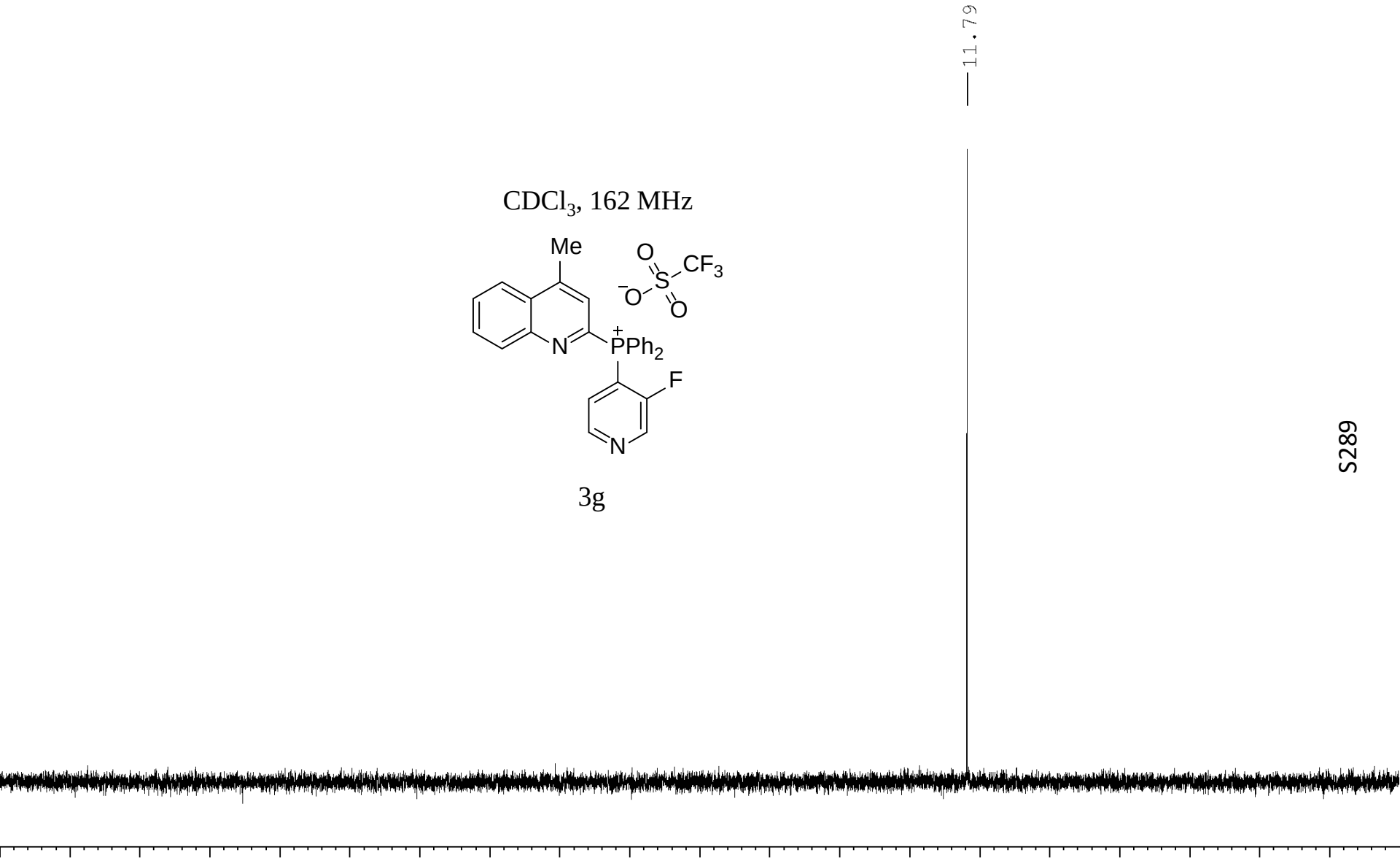
19.03
19.01

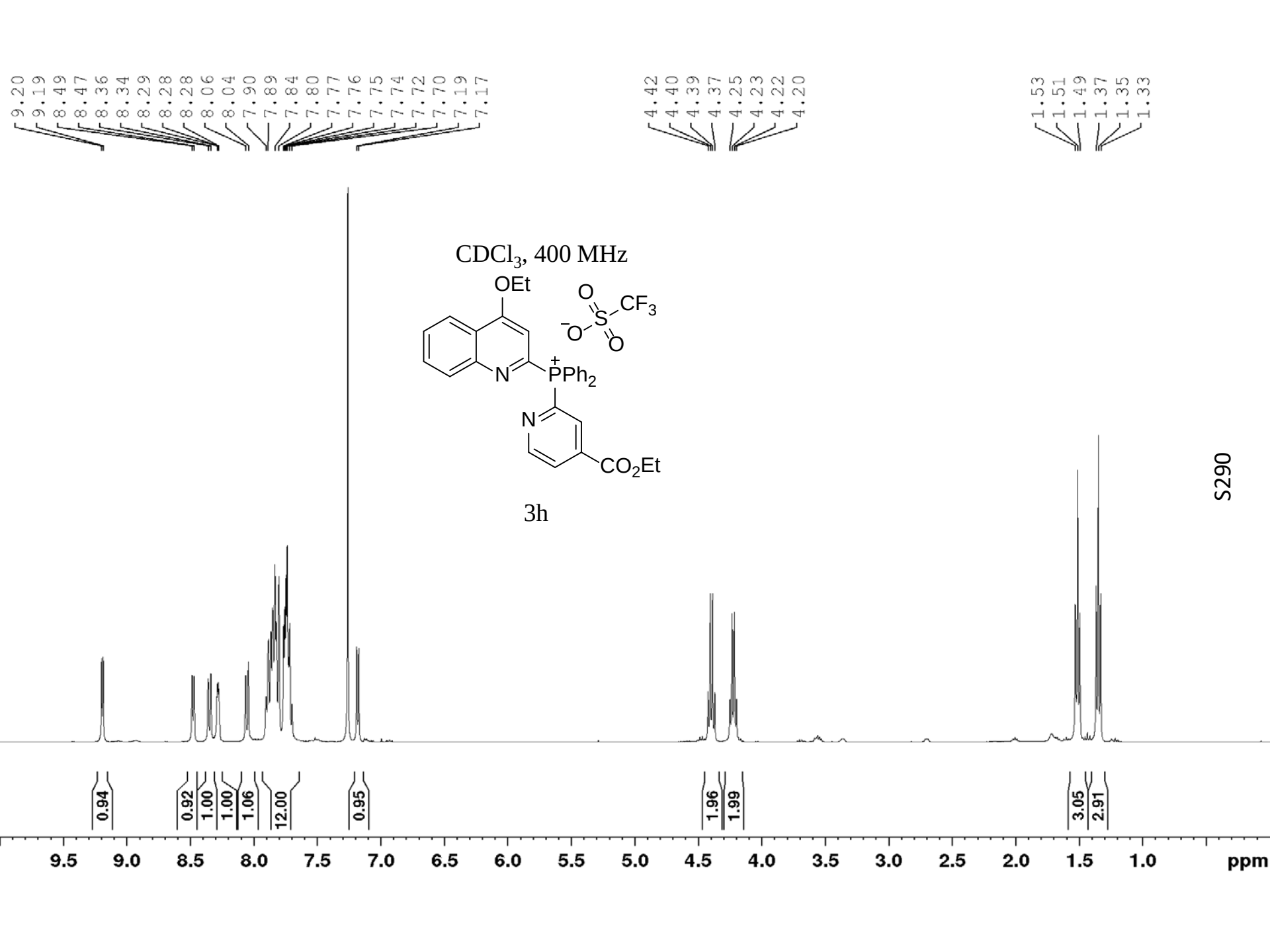
$CDCl_3$, 100 MHz

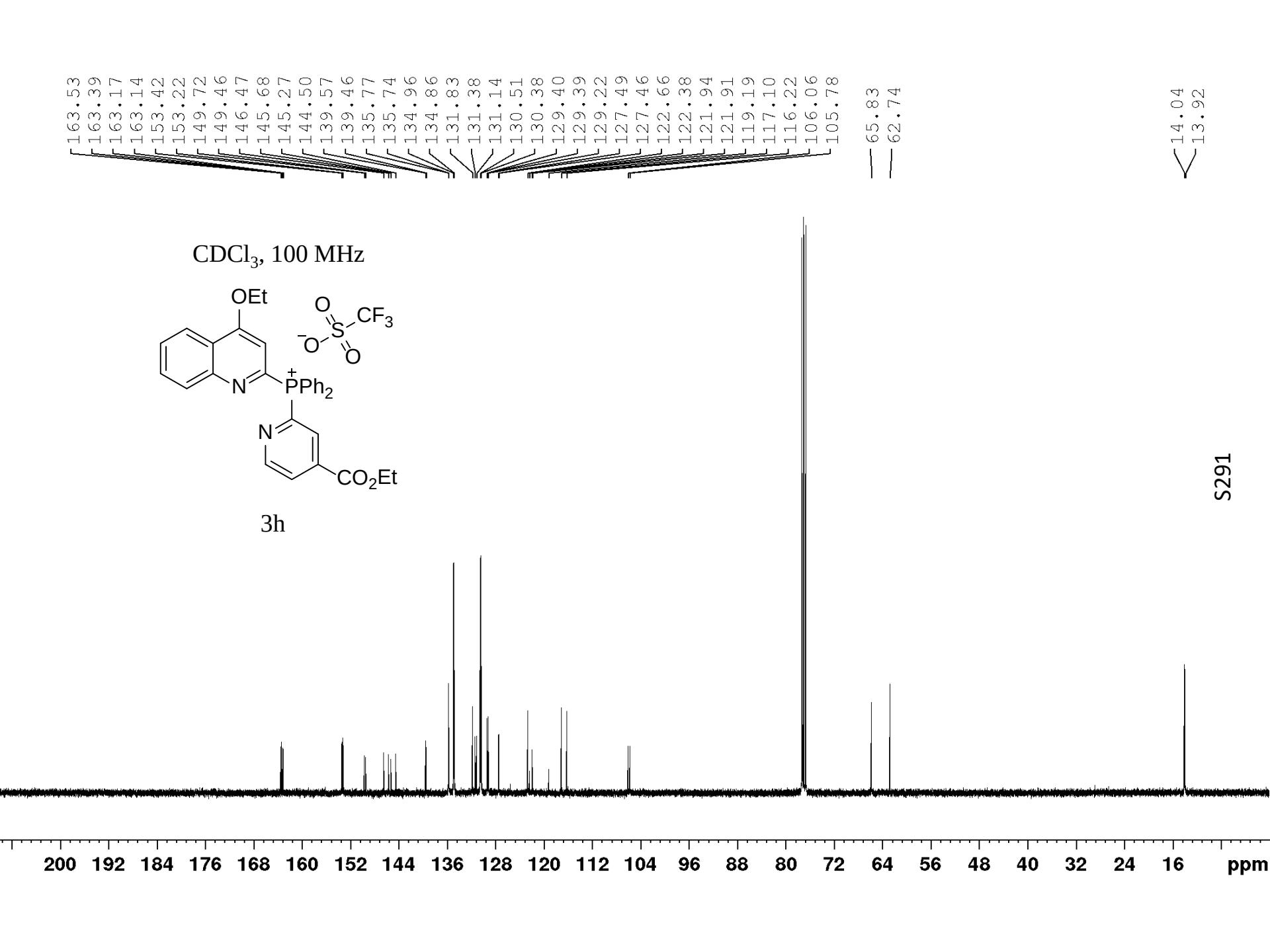


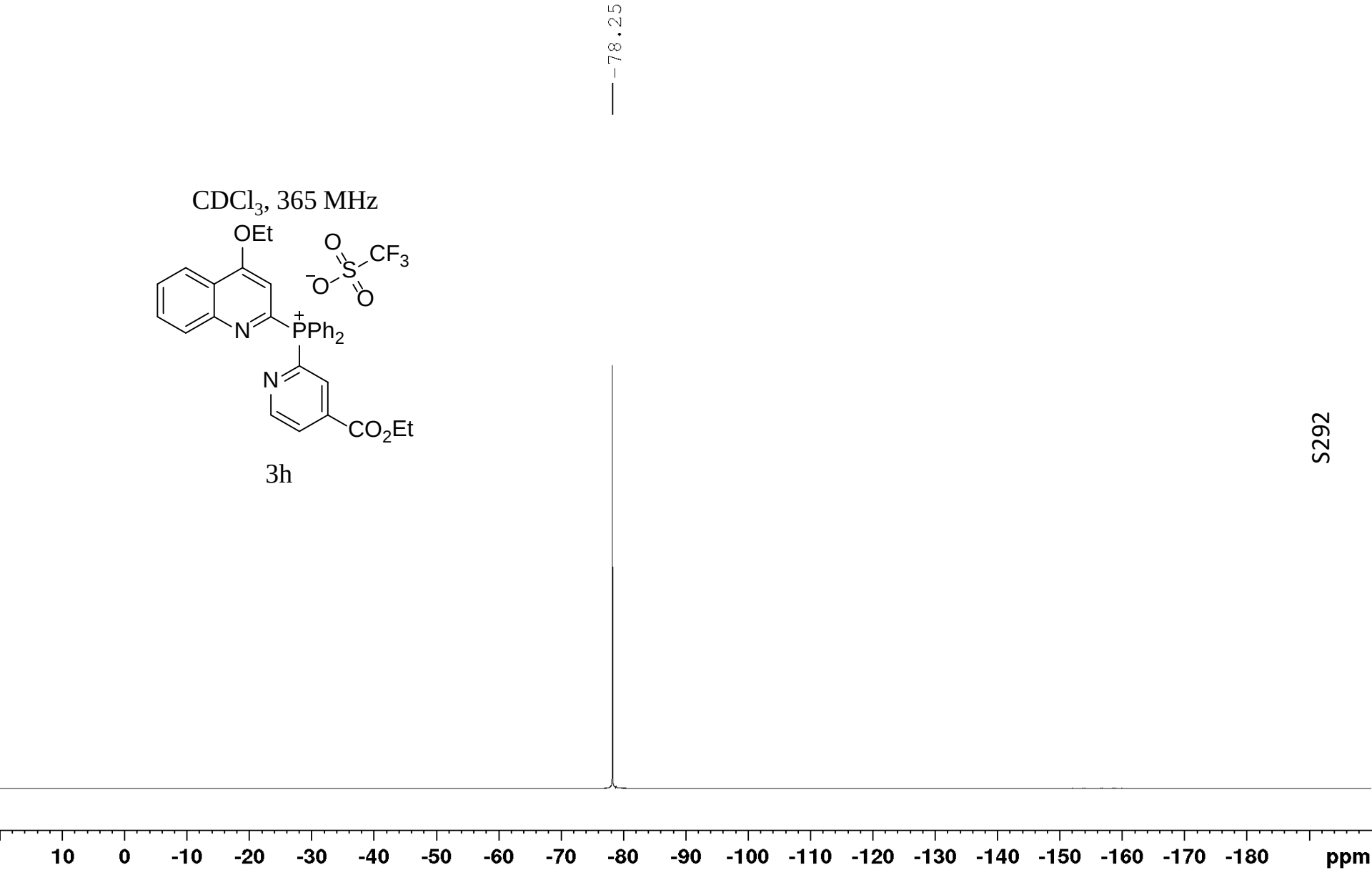
3g


-78.25
-109.72
-109.74
CDCl3, 365 MHz
Me
O
CF3
O
S
O
N
PPh2
F
N
3g
S288
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
ppm


11.79
CDCl3, 162 MHz
Me
O
CF3
S
O
O
N
PPh2
F
N
3g
S289
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
ppm

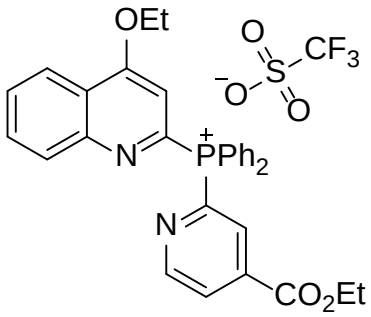

9.20
9.19
8.49
8.47
8.36
8.34
8.29
8.28
8.28
8.06
8.04
7.90
7.89
7.84
7.80
7.77
7.76
7.75
7.74
7.72
7.70
7.19
7.17
4.42
4.40
4.39
4.37
4.25
4.23
4.22
4.20
1.53
1.51
1.49
1.37
1.35
1.33
CDCl3, 400 MHz
OEt
O
CF3
S
O
O
O
N
PPh2
N
CO2Et
3h
S290
0.94
0.92
1.00
1.00
1.06
12.00
0.95
1.96
1.99
3.05
2.91
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm


163.53
163.39
163.17
163.14
153.42
153.22
149.72
149.46
146.47
145.68
145.27
144.50
139.57
139.46
135.77
135.74
134.96
134.86
131.83
131.38
131.14
130.51
130.38
129.40
129.39
129.22
127.49
127.46
122.66
122.38
121.94
121.91
119.19
117.10
116.22
106.06
105.78
65.83
62.74
14.04
13.92
CDCl3, 100 MHz
OEt
O
CF3
S
O
O
N
PPh2
N
CO2Et
3h
S291
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


-78.25
CDCl3, 365 MHz
OEt
O
CF3
S
O
O
N
PPh2
N
CO2Et
3h
S292
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
ppm

9.58

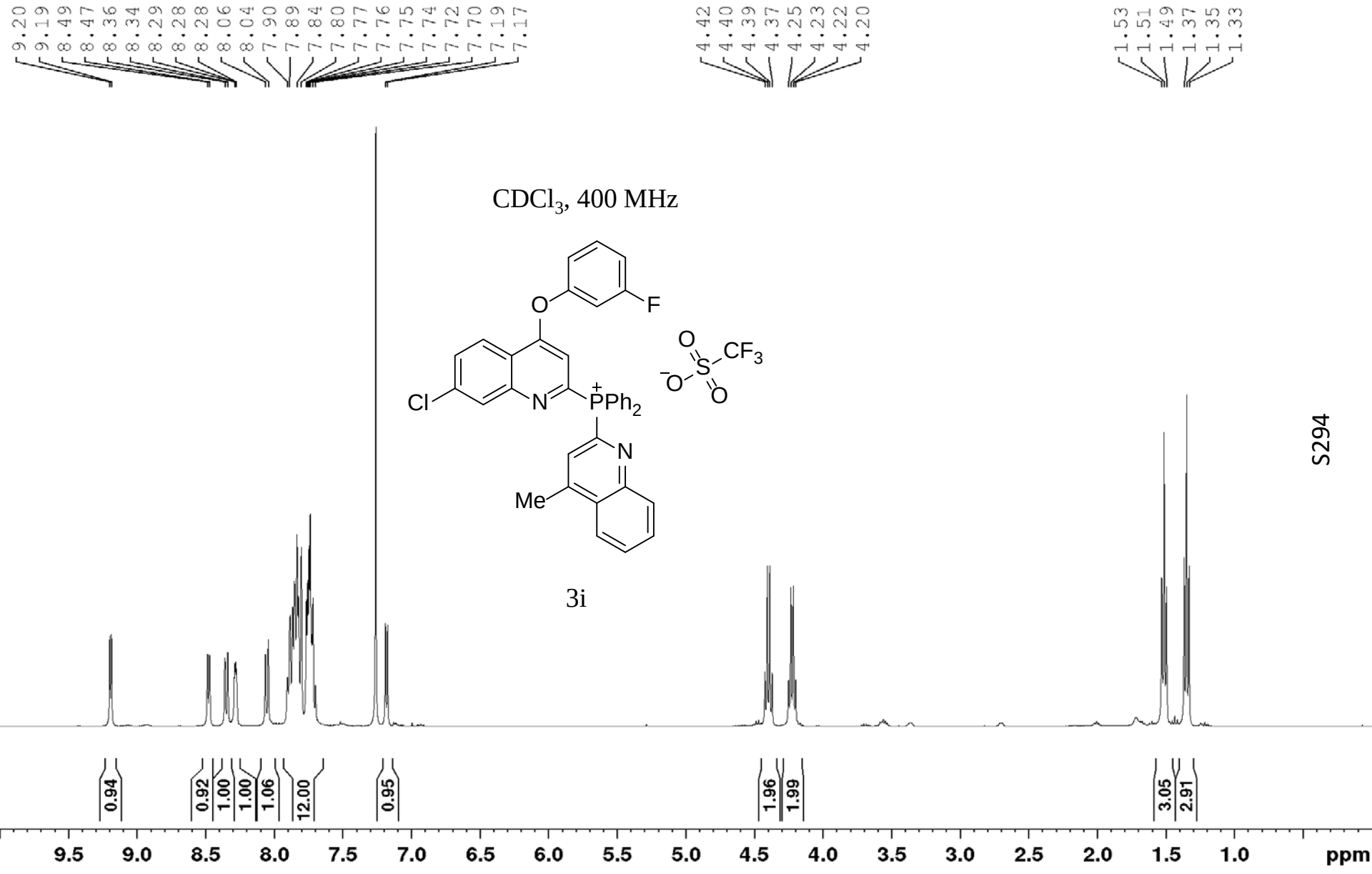
$CDCl_3$, 162 MHz

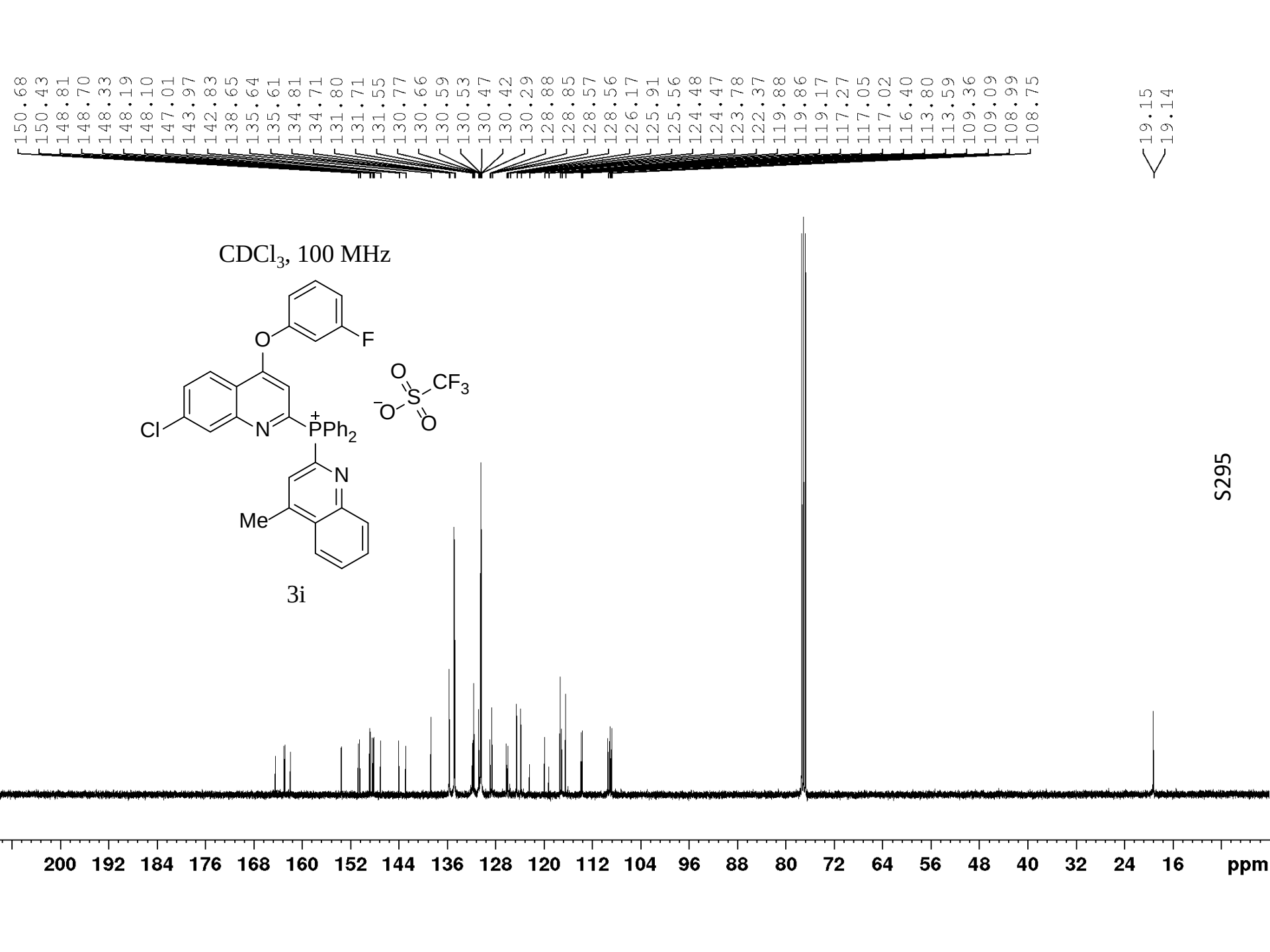


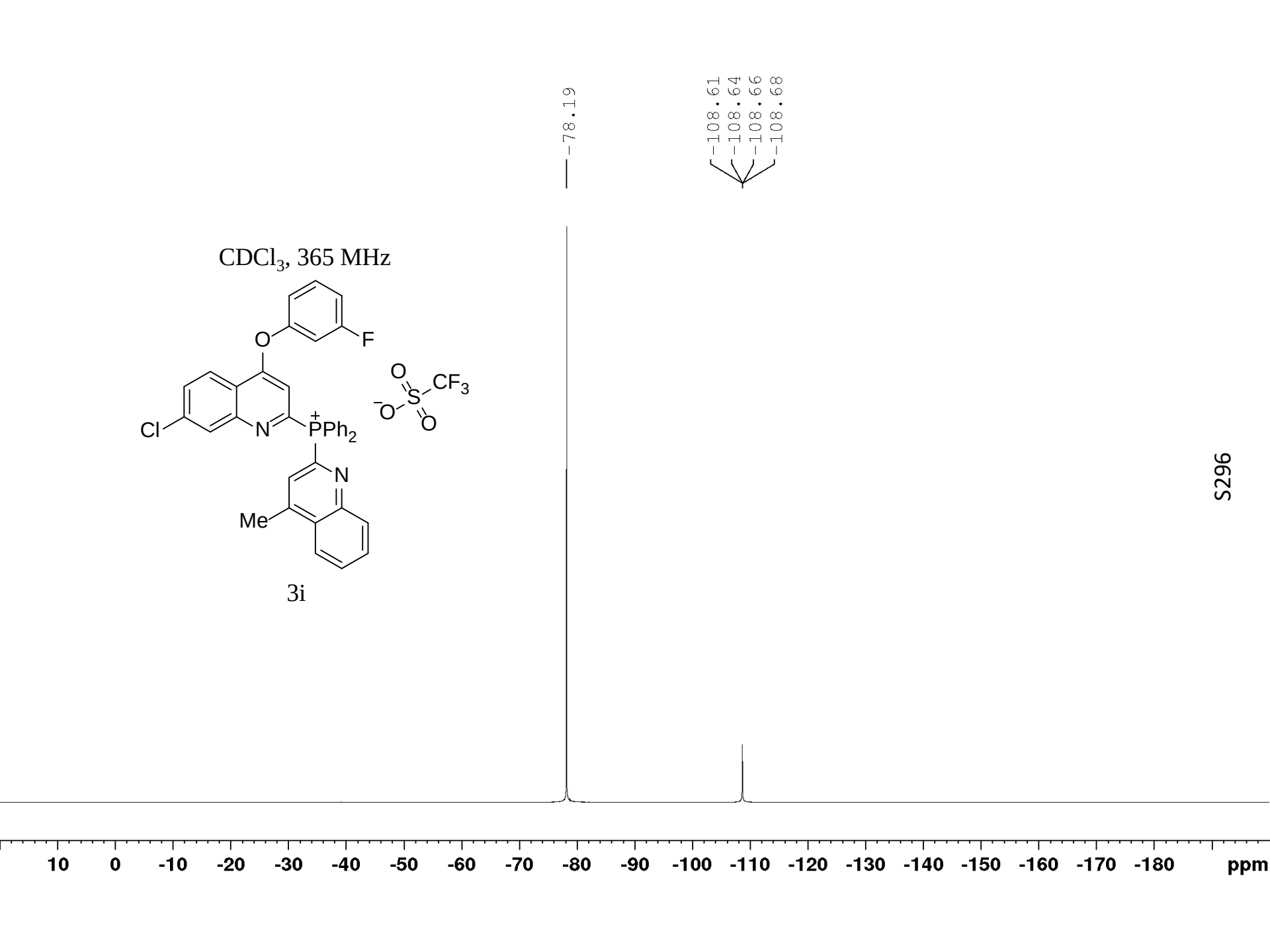
3h

S293

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

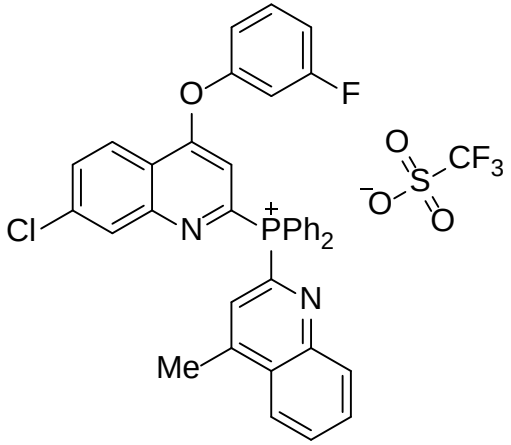

9.20
9.19
8.49
8.47
8.36
8.34
8.29
8.28
8.28
8.06
8.04
7.90
7.89
7.84
7.80
7.77
7.76
7.75
7.74
7.72
7.70
7.19
7.17
4.42
4.40
4.39
4.37
4.25
4.23
4.22
4.20
1.53
1.51
1.49
1.37
1.35
1.33
CDCl3, 400 MHz
O
F
O
CF3
O
S
O
Cl
N
PPh2
N
Me
3i
S294
0.94
0.92
1.00
1.00
1.06
12.00
0.95
1.96
1.99
3.05
2.91
9.5
9.0
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


150.68
150.43
148.81
148.70
148.33
148.19
148.10
147.01
143.97
142.83
138.65
135.64
135.61
134.81
134.71
131.80
131.71
131.55
130.77
130.66
130.59
130.53
130.47
130.42
130.29
128.88
128.85
128.57
128.56
126.17
125.91
125.56
124.48
124.47
123.78
122.37
119.88
119.86
119.17
117.27
117.05
117.02
116.40
113.80
113.59
109.36
109.09
108.99
108.75
19.15
19.14
CDCl3, 100 MHz
O
F
O
CF3
S
O
O
Cl
N
PPh2
N
Me
3i
S295
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


-78.19
-108.61
-108.64
-108.66
-108.68
CDCl3, 365 MHz
O
F
O
CF3
O
S
O
Cl
N
PPh2
N
Me
3i
S296
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
ppm

8.06

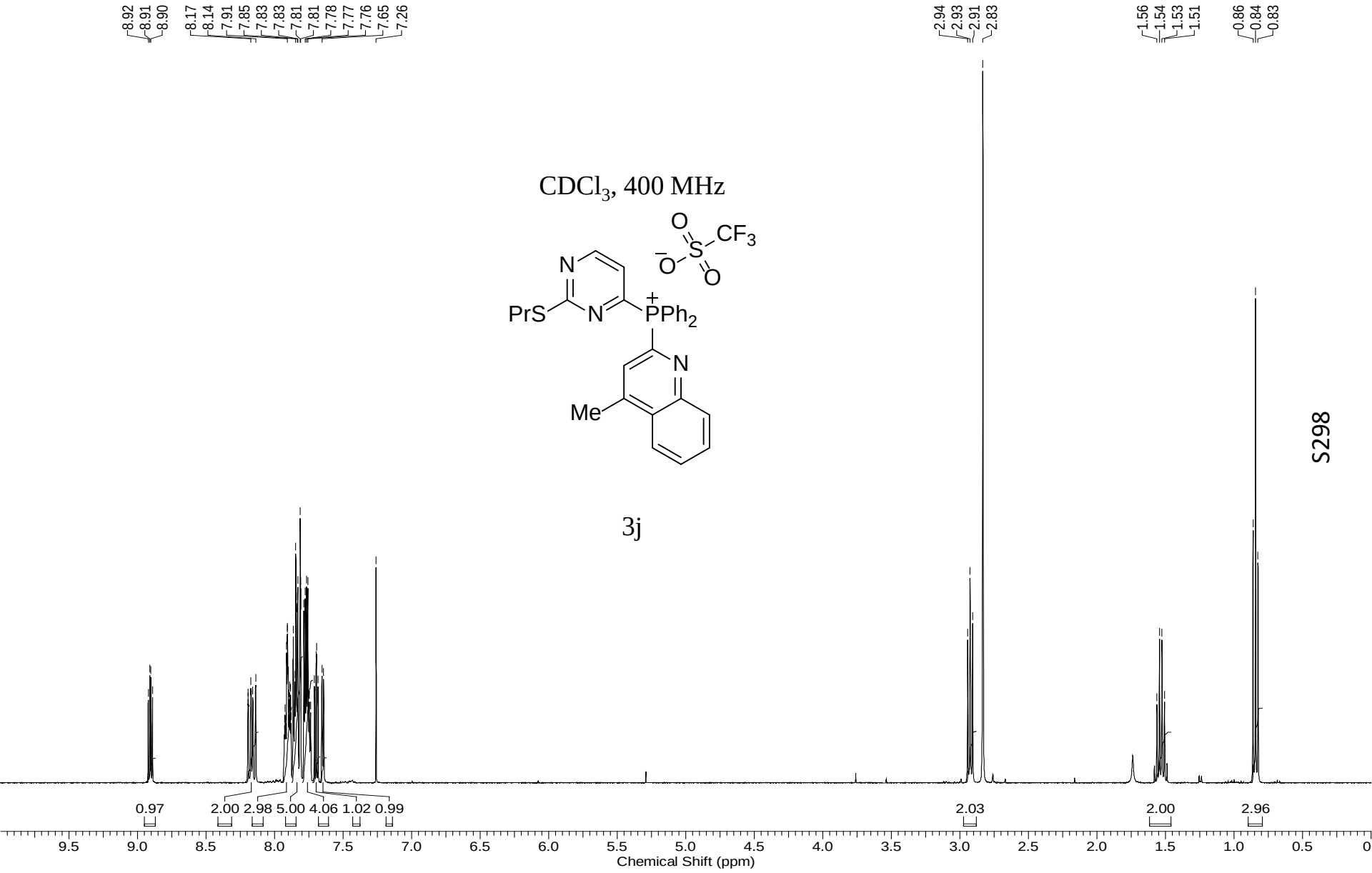
$CDCl_3$, 162 MHz

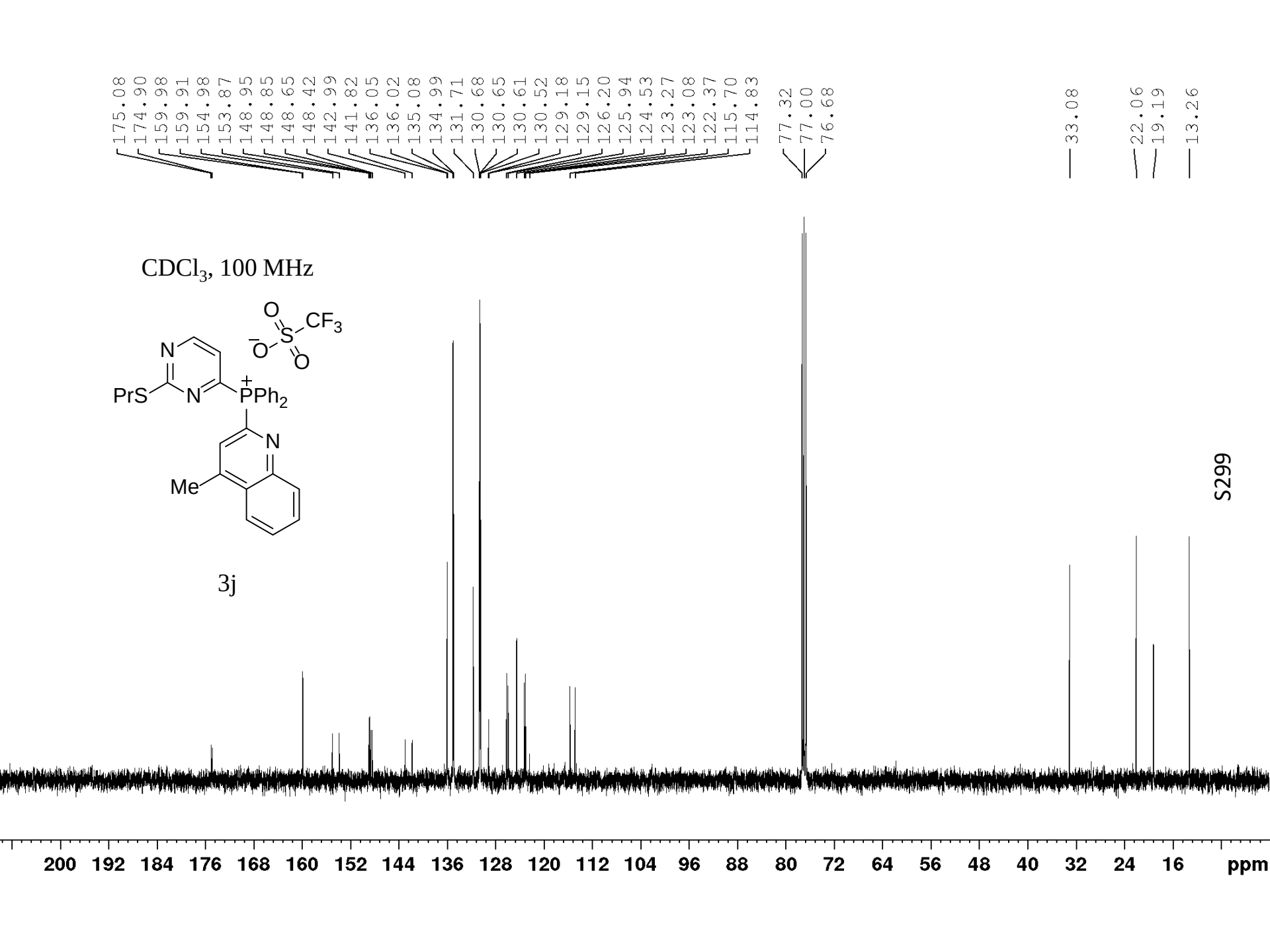


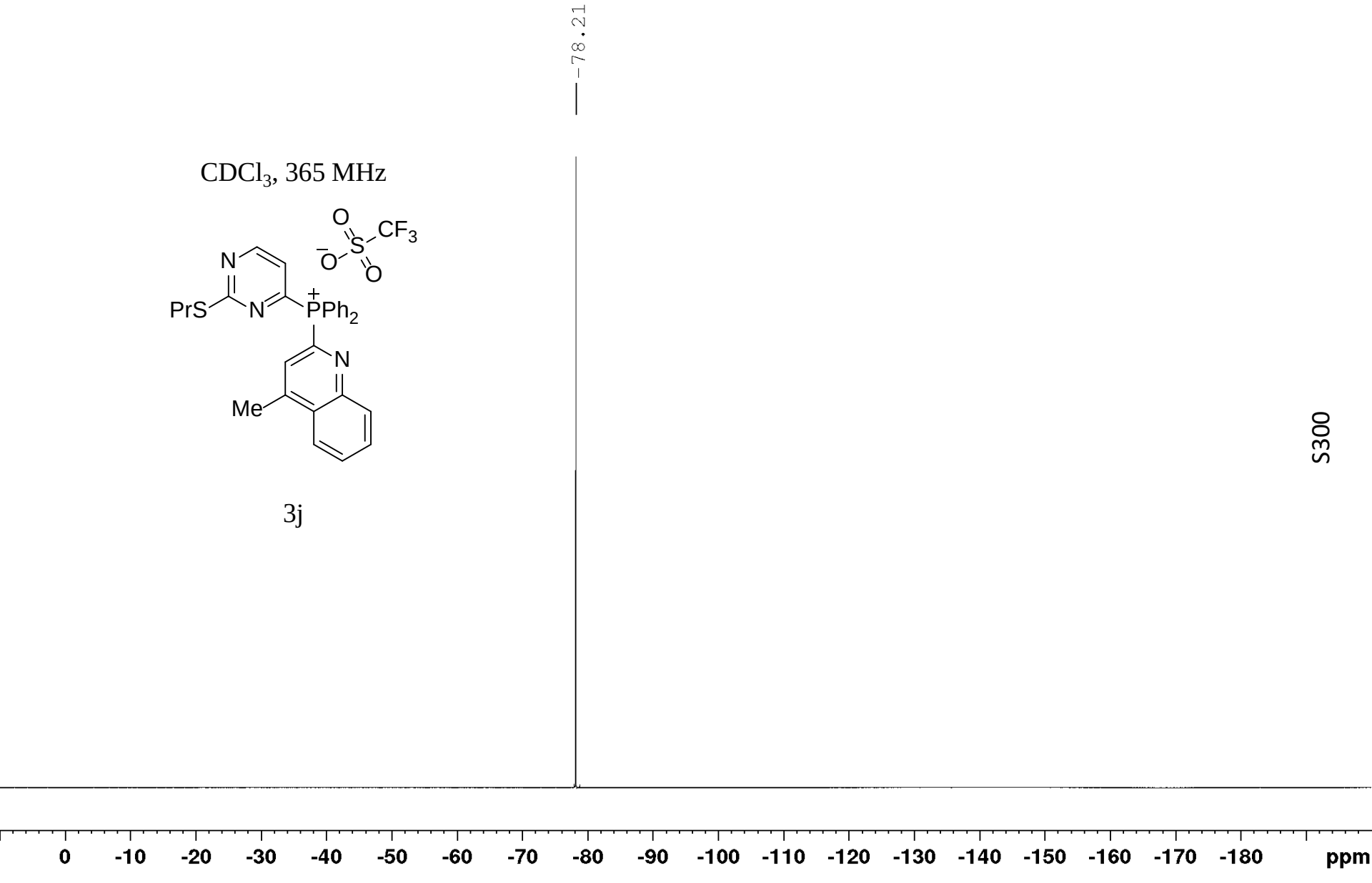
3i

S297

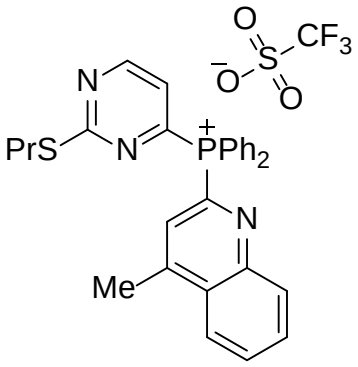
140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 ppm


8.92
8.91
8.90
8.17
8.14
7.91
7.85
7.83
7.83
7.81
7.81
7.78
7.77
7.76
7.65
7.26
2.94
2.93
2.91
2.83
1.56
1.54
1.53
1.51
0.86
0.84
0.83
CDCl3, 400 MHz
O
S
CF3
O
O
N
PrS
N
PPh2
N
Me
3j
S298
0.97
2.00
2.98
5.00
4.06
1.02
0.99
2.03
2.00
2.96
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)


175.08
174.90
159.98
159.91
154.98
153.87
148.95
148.85
148.65
148.42
142.99
141.82
136.05
136.02
135.08
134.99
131.71
130.68
130.65
130.61
130.52
129.18
129.15
126.20
125.94
124.53
123.27
123.08
122.37
115.70
114.83
77.32
77.00
76.68
33.08
22.06
19.19
13.26
CDCl3, 100 MHz
PrS
PPh2
Me
3j
S299
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


-78.21
CDCl3, 365 MHz
O
CF3
S
O
O
N
PrS
N
PPh2
N
Me
3j
S300
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
ppm

$CDCl_3$, 162 MHz

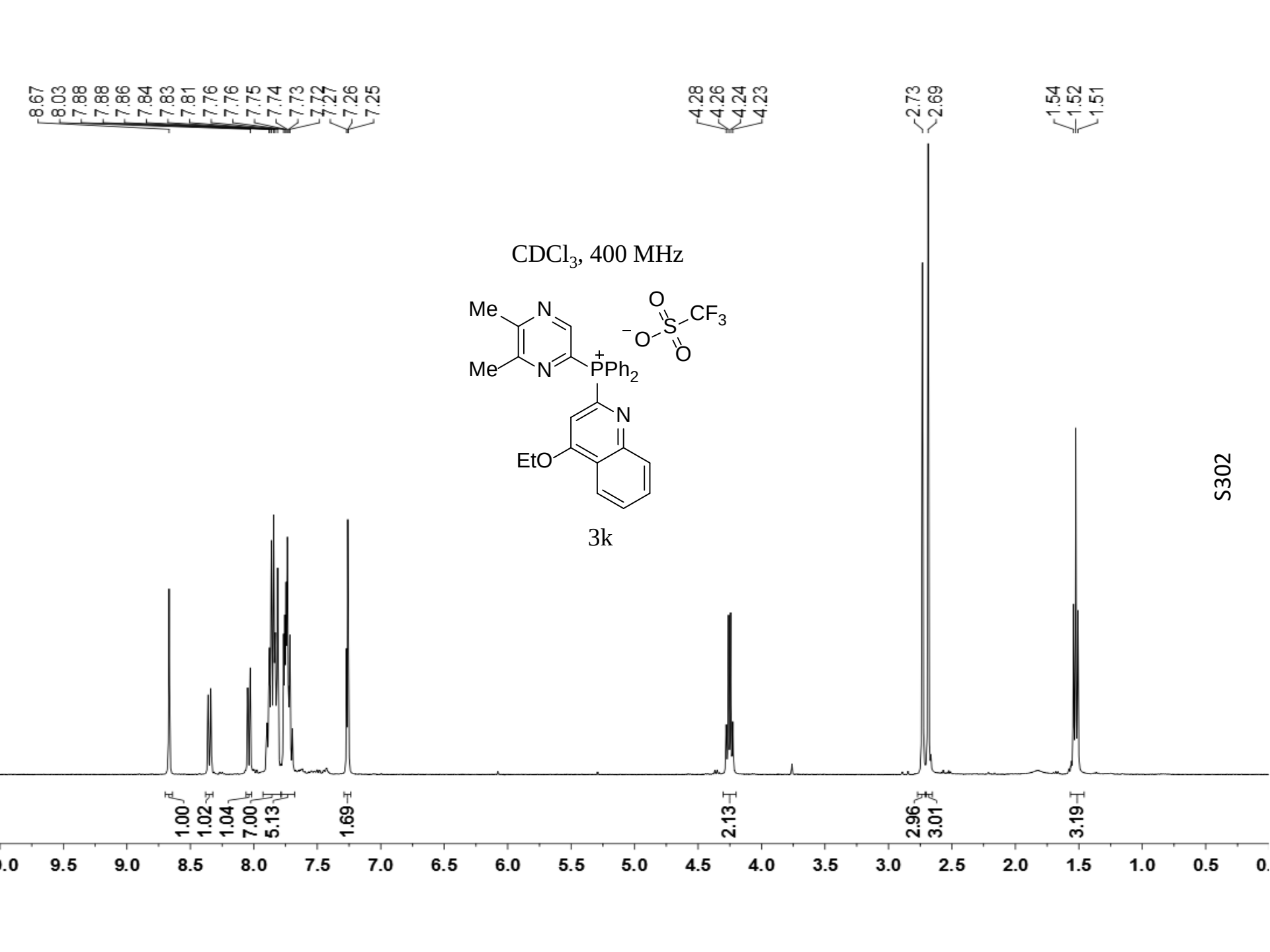


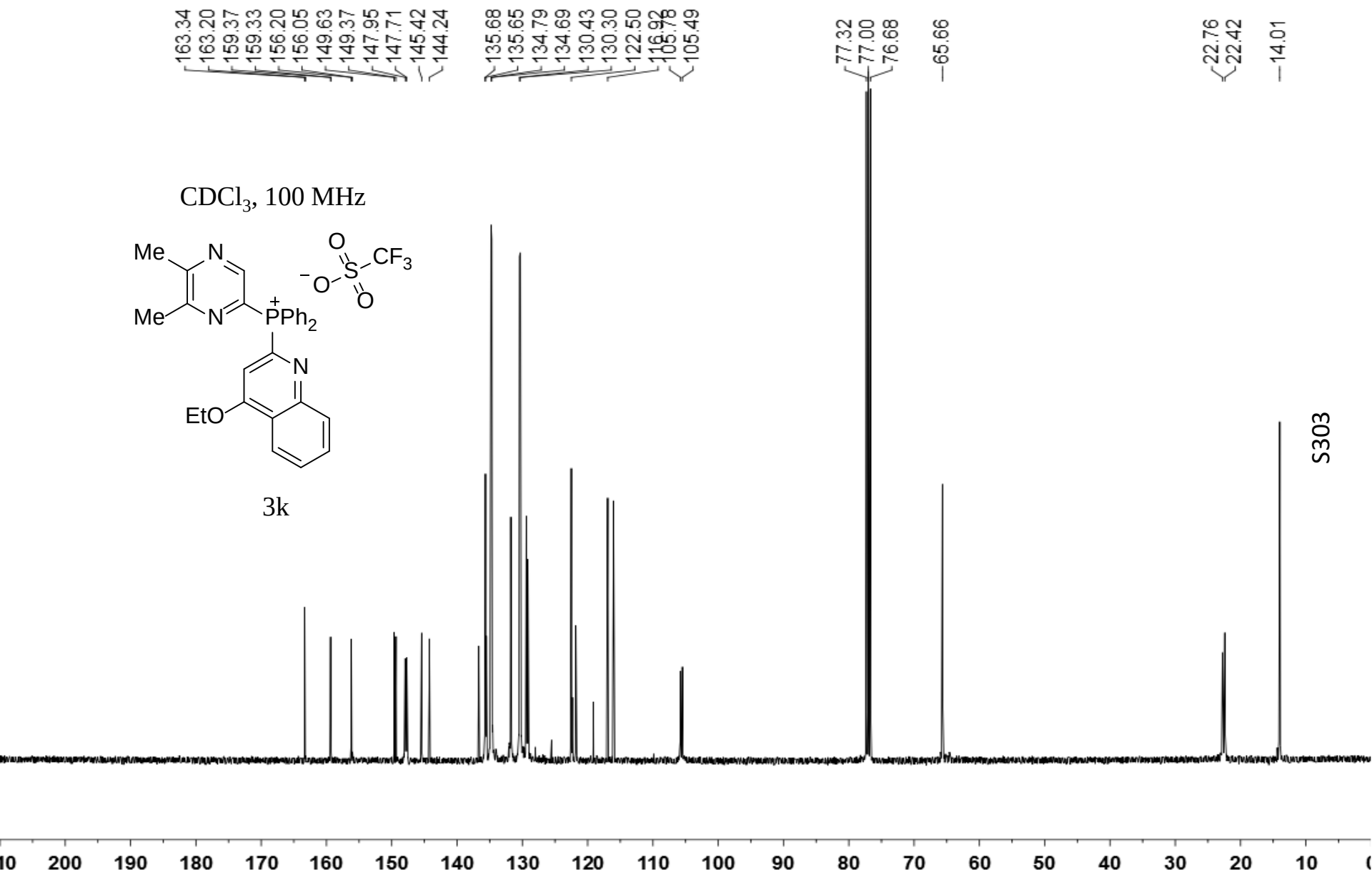
3j

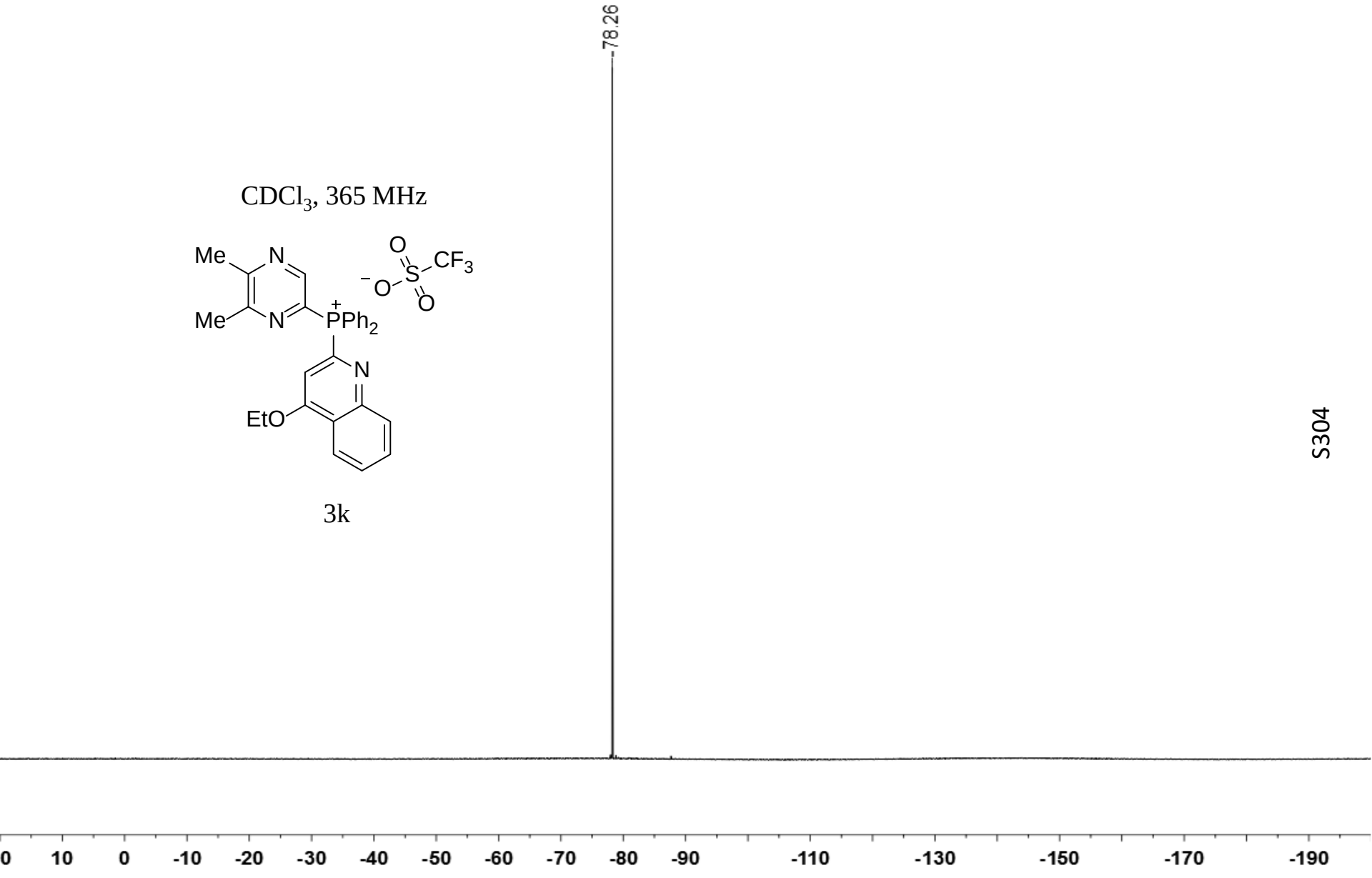
9.49

S301

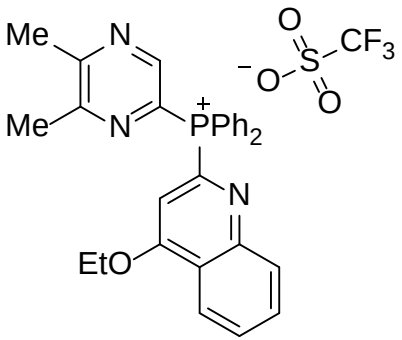
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 ppm


8.67
8.03
7.88
7.88
7.86
7.84
7.83
7.81
7.76
7.76
7.75
7.74
7.73
7.72
7.27
7.26
7.25
4.28
4.26
4.24
4.23
2.73
2.69
1.54
1.52
1.51
CDCl3, 400 MHz
Me
N
Me
N
PPh2
O
S
CF3
O
O
O
N
EtO
3k
S302
1.00
1.02
1.04
7.00
5.13
1.69
2.13
2.96
3.01
3.19
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

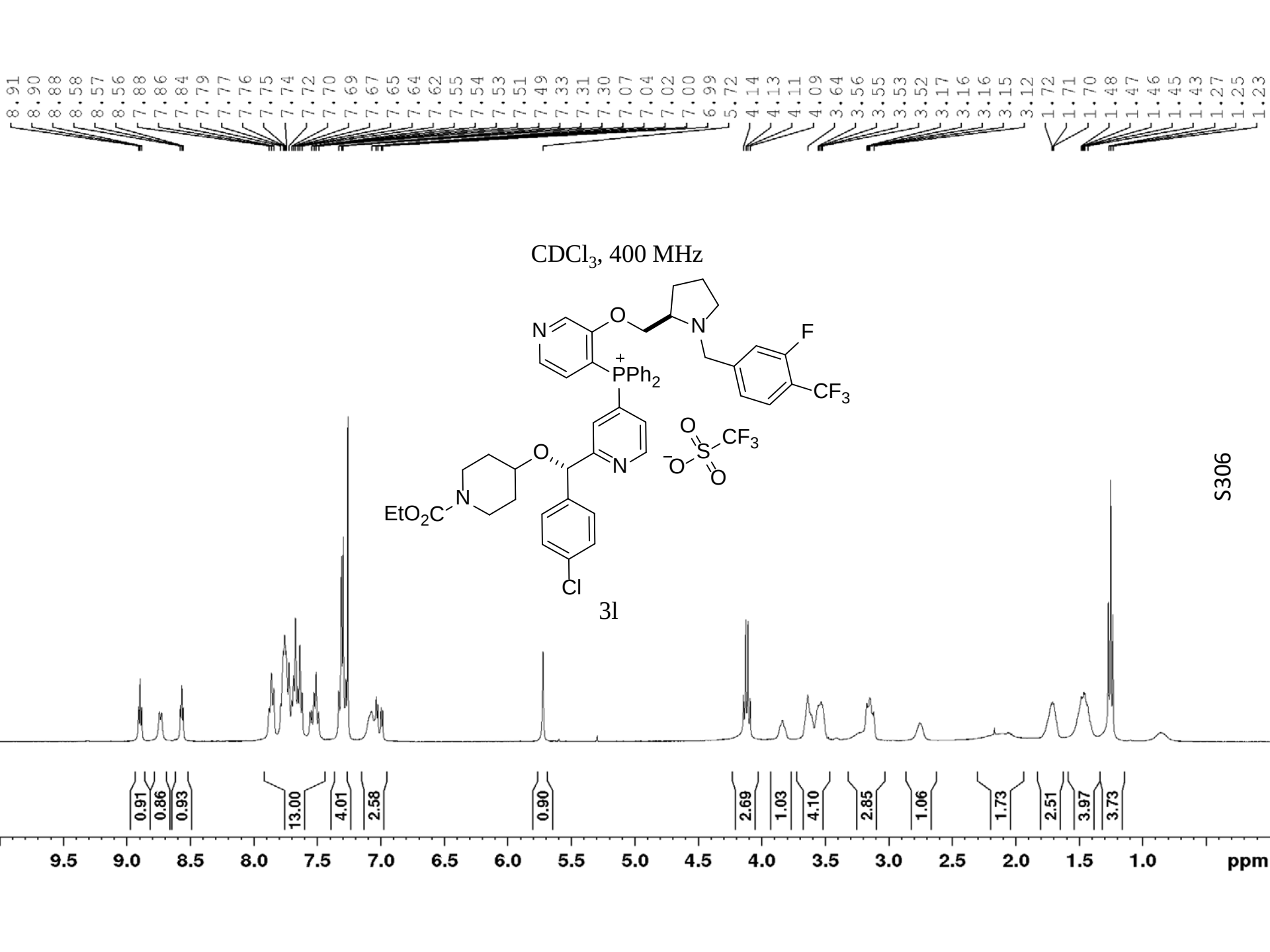

163.34
163.20
159.37
159.33
156.20
156.05
149.63
149.37
147.95
147.71
145.42
144.24
135.68
135.65
134.79
134.69
130.43
130.30
122.50
116.92
105.78
105.49
77.32
77.00
76.68
65.66
22.76
22.42
14.01
CDCl3, 100 MHz
Me
N
Me
N
PPh2
O
S
CF3
O
O
O
N
EtO
3k
S303
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

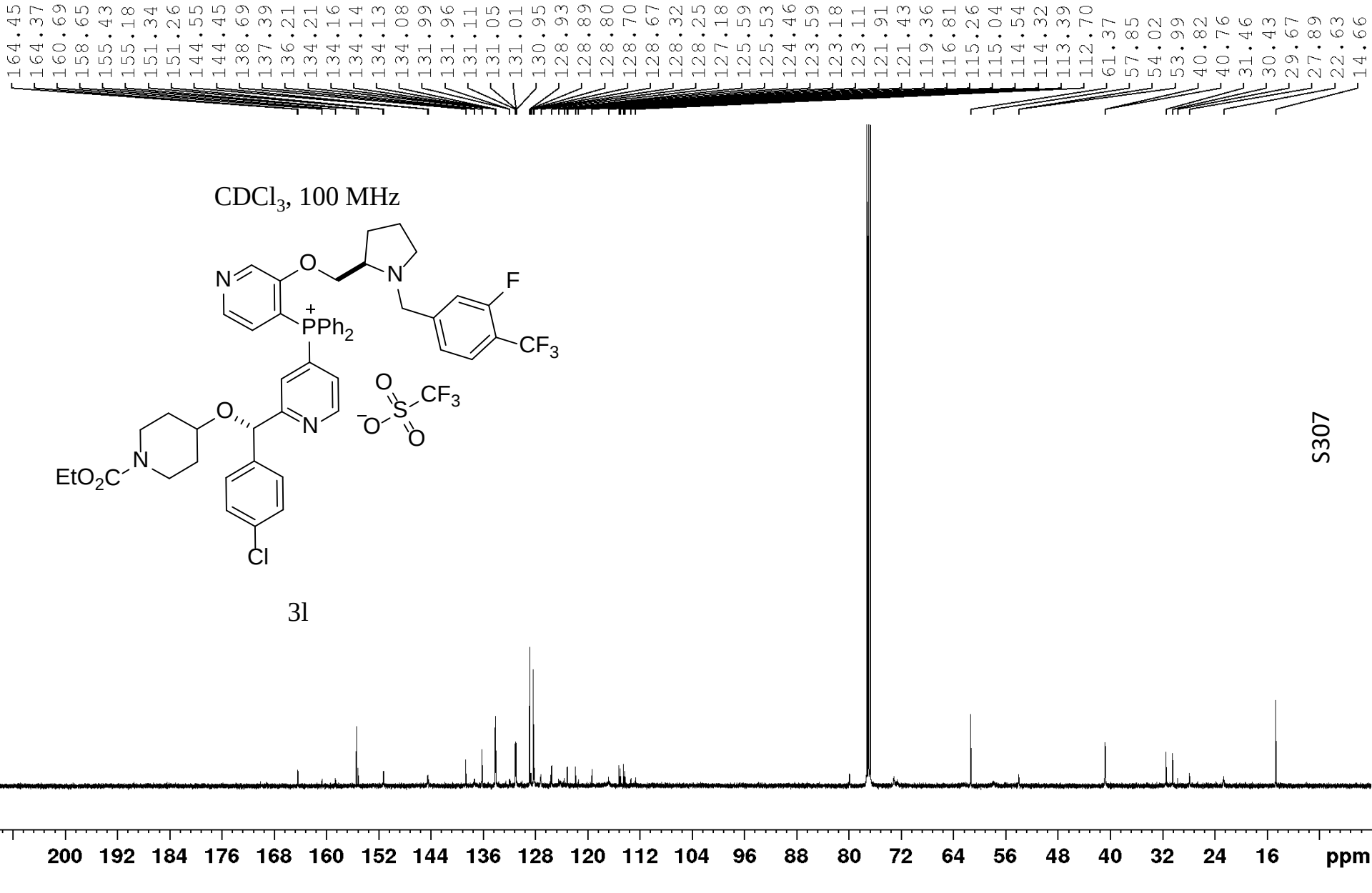

-78.26
CDCl3, 365 MHz
Me
N
Me
N
PPh2
O
CF3
O
S
O
O
N
EtO
3k
S304
0
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-110
-130
-150
-170
-190

$CDCl_3$, 162 MHz

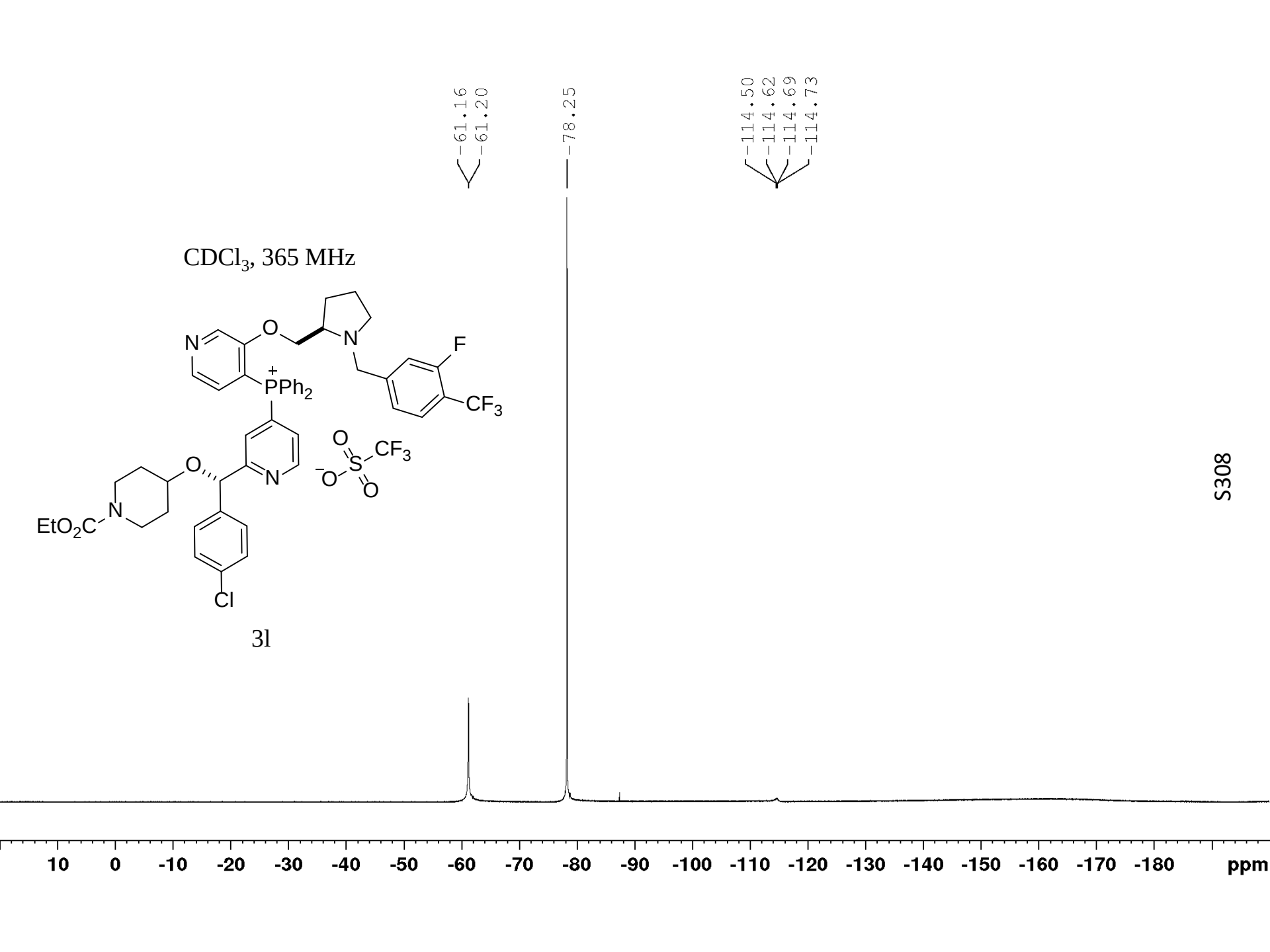


3k


8.91
8.90
8.88
8.58
8.57
8.56
7.88
7.86
7.84
7.79
7.77
7.76
7.75
7.74
7.72
7.70
7.69
7.67
7.65
7.64
7.62
7.55
7.54
7.53
7.51
7.49
7.33
7.31
7.30
7.07
7.04
7.02
7.00
6.99
5.72
4.14
4.13
4.11
4.09
3.64
3.56
3.55
3.53
3.52
3.17
3.16
3.16
3.15
3.12
1.72
1.71
1.70
1.48
1.47
1.46
1.45
1.43
1.27
1.25
1.23
CDCl3, 400 MHz
N
O
N
F
PPh2
CF3
O
CF3
O
S
O
N
EtO2C
Cl
3l
S306
0.91
0.86
0.93
13.00
4.01
2.58
0.90
2.69
1.03
4.10
2.85
1.06
1.73
2.51
3.97
3.73
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

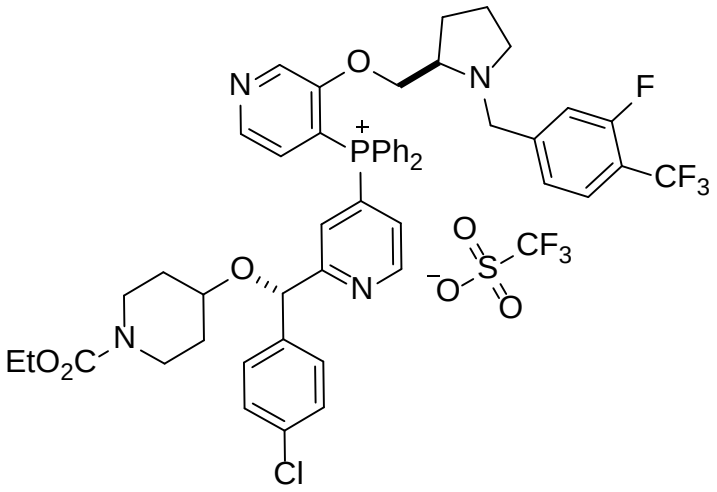

164.45
164.37
160.69
158.65
155.43
155.18
151.34
151.26
144.55
144.45
138.69
137.39
136.21
134.21
134.16
134.14
134.13
134.08
131.99
131.96
131.11
131.05
131.01
130.95
128.93
128.89
128.80
128.70
128.67
128.32
128.25
127.18
125.59
125.53
124.46
123.59
123.18
123.11
121.91
121.43
119.36
116.81
115.26
115.04
114.54
114.32
113.39
112.70
61.37
57.85
54.02
53.99
40.82
40.76
31.46
30.43
29.67
27.89
22.63
14.66
CDCl3, 100 MHz
S307
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

3l


-61.16
-61.20
-78.25
-114.50
-114.62
-114.69
-114.73
CDCl3, 365 MHz
3l
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
ppm

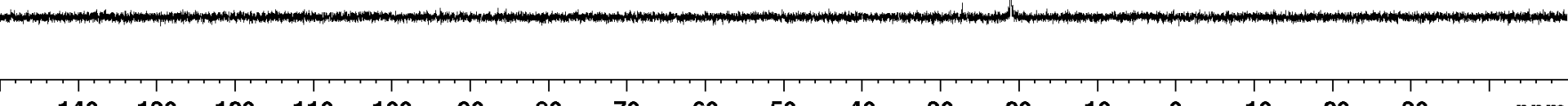
21.01

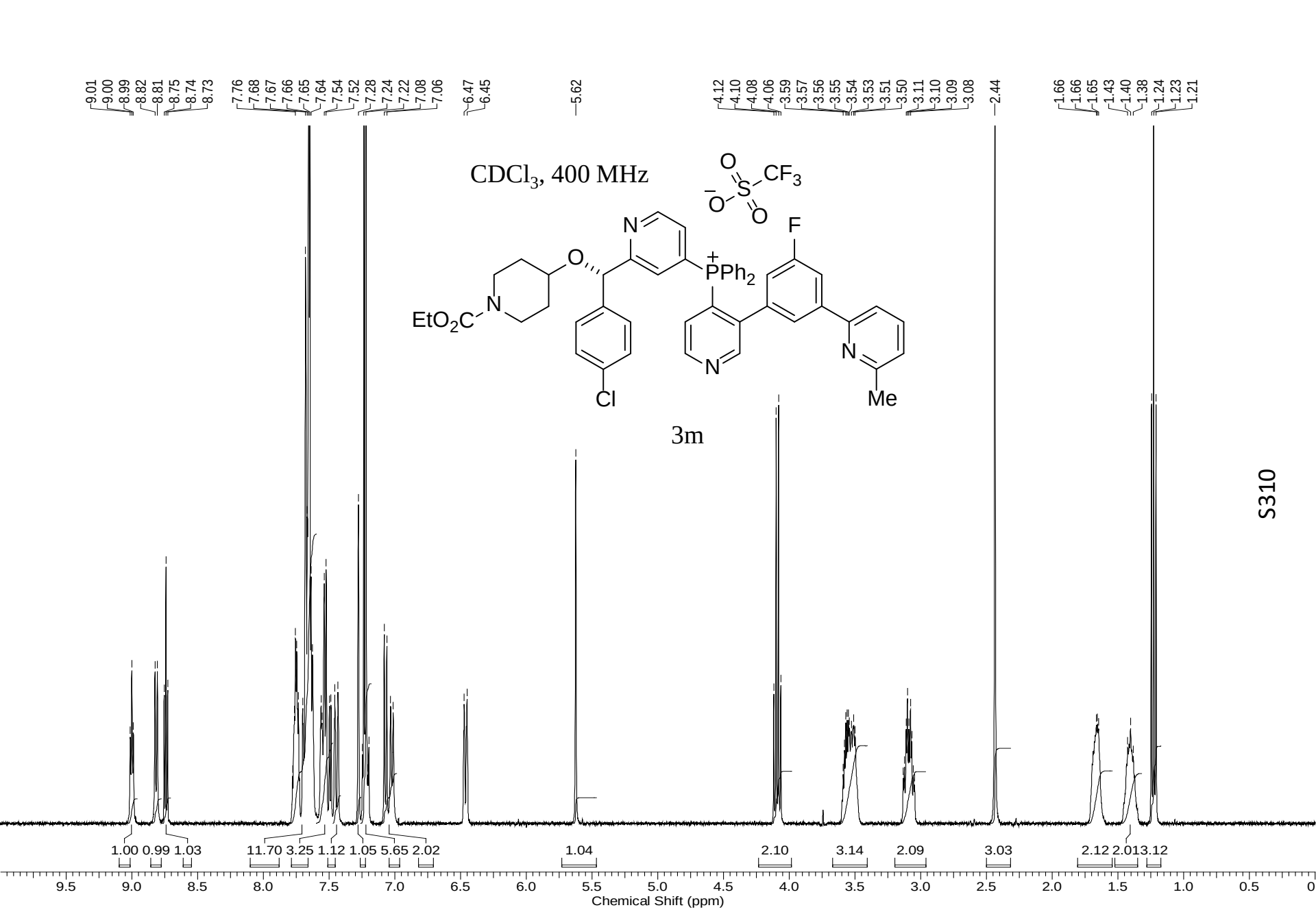
$CDCl_3$, 162 MHz

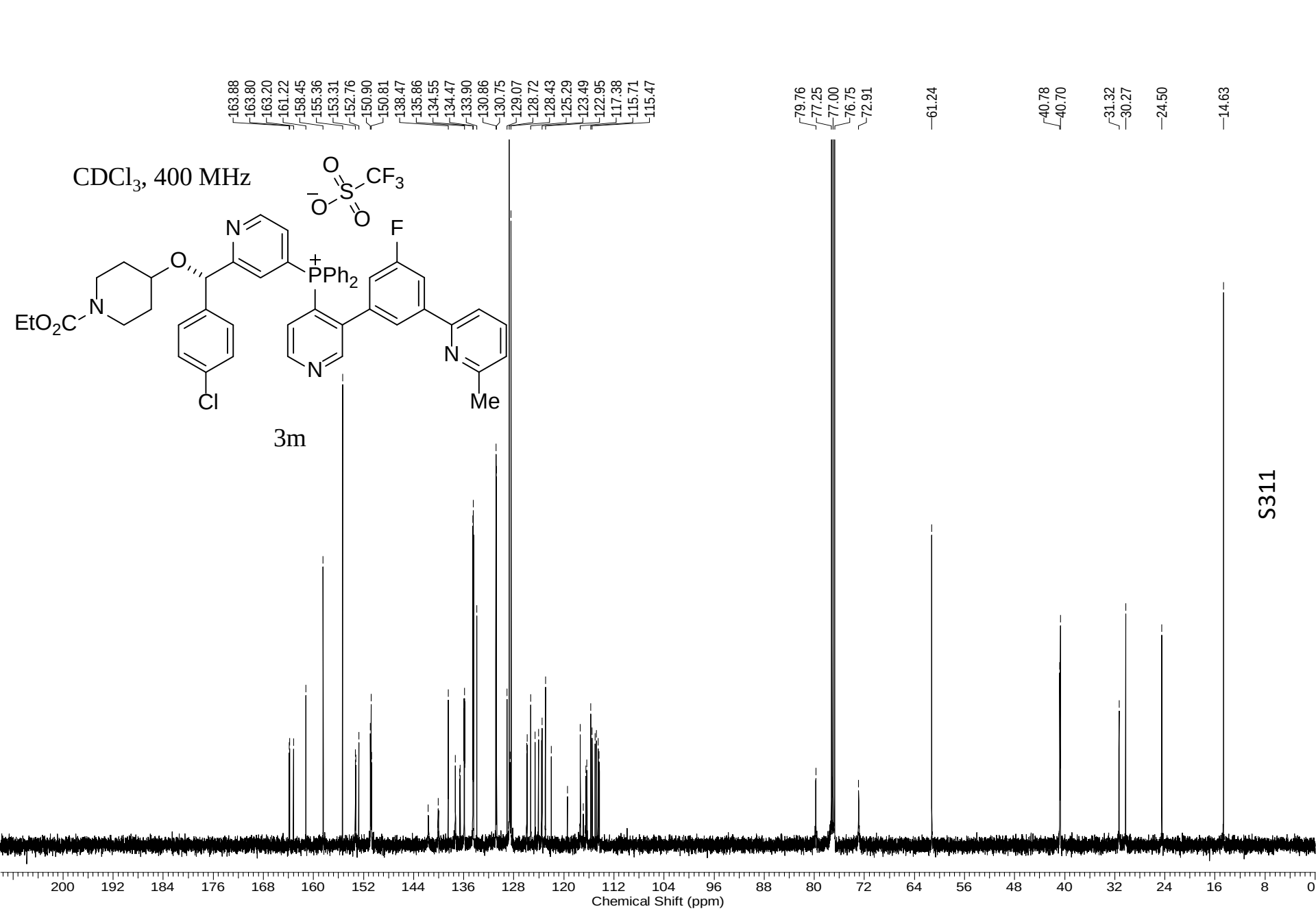


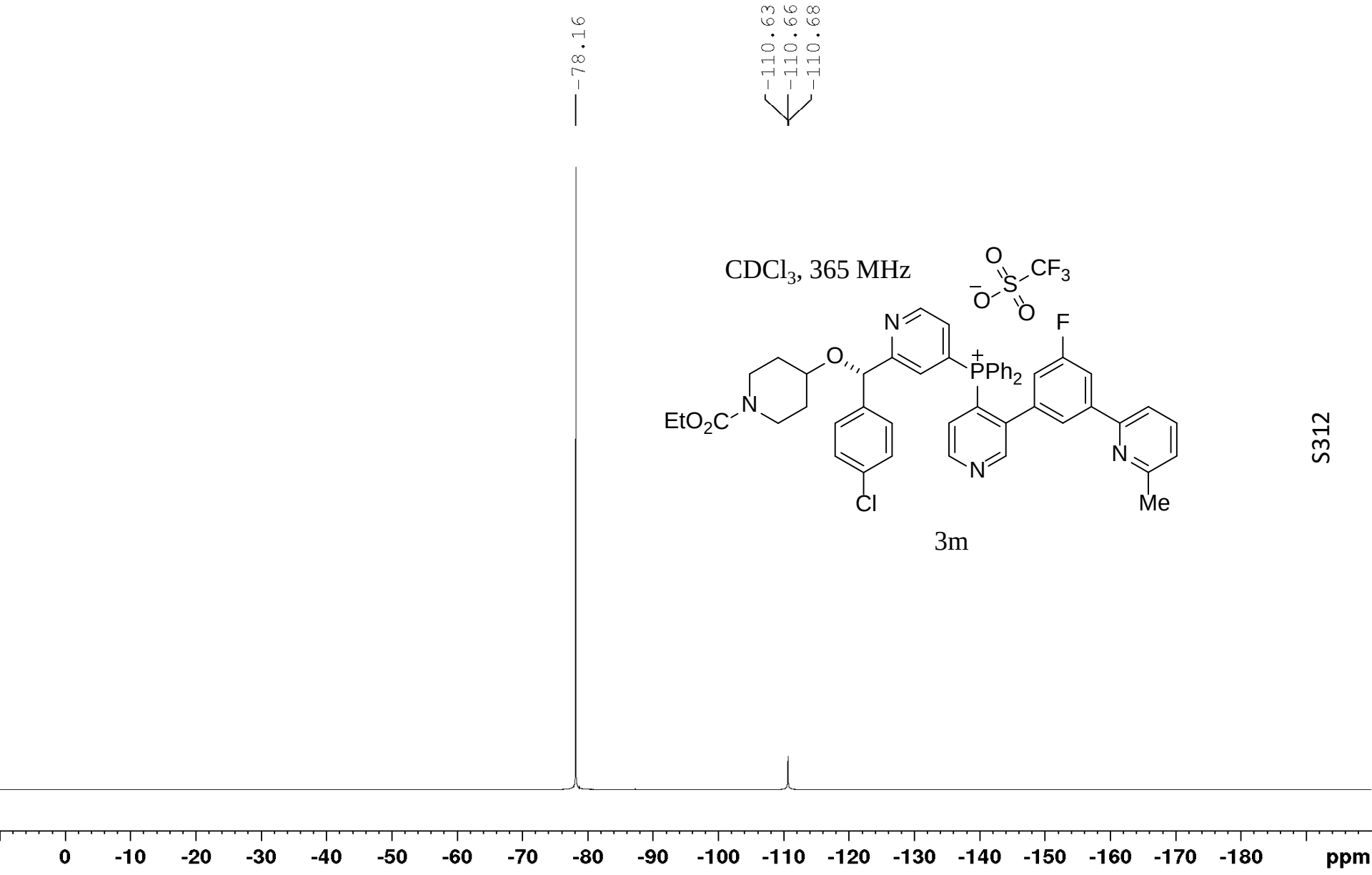
3l

S309

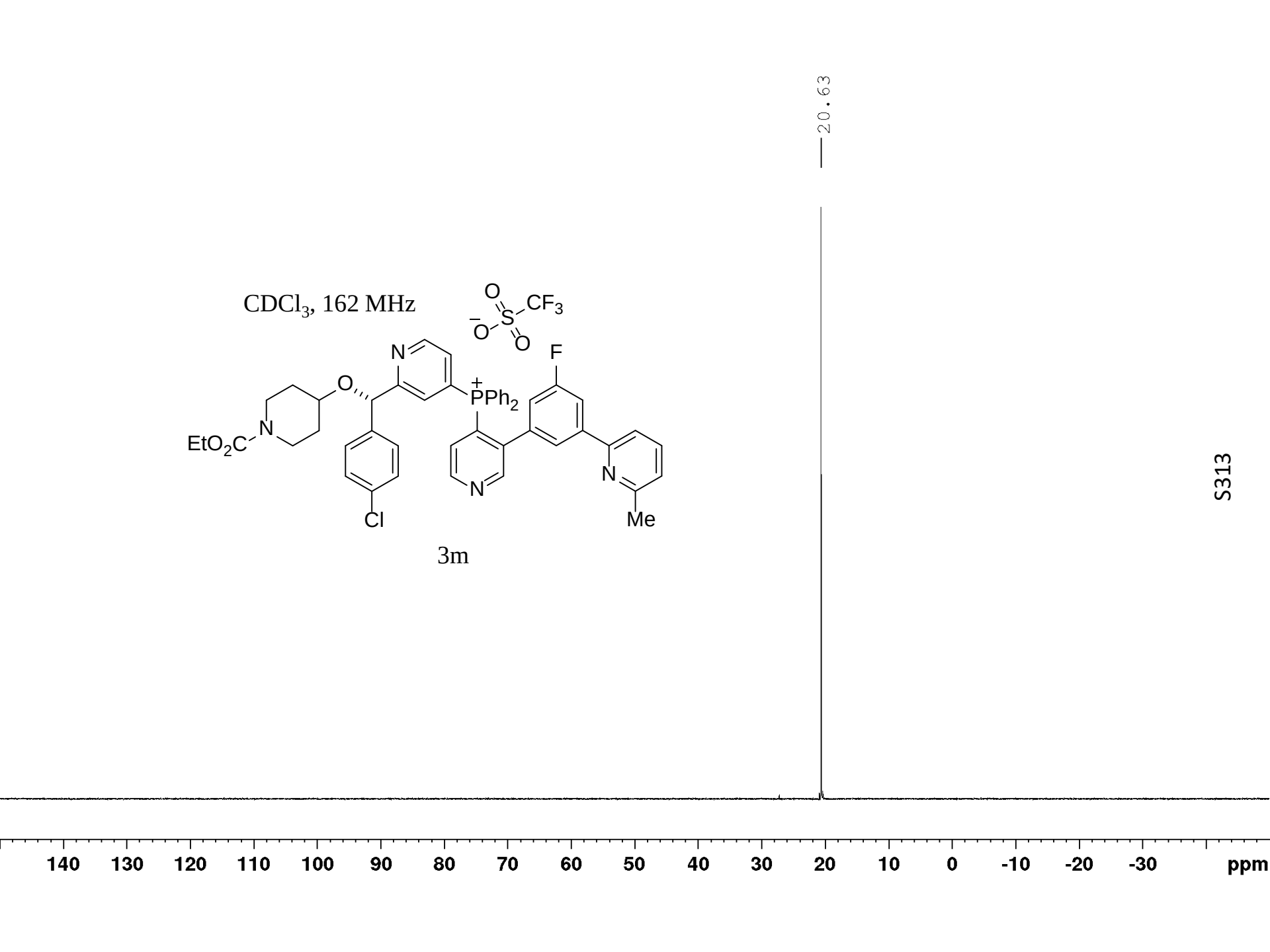


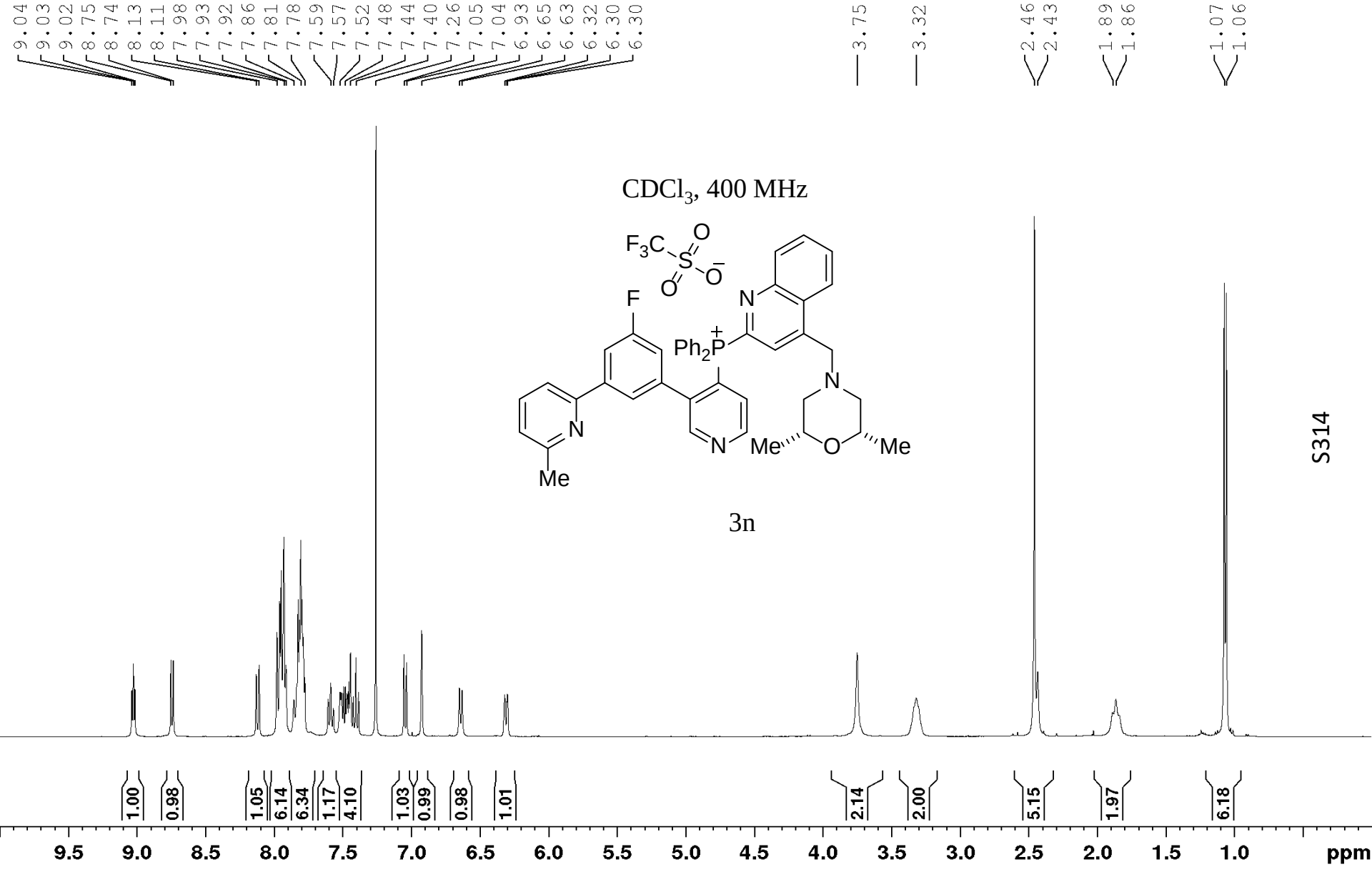

9.01 9.00 8.99 8.82 8.81 8.75 8.74 8.73 7.76 7.68 7.67 7.66 7.65 7.64 7.54 7.52 7.28 7.24 7.22 7.08 7.06 6.47 6.45 5.62 4.12 4.10 4.08 4.06 3.59 3.57 3.56 3.55 3.54 3.53 3.51 3.50 3.11 3.10 3.09 3.08 2.44 1.66 1.66 1.65 1.43 1.40 1.38 1.24 1.23 1.21
CDCl3, 400 MHz
3m
S310
1.00 0.99 1.03 11.70 3.25 1.12 1.05 5.65 2.02 1.04 2.10 3.14 2.09 3.03 2.12 2.01 3.12
Chemical Shift (ppm)

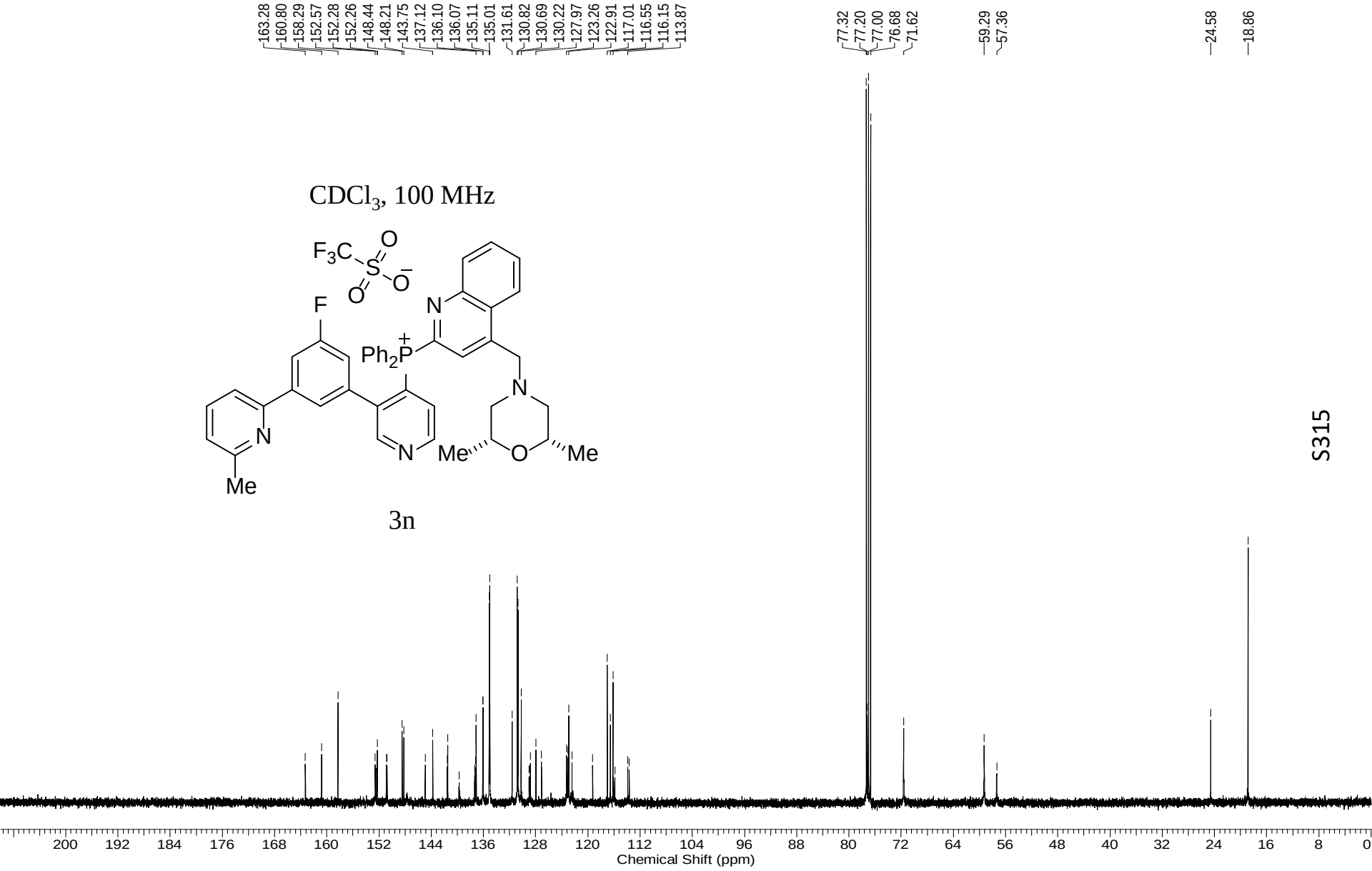

163.88
163.80
163.20
161.22
158.45
155.36
153.31
152.76
150.90
150.81
138.47
135.86
134.55
134.47
133.90
130.86
130.75
129.07
128.72
128.43
125.29
123.49
122.95
117.38
115.71
115.47
79.76
77.25
77.00
76.75
72.91
61.24
40.78
40.70
31.32
30.27
24.50
14.63
CDCl3, 400 MHz
3m
S311
200
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)

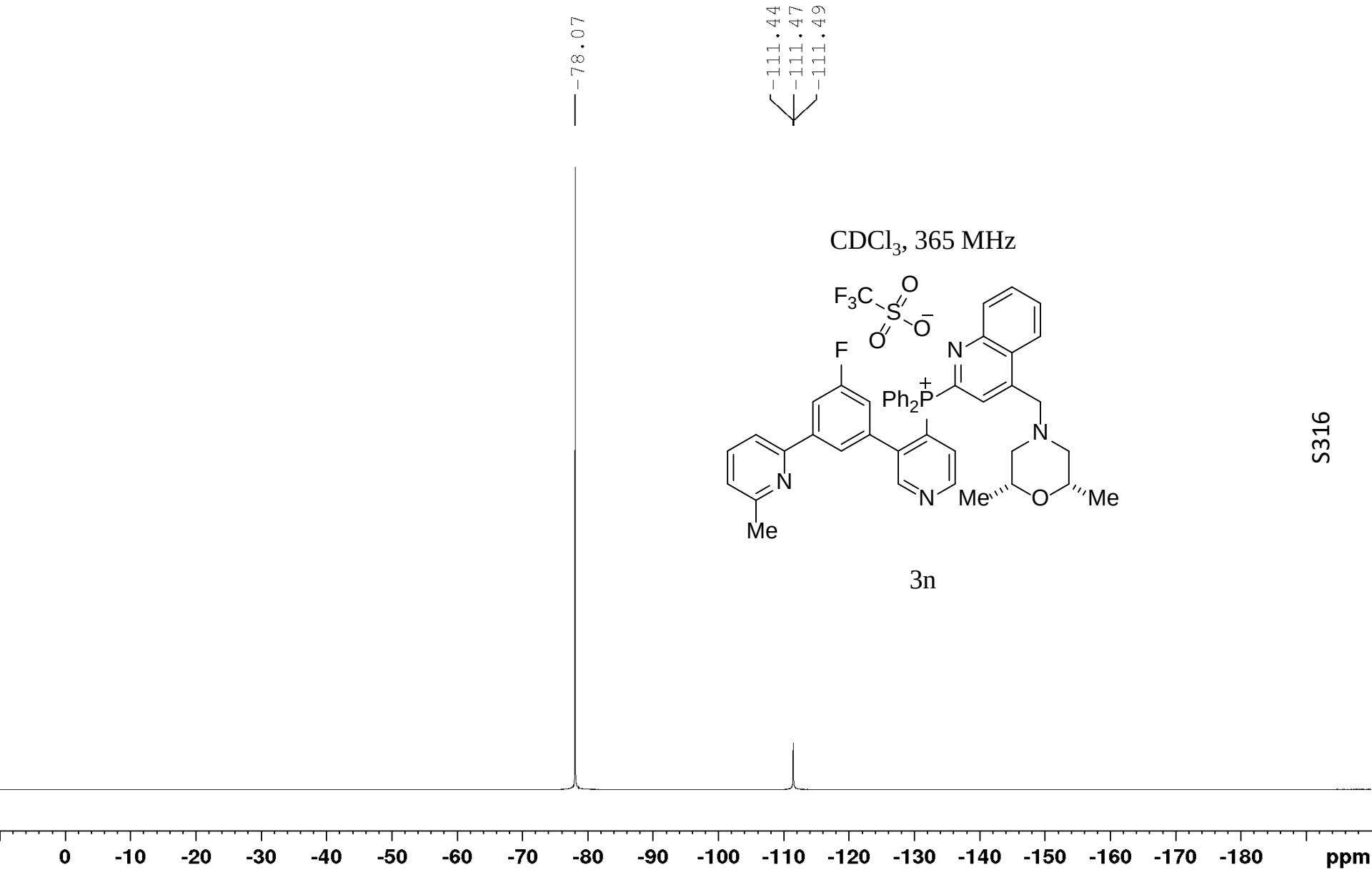

-78.16
-110.63
-110.66
-110.68
CDCl3, 365 MHz
EtO2C
Cl
Me
F
PPh2
CF3
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
ppm

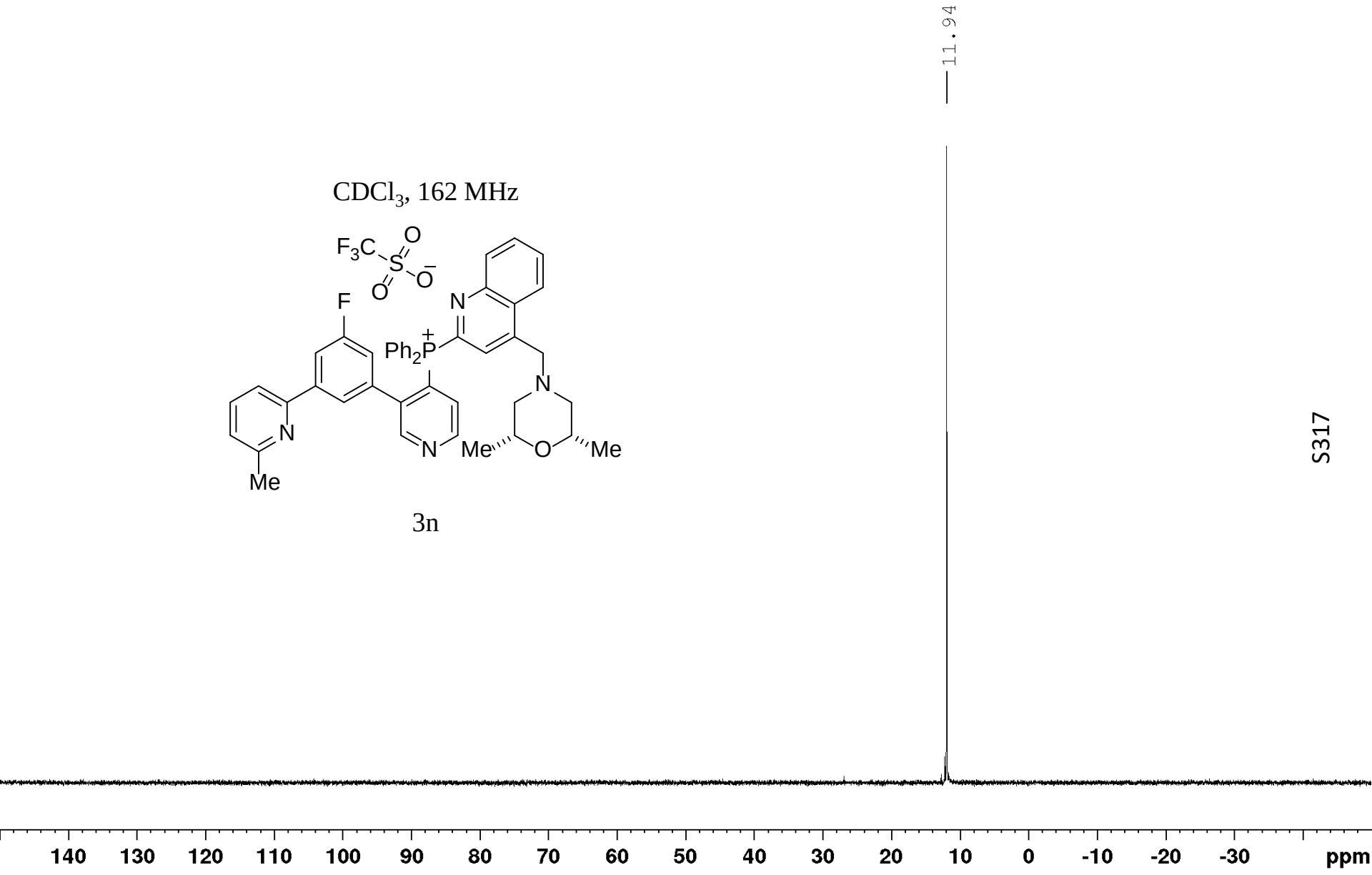
3m

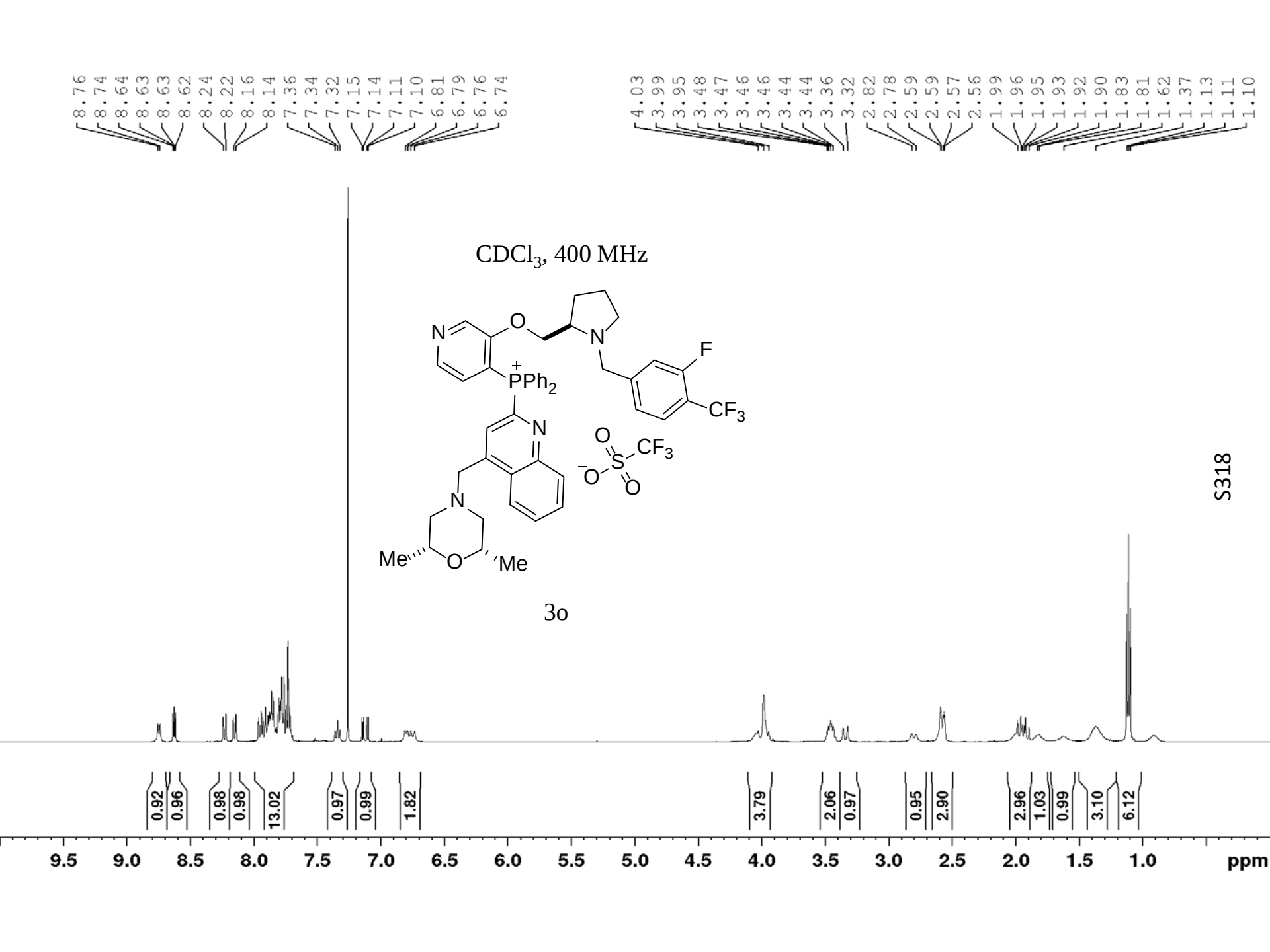

20.63
CDCl3, 162 MHz
O
S
CF3
O
O
N
F
O
PPh2
N
EtO2C
N
N
Cl
Me
3m
S313
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
ppm

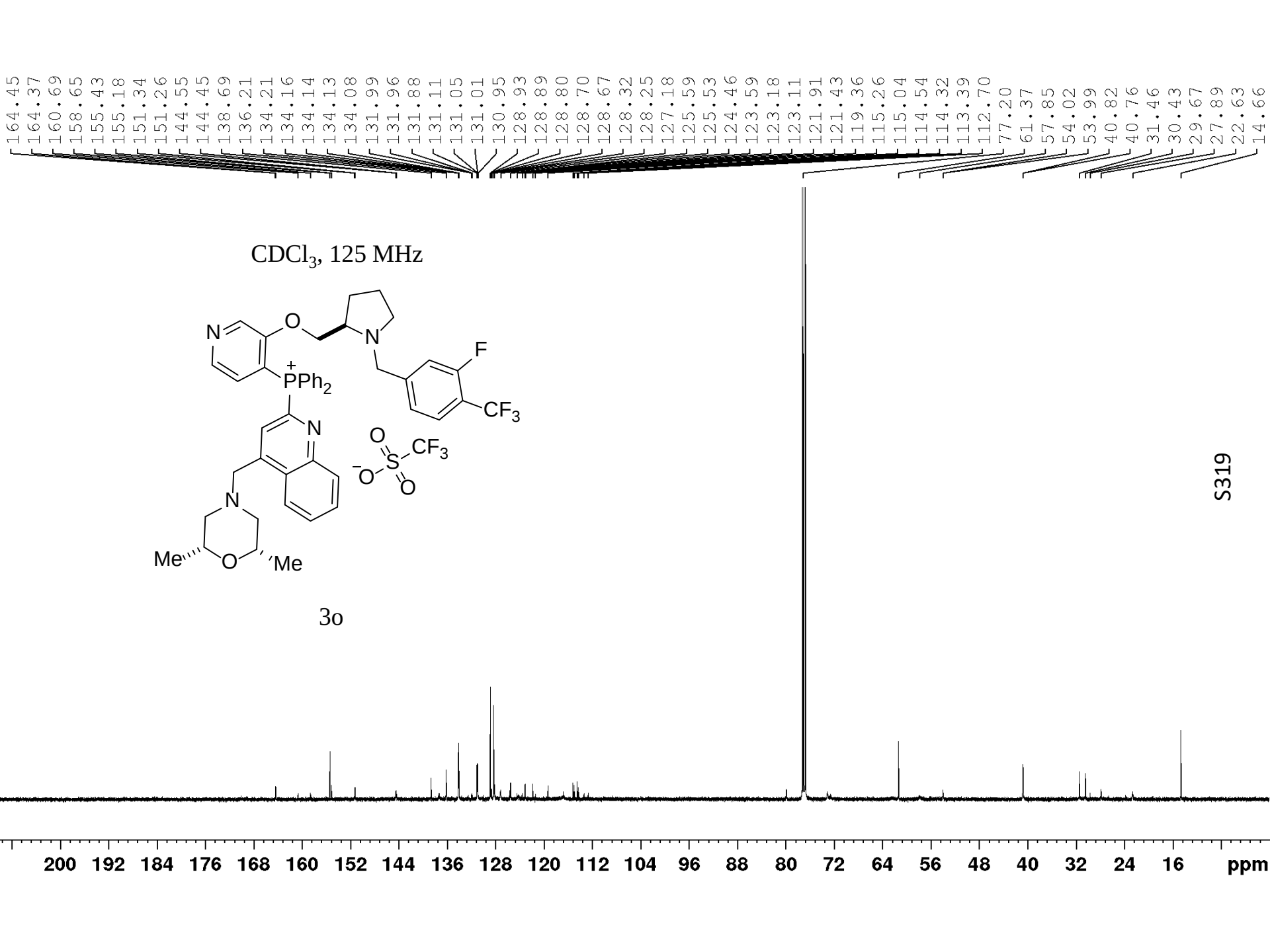

9.04
9.03
9.02
8.75
8.74
8.13
8.11
7.98
7.93
7.92
7.86
7.81
7.78
7.59
7.57
7.52
7.48
7.44
7.40
7.26
7.05
7.04
6.93
6.65
6.63
6.32
6.30
6.30
3.75
3.32
2.46
2.43
1.89
1.86
1.07
1.06
CDCl3, 400 MHz
F3C
S
O
O
O
F
N
Ph2P
N
N
Me
N
Me
O
Me
Me
3n
S314
1.00
0.98
1.05
6.14
6.34
1.17
4.10
1.03
0.99
0.98
1.01
2.14
2.00
5.15
1.97
6.18
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm


163.28
160.80
158.29
152.57
152.28
152.26
148.44
148.21
143.75
137.12
136.10
136.07
135.11
135.01
131.61
130.82
130.69
130.22
127.97
123.26
122.91
117.01
116.55
116.15
113.87
77.32
77.20
77.00
76.68
71.62
59.29
57.36
24.58
18.86
CDCl3, 100 MHz
F3C
O
S
O
O
O
F
N
Ph2P
+
N
N
Me
N
Me
O
Me
Me
3n
S315
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
Chemical Shift (ppm)


-78.07
-111.44
-111.47
-111.49
CDCl3, 365 MHz
3n
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
ppm

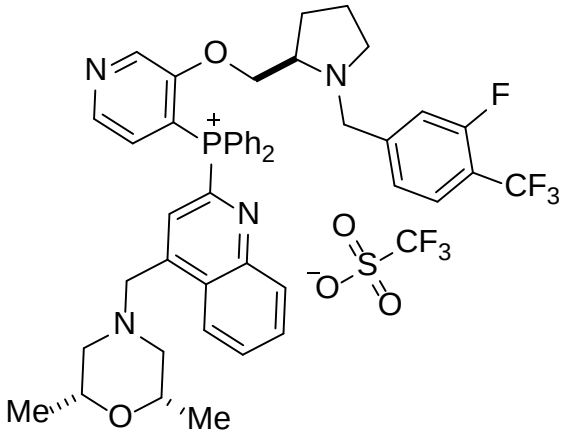

11.94
CDCl3, 162 MHz
F3C
O
S
O
O
F
N
Ph2P
+
N
N
Me
O
Me
N
Me
3n
S317
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
ppm


8.76
8.74
8.64
8.63
8.63
8.62
8.24
8.22
8.16
8.14
7.36
7.34
7.32
7.15
7.14
7.11
7.10
6.81
6.79
6.76
6.74
4.03
3.99
3.95
3.48
3.47
3.46
3.46
3.44
3.44
3.36
3.32
2.82
2.78
2.59
2.59
2.57
2.56
1.99
1.96
1.95
1.93
1.92
1.90
1.83
1.81
1.62
1.37
1.13
1.11
1.10
CDCl3, 400 MHz
N
O
N
F
PPh2
CF3
N
O
CF3
S
O
O
O
N
Me
O
Me
3o
S318
0.92
0.96
0.98
0.98
13.02
0.97
0.99
1.82
3.79
2.06
0.97
0.95
2.90
2.96
1.03
0.99
3.10
6.12
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm


164.45
164.37
160.69
158.65
155.43
155.18
151.34
151.26
144.55
144.45
138.69
136.21
134.21
134.16
134.14
134.13
134.08
131.99
131.96
131.88
131.11
131.05
131.01
130.95
128.93
128.89
128.80
128.70
128.67
128.32
128.25
127.18
125.59
125.53
124.46
123.59
123.18
123.11
121.91
121.43
119.36
115.26
115.04
114.54
114.32
113.39
112.70
77.20
61.37
57.85
54.02
53.99
40.82
40.76
31.46
30.43
29.67
27.89
22.63
14.66
CDCl3, 125 MHz
N
O
N
F
PPh2
CF3
N
O
CF3
S
O
O
N
Me
O
Me
3o
S319
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

-61.11
-61.15
-78.14
-114.67
-114.70

$CDCl_3$, 365 MHz



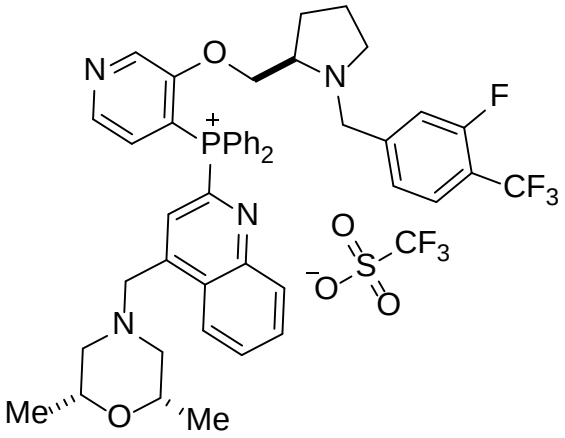
3o

S320

10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 ppm

12.52

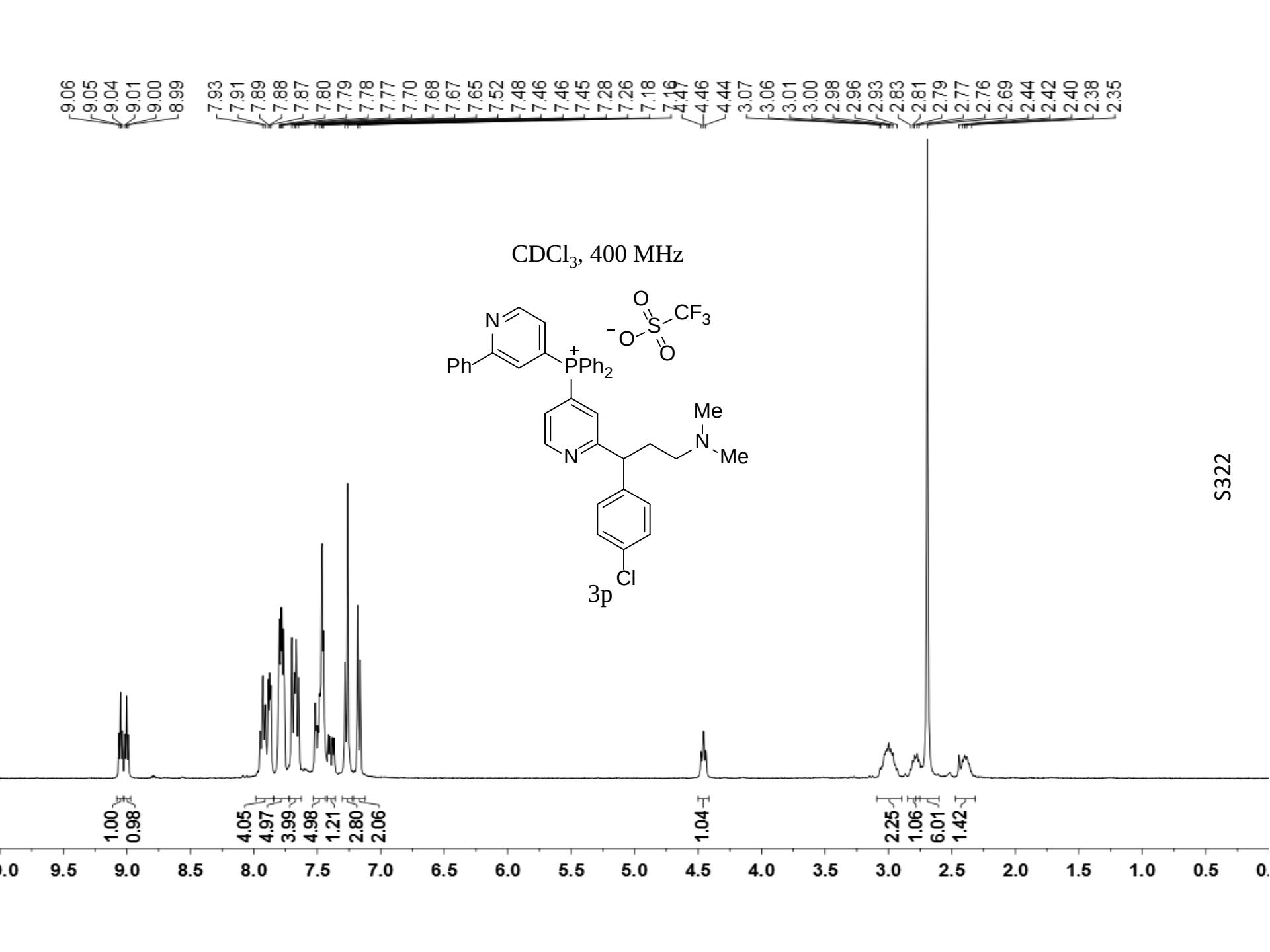
$CDCl_3$, 162 MHz

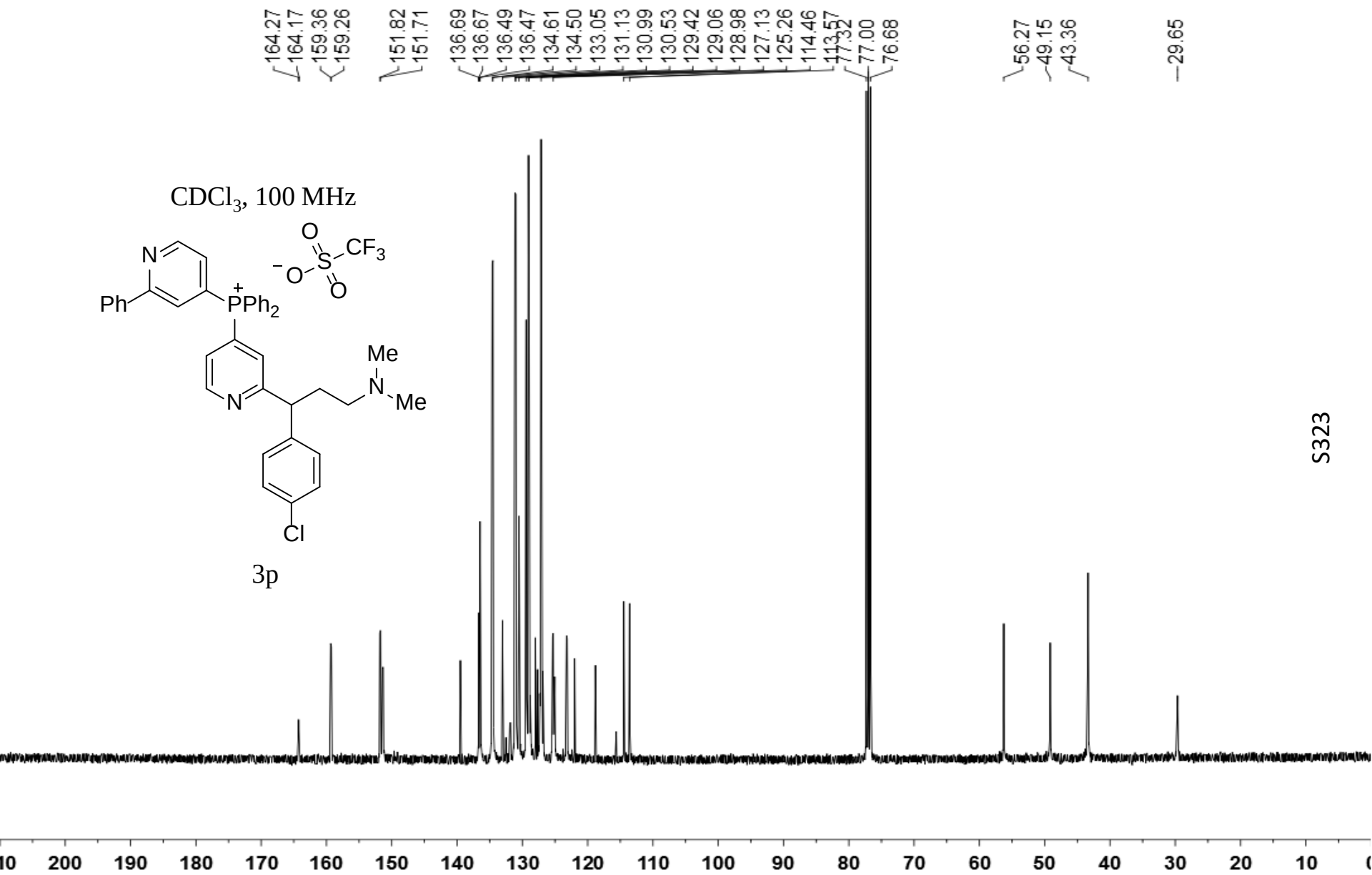


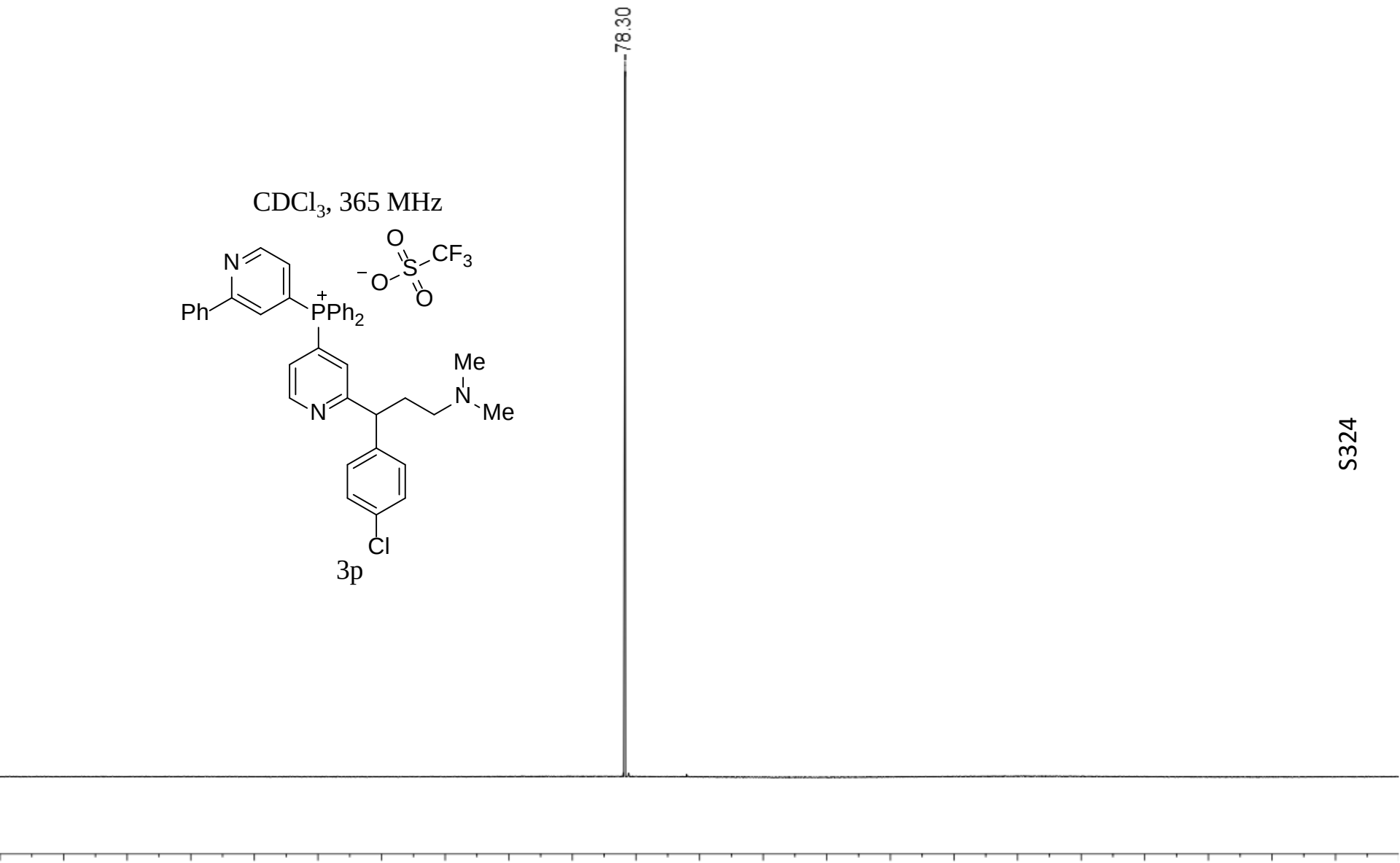
3o

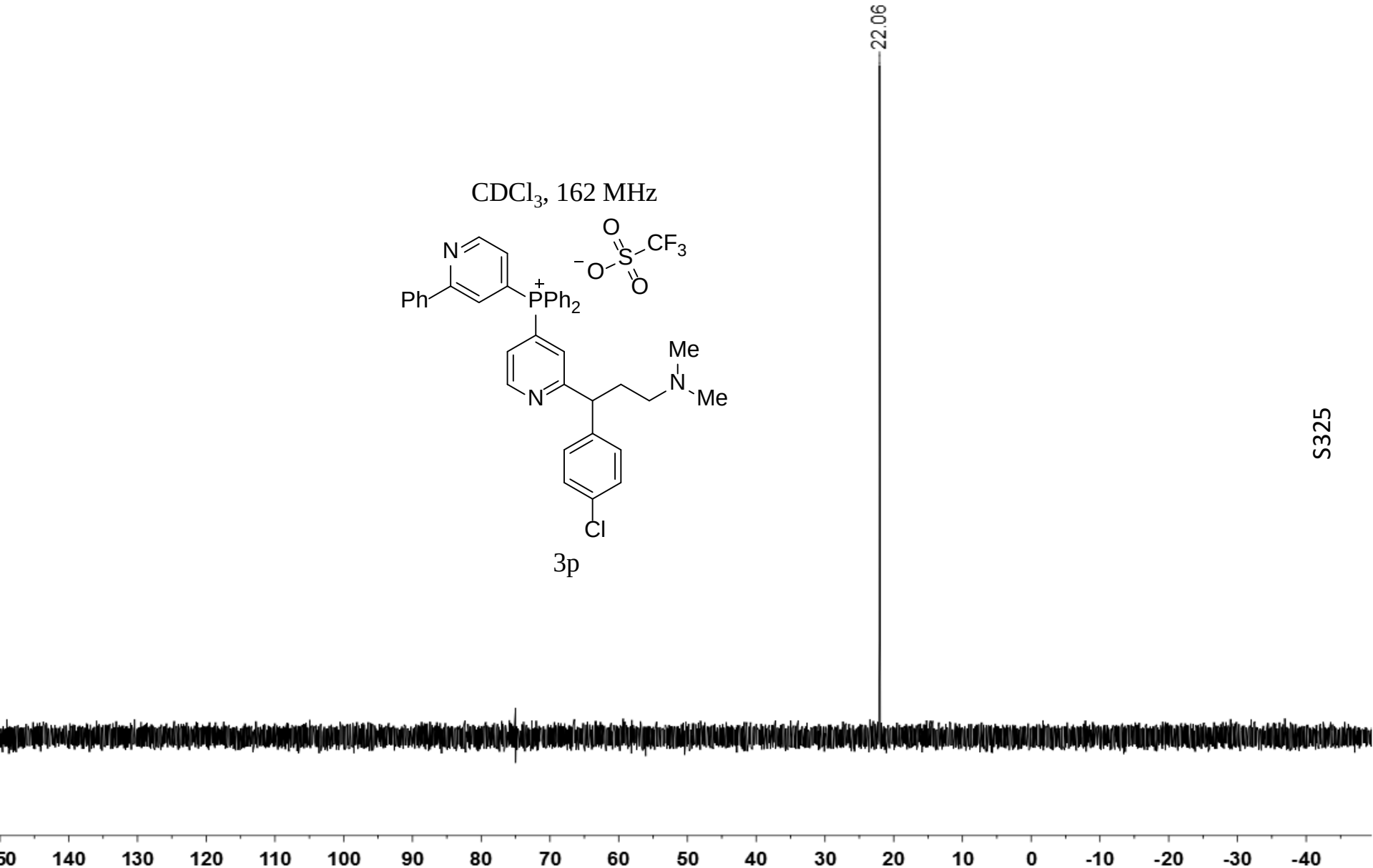
S321

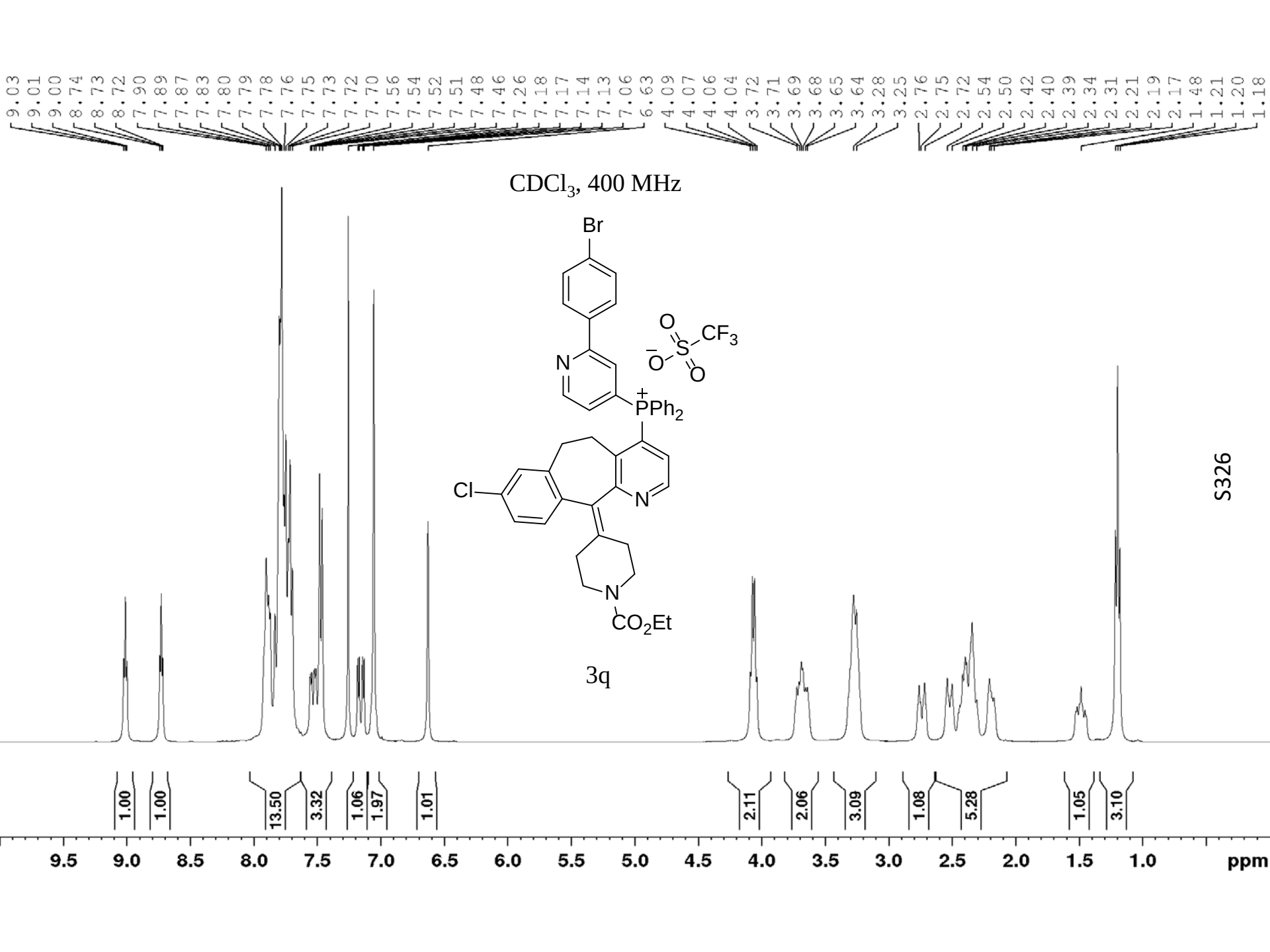
140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 ppm

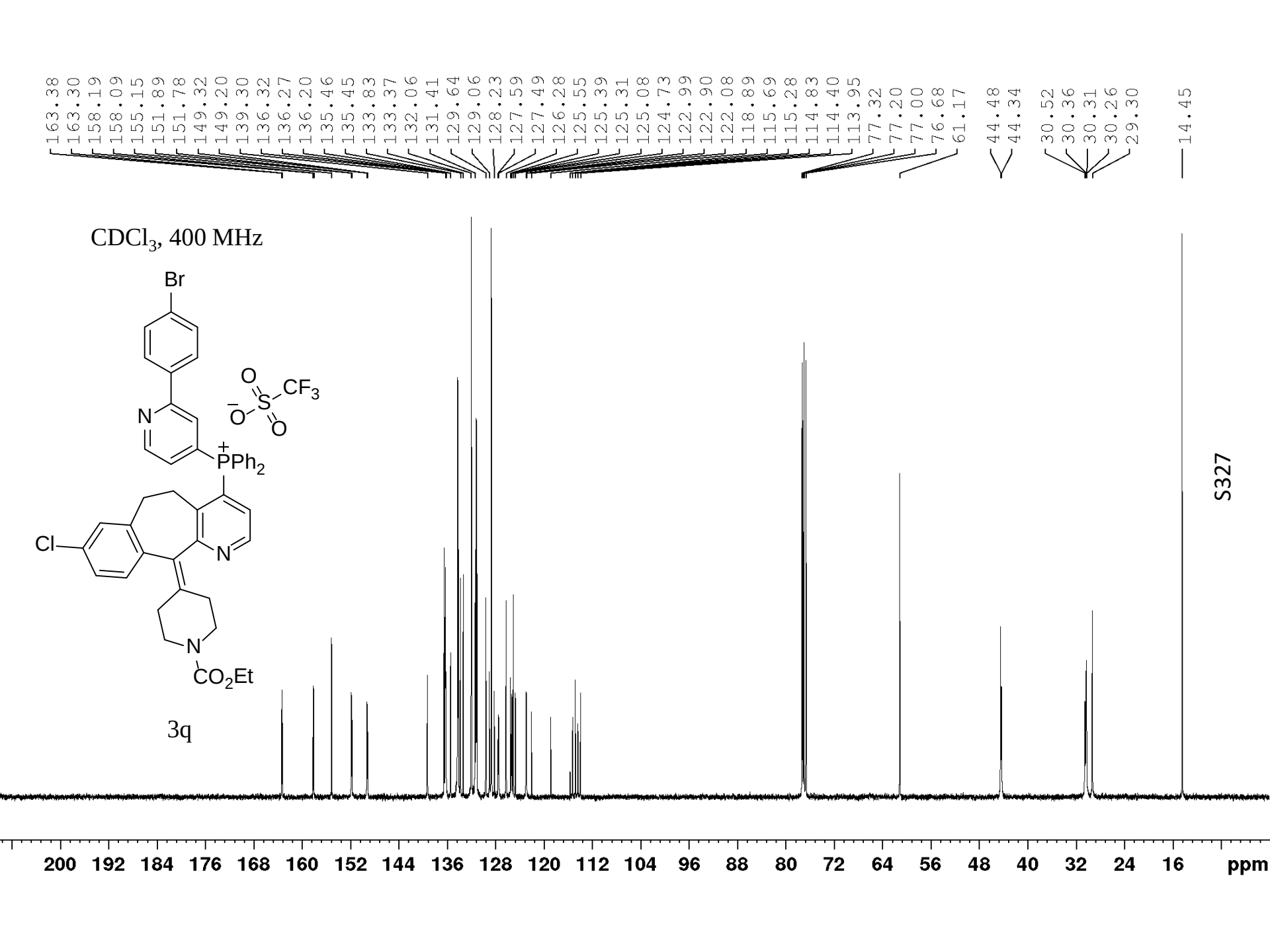

9.06
9.05
9.04
9.01
9.00
8.99
7.93
7.91
7.89
7.88
7.87
7.80
7.79
7.78
7.77
7.70
7.68
7.67
7.65
7.52
7.48
7.46
7.46
7.45
7.28
7.26
7.18
7.16
4.47
4.46
4.44
3.07
3.06
3.01
3.00
2.98
2.96
2.93
2.83
2.81
2.79
2.77
2.76
2.69
2.44
2.42
2.40
2.38
2.35
CDCl3, 400 MHz
Ph
PPh2
CF3
Me
Me
Cl
3p
S322
1.00
0.98
4.05
4.97
3.99
4.98
1.21
2.80
2.06
1.04
2.25
1.06
6.01
1.42
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

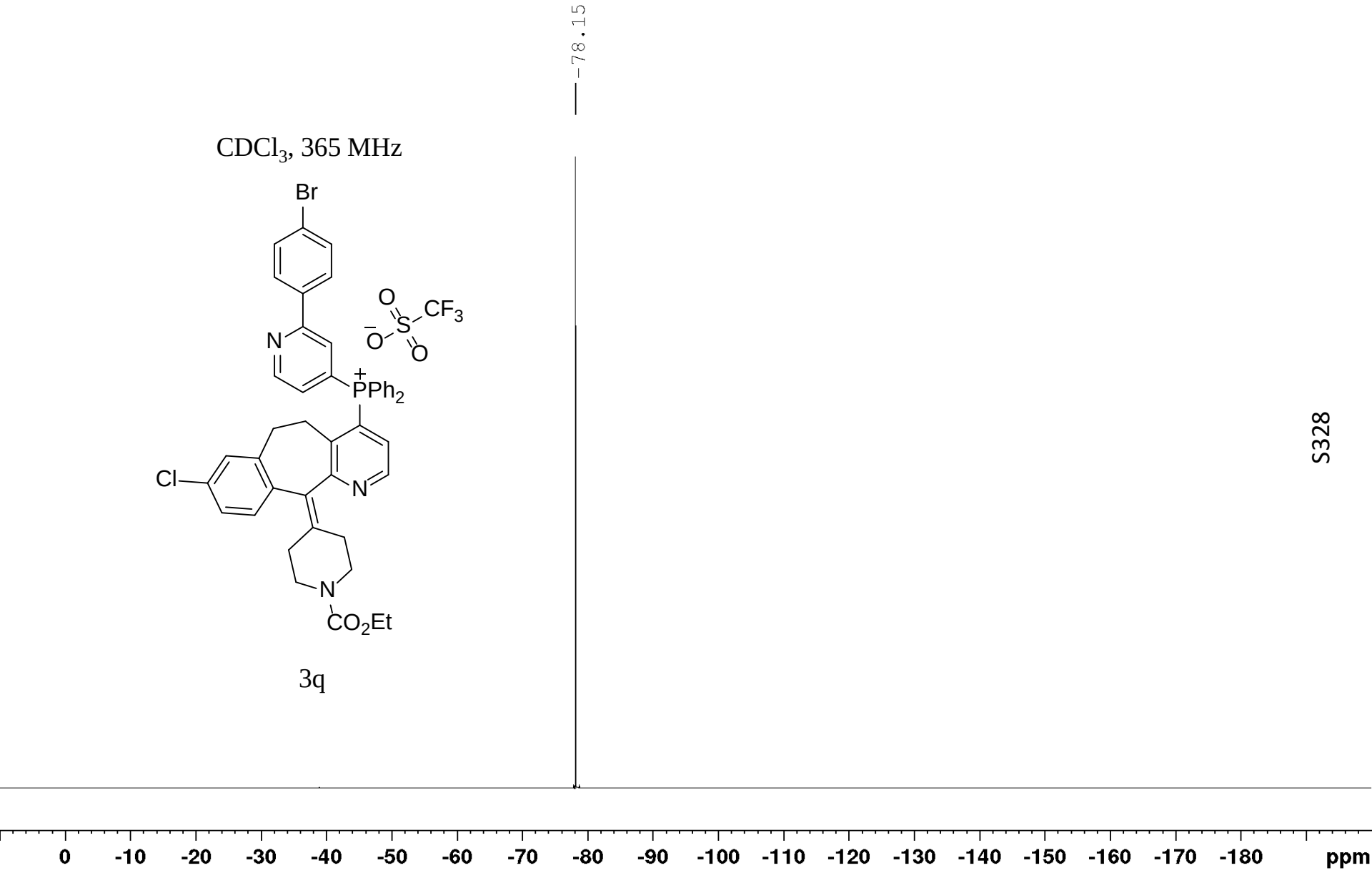

164.27
164.17
159.36
159.26
151.82
151.71
136.69
136.67
136.49
136.47
134.61
134.50
133.05
131.13
130.99
130.53
129.42
129.06
128.98
127.13
125.26
114.46
113.57
77.32
77.00
76.68
56.27
49.15
43.36
29.65
CDCl3, 100 MHz
3p
S323


78.30
CDCl3, 365 MHz
3p
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-110
-130
-150
-170
-190

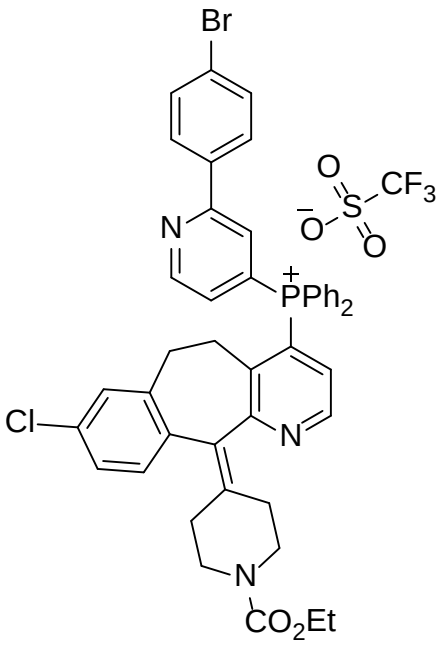

22.06
CDCl3, 162 MHz
N
Ph
PPh2
O
S
CF3
O
O
Me
N
Me
N
Cl
3p
S325
50
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40


9.03 9.01 9.00 8.74 8.73 8.72 7.90 7.89 7.87 7.83 7.80 7.79 7.78 7.76 7.75 7.73 7.72 7.70 7.56 7.54 7.52 7.51 7.48 7.46 7.26 7.18 7.17 7.14 7.13 7.06 6.63 4.09 4.07 4.06 4.04 3.72 3.71 3.69 3.68 3.65 3.64 3.28 3.25 2.76 2.75 2.72 2.54 2.50 2.42 2.40 2.39 2.34 2.31 2.21 2.19 2.17 1.48 1.21 1.20 1.18
CDCl3, 400 MHz
Br
O
CF3
S
O
O
N
PPh2
Cl
N
N
CO2Et
3q
S326
1.00
1.00
13.50
3.32
1.06
1.97
1.01
2.11
2.06
3.09
1.08
5.28
1.05
3.10
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0
ppm

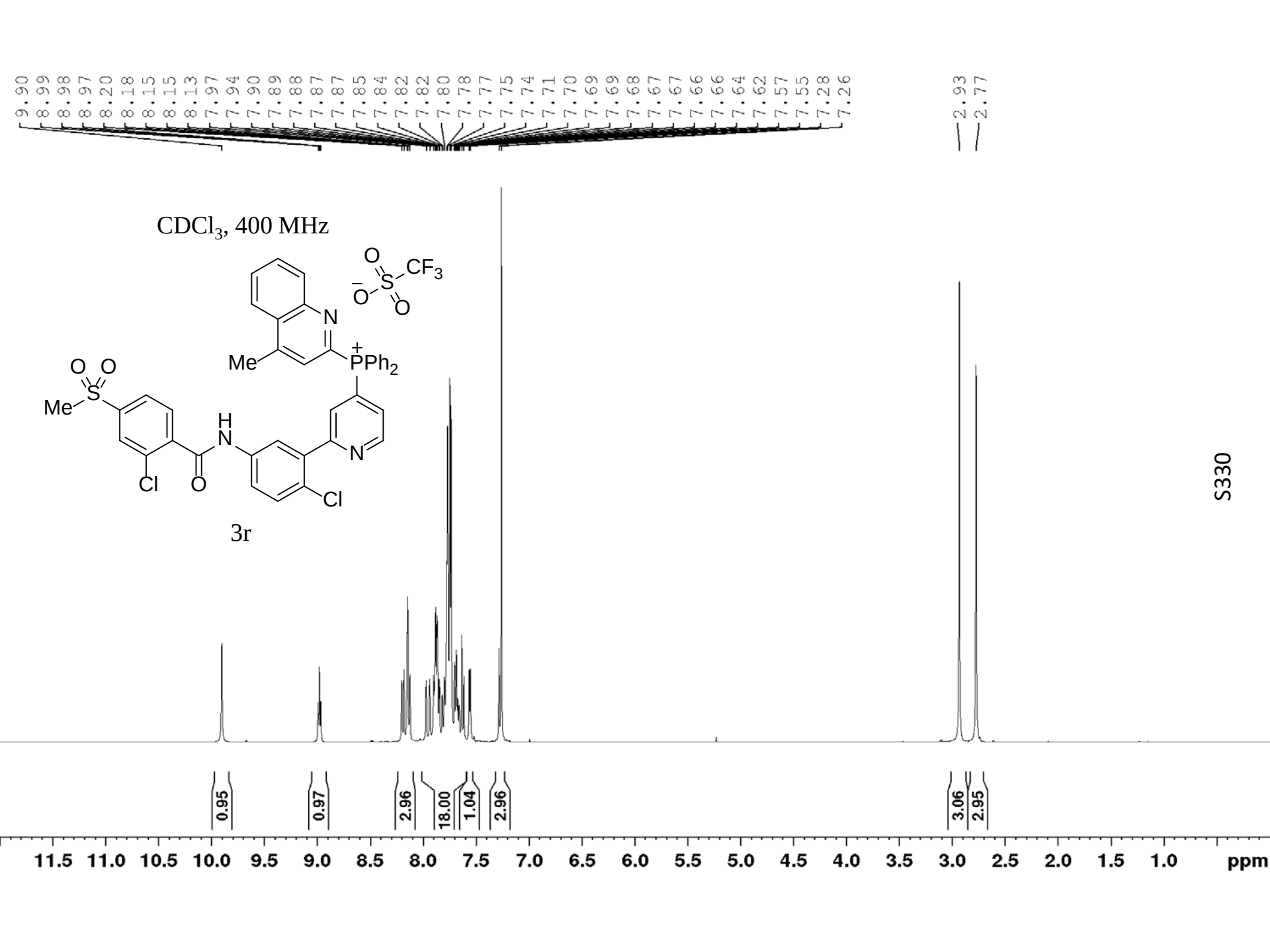

163.38
163.30
158.19
158.09
155.15
151.89
151.78
149.32
149.20
139.30
136.32
136.27
136.20
135.46
135.45
133.83
133.37
132.06
131.41
129.64
129.06
128.23
127.59
127.49
126.28
125.55
125.39
125.31
125.08
124.73
122.99
122.90
122.08
118.89
115.69
115.28
114.83
114.40
113.95
77.32
77.20
77.00
76.68
61.17
44.48
44.34
30.52
30.36
30.31
30.26
29.30
14.45
CDCl3, 400 MHz
Br
O
CF3
S
O
O
N
PPh2
Cl
N
N
CO2Et
3q
S327
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 ppm

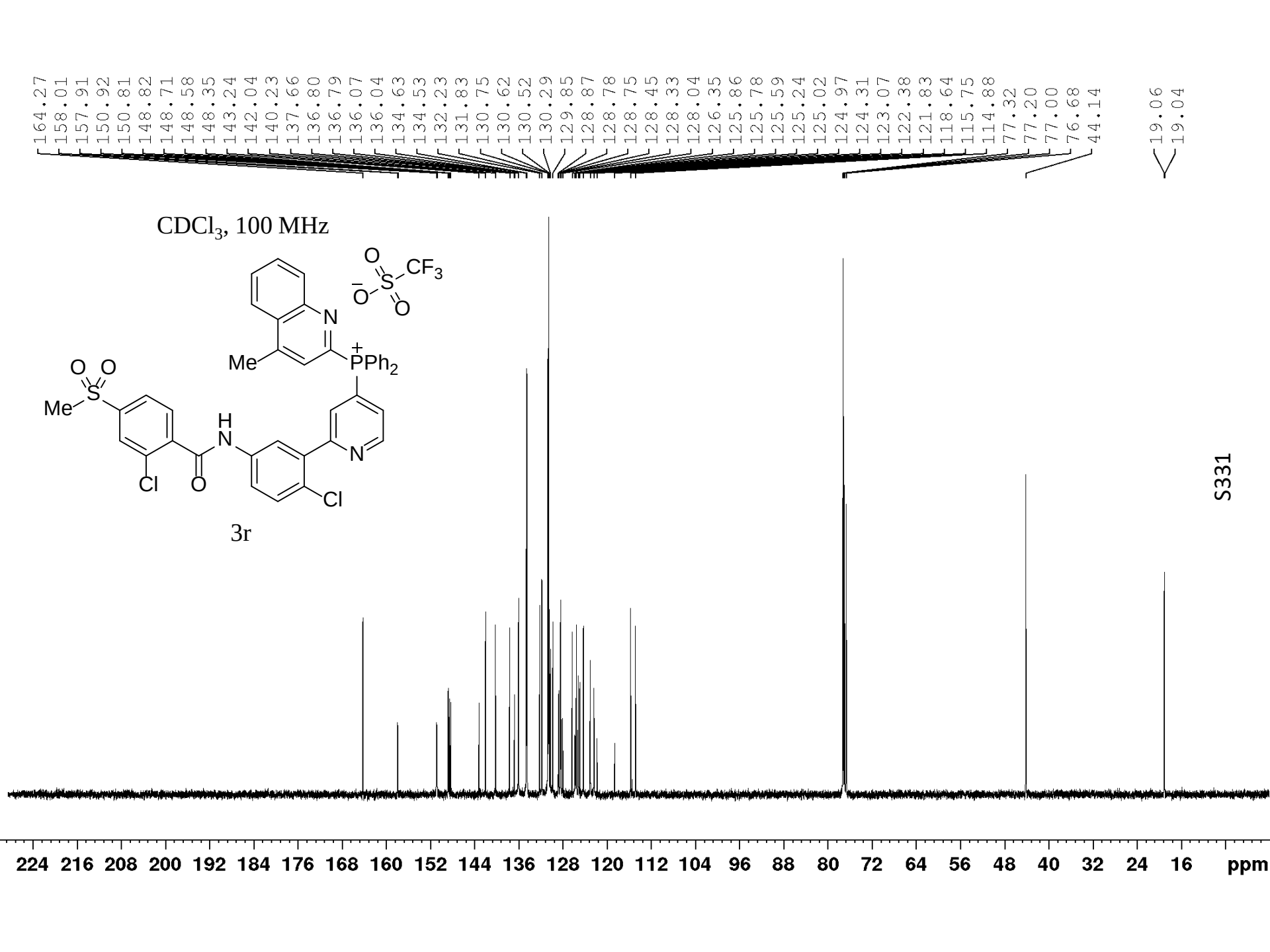

-78.15
CDCl3, 365 MHz
Br
O
CF3
S
O
O
N
PPh2
Cl
N
N
CO2Et
3q
S328
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
ppm

$CDCl_3$, 162 MHz

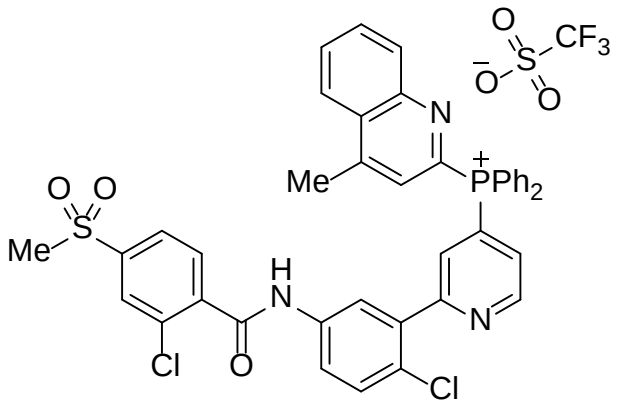


3q


9.90
8.99
8.98
8.97
8.20
8.18
8.15
8.15
8.13
7.97
7.94
7.90
7.89
7.88
7.87
7.87
7.85
7.84
7.82
7.82
7.80
7.78
7.77
7.75
7.74
7.71
7.70
7.69
7.69
7.68
7.67
7.67
7.66
7.66
7.64
7.62
7.57
7.55
7.28
7.26
2.93
2.77
CDCl3, 400 MHz
3r
S330
0.95
0.97
2.96
18.00
1.04
2.96
3.06
2.95
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm


164.27
158.01
157.91
150.92
150.81
148.82
148.71
148.58
148.35
143.24
142.04
140.23
137.66
136.80
136.79
136.07
136.04
134.63
134.53
132.23
131.83
130.75
130.62
130.52
130.29
129.85
128.87
128.78
128.75
128.45
128.33
128.04
126.35
125.86
125.78
125.59
125.24
125.02
124.97
124.31
123.07
122.38
121.83
118.64
115.75
114.88
77.32
77.20
77.00
76.68
44.14
19.06
19.04
CDCl3, 100 MHz
3r
S331
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 ppm

$CDCl_3$, 365 MHz



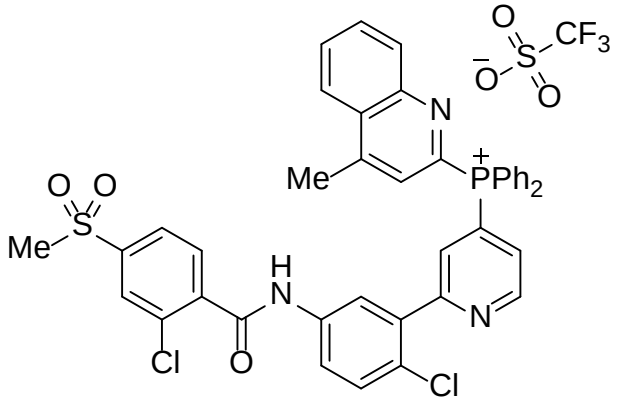
3r

-78.30

S332

0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 ppm

$CDCl_3$, 162 MHz

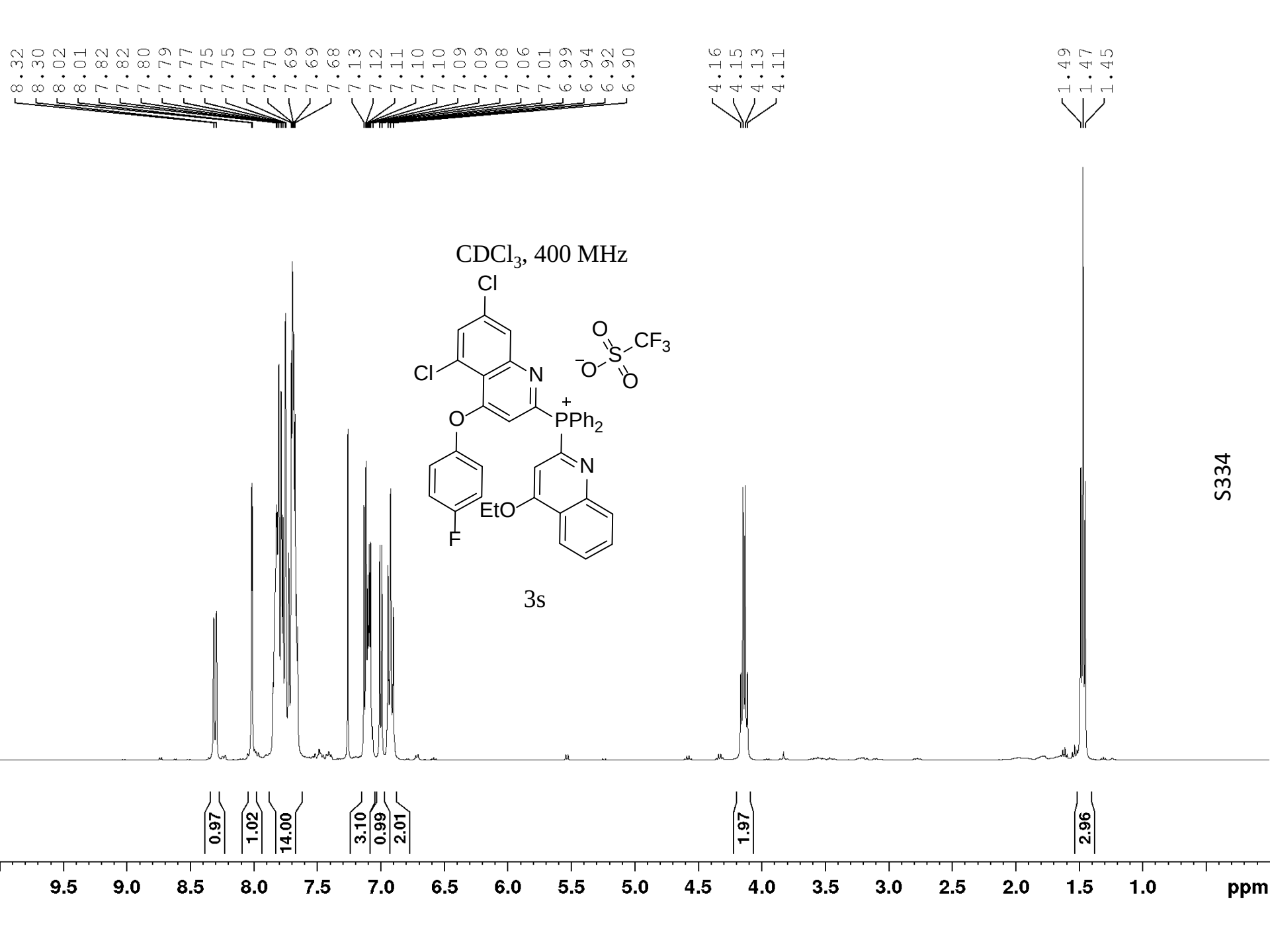


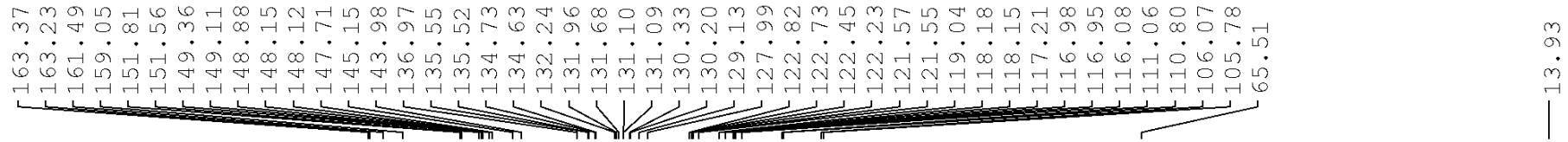
3r

13.30

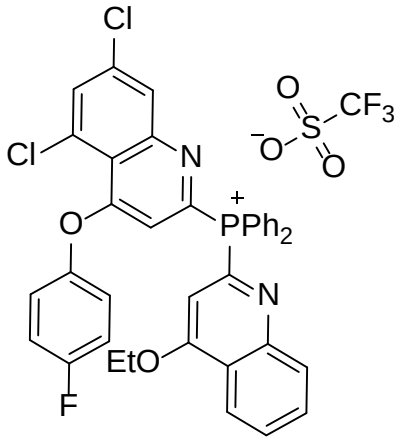
S333

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


8.32
8.30
8.02
8.01
7.82
7.82
7.80
7.79
7.77
7.75
7.75
7.70
7.70
7.69
7.69
7.68
7.13
7.12
7.11
7.10
7.10
7.09
7.09
7.08
7.06
7.01
6.99
6.94
6.92
6.90
4.16
4.15
4.13
4.11
1.49
1.47
1.45
CDCl3, 400 MHz
Cl
Cl
N
O
S
CF3
O
O
O
PPh2
+
N
EtO
F
3s
S334
0.97
1.02
14.00
3.10
0.99
2.01
1.97
2.96
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

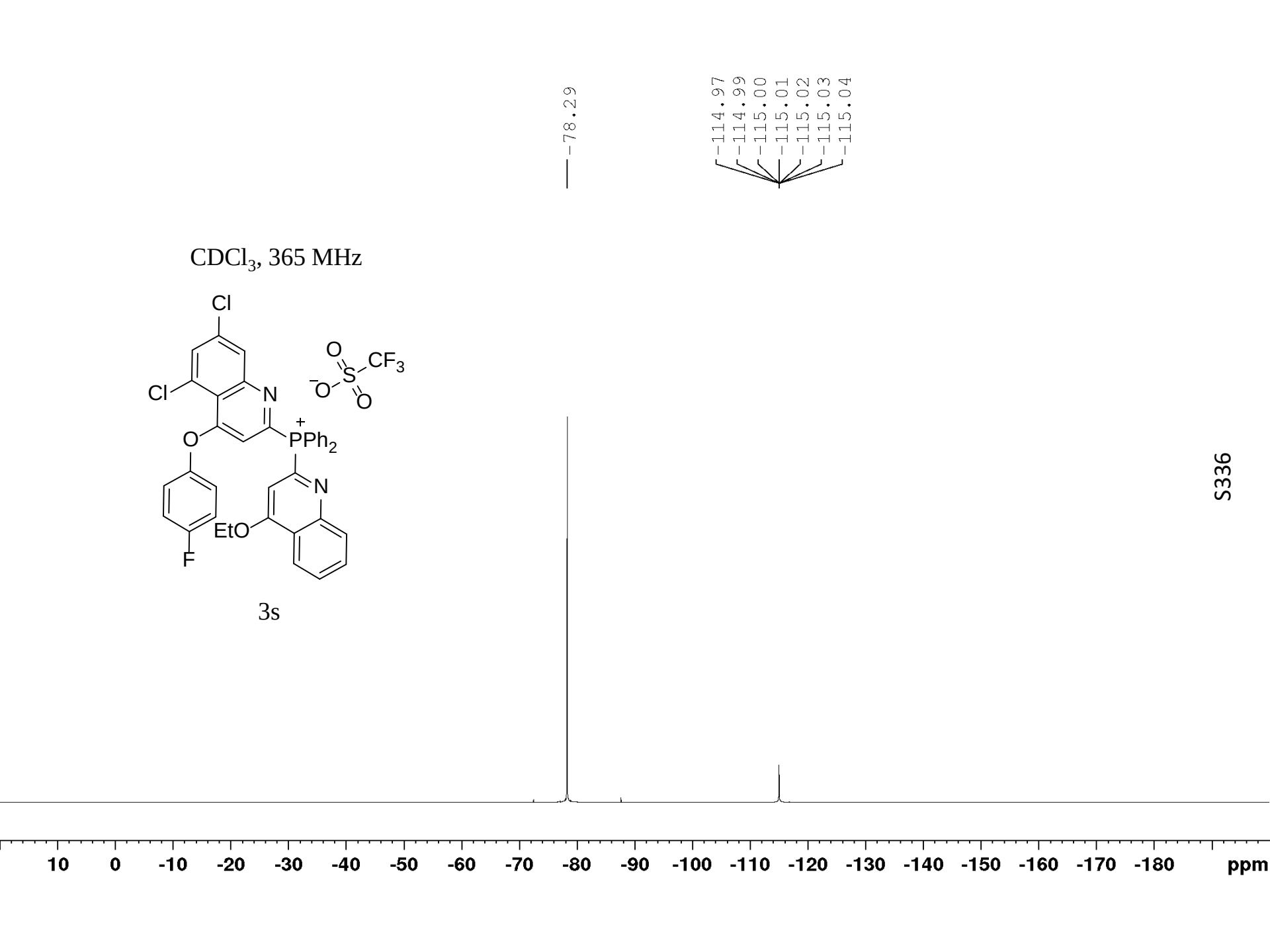


$CDCl_3$, 100 MHz



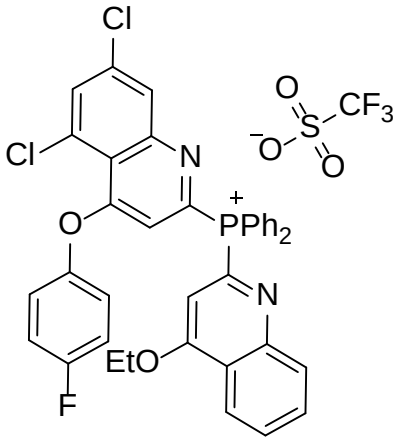
3s

S335


-78.29
-114.97
-114.99
-115.00
-115.01
-115.02
-115.03
-115.04
CDCl3, 365 MHz
Cl
Cl
N
O
S
CF3
O
O
O
PPh2
+
N
EtO
F
3s
S336
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
ppm

8.41

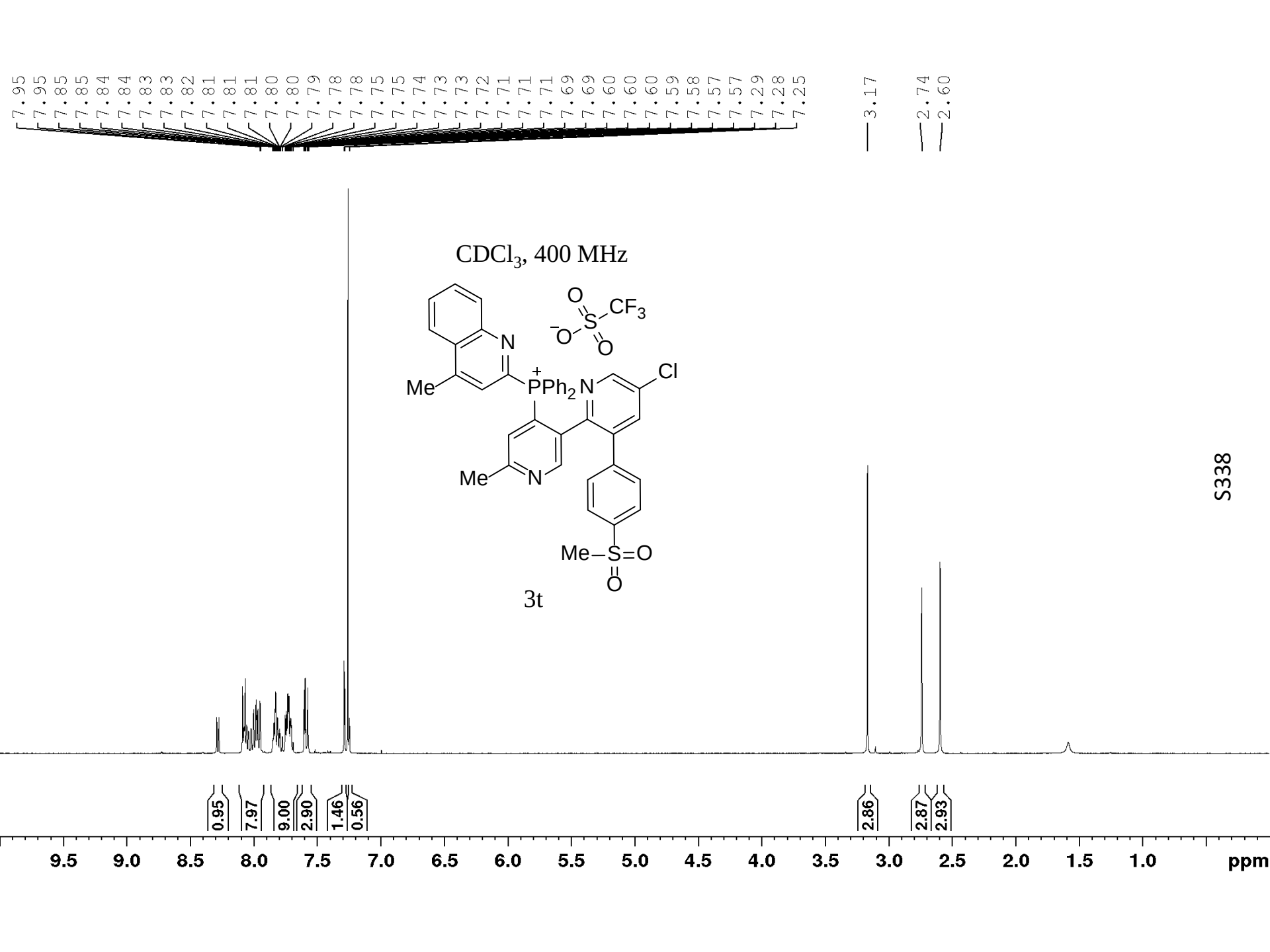
$CDCl_3$, 162 MHz

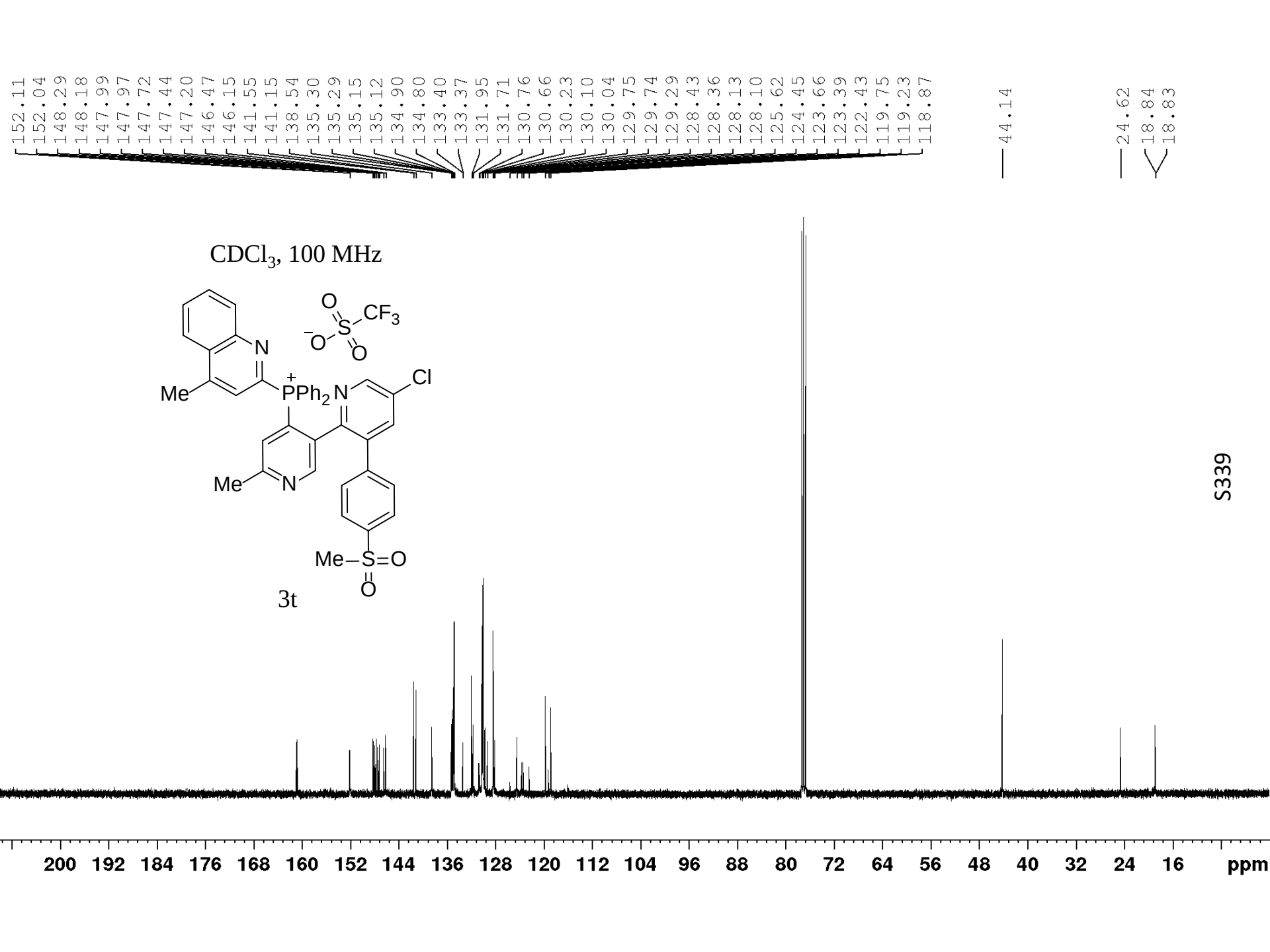


3s

S337

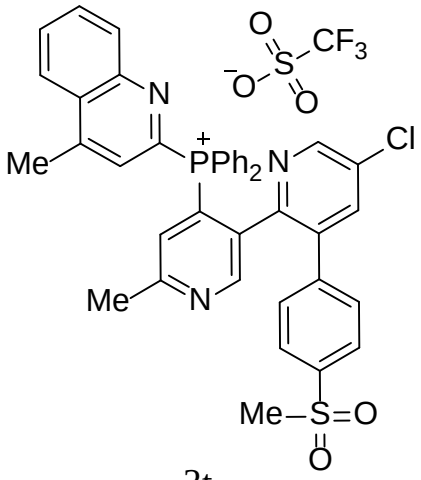
140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 ppm


7.95
7.95
7.85
7.85
7.84
7.84
7.83
7.83
7.82
7.81
7.81
7.81
7.80
7.80
7.79
7.78
7.78
7.75
7.75
7.74
7.73
7.73
7.72
7.71
7.71
7.71
7.69
7.69
7.60
7.60
7.60
7.59
7.58
7.57
7.57
7.29
7.28
7.25
3.17
2.74
2.60
CDCl3, 400 MHz
Me
PPh2
Cl
Me
Me–S=O
3t
S338
0.95
7.97
9.00
2.90
1.46
0.56
2.86
2.87
2.93
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm


152.11
152.04
148.29
148.18
147.99
147.97
147.72
147.44
147.20
146.47
146.15
141.55
141.15
138.54
135.30
135.29
135.15
135.12
134.90
134.80
133.40
133.37
131.95
131.71
130.76
130.66
130.23
130.10
130.04
129.75
129.74
129.29
128.43
128.36
128.13
128.10
125.62
124.45
123.66
123.39
122.43
119.75
119.23
118.87
44.14
24.62
18.84
18.83
CDCl3, 100 MHz
Me
PPh2
Cl
Me
Me—S=O
3t
S339
200
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
ppm

—78.15

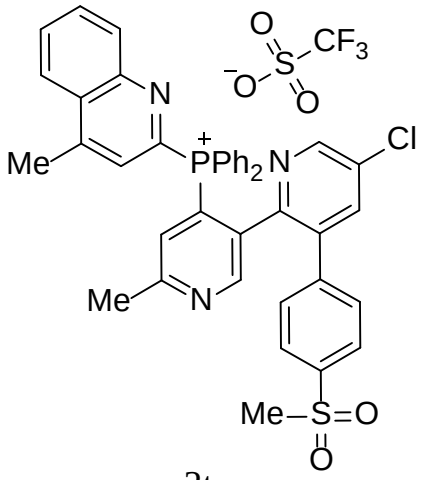
$CDCl_3$, 365 MHz



3t

16.31

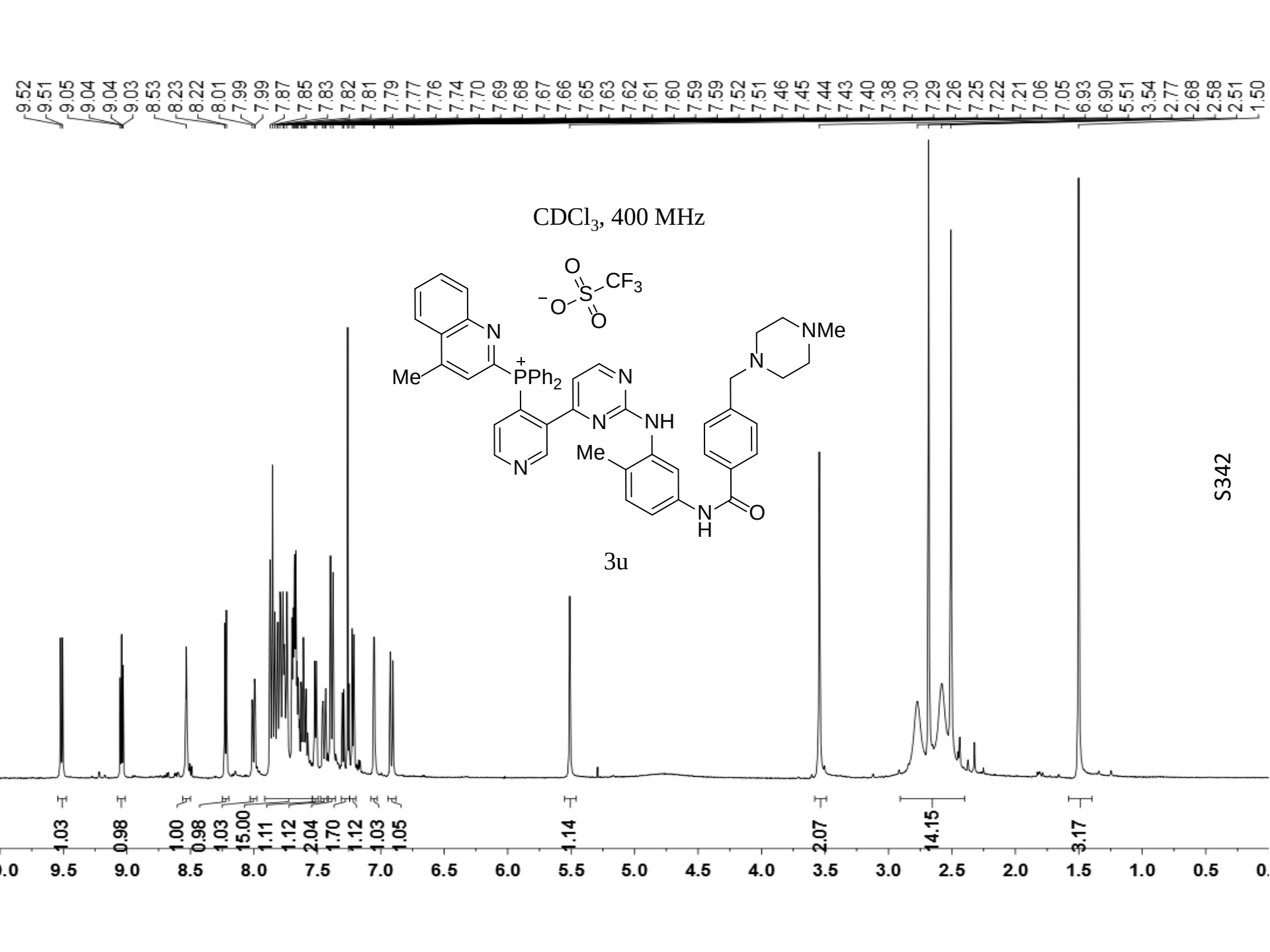
$CDCl_3$, 162 MHz

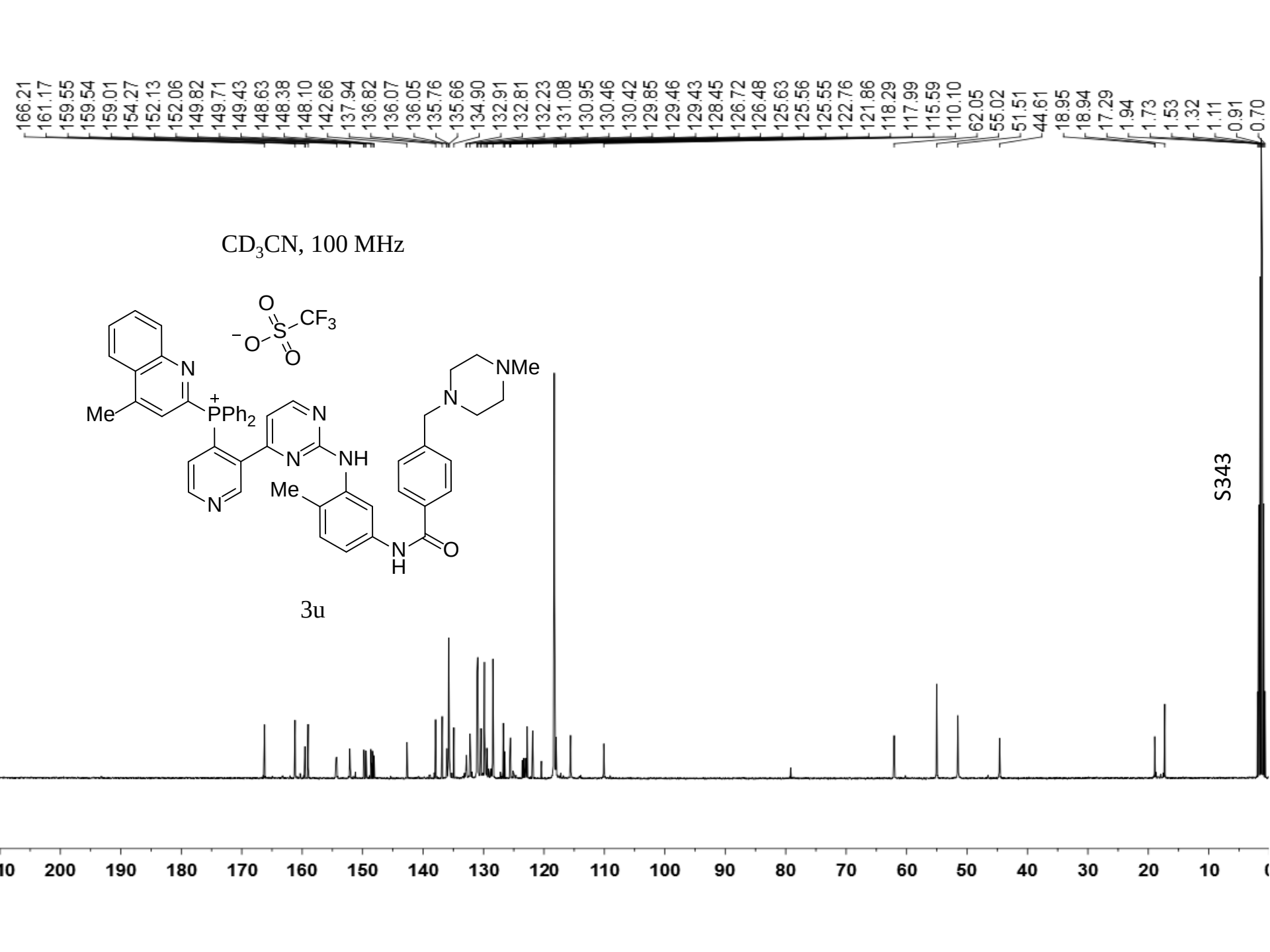


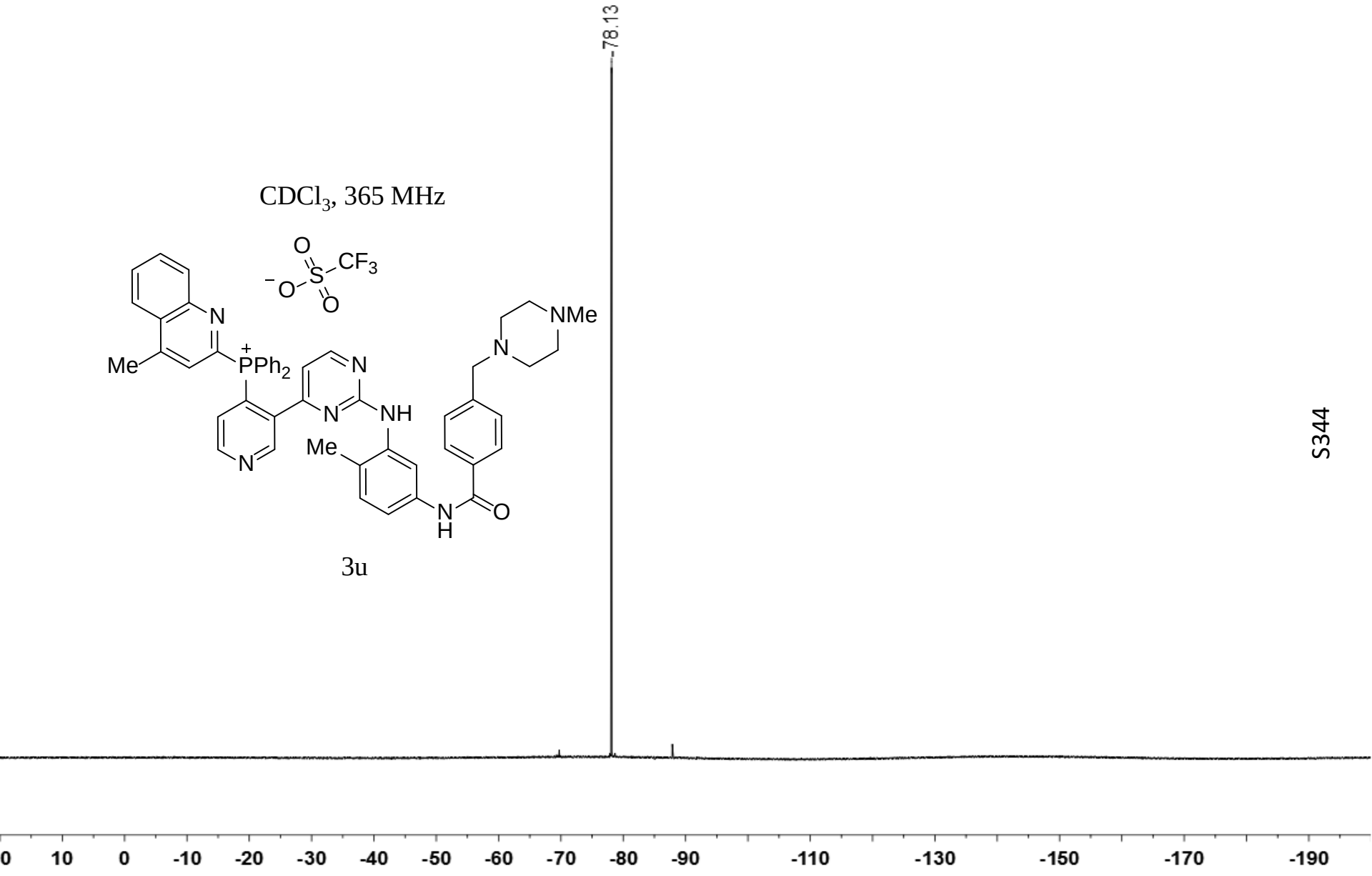
3t

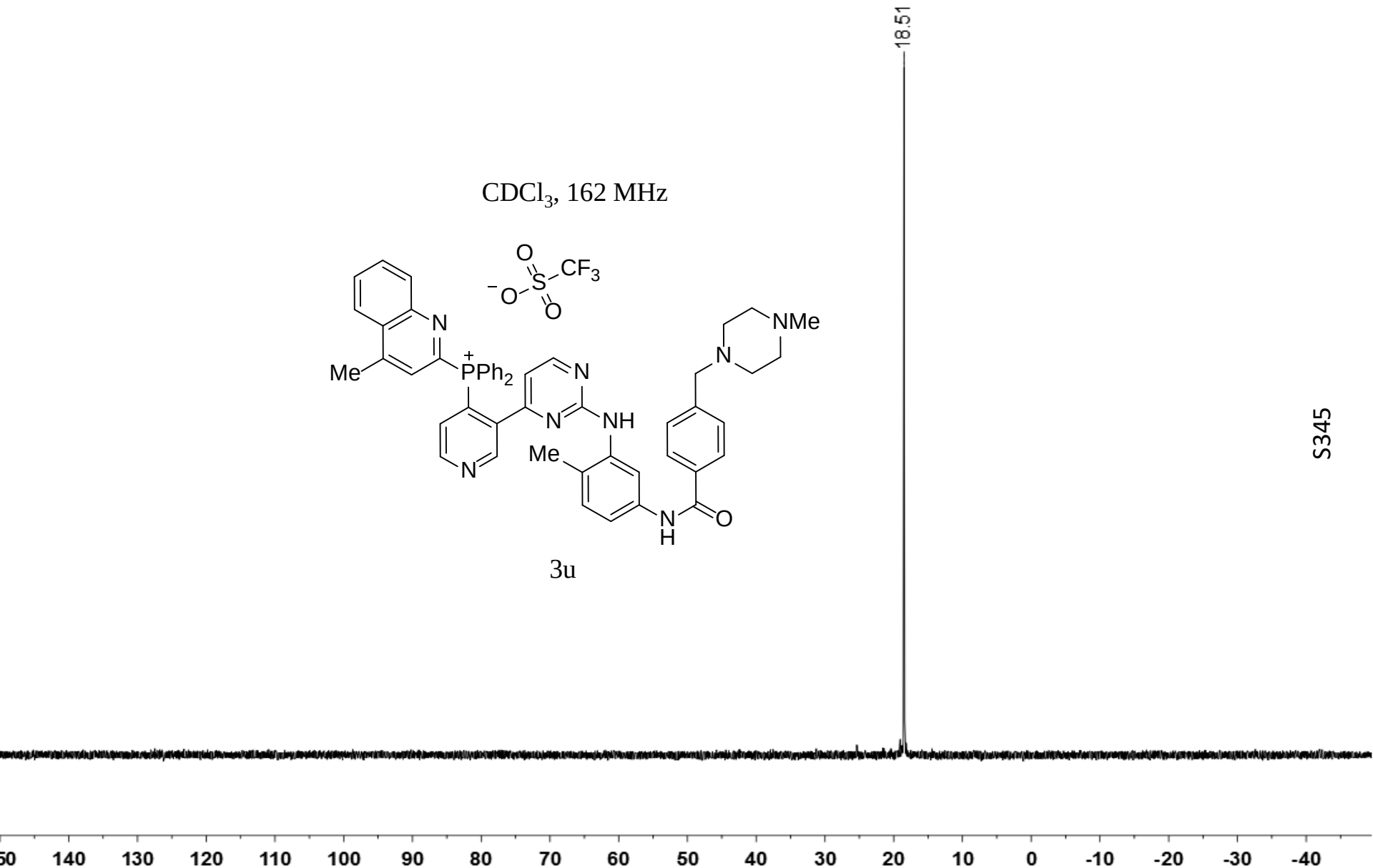
S341

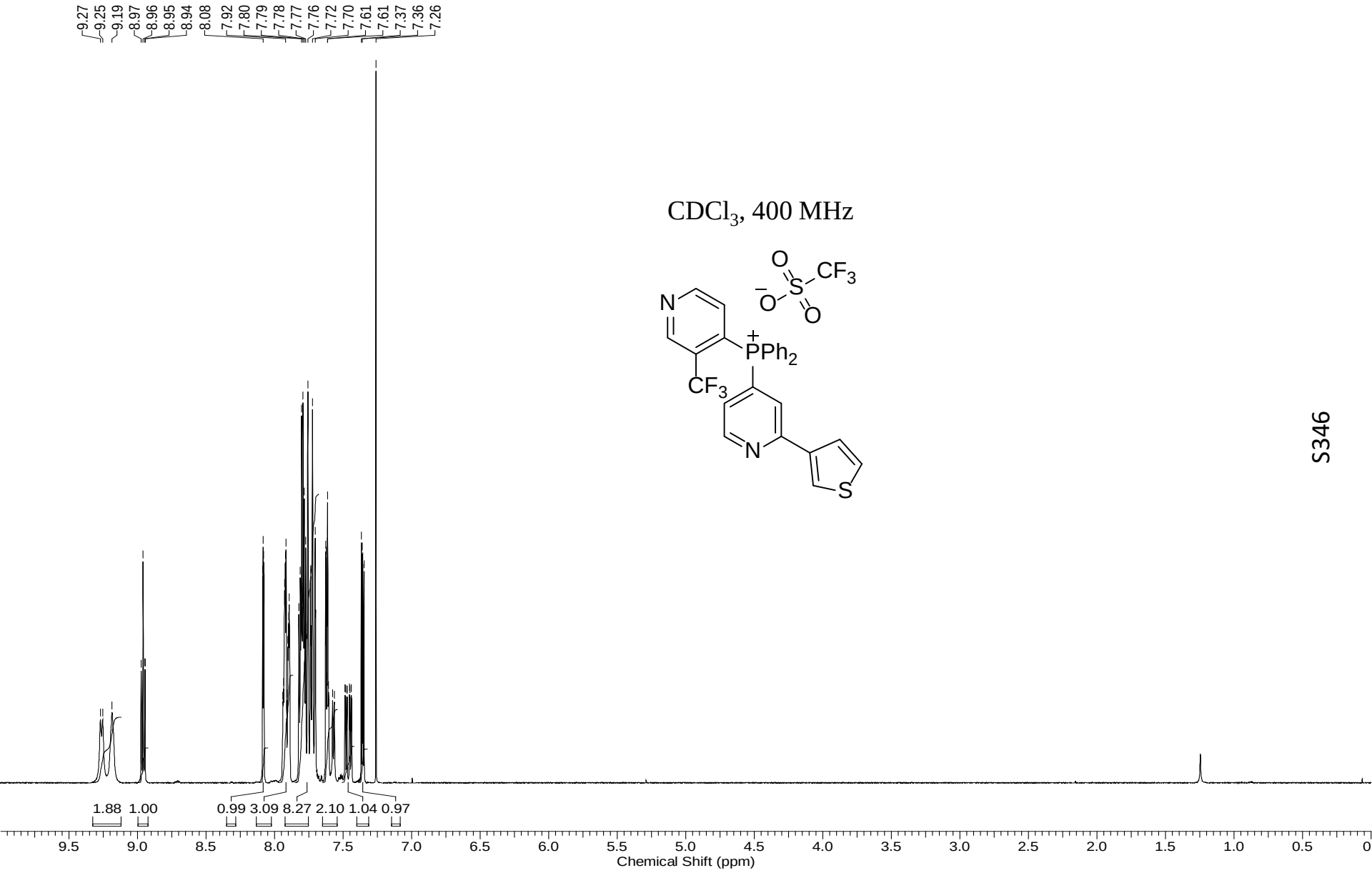
140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 ppm

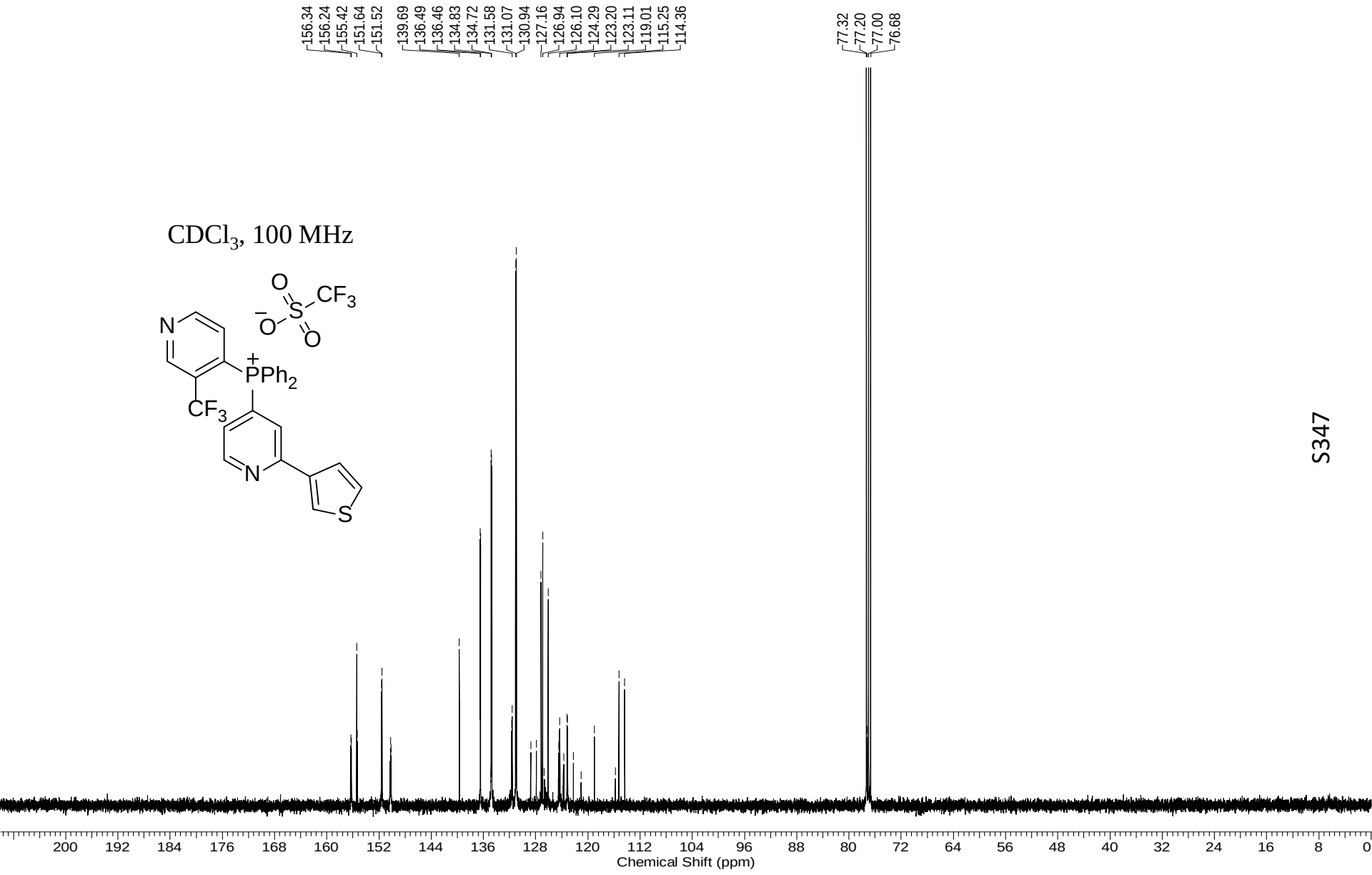

CDCl3, 400 MHz
3u
S342

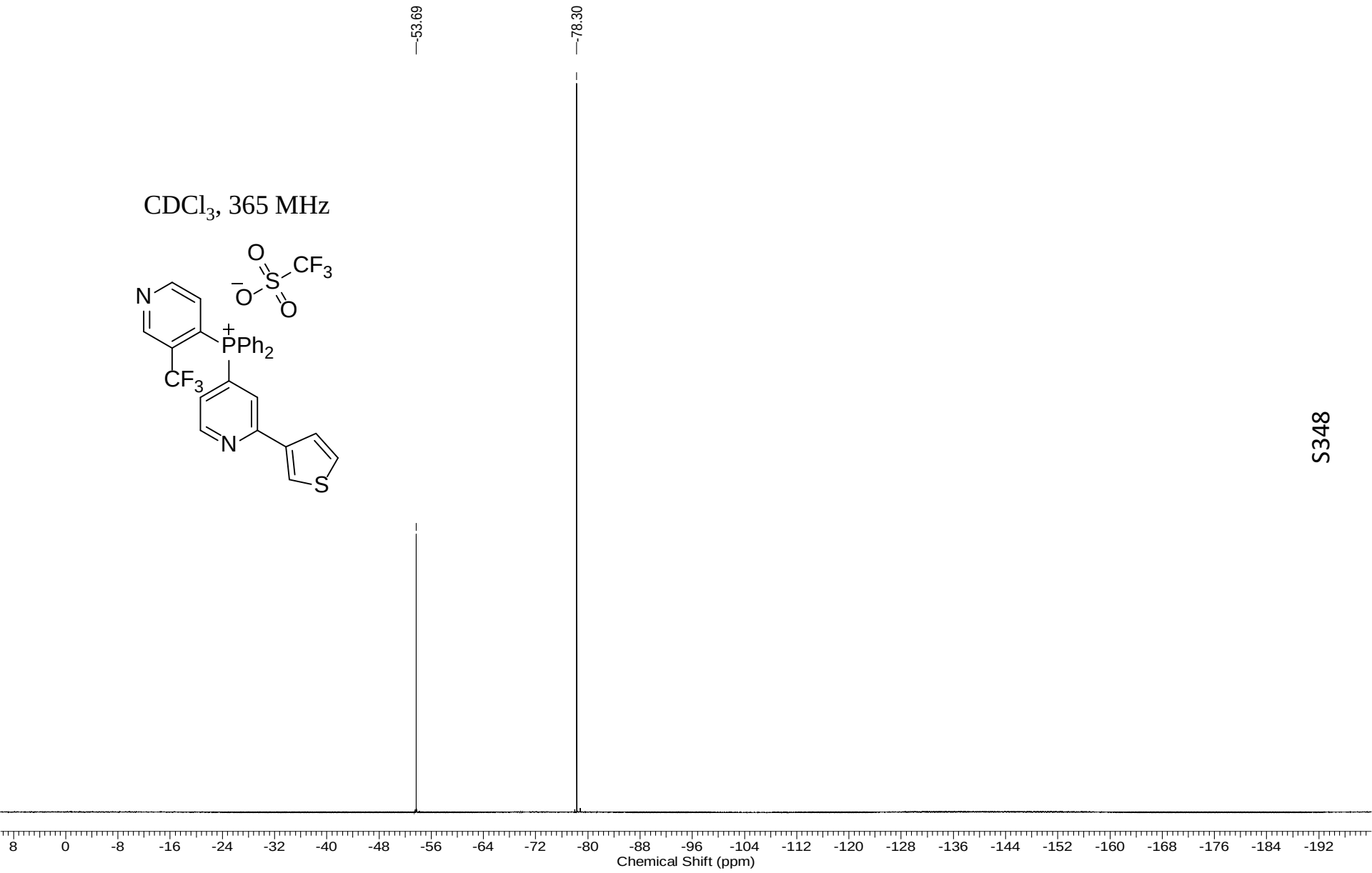

166.21
161.17
159.55
159.54
159.01
154.27
152.13
152.06
149.82
149.71
149.43
148.63
148.38
148.10
142.66
137.94
136.82
136.07
136.05
135.76
135.66
134.90
132.91
132.81
132.23
131.08
130.95
130.46
130.42
129.85
129.46
129.43
128.45
126.72
126.48
125.63
125.56
125.55
122.76
121.86
118.29
117.99
115.59
110.10
62.05
55.02
51.51
44.61
18.95
18.94
17.29
1.94
1.73
1.53
1.32
1.11
0.91
0.70
CD3CN, 100 MHz
S343
3u
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

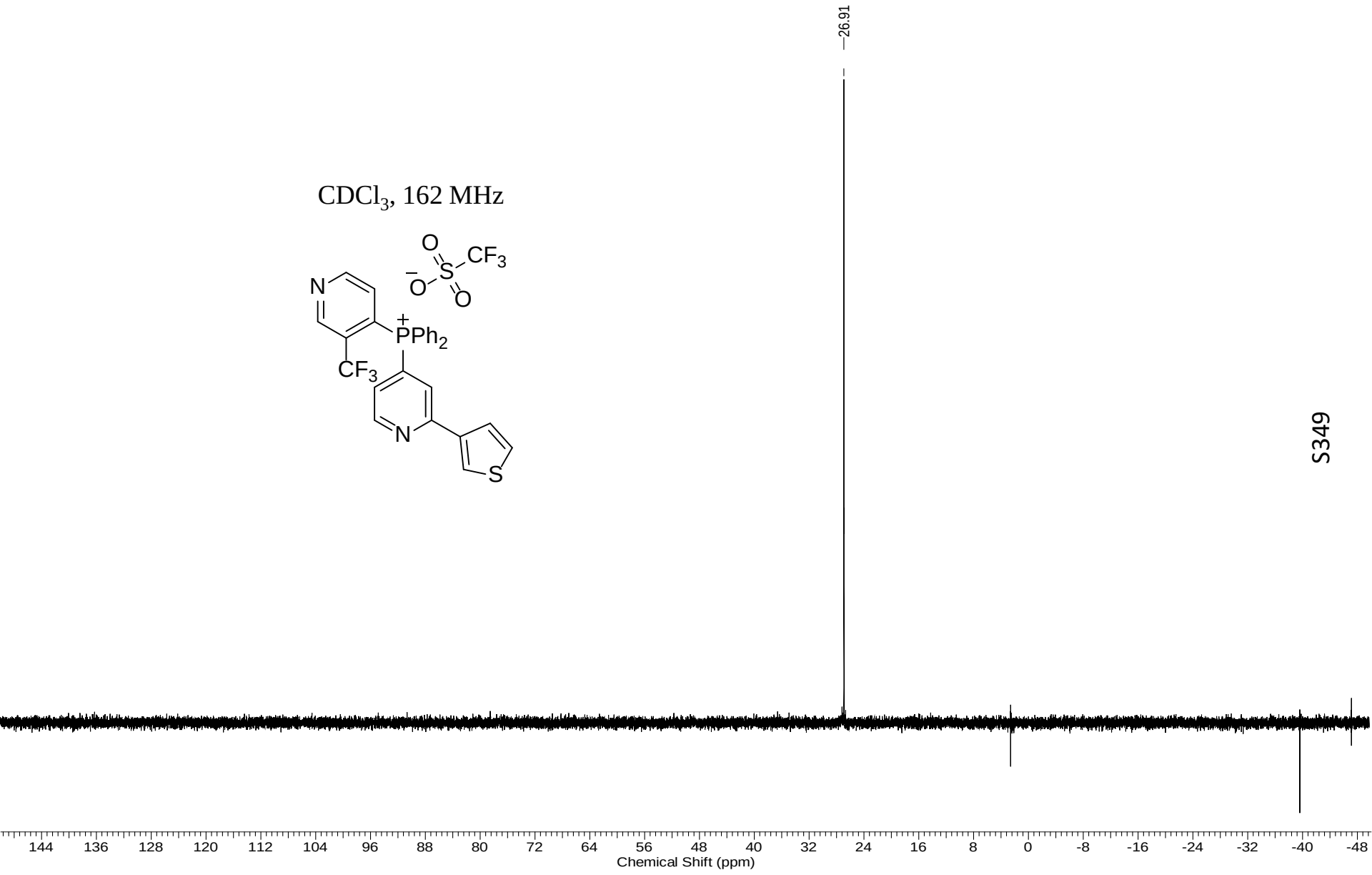

-78.13
CDCl3, 365 MHz
O
CF3
O
S
O
O
N
Me
PPh2
N
N
NH
N
Me
N
NMe
N
N
H
O
3u
S344
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-110
-130
-150
-170
-190

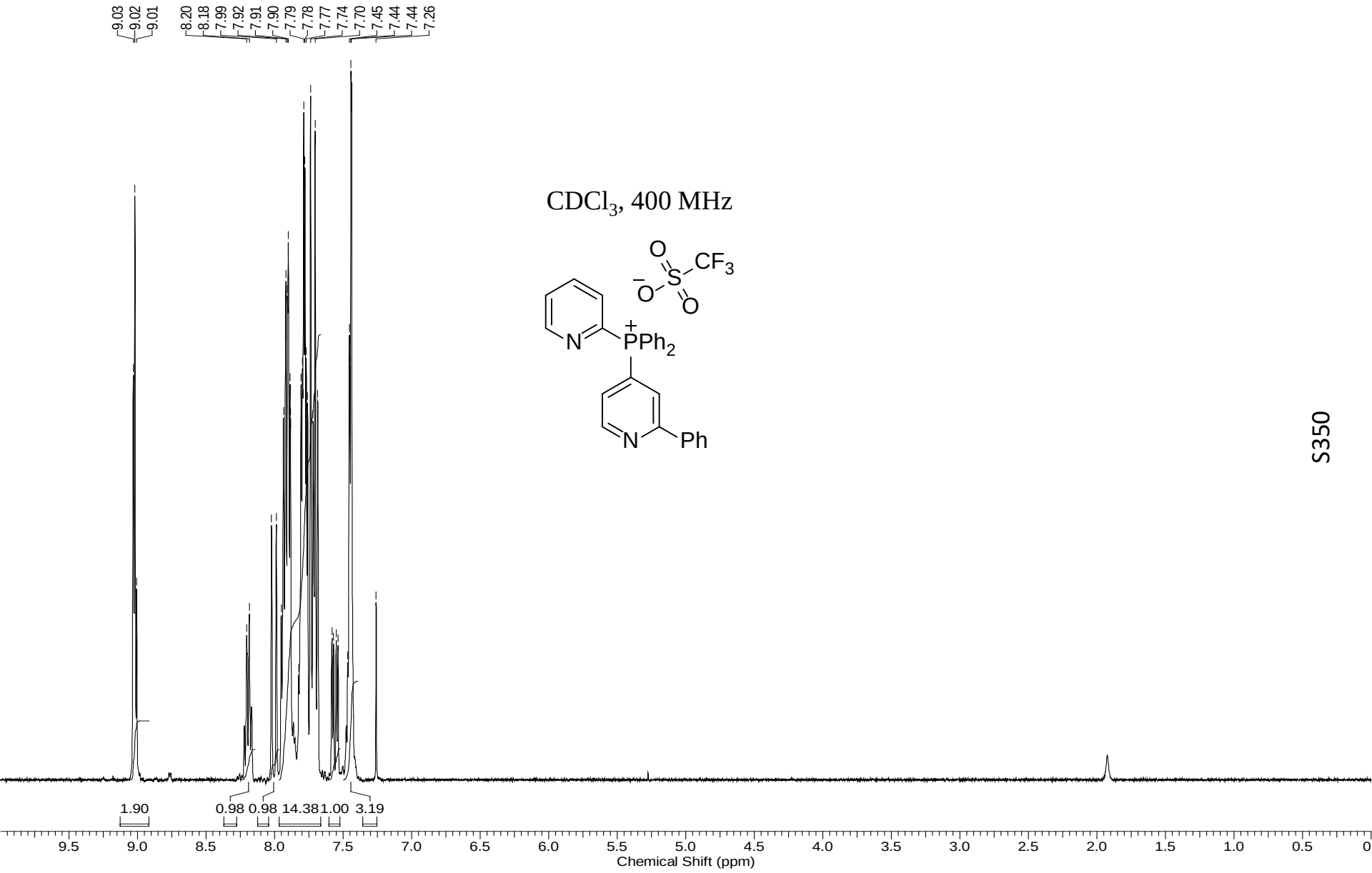

18.51
CDCl3, 162 MHz
3u
S345
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40

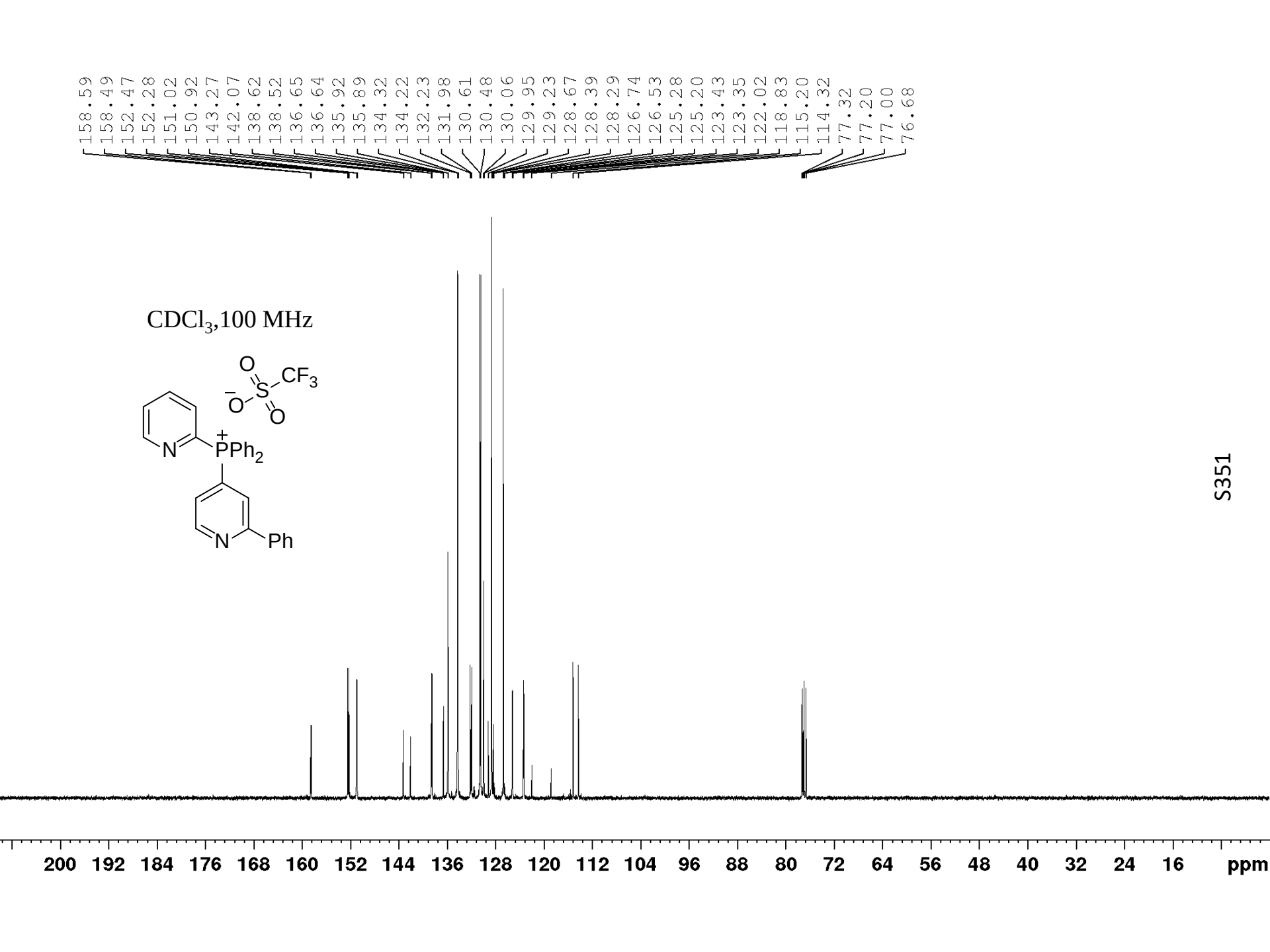

9.27
9.25
9.19
8.97
8.96
8.95
8.94
8.08
7.92
7.80
7.79
7.78
7.77
7.76
7.72
7.70
7.61
7.61
7.37
7.36
7.26
CDCl3, 400 MHz
O
CF3
S
O
O
N
PPh2
CF3
N
S
1.88
1.00
0.99
3.09
8.27
2.10
1.04
0.97
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

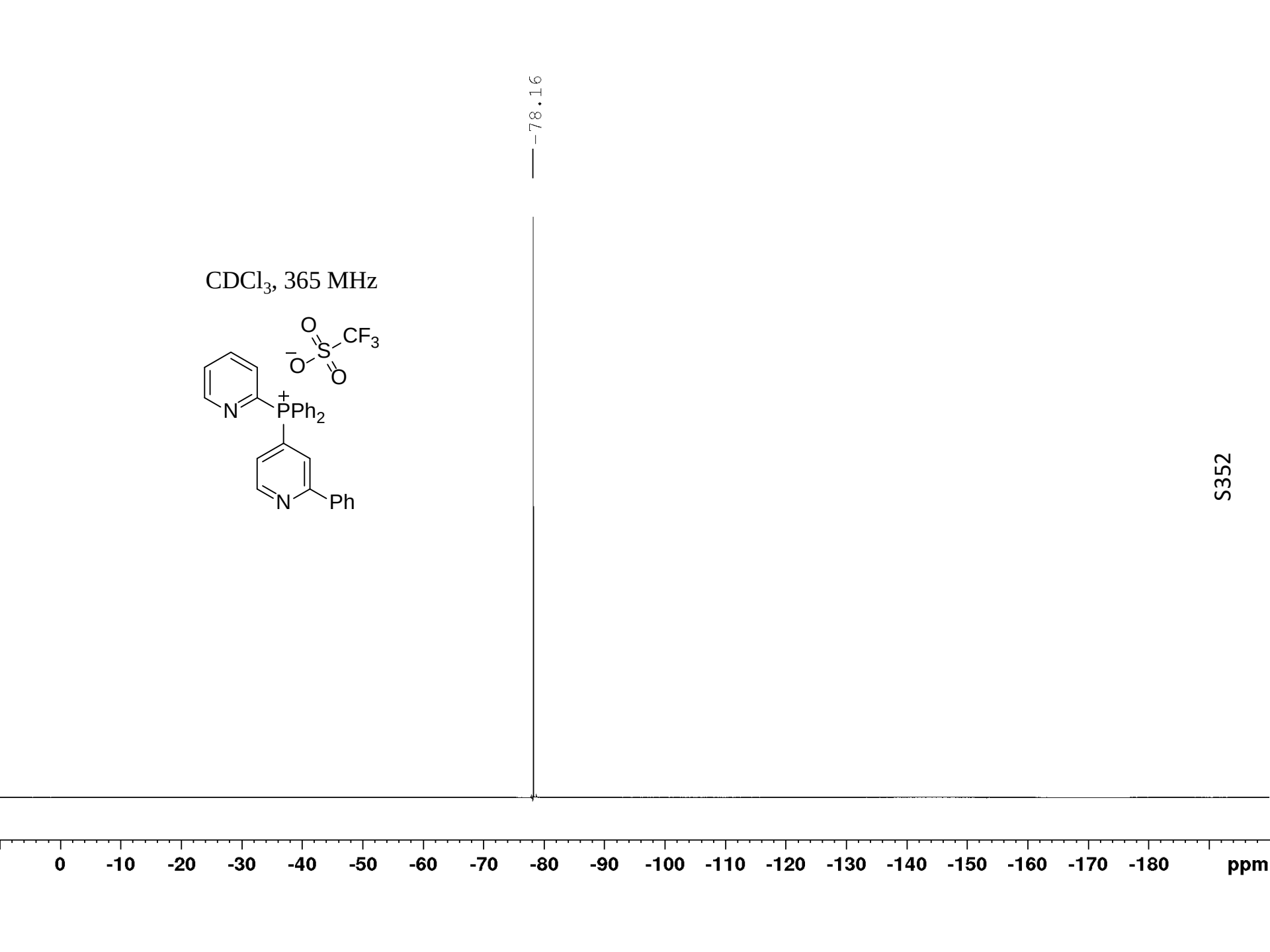

156.34
156.24
155.42
151.64
151.52
139.69
136.49
136.46
134.83
134.72
131.58
131.07
130.94
127.16
126.94
126.10
124.29
123.20
123.11
119.01
115.25
114.36
77.32
77.20
77.00
76.68
CDCl3, 100 MHz
O
S
CF3
O
O
N
PPh2
CF3
N
S
200
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)

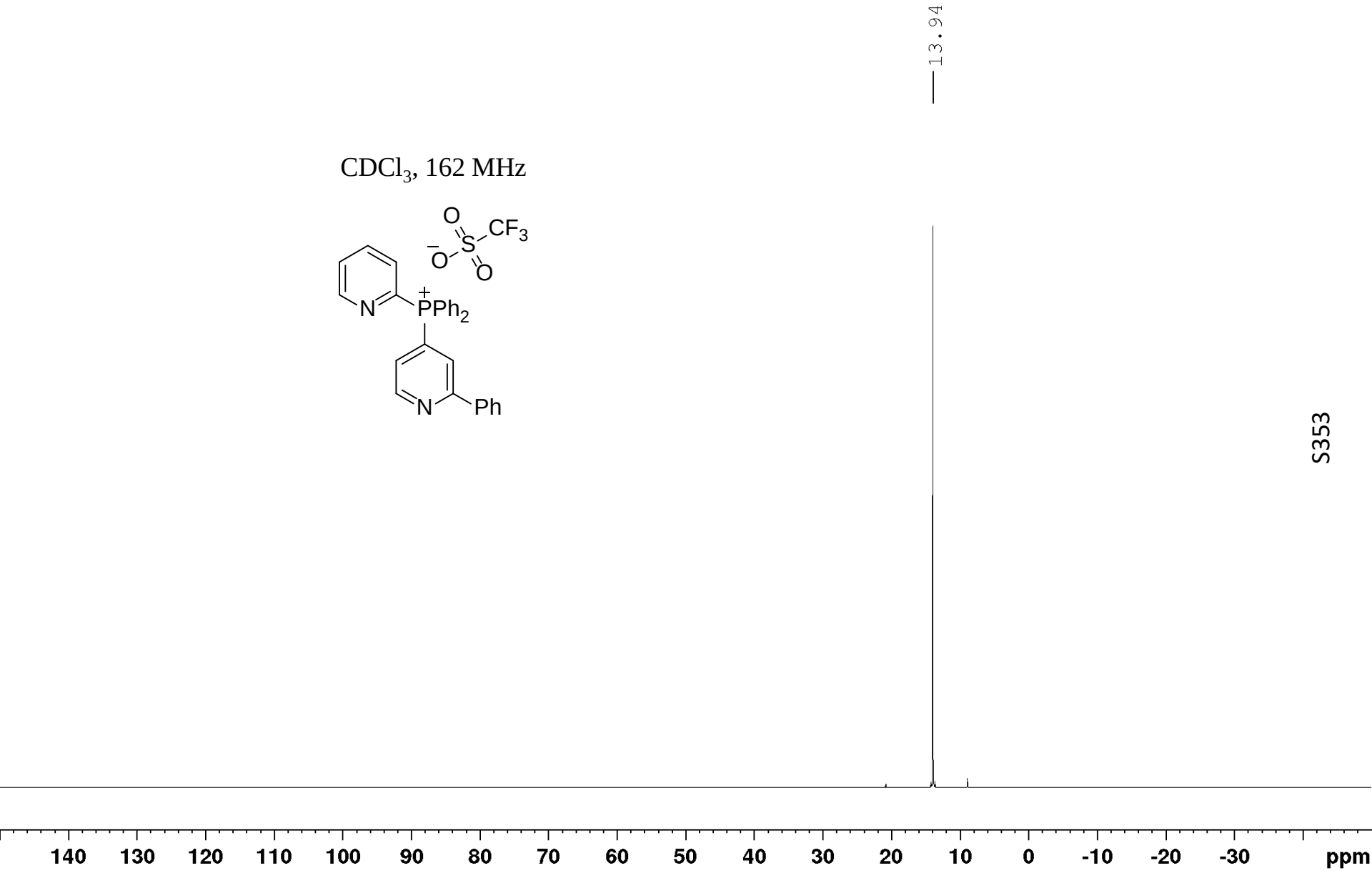

-53.69
-78.30
CDCl3, 365 MHz
O
CF3
S
O
O
N
PPh2
CF3
N
S
8
0
-8
-16
-24
-32
-40
-48
-56
-64
-72
-80
-88
-96
-104
-112
-120
-128
-136
-144
-152
-160
-168
-176
-184
-192
Chemical Shift (ppm)

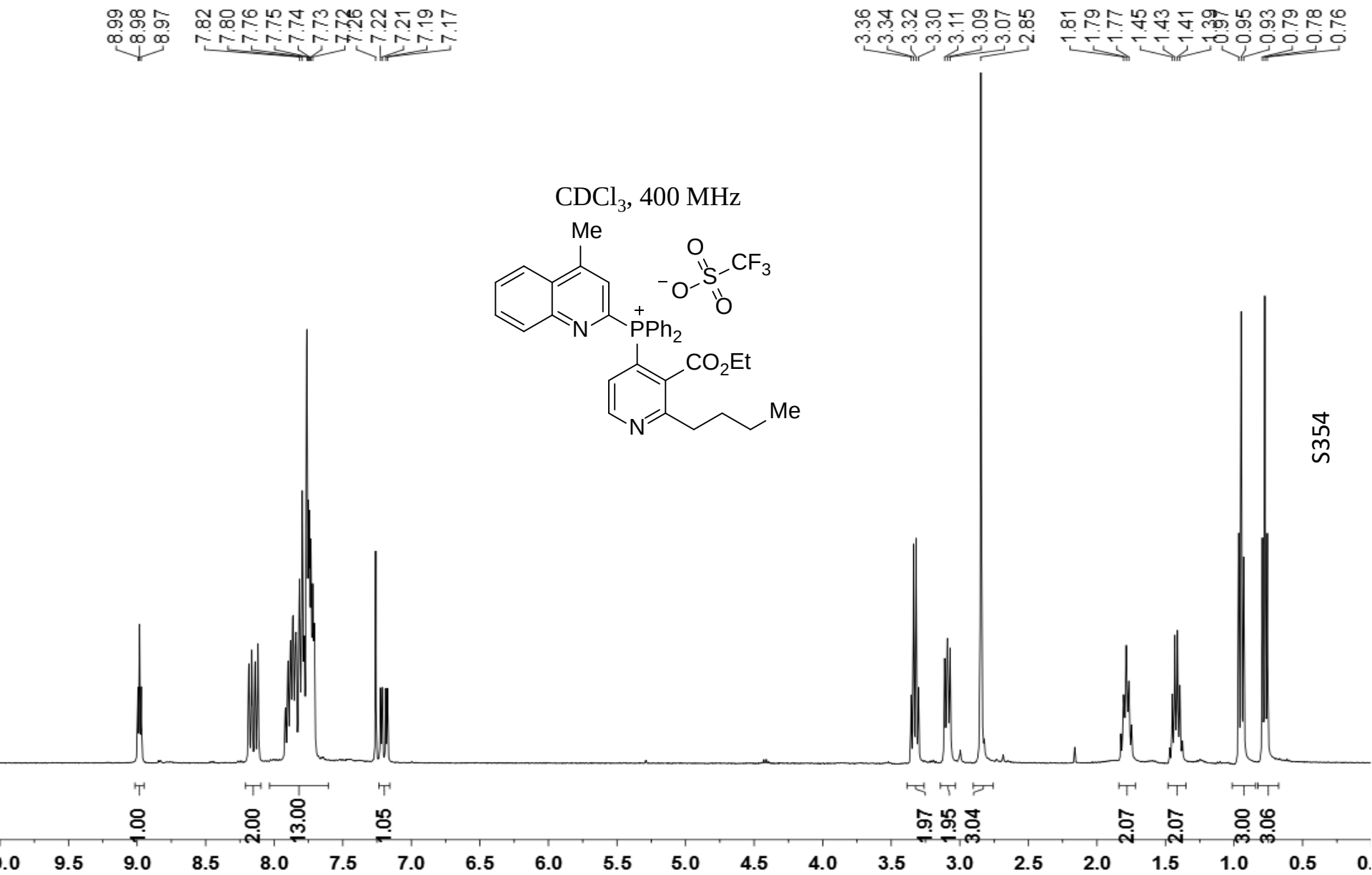

26.91
CDCl3, 162 MHz
O
CF3
S
O
O
N
PPh2
CF3
N
S
S349
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
-8
-16
-24
-32
-40
-48
Chemical Shift (ppm)

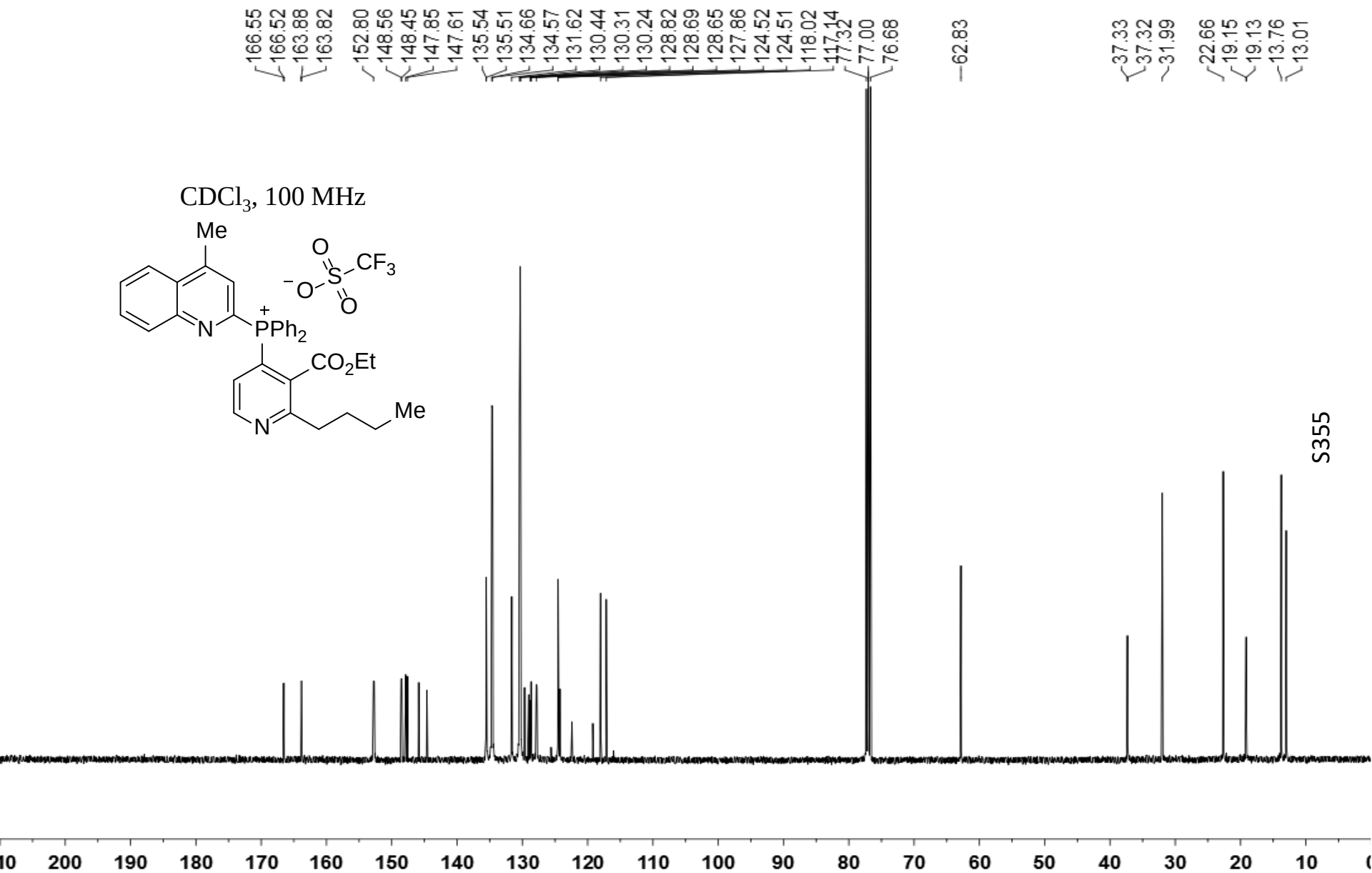

9.03
9.02
9.01
8.20
8.18
7.99
7.92
7.91
7.90
7.79
7.78
7.77
7.74
7.70
7.45
7.44
7.44
7.26
CDCl3, 400 MHz
O
CF3
S
O
O
N
PPh2
N
Ph
1.90
0.98
0.98
14.38
1.00
3.19
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)


158.59
158.49
152.47
152.28
151.02
150.92
143.27
142.07
138.62
138.52
136.65
136.64
135.92
135.89
134.32
134.22
132.23
131.98
130.61
130.48
130.06
129.95
129.23
128.67
128.39
128.29
126.74
126.53
125.28
125.20
123.43
123.35
122.02
118.83
115.20
114.32
77.32
77.20
77.00
76.68
CDCl3,100 MHz
O
CF3
S
O
O
N
PPh2
N
Ph
S351
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

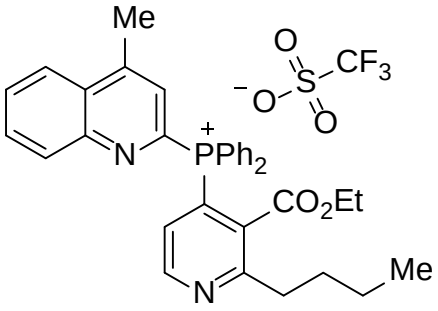

-78.16
CDCl3, 365 MHz
O
S
CF3
O
O
N
PPh2
N
Ph
S352
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
ppm


13.94
CDCl3, 162 MHz
O
CF3
S
O
O
N
PPh2
N
Ph
S353
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
ppm


8.99
8.98
8.97
7.82
7.80
7.76
7.75
7.74
7.73
7.72
7.26
7.22
7.21
7.19
7.17
3.36
3.34
3.32
3.30
3.11
3.09
3.07
2.85
1.81
1.79
1.77
1.45
1.43
1.41
1.39
0.97
0.95
0.93
0.79
0.78
0.76
CDCl3, 400 MHz
Me
O
CF3
O
S
O
O
N
PPh2
CO2Et
Me
N
S354
1.00
2.00
13.00
1.05
1.97
1.95
3.04
2.07
2.07
3.00
3.06
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5


166.55
166.52
163.88
163.82
152.80
148.56
148.45
147.85
147.61
135.54
135.51
134.66
134.57
131.62
130.44
130.31
130.24
128.82
128.69
128.65
127.86
124.52
124.51
118.02
117.14
77.32
77.00
76.68
62.83
37.33
37.32
31.99
22.66
19.15
19.13
13.76
13.01
CDCl3, 100 MHz
Me
O
CF3
O
S
O
O
N
PPh2
CO2Et
Me
N
S355
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

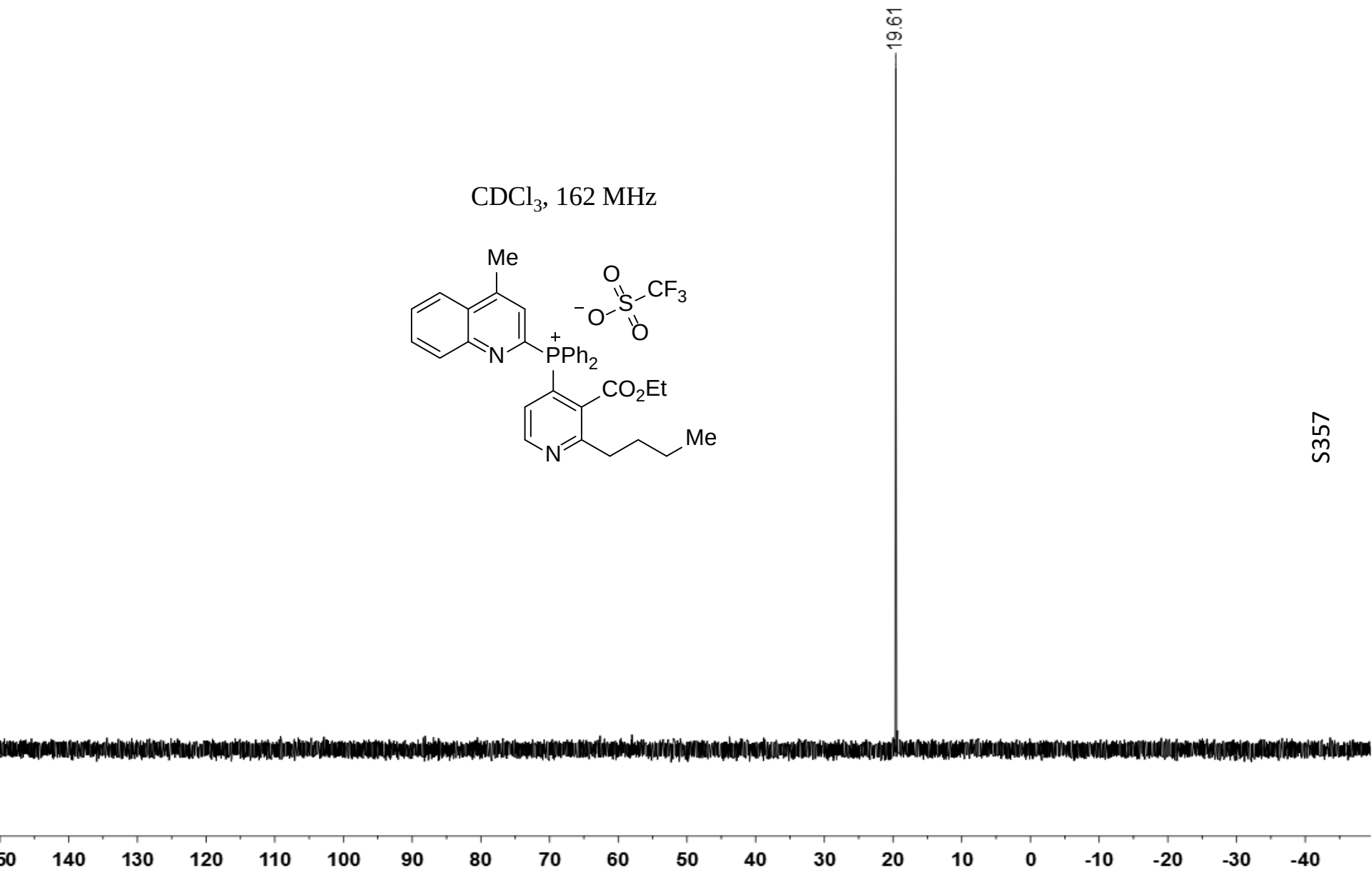
$CDCl_3$, 365 MHz

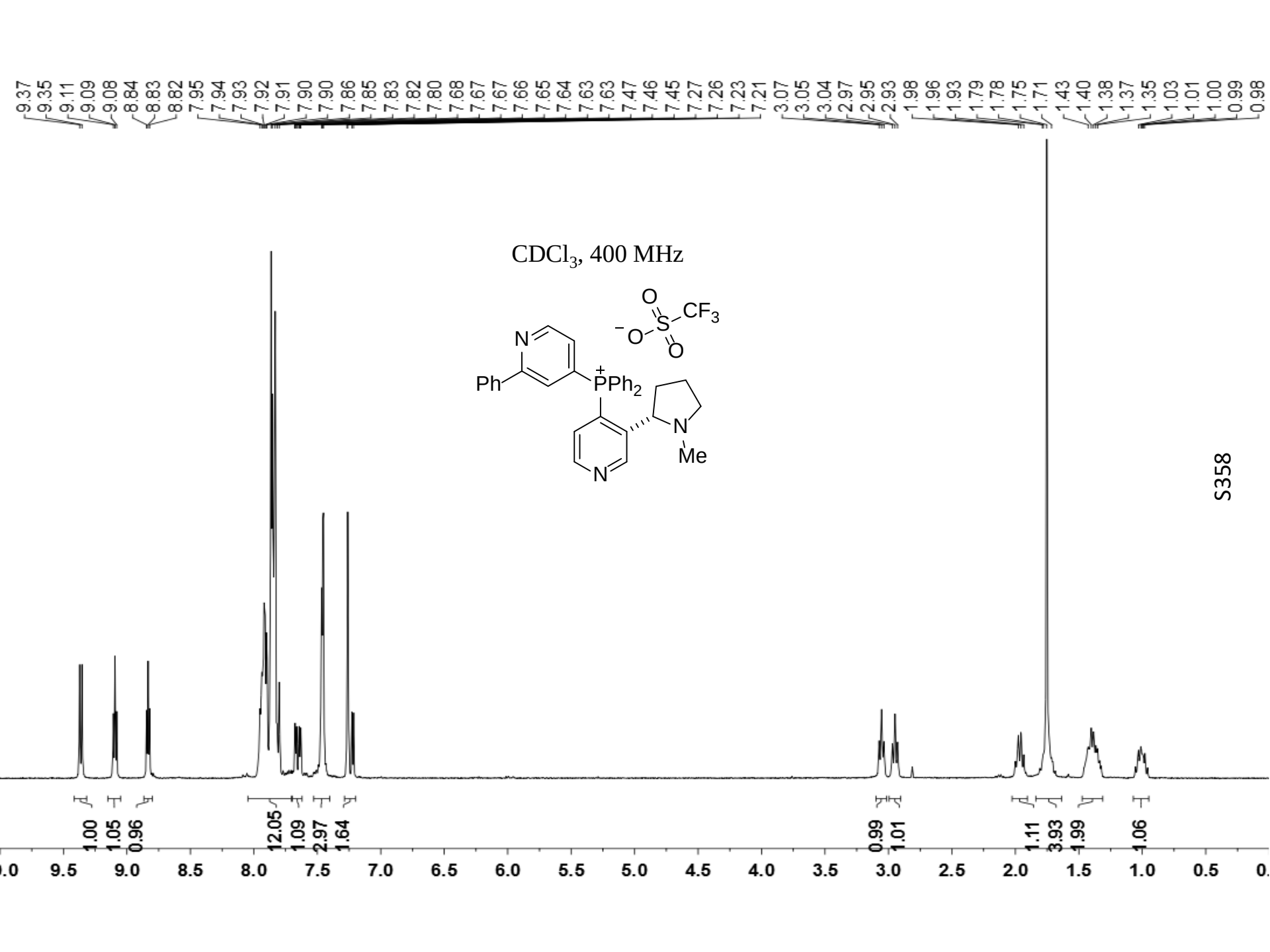


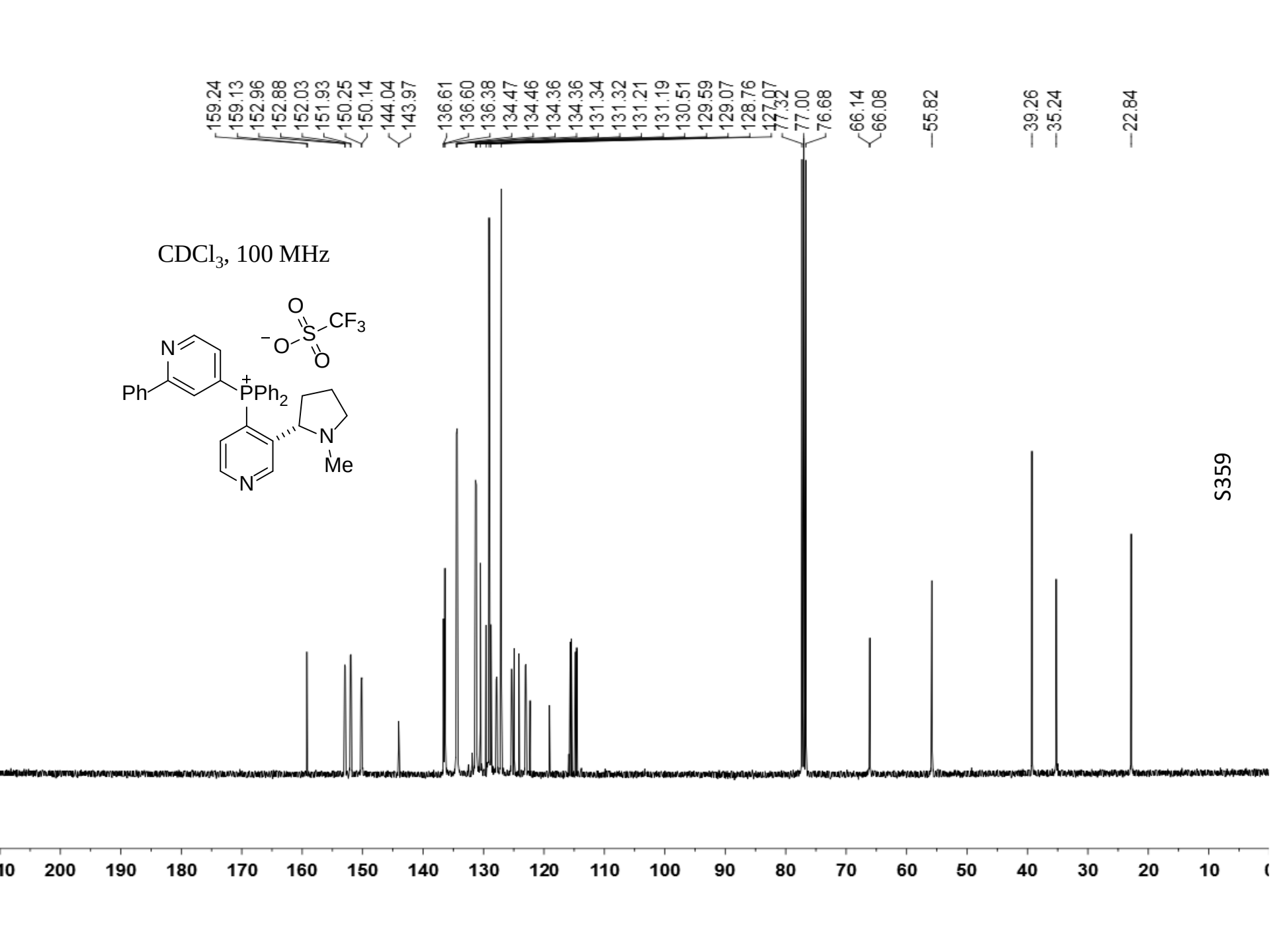
-78.15

S356

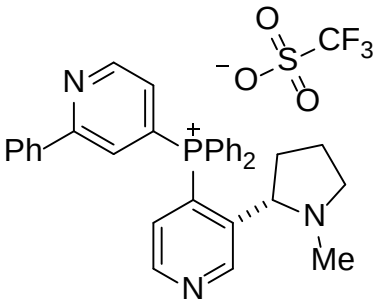
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -110 -130 -150 -170 -190


19.61
CDCl3, 162 MHz
Me
O
S
CF3
O
O
N
PPh2
CO2Et
Me
N
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40


9.37
9.35
9.11
9.09
9.08
8.84
8.83
8.82
7.95
7.94
7.93
7.92
7.91
7.90
7.90
7.86
7.85
7.83
7.82
7.80
7.68
7.67
7.67
7.66
7.65
7.64
7.63
7.63
7.47
7.46
7.45
7.27
7.26
7.23
7.21
3.07
3.05
3.04
2.97
2.95
2.93
1.98
1.96
1.93
1.79
1.78
1.75
1.71
1.43
1.40
1.38
1.37
1.35
1.03
1.01
1.00
0.99
0.98
CDCl3, 400 MHz
O
CF3
S
O
O
N
Ph
PPh2
N
Me
N
1.00
1.05
0.96
12.05
1.09
2.97
1.64
0.99
1.01
1.11
3.93
1.99
1.06
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
S358


159.24
159.13
152.96
152.88
152.03
151.93
150.25
150.14
144.04
143.97
136.61
136.60
136.38
134.47
134.46
134.36
134.36
131.34
131.32
131.21
131.19
130.51
129.59
129.07
128.76
127.32
127.07
77.00
76.68
66.14
66.08
55.82
39.26
35.24
22.84
CDCl3, 100 MHz
S359
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

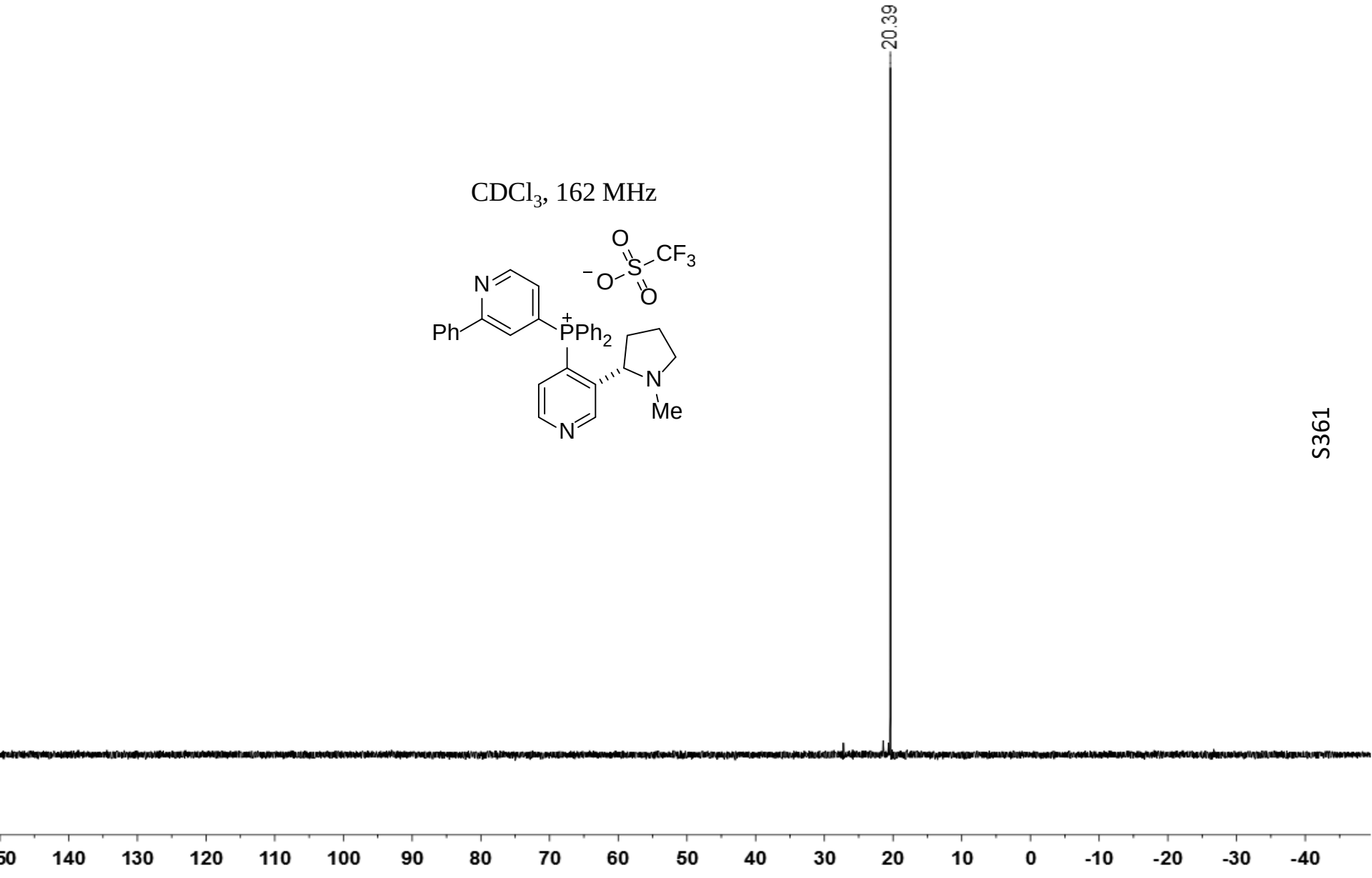
$CDCl_3$, 365 MHz

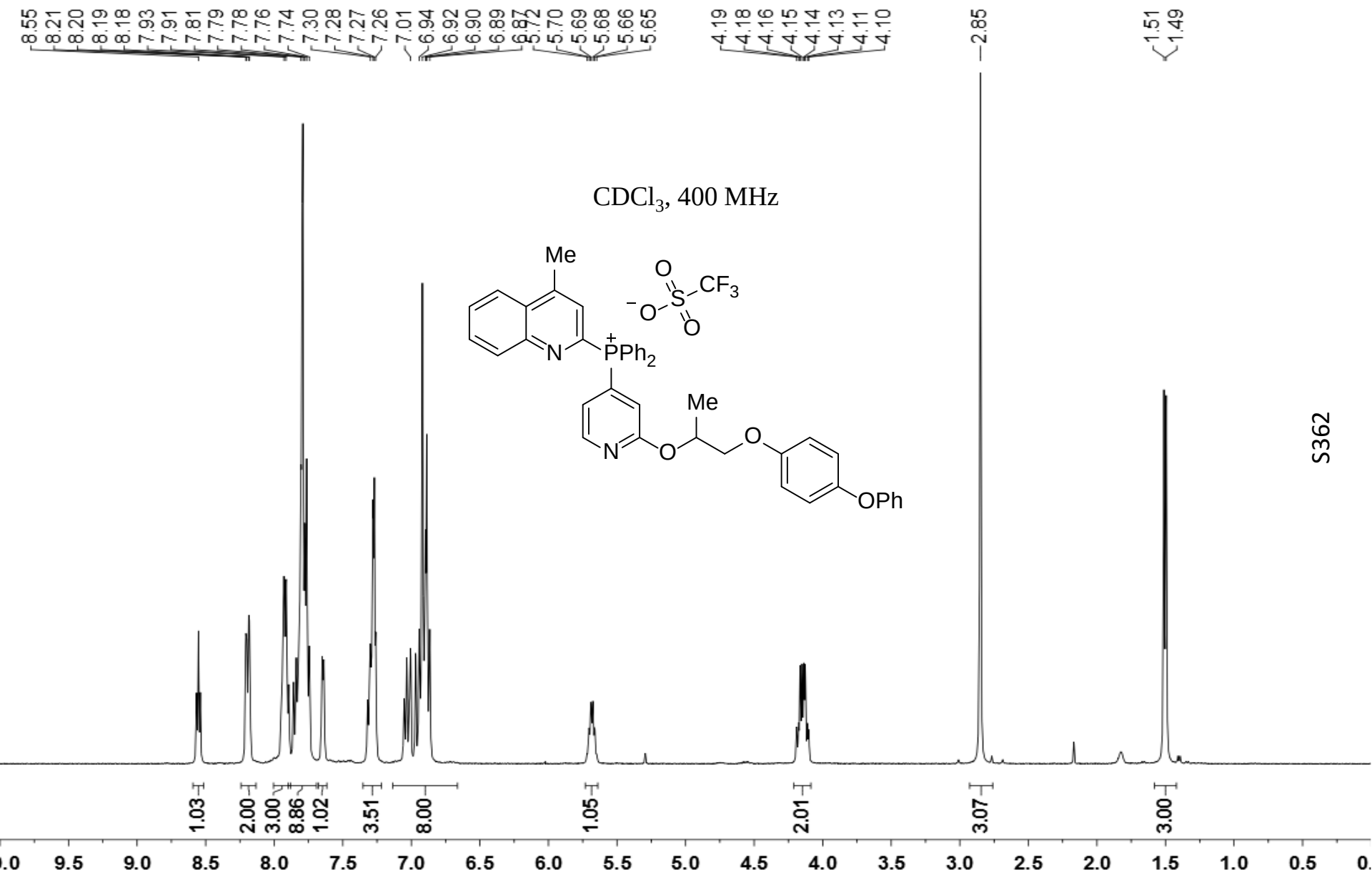


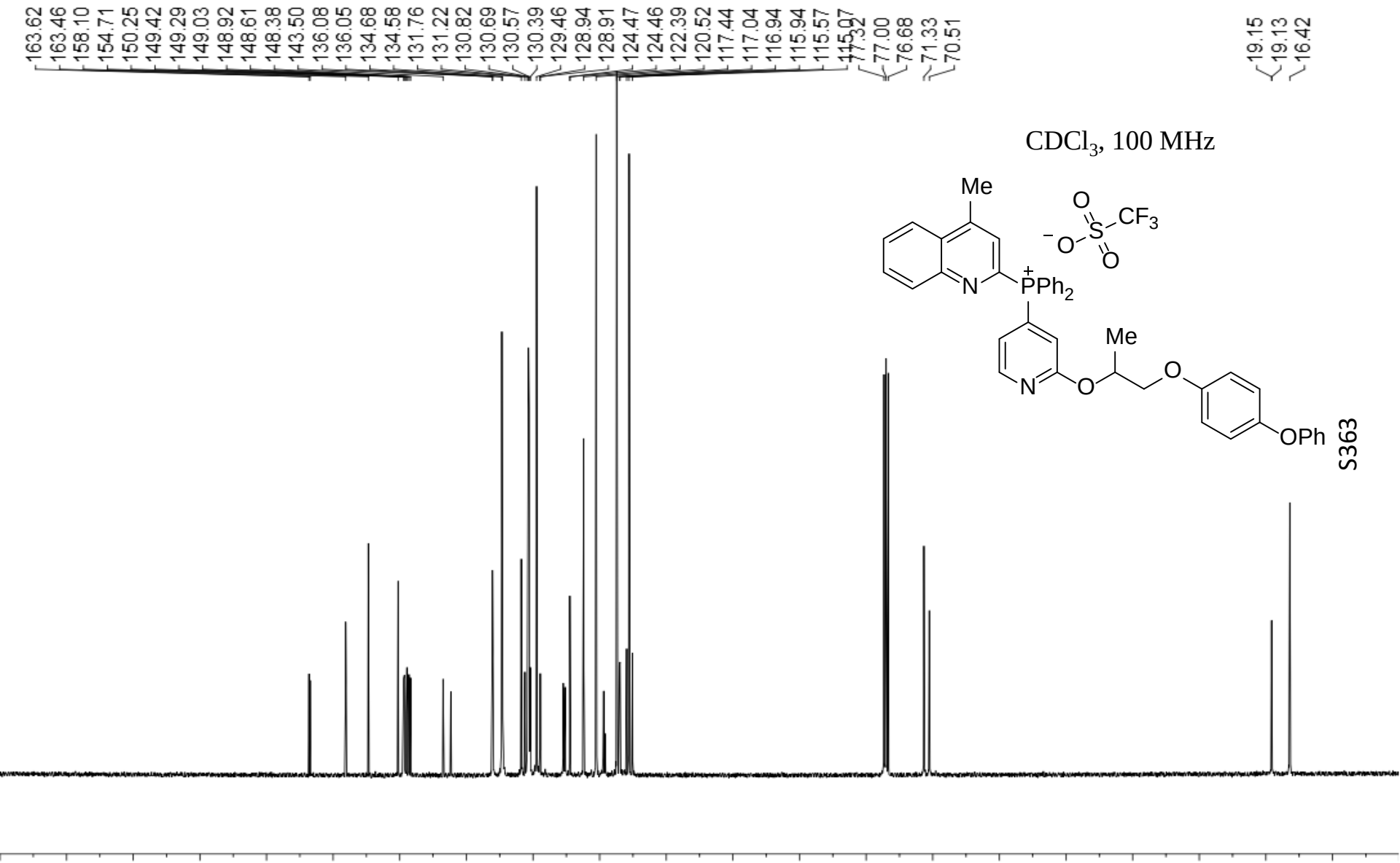
-78.13

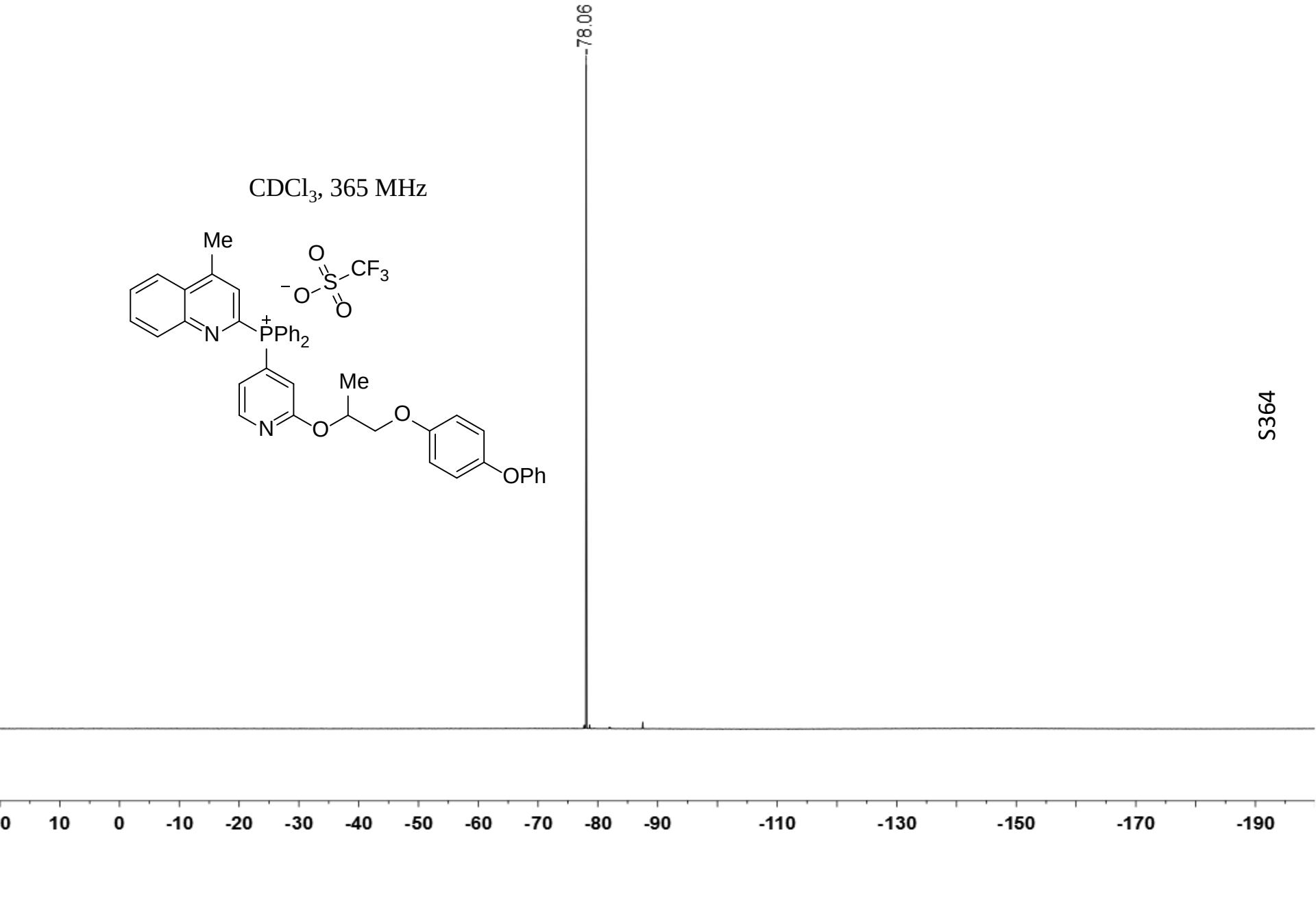
S360

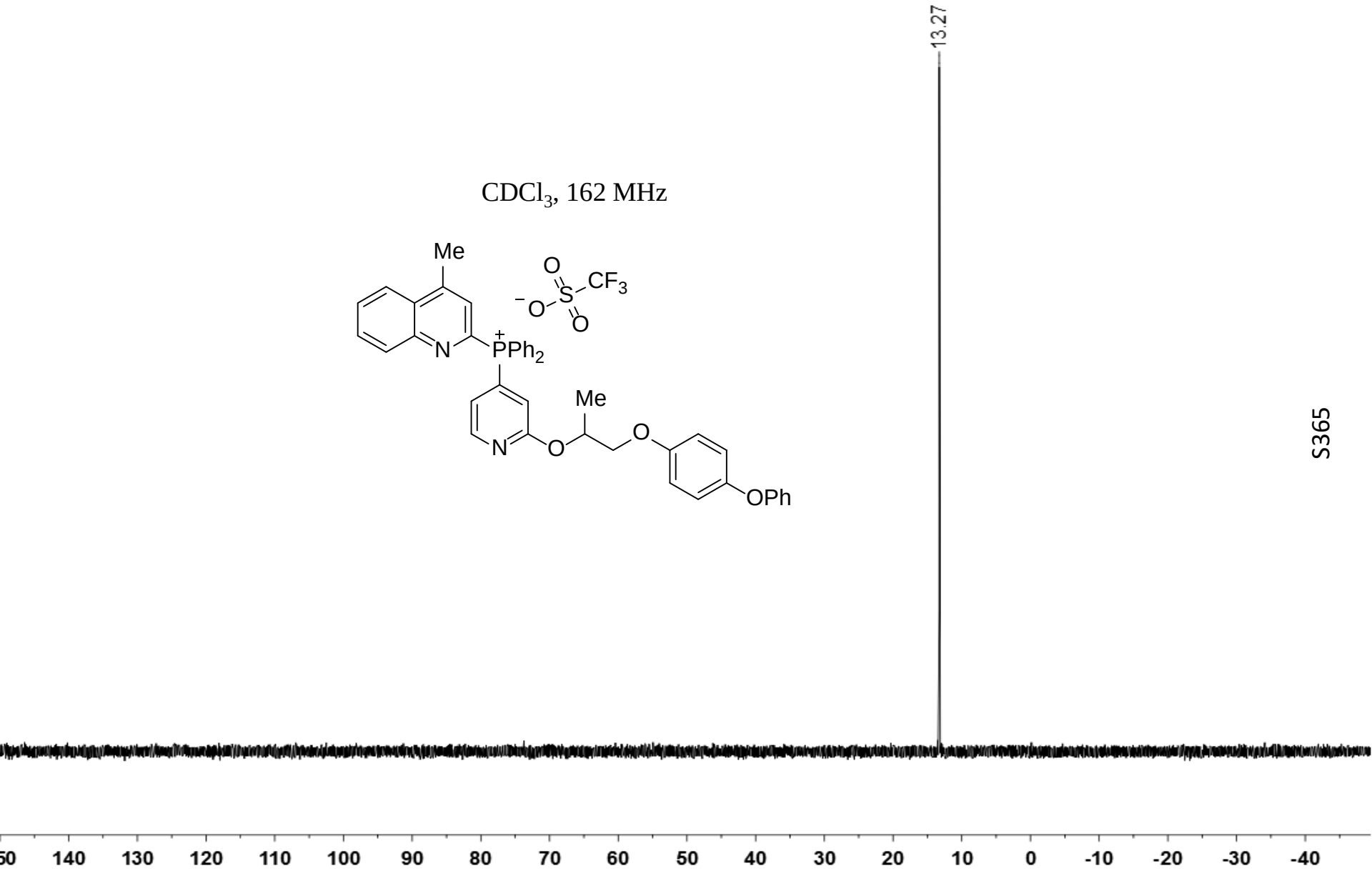
0 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -110 -130 -150 -170 -190

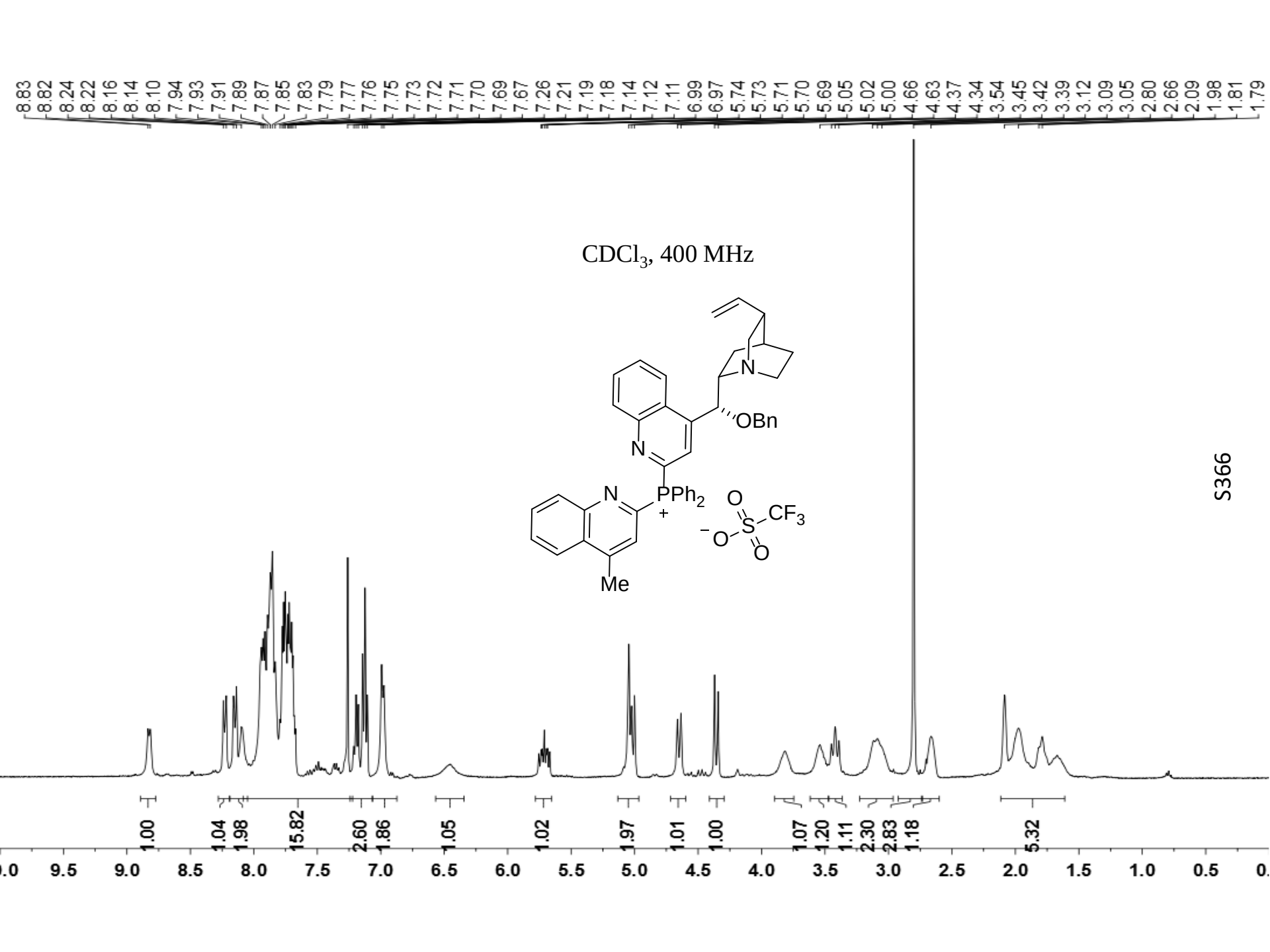

20.39
CDCl3, 162 MHz
O
CF3
S
O
O
N
Ph
PPh2
N
Me
N
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40

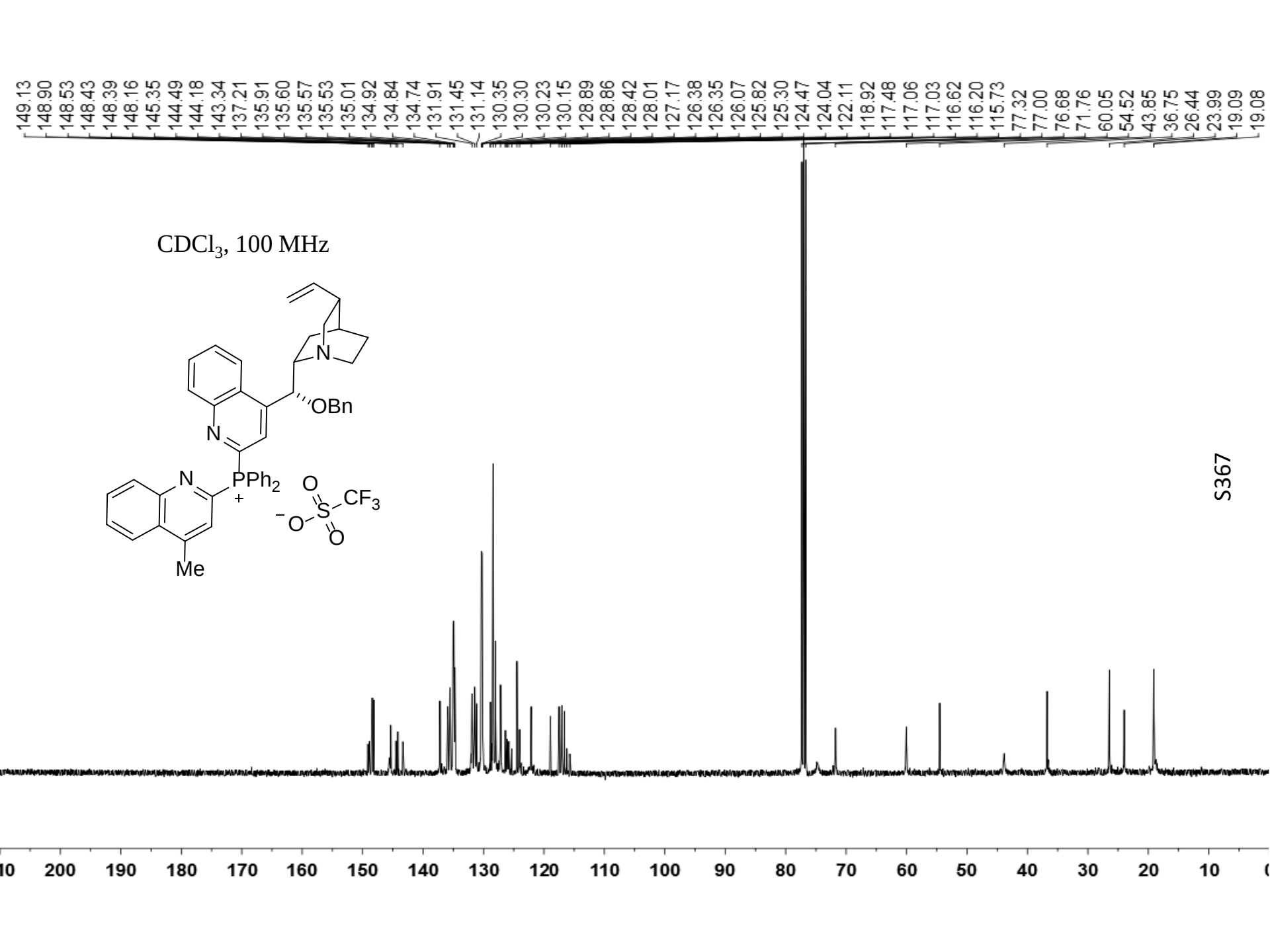

8.55
8.21
8.20
8.19
8.18
7.93
7.91
7.81
7.79
7.78
7.76
7.74
7.30
7.28
7.27
7.26
7.01
6.94
6.92
6.90
6.89
6.87
5.72
5.70
5.69
5.68
5.66
5.65
4.19
4.18
4.16
4.15
4.14
4.13
4.11
4.10
2.85
1.51
1.49
CDCl3, 400 MHz
Me
O
CF3
O
S
O
O
N
PPh2
Me
N
O
O
OPh
S362
1.03
2.00
3.00
8.86
1.02
3.51
8.00
1.05
2.01
3.07
3.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5


163.62
163.46
158.10
154.71
150.25
149.42
149.29
149.03
148.92
148.61
148.38
143.50
136.08
136.05
134.68
134.58
131.76
131.22
130.82
130.69
130.57
130.39
129.46
128.94
128.91
124.47
124.46
122.39
120.52
117.44
117.04
116.94
115.94
115.57
115.07
77.32
77.00
76.68
71.33
70.51
19.15
19.13
16.42
CDCl3, 100 MHz
Me
O
CF3
O
S
O
O
N
PPh2
Me
N
O
O
OPh
S363
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

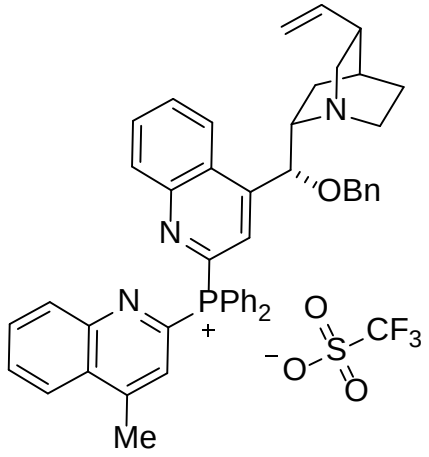

78.06
CDCl3, 365 MHz
Me
O
CF3
O
S
O
O
N
PPh2
Me
N
O
O
OPh
S364
0
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-110
-130
-150
-170
-190


13.27
CDCl3, 162 MHz
Me
O
S
CF3
O
O
N
PPh2
Me
N
O
O
OPh
S365
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40


8.83 8.82 8.24 8.22 8.16 8.14 8.10 7.94 7.93 7.91 7.89 7.87 7.85 7.83 7.79 7.77 7.76 7.75 7.73 7.72 7.71 7.70 7.69 7.67 7.26 7.21 7.19 7.18 7.14 7.12 7.11 6.99 6.97 5.74 5.73 5.71 5.70 5.69 5.05 5.02 5.00 4.66 4.63 4.37 4.34 3.54 3.45 3.42 3.39 3.12 3.09 3.05 2.80 2.66 2.09 1.98 1.81 1.79
CDCl3, 400 MHz
OBn
N
PPh2
CF3
Me
S366
1.00 1.04 1.98 15.82 2.60 1.86 1.05 1.02 1.97 1.01 1.00 1.07 1.20 1.11 2.30 2.83 1.18 5.32
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5


149.13
148.90
148.53
148.43
148.39
148.16
145.35
144.49
144.18
143.34
137.21
135.91
135.60
135.57
135.53
135.01
134.92
134.84
134.74
131.91
131.45
131.14
130.35
130.30
130.23
130.15
128.89
128.86
128.42
128.01
127.17
126.38
126.35
126.07
125.82
125.30
124.47
124.04
122.11
118.92
117.48
117.06
117.03
116.62
116.20
115.73
77.32
77.00
76.68
71.76
60.05
54.52
43.85
36.75
26.44
23.99
19.09
19.08
CDCl3, 100 MHz
N
OBn
N
N
PPh2
+
O
S
CF3
O
O
Me
S367
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

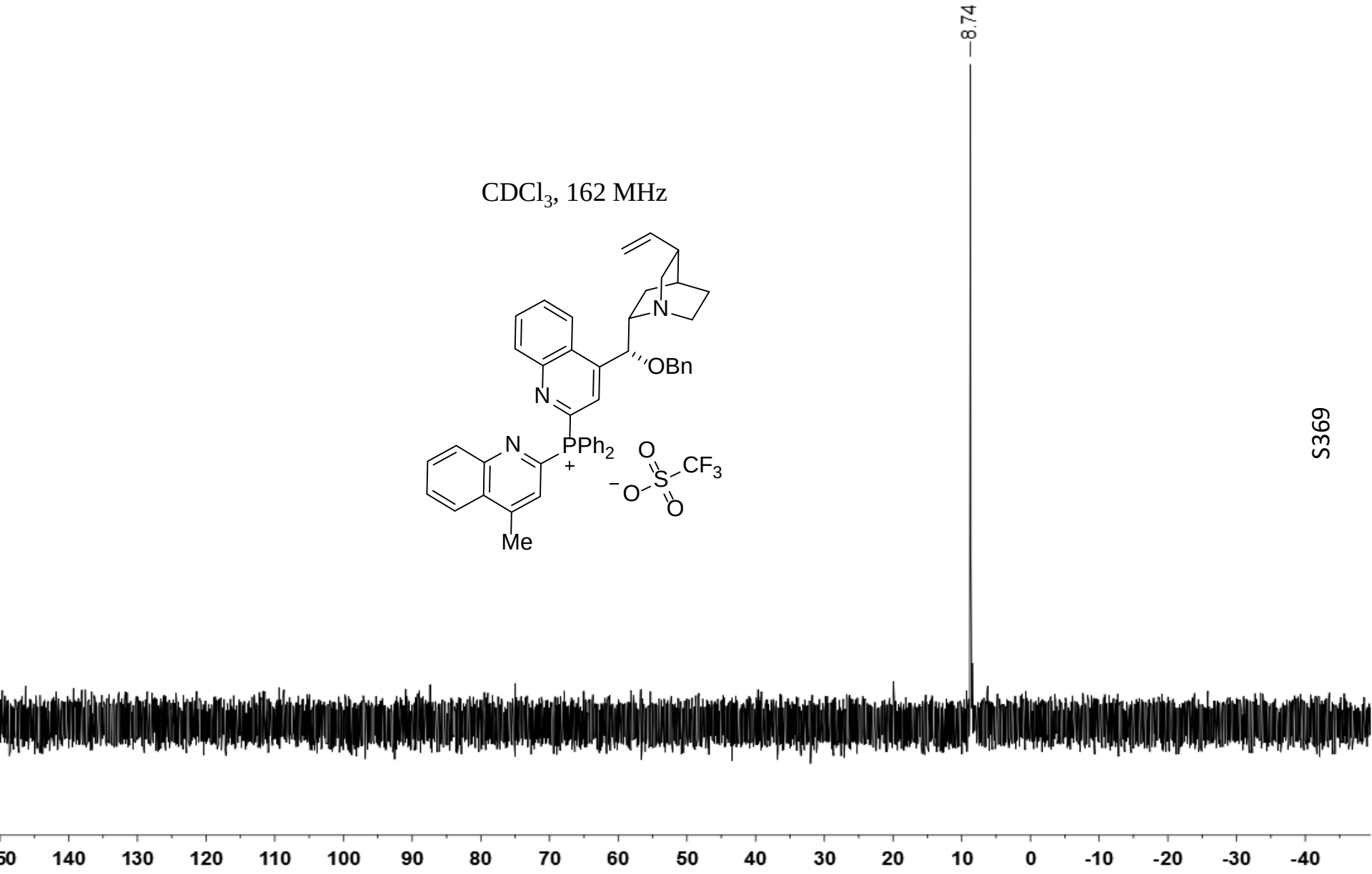
$CDCl_3$, 365 MHz

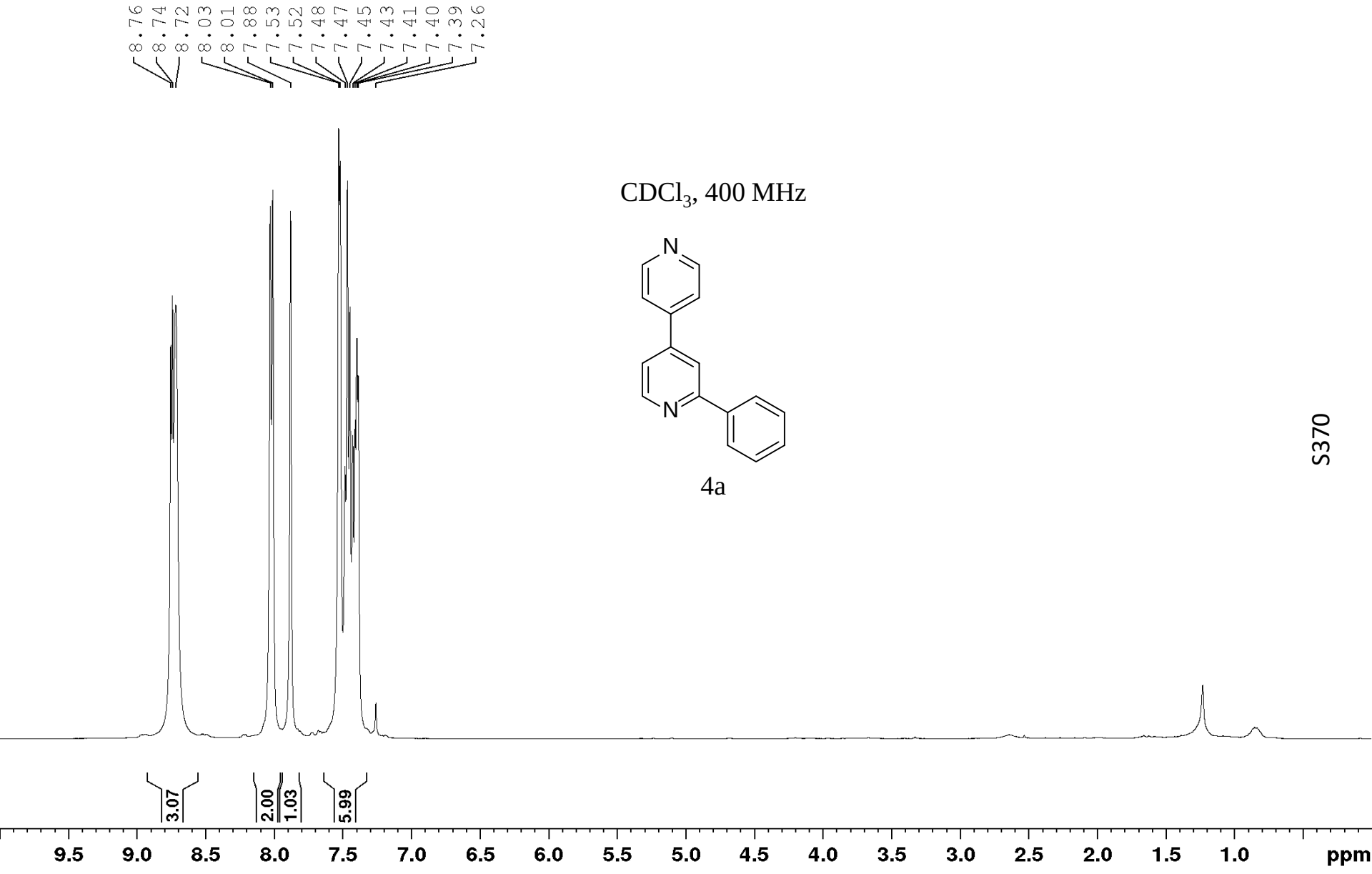


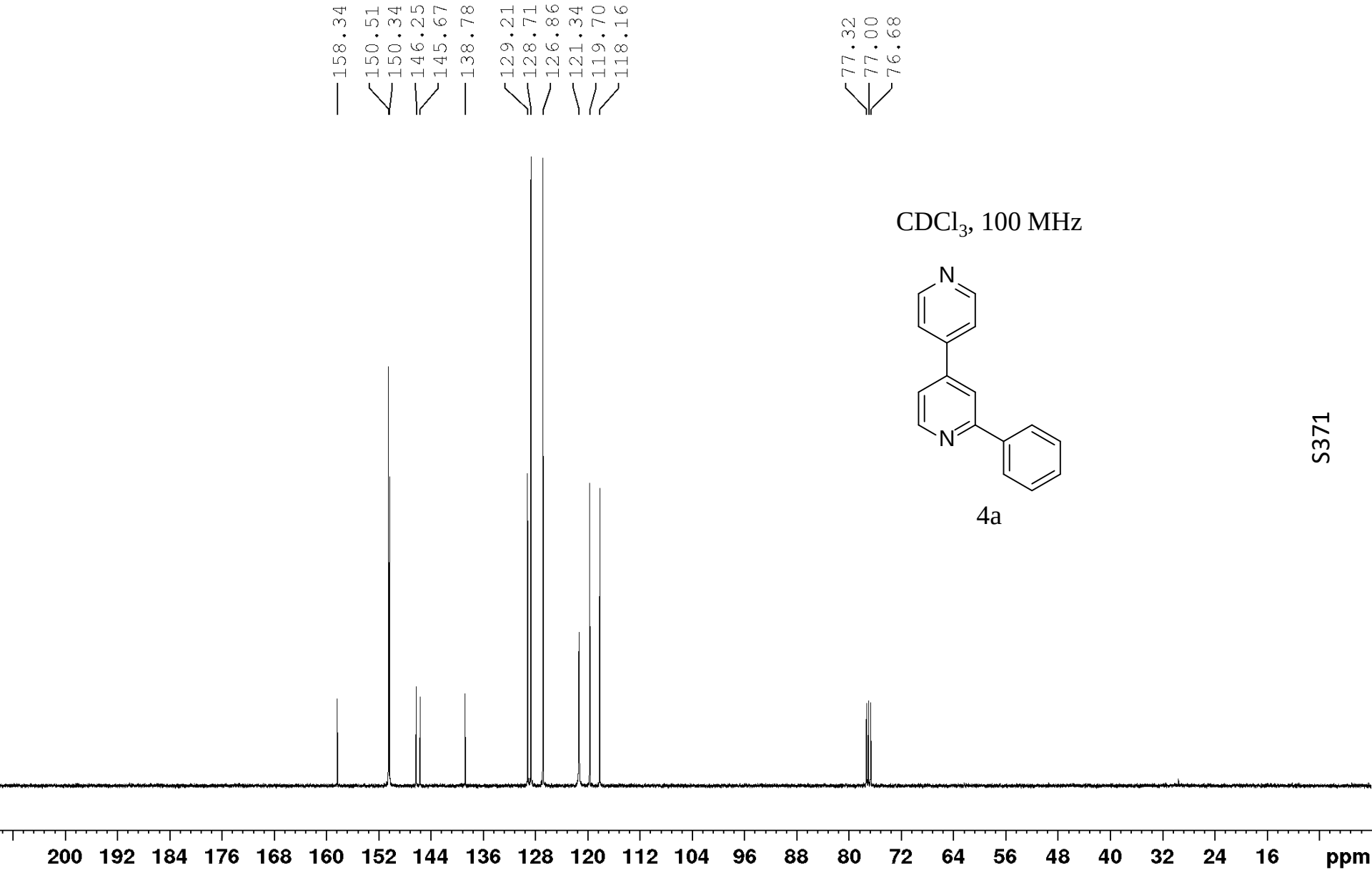
-78.23

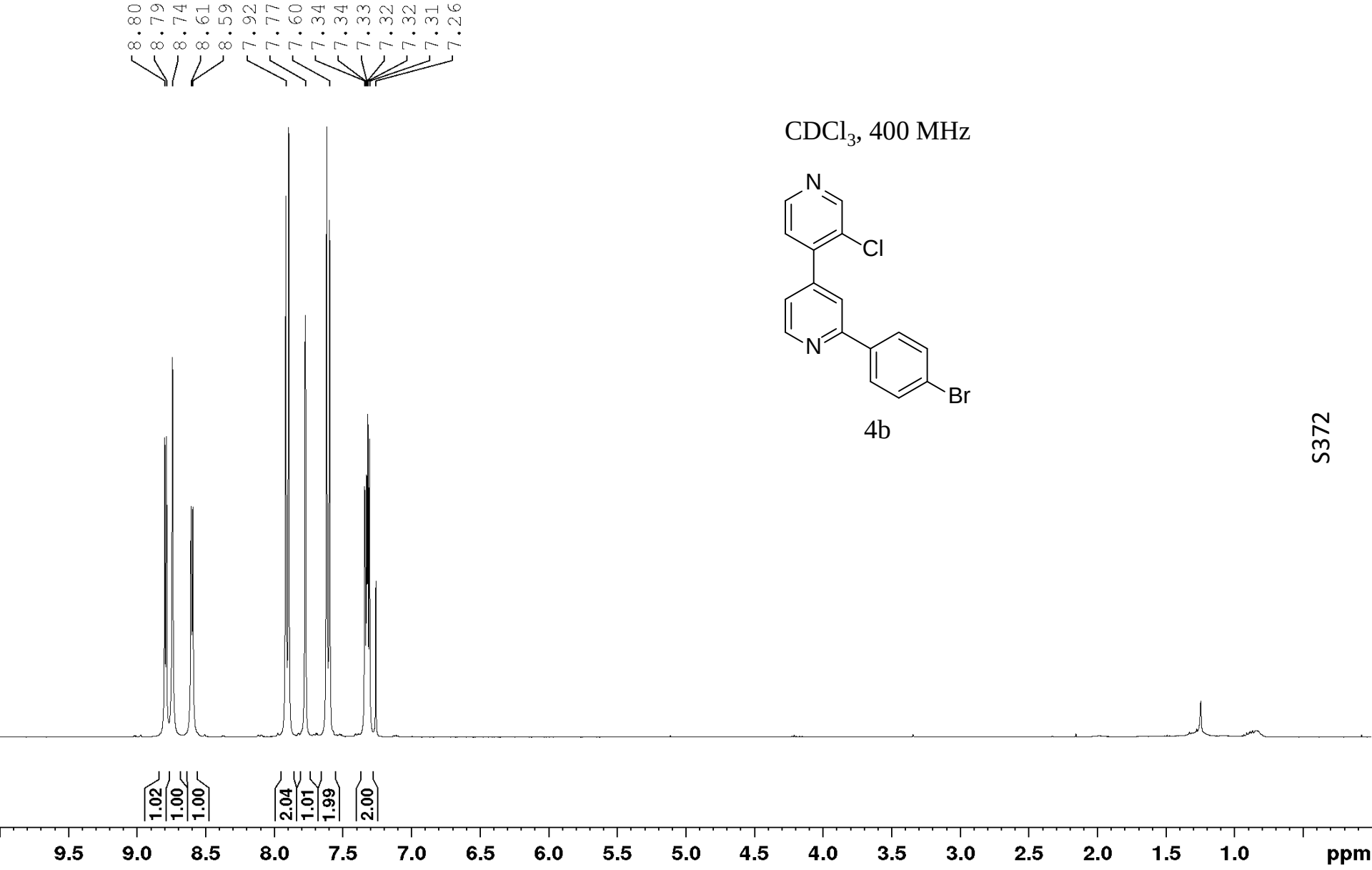
S368

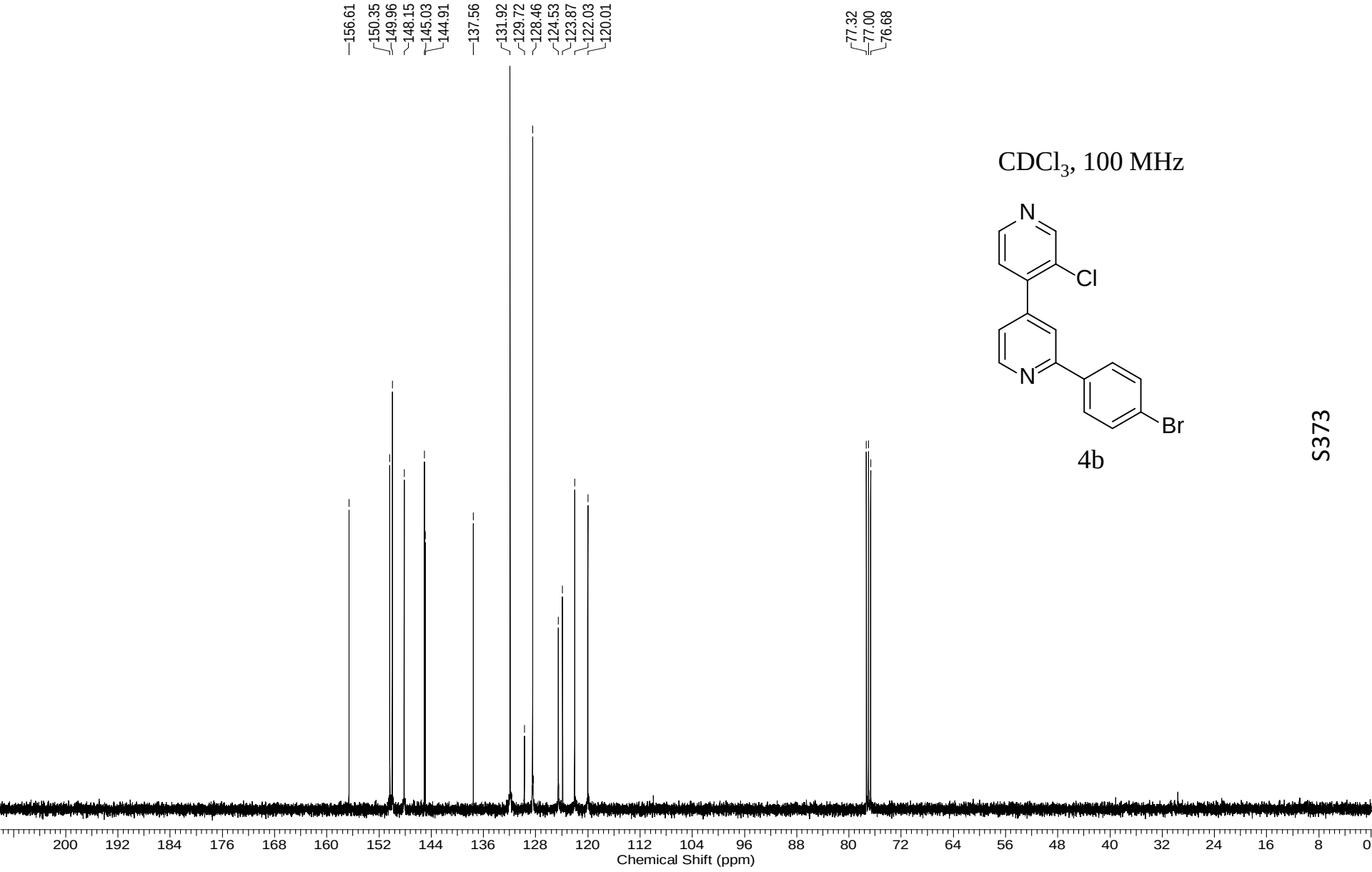
0 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -110 -130 -150 -170 -190

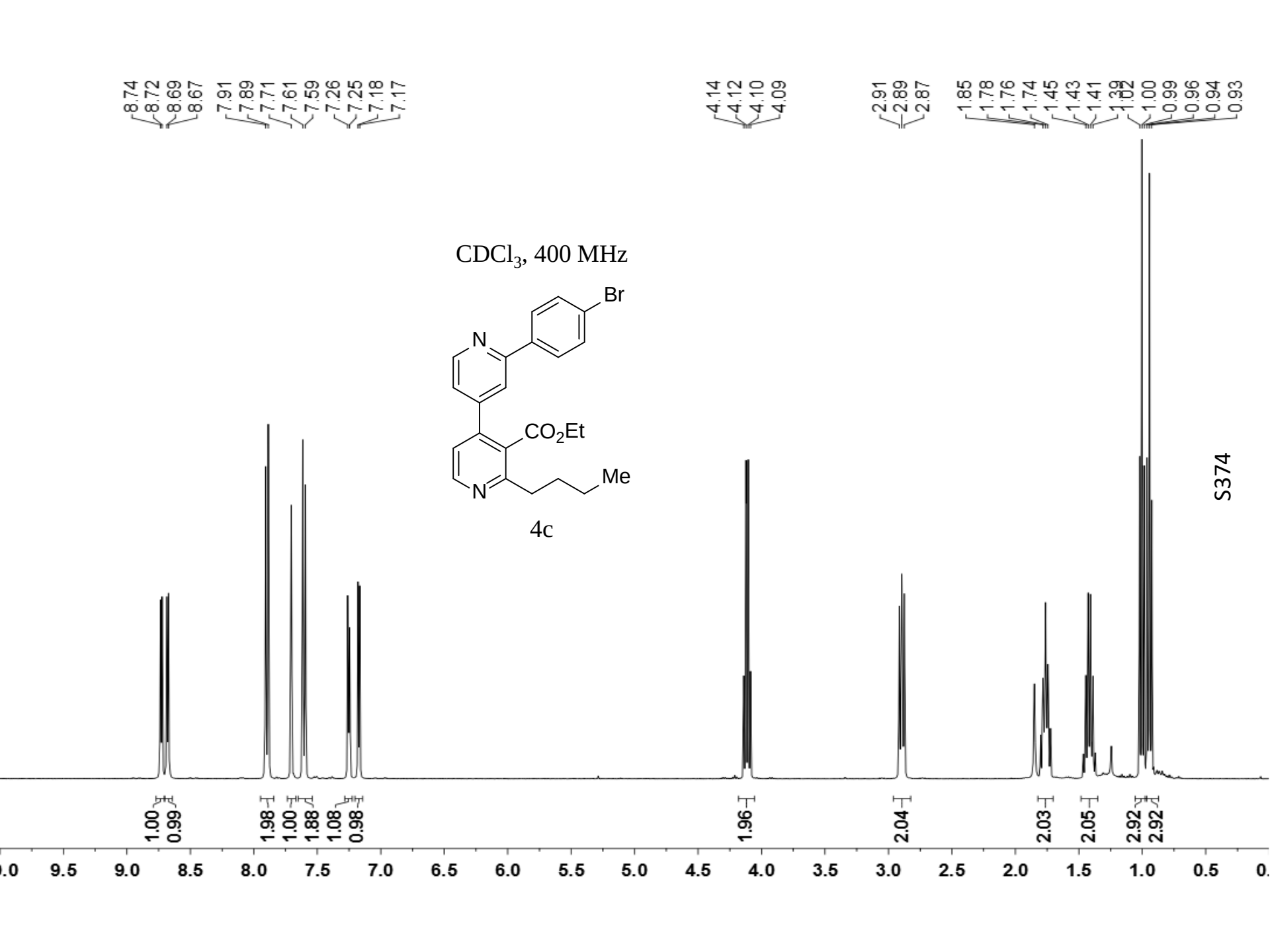

8.74
CDCl3, 162 MHz
N
OBn
N
N
PPh2
+
O
S
CF3
O
O
Me
S369
50
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40

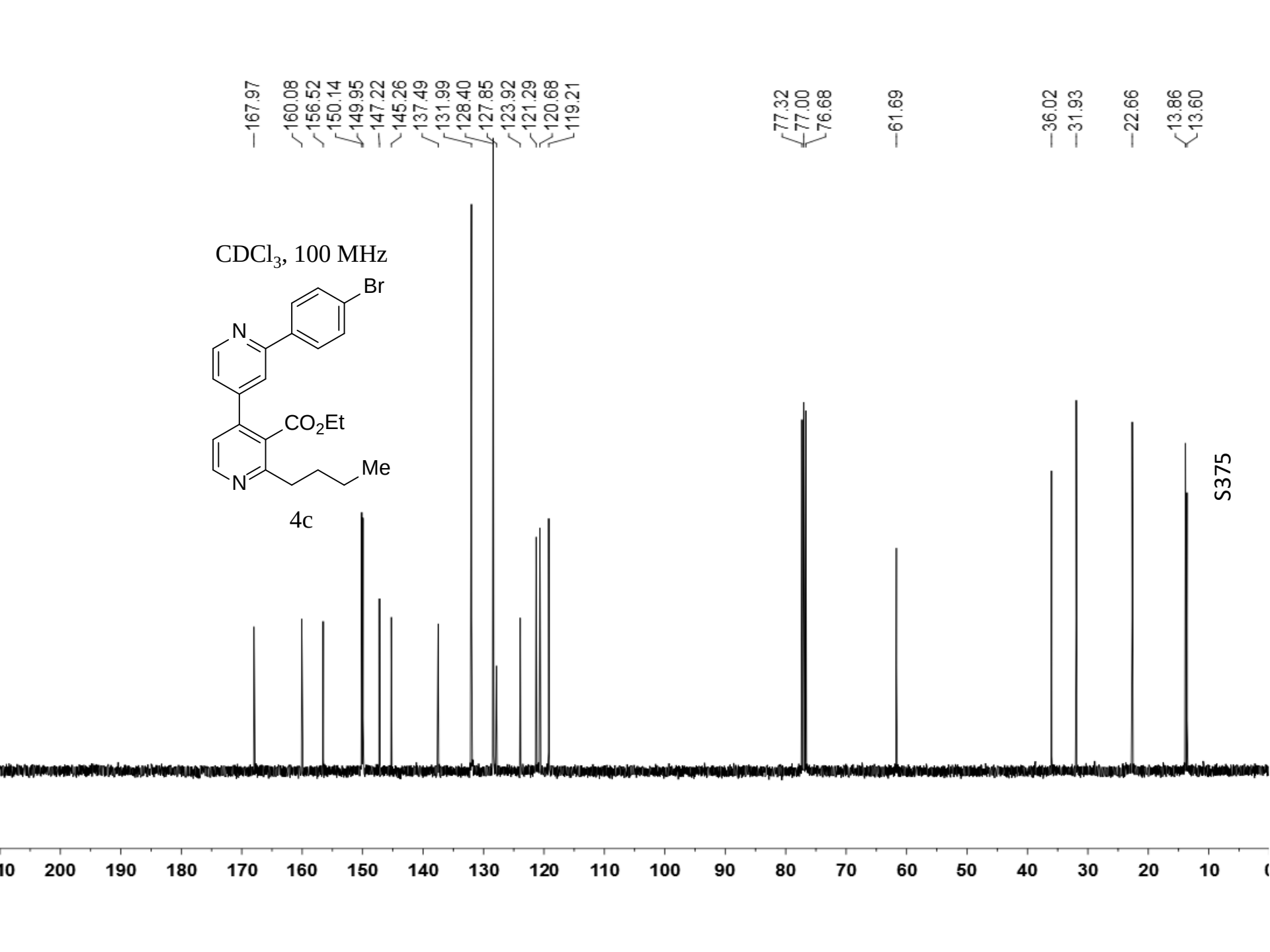

8.76
8.74
8.72
8.03
8.01
7.88
7.53
7.52
7.48
7.47
7.45
7.43
7.41
7.40
7.39
7.26
CDCl3, 400 MHz
N
N
4a
S370
3.07
2.00
1.03
5.99
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

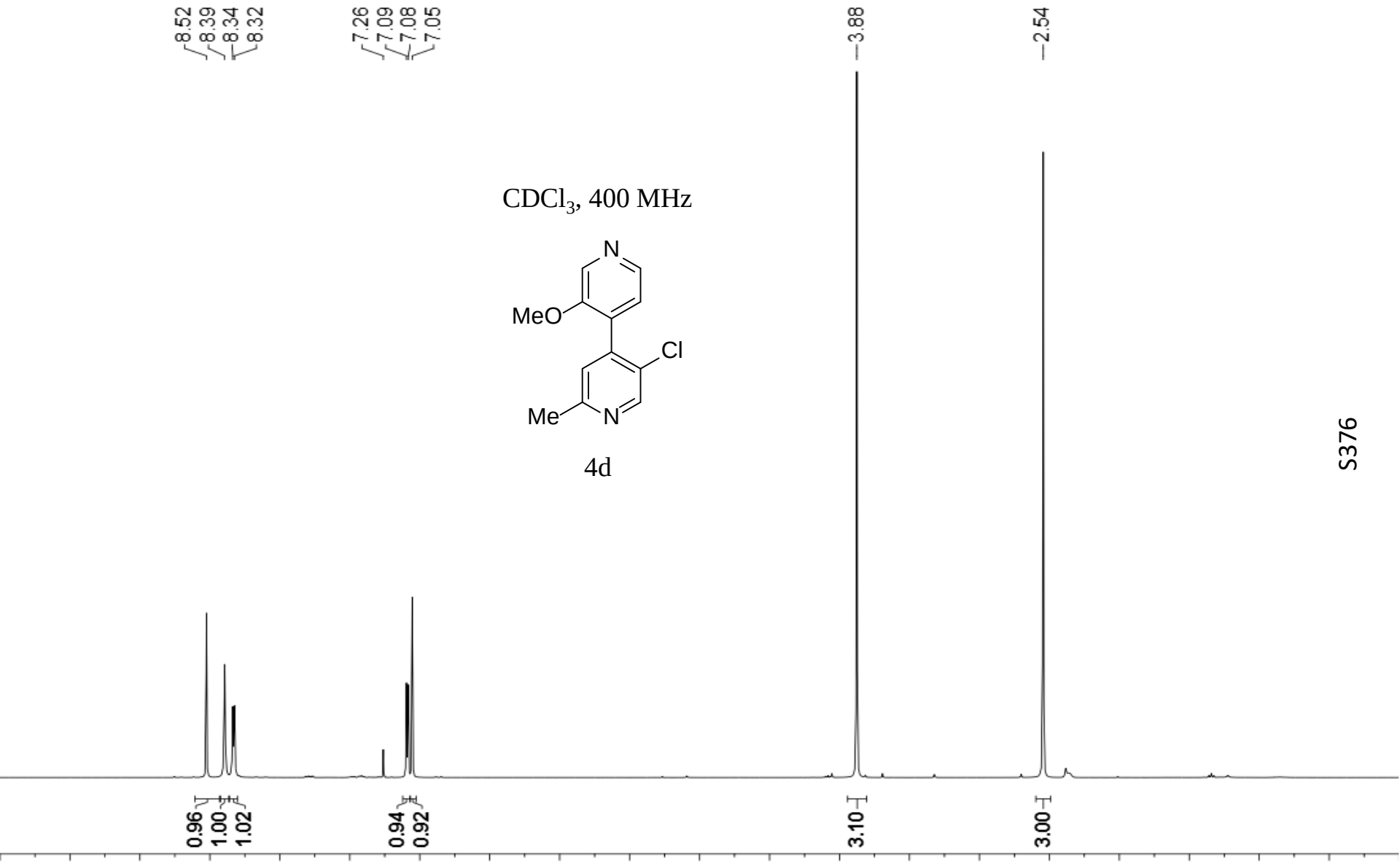

158.34
150.51
150.34
146.25
145.67
138.78
129.21
128.71
126.86
121.34
119.70
118.16
77.32
77.00
76.68
CDCl3, 100 MHz
N
N
4a
S371
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 ppm

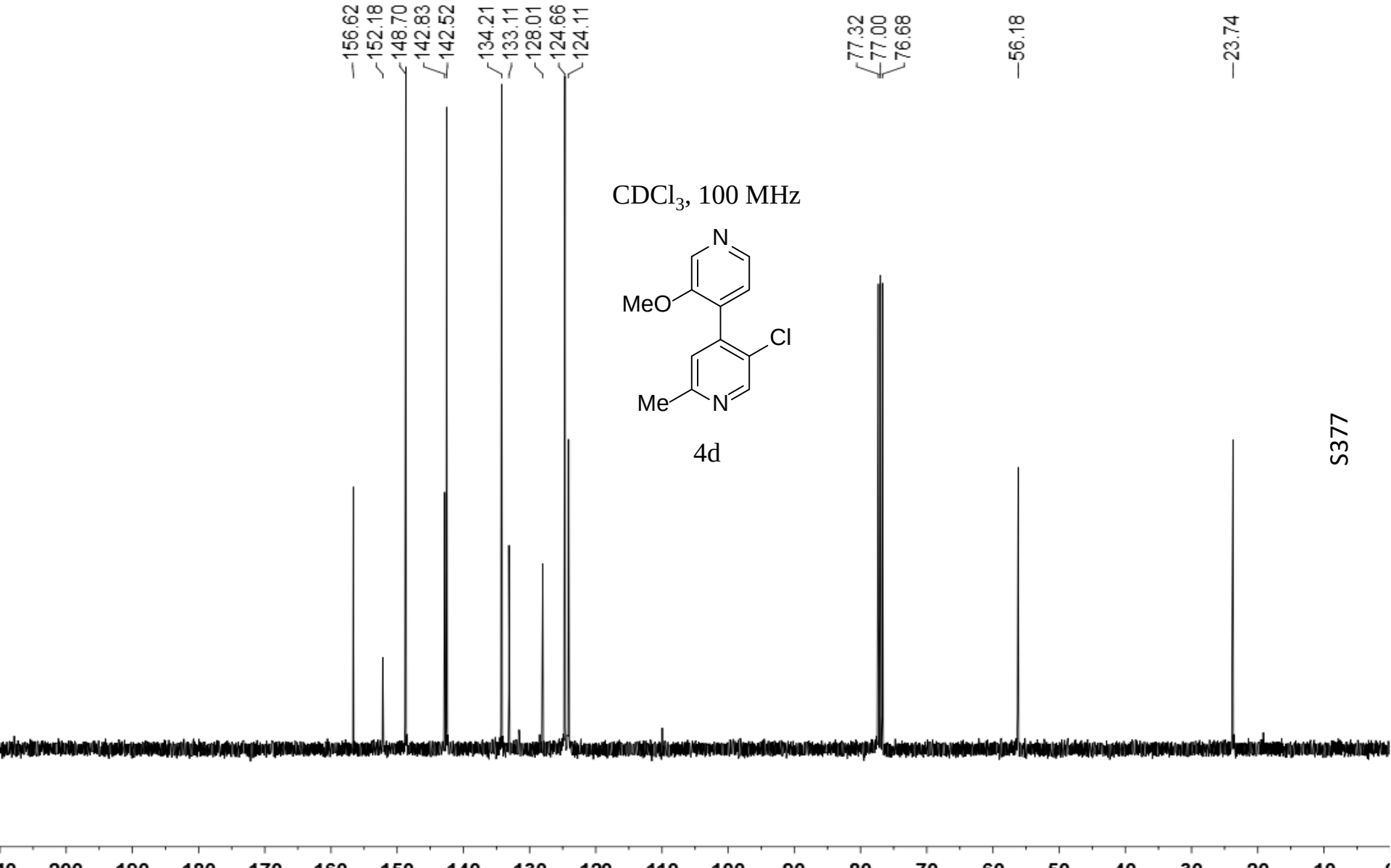

8.80
8.79
8.74
8.61
8.59
7.92
7.77
7.60
7.34
7.34
7.33
7.32
7.32
7.31
7.26
CDCl3, 400 MHz
N
Cl
N
Br
4b
S372
1.02
1.00
1.00
2.04
1.01
1.99
2.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

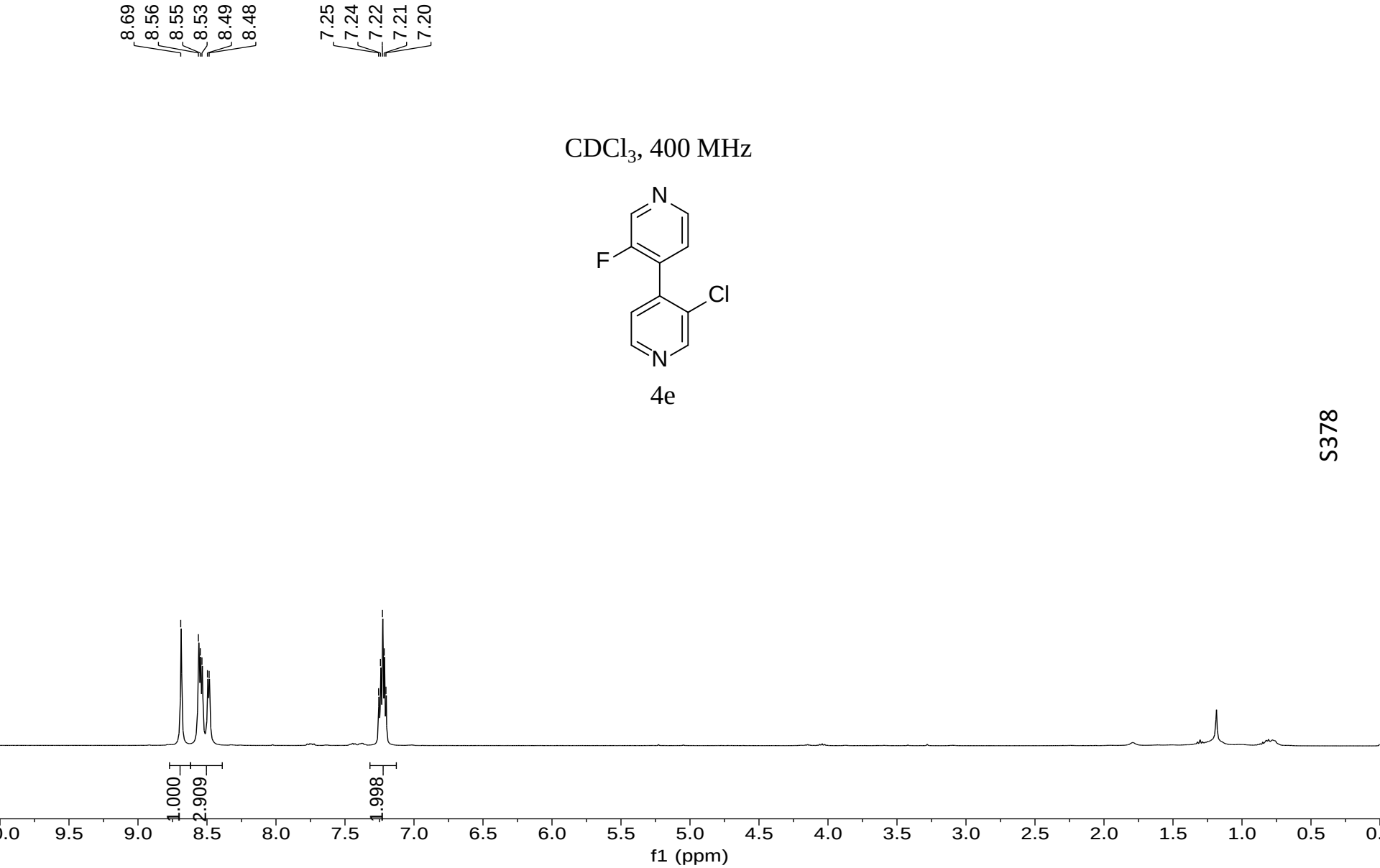

156.61
150.35
149.96
148.15
145.03
144.91
137.56
131.92
129.72
128.46
124.53
123.87
122.03
120.01
77.32
77.00
76.68
CDCl3, 100 MHz
N
Cl
N
Br
4b
200
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)

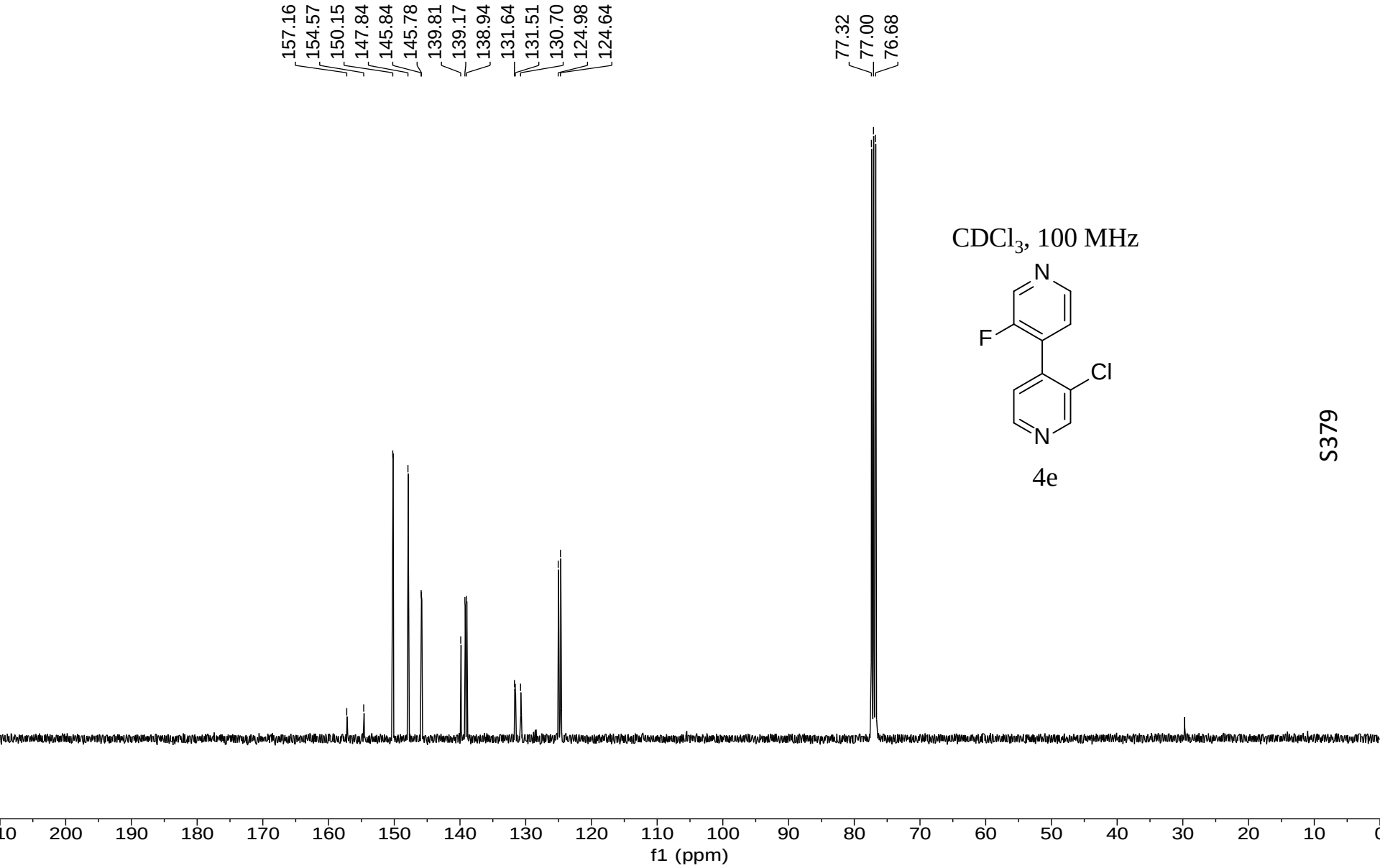

8.74
8.72
8.69
8.67
7.91
7.89
7.71
7.61
7.59
7.26
7.25
7.18
7.17
4.14
4.12
4.10
4.09
2.91
2.89
2.87
1.85
1.78
1.76
1.74
1.45
1.43
1.41
1.00
0.99
0.96
0.94
0.93
CDCl3, 400 MHz
Br
N
CO2Et
Me
N
4c
S374
1.00
0.99
1.98
1.00
1.88
1.08
0.98
1.96
2.04
2.03
2.05
2.92
2.92
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5


167.97
160.08
156.52
150.14
149.95
147.22
145.26
137.49
131.99
128.40
127.85
123.92
121.29
120.68
119.21
77.32
77.00
76.68
61.69
36.02
31.93
22.66
13.86
13.60
CDCl3, 100 MHz
Br
N
CO2Et
Me
N
4c
S375
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10


8.52
8.39
8.34
8.32
7.26
7.09
7.08
7.05
3.88
2.54
CDCl3, 400 MHz
N
MeO
Cl
Me
N
4d
0.96
1.00
1.02
0.94
0.92
3.10
3.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

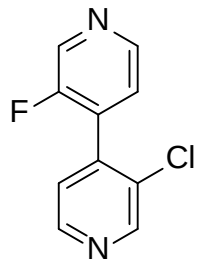

156.62
152.18
148.70
142.83
142.52
134.21
133.11
128.01
124.66
124.11
77.32
77.00
76.68
56.18
23.74
CDCl3, 100 MHz
N
MeO
Cl
Me
N
4d
S377
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10


8.69
8.56
8.55
8.53
8.49
8.48
7.25
7.24
7.22
7.21
7.20
CDCl3, 400 MHz
N
F
Cl
N
4e
S378
1.000
2.909
1.998
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


157.16
154.57
150.15
147.84
145.84
145.78
139.81
139.17
138.94
131.64
131.51
130.70
124.98
124.64
77.32
77.00
76.68
CDCl3, 100 MHz
N
F
Cl
N
4e
S379
f1 (ppm)

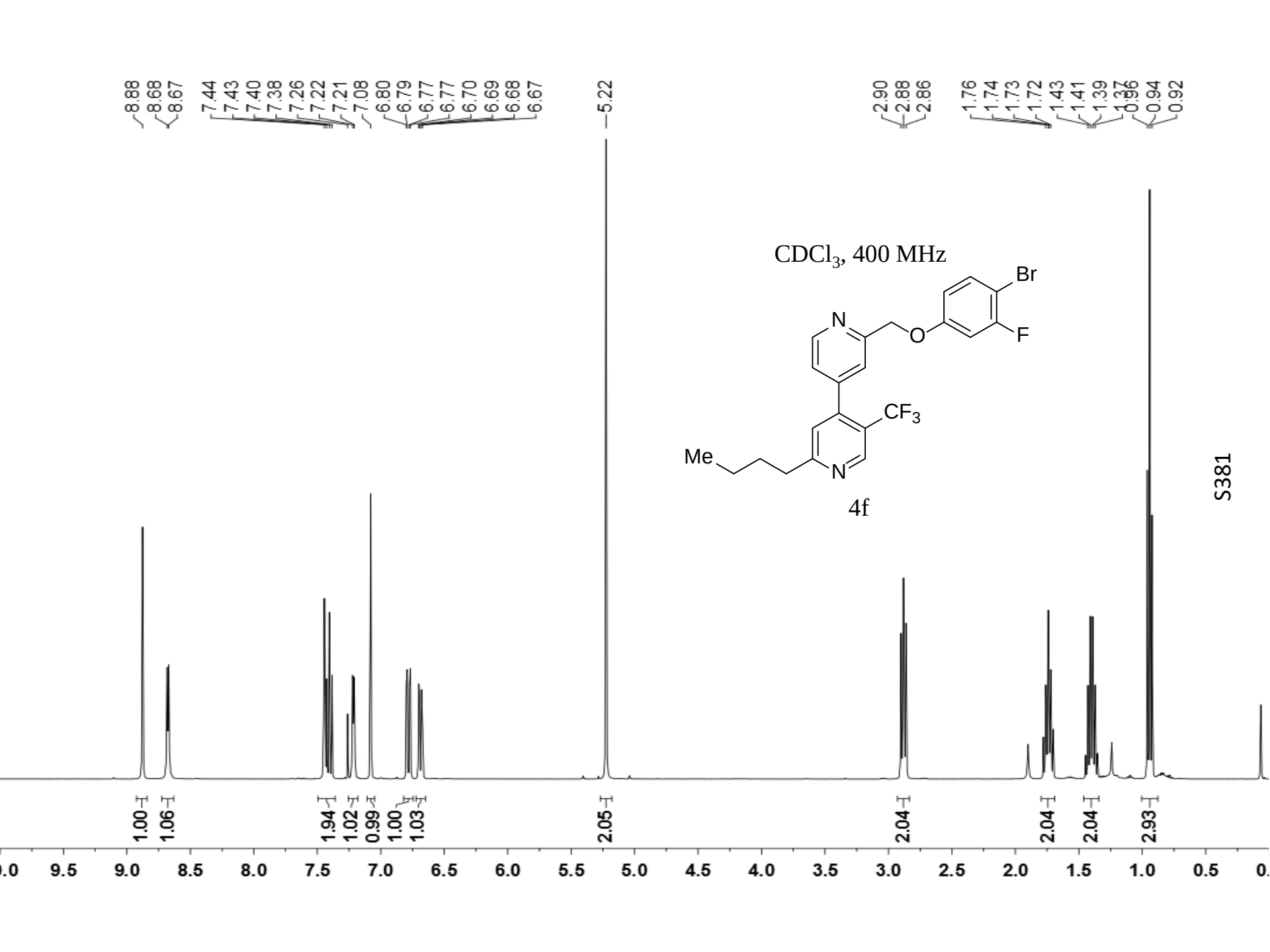
-128.05
-128.07

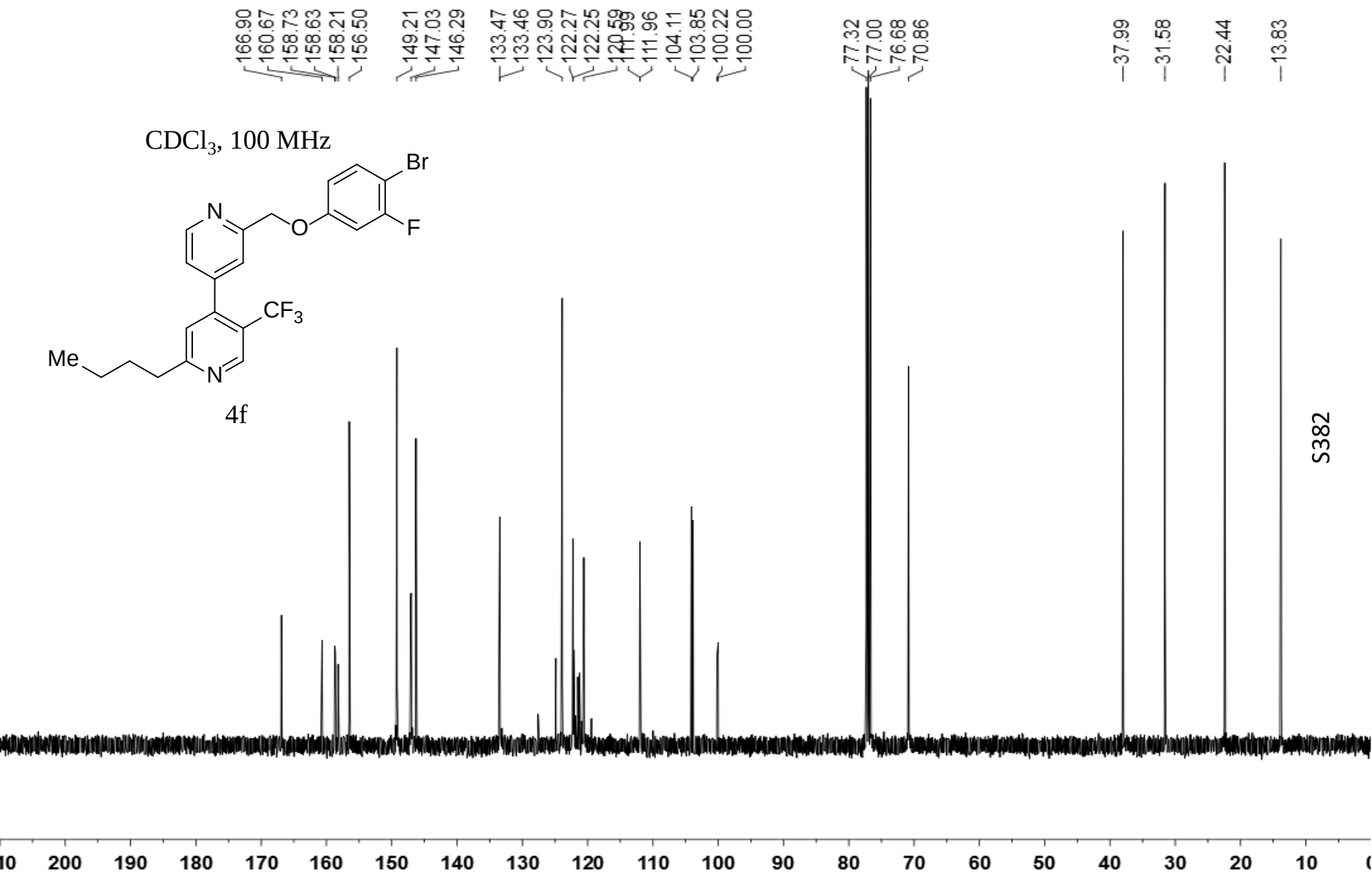
$CDCl_3$, 365 MHz

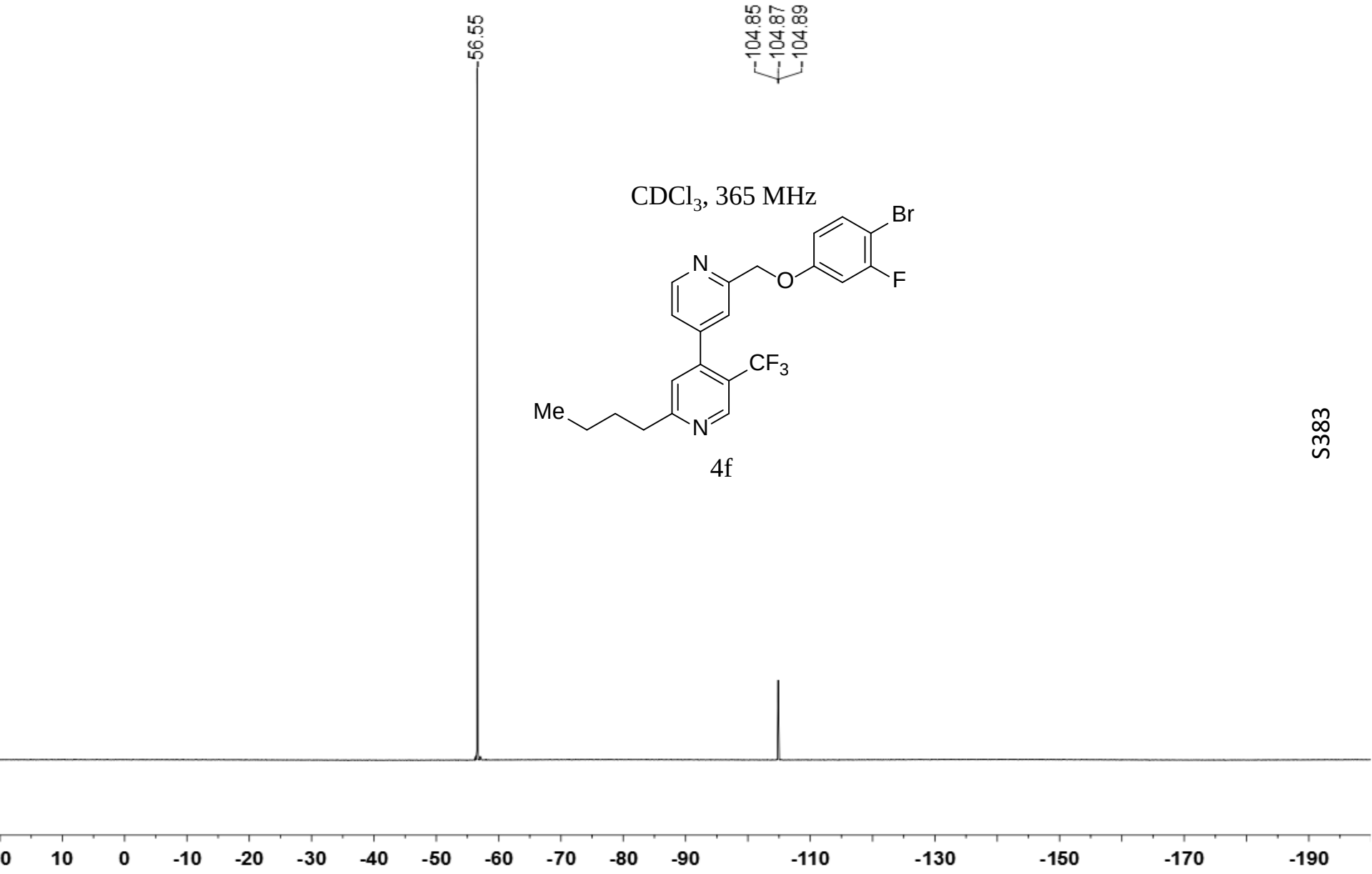


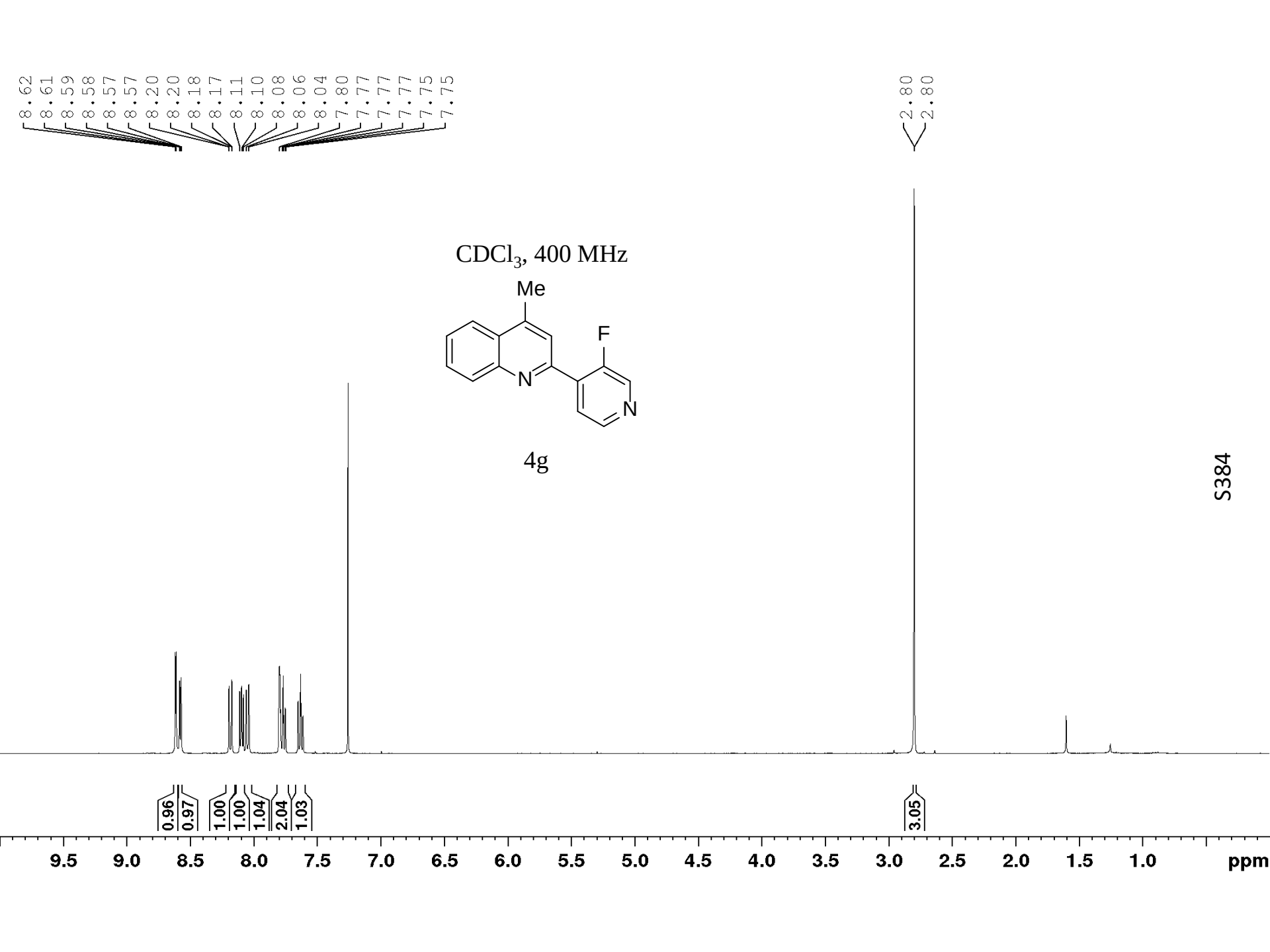
4e

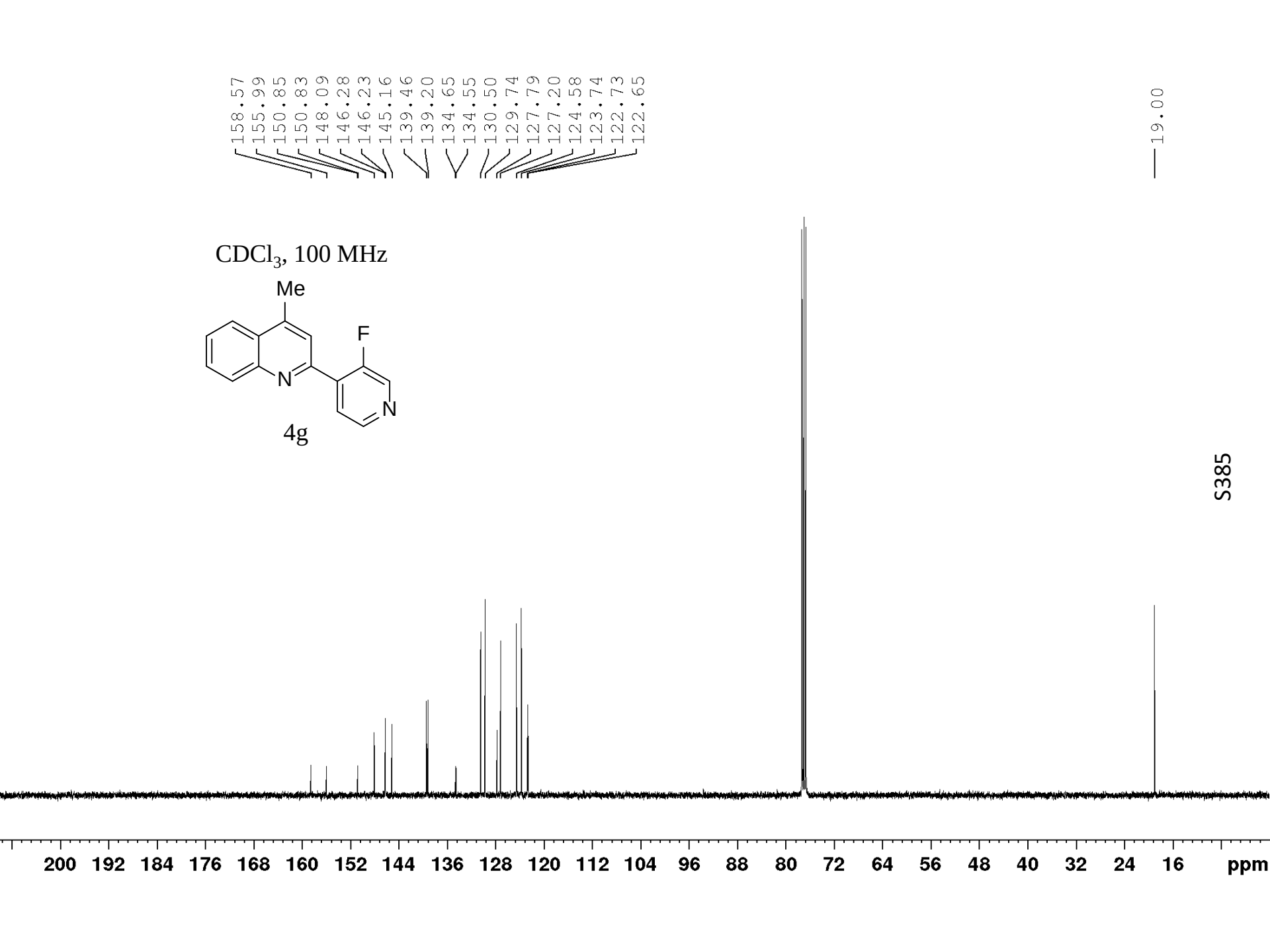
S380

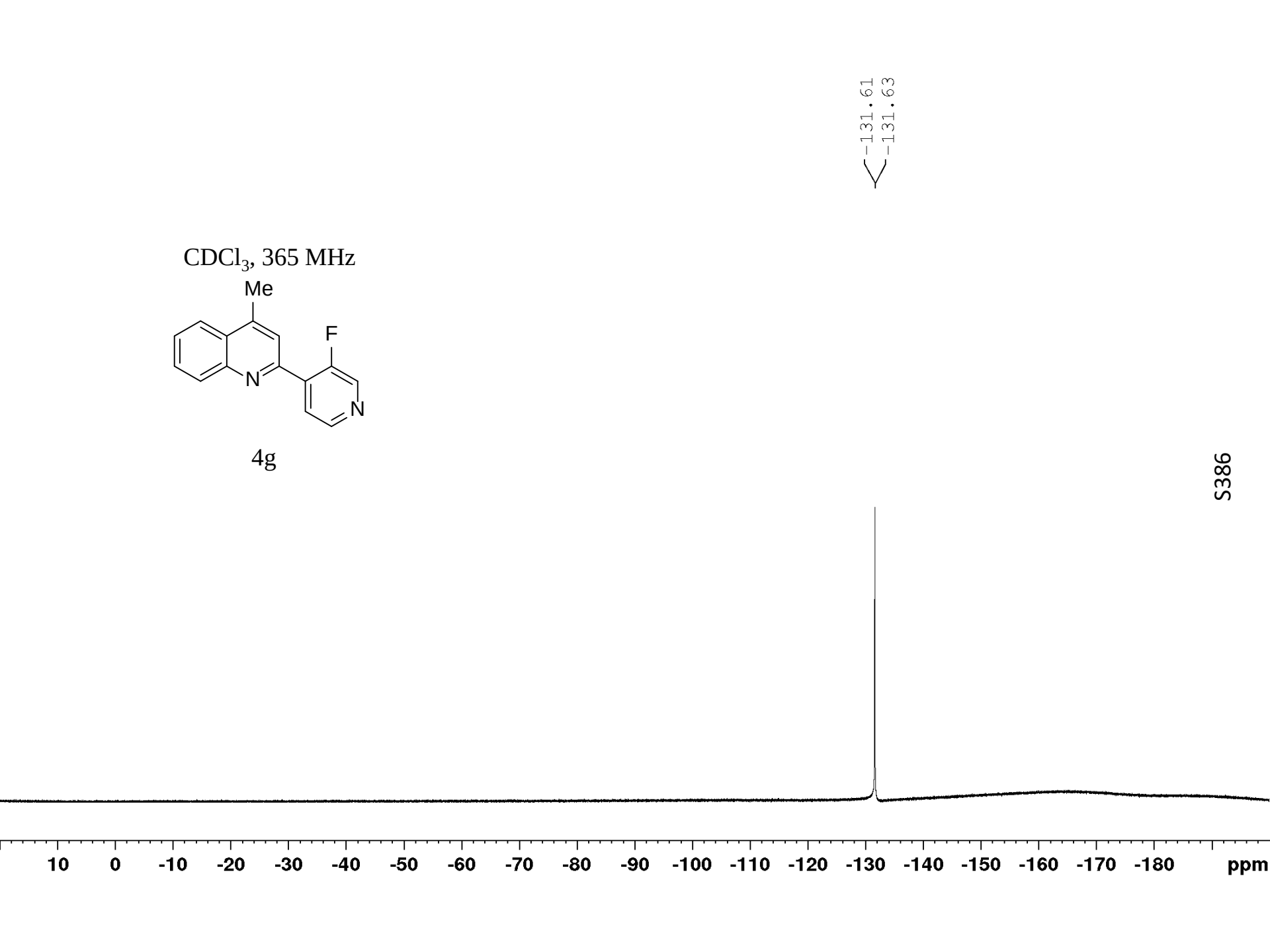

8.88
8.68
8.67
7.44
7.43
7.40
7.38
7.26
7.22
7.21
7.08
6.80
6.79
6.77
6.77
6.70
6.69
6.68
6.67
5.22
2.90
2.88
2.86
1.76
1.74
1.73
1.72
1.43
1.41
1.39
0.96
0.94
0.92
CDCl3, 400 MHz
Br
F
O
N
CF3
Me
N
4f
S381
1.00
1.06
1.94
1.02
0.99
1.00
1.03
2.05
2.04
2.04
2.04
2.93
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

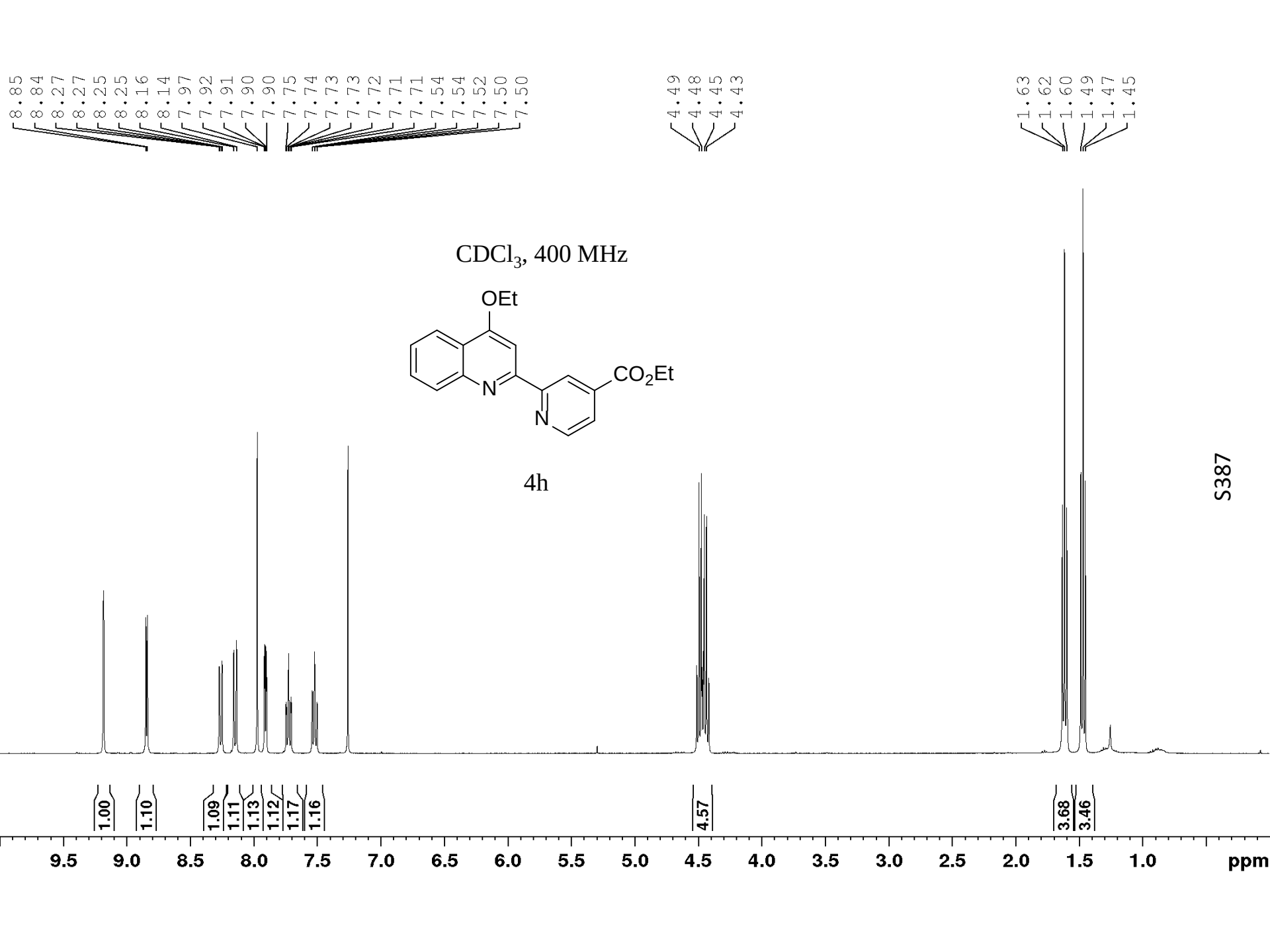

166.90
160.67
158.73
158.63
158.21
156.50
149.21
147.03
146.29
133.47
133.46
123.90
122.27
122.25
120.59
111.99
111.96
104.11
103.85
100.22
100.00
77.32
77.00
76.68
70.86
37.99
31.58
22.44
13.83
CDCl3, 100 MHz
Br
F
O
N
CF3
Me
N
4f
S382
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

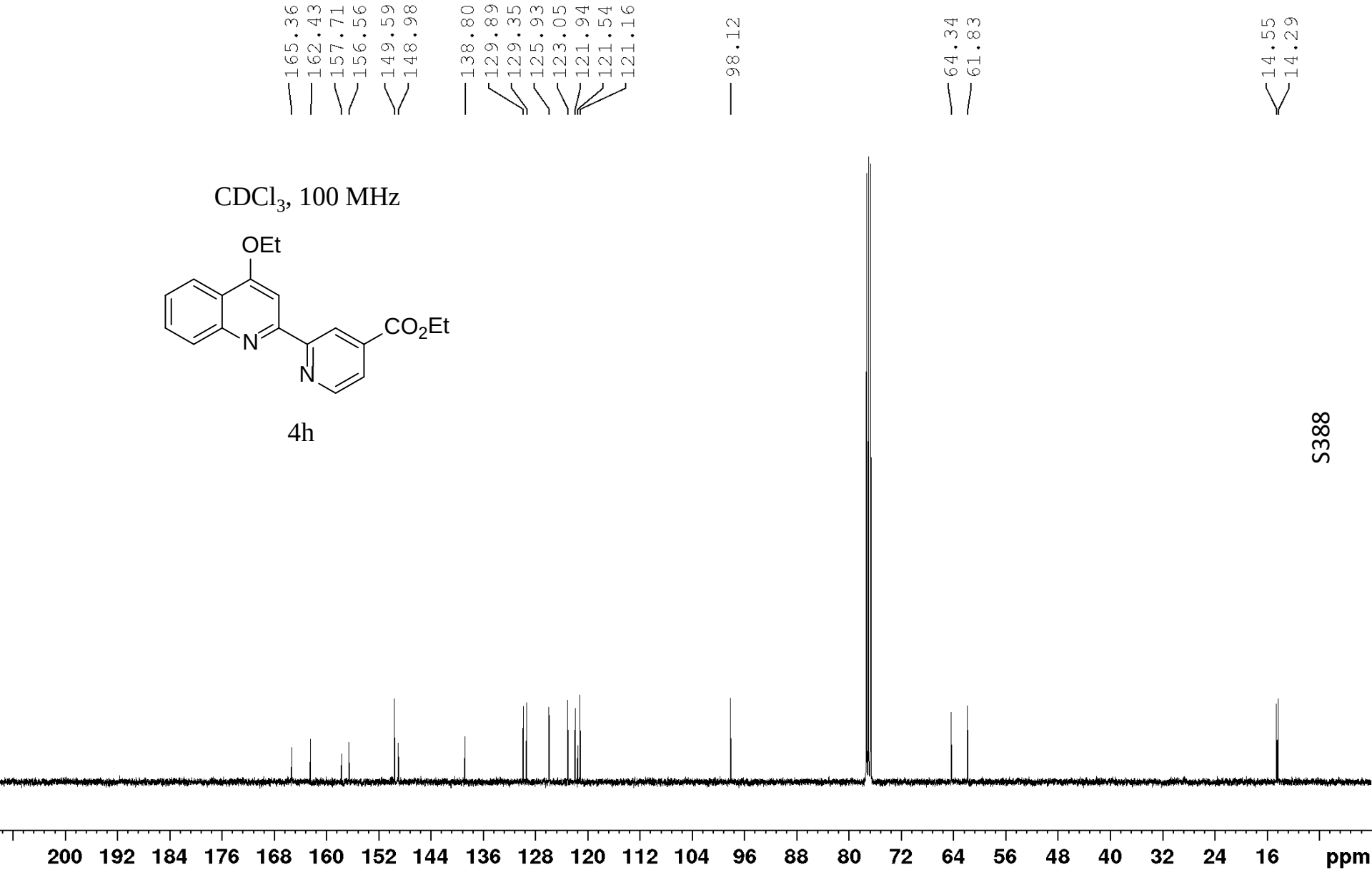

56.55
-104.85
-104.87
-104.89
CDCl3, 365 MHz
Br
F
O
N
CF3
Me
N
4f
0
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-110
-130
-150
-170
-190

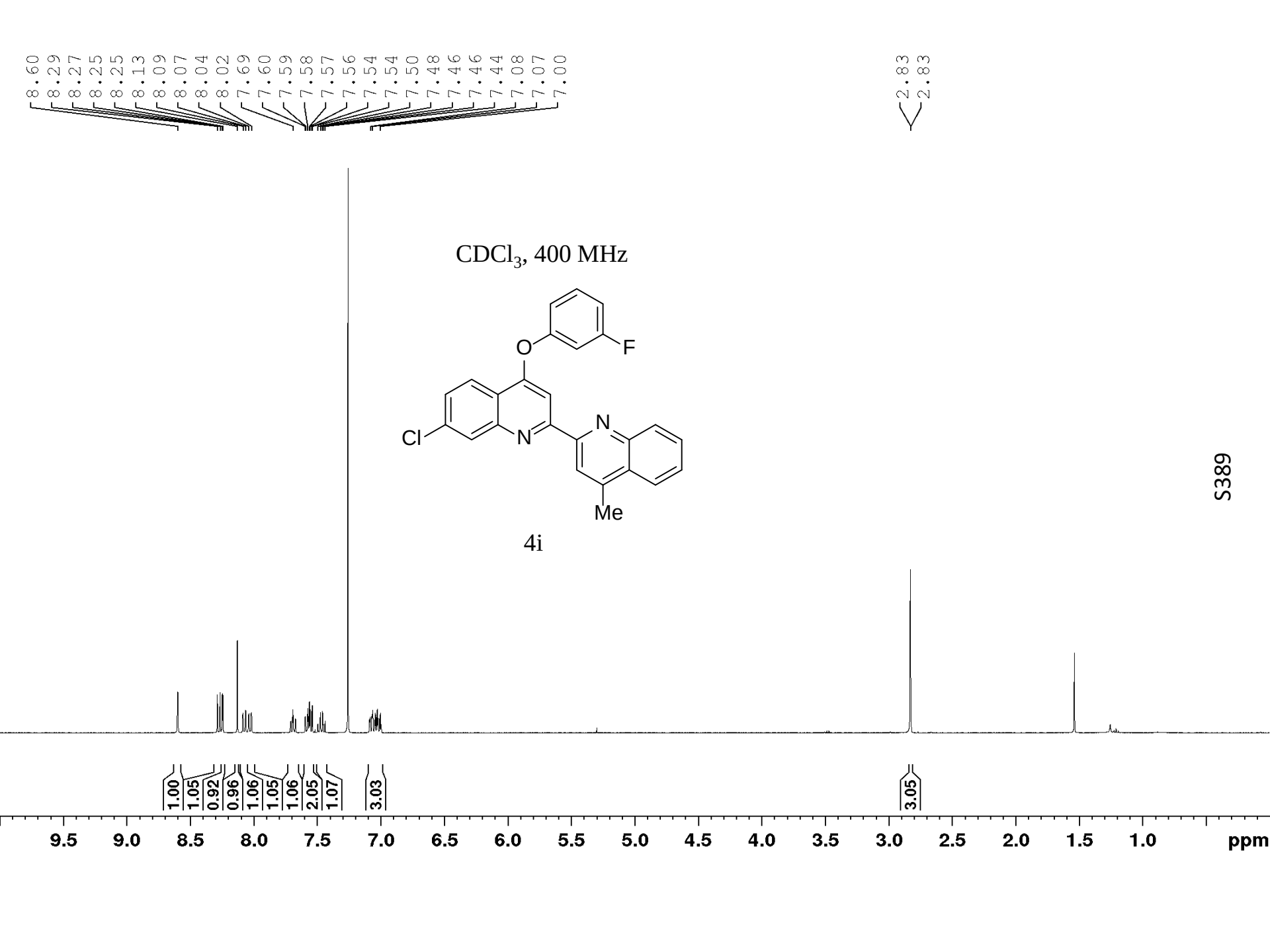

8.62
8.61
8.59
8.58
8.57
8.57
8.20
8.20
8.18
8.17
8.11
8.10
8.08
8.06
8.04
7.80
7.77
7.77
7.77
7.75
7.75
2.80
2.80
CDCl3, 400 MHz
Me
F
N
N
4g
S384
0.96
0.97
1.00
1.00
1.04
2.04
1.03
3.05
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

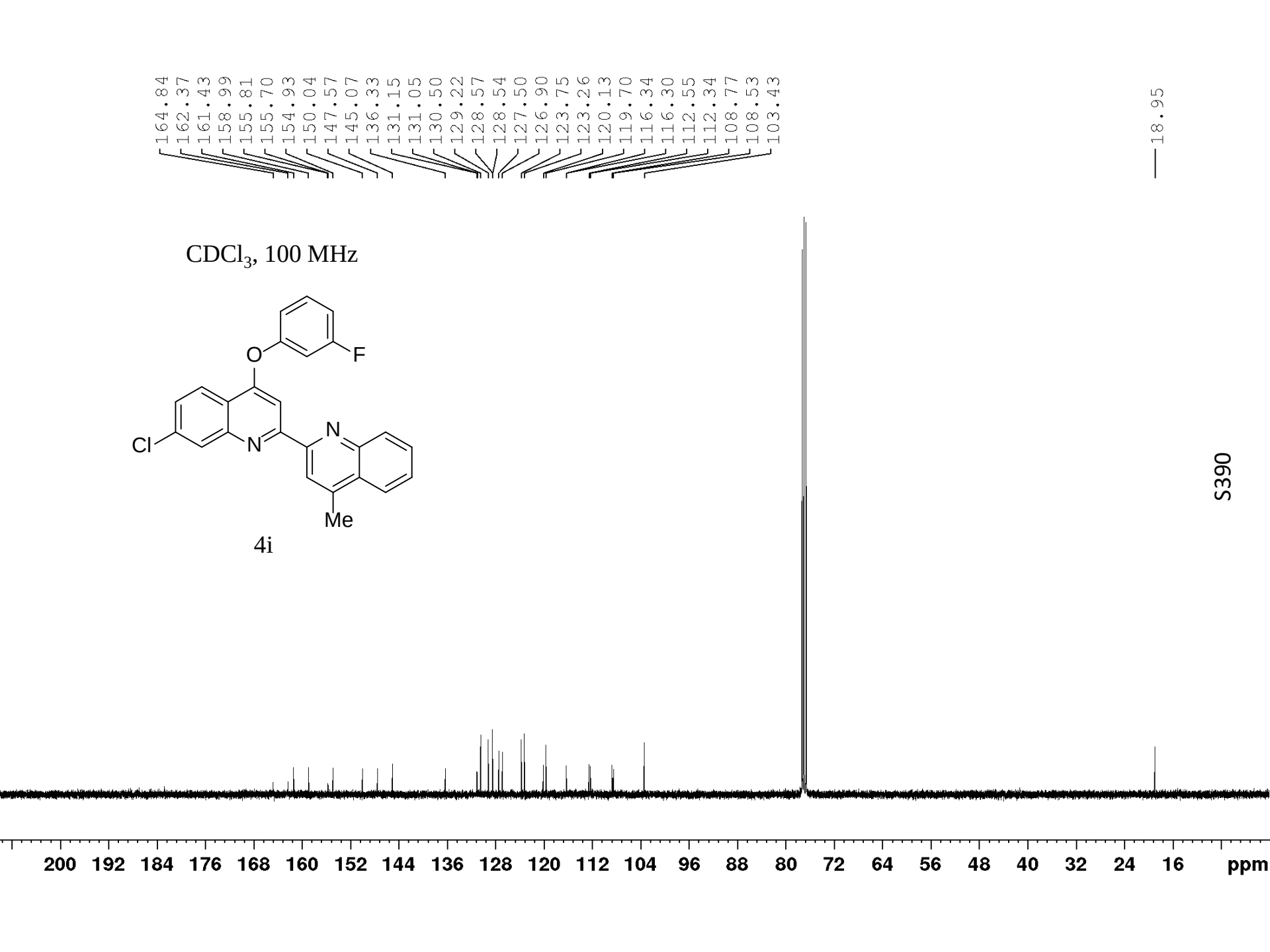

158.57
155.99
150.85
150.83
148.09
146.28
146.23
145.16
139.46
139.20
134.65
134.55
130.50
129.74
127.79
127.20
124.58
123.74
122.73
122.65
19.00
CDCl3, 100 MHz
Me
F
N
N
4g
S385
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 ppm

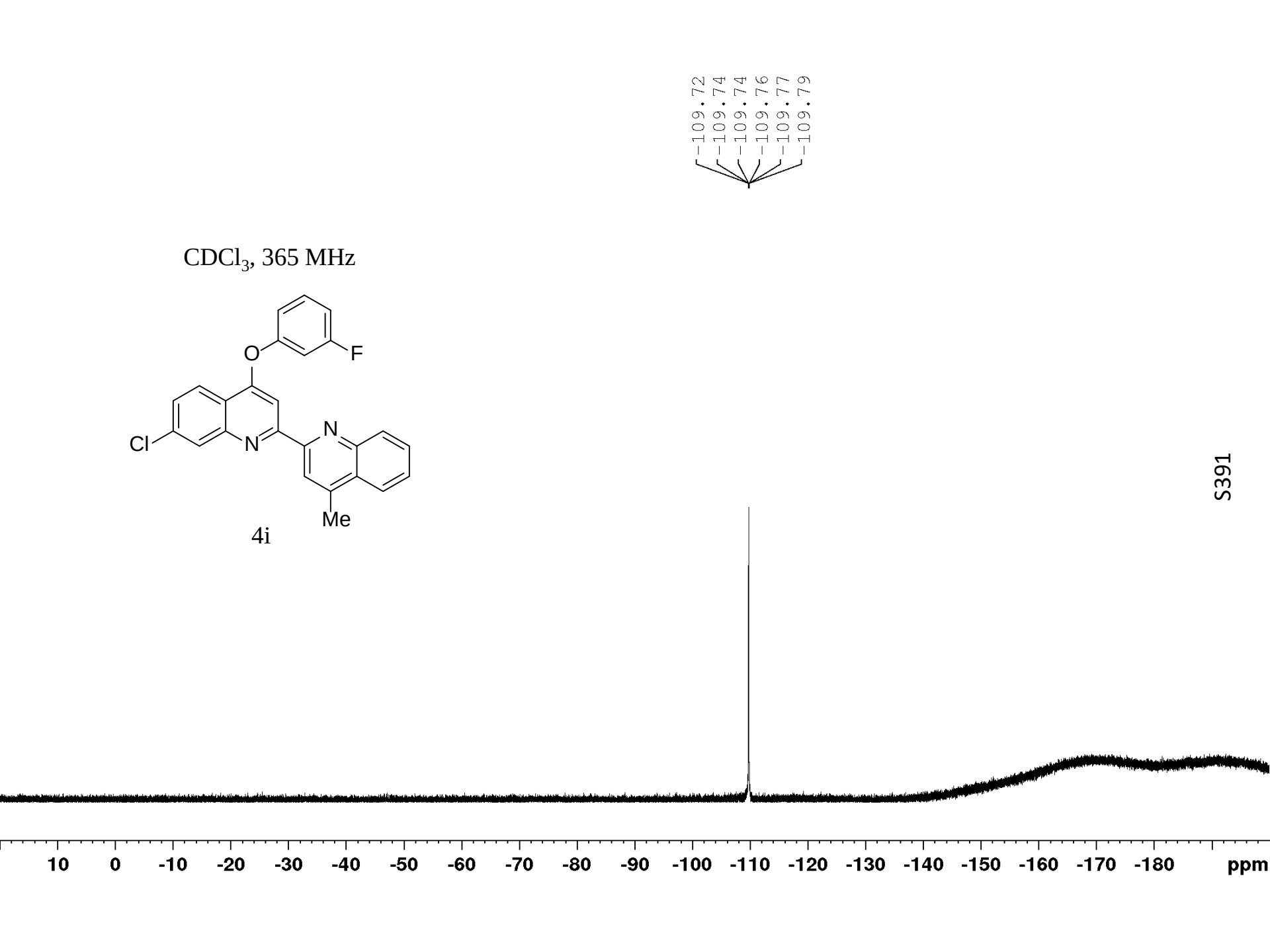

-131.61
-131.63
CDCl3, 365 MHz
Me
F
N
N
4g
S386
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
ppm

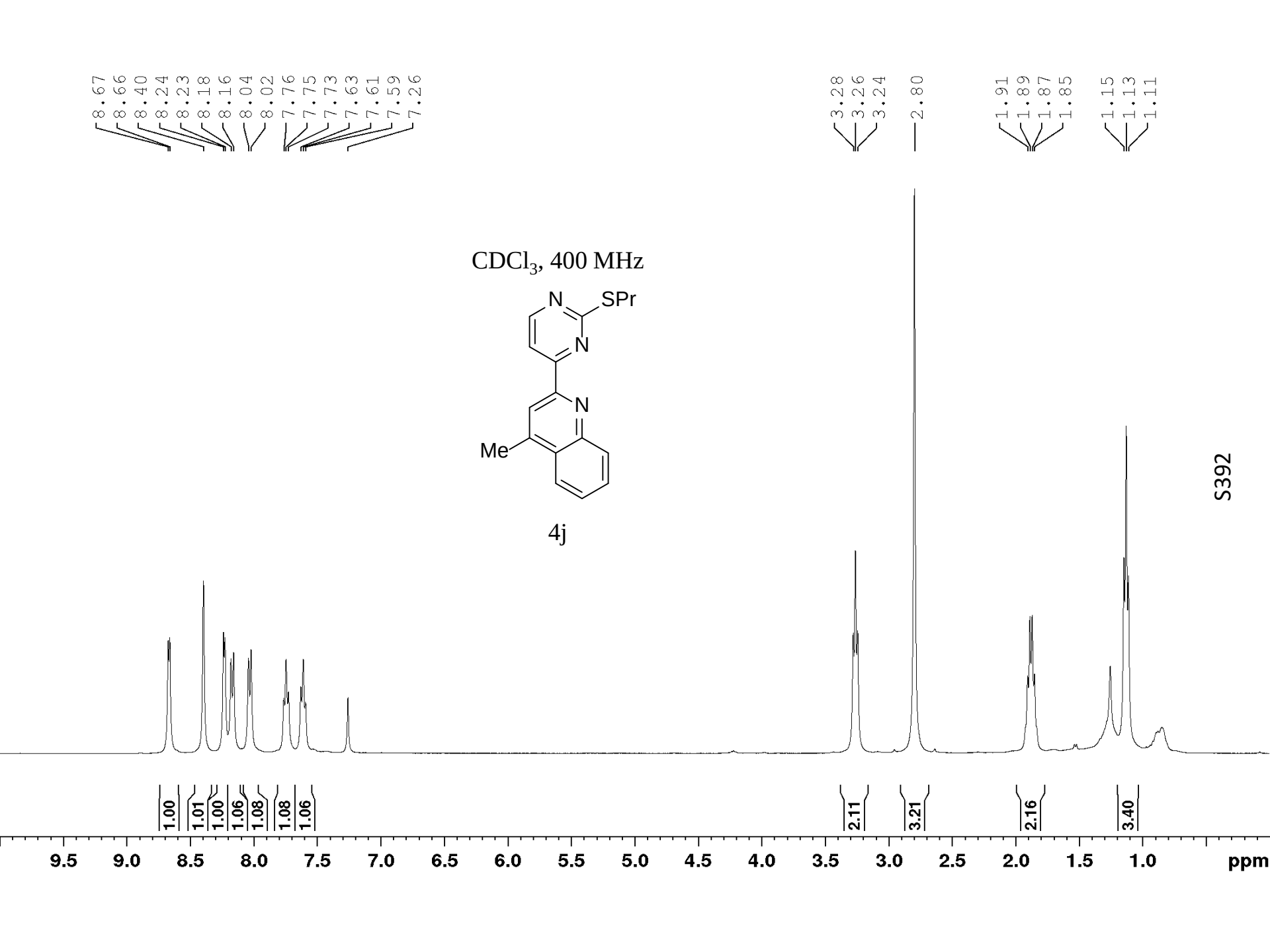

8.85
8.84
8.27
8.27
8.25
8.25
8.16
8.14
7.97
7.92
7.91
7.90
7.90
7.75
7.74
7.73
7.73
7.72
7.71
7.71
7.54
7.54
7.52
7.50
7.50
4.49
4.48
4.45
4.43
1.63
1.62
1.60
1.49
1.47
1.45
CDCl3, 400 MHz
OEt
CO2Et
N
N
4h
S387
1.00
1.10
1.09
1.11
1.13
1.12
1.17
1.16
4.57
3.68
3.46
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

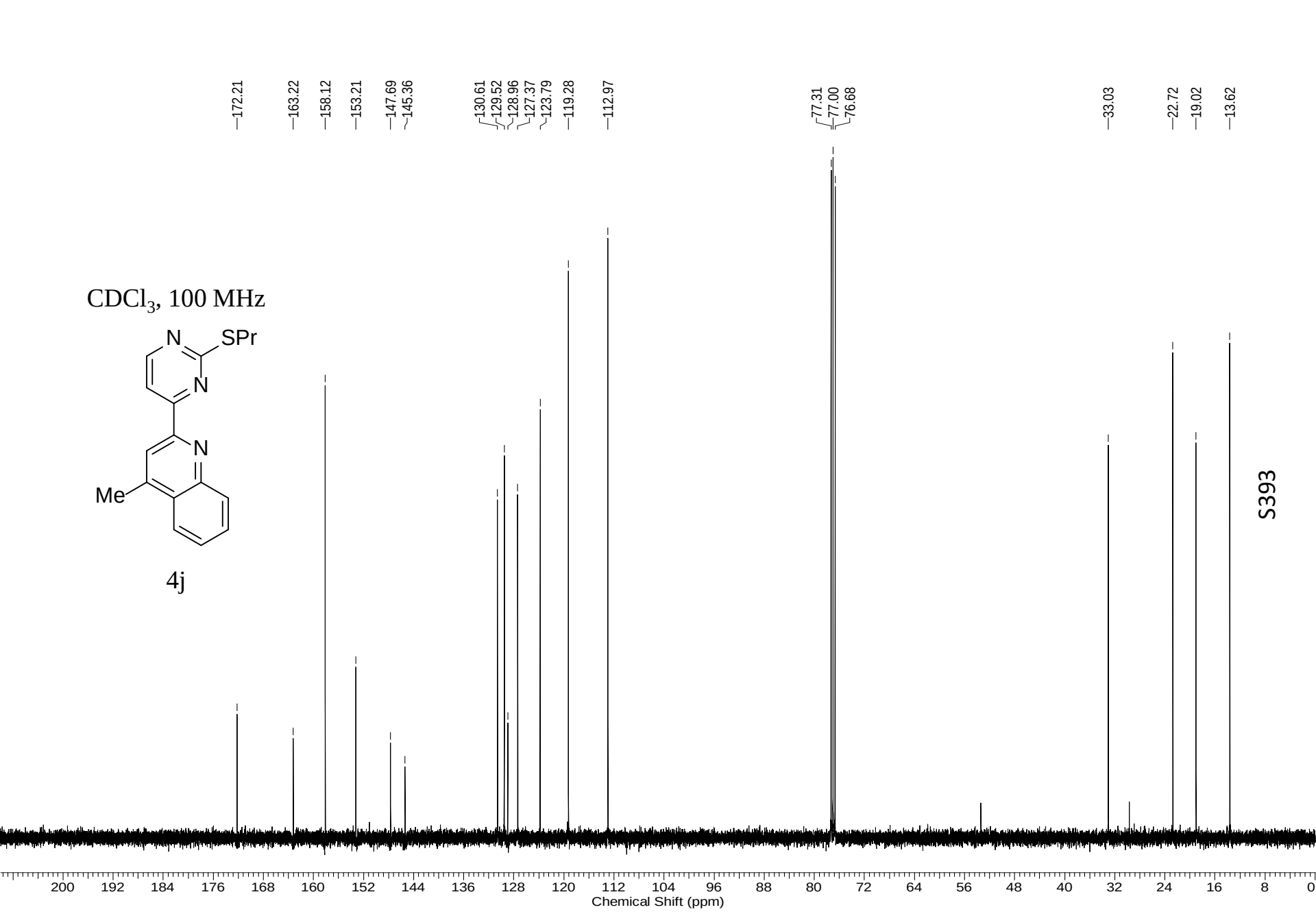

165.36
162.43
157.71
156.56
149.59
148.98
138.80
129.89
129.35
125.93
123.05
121.94
121.54
121.16
98.12
64.34
61.83
14.55
14.29
CDCl3, 100 MHz
OEt
CO2Et
N
N
4h
S388
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 ppm

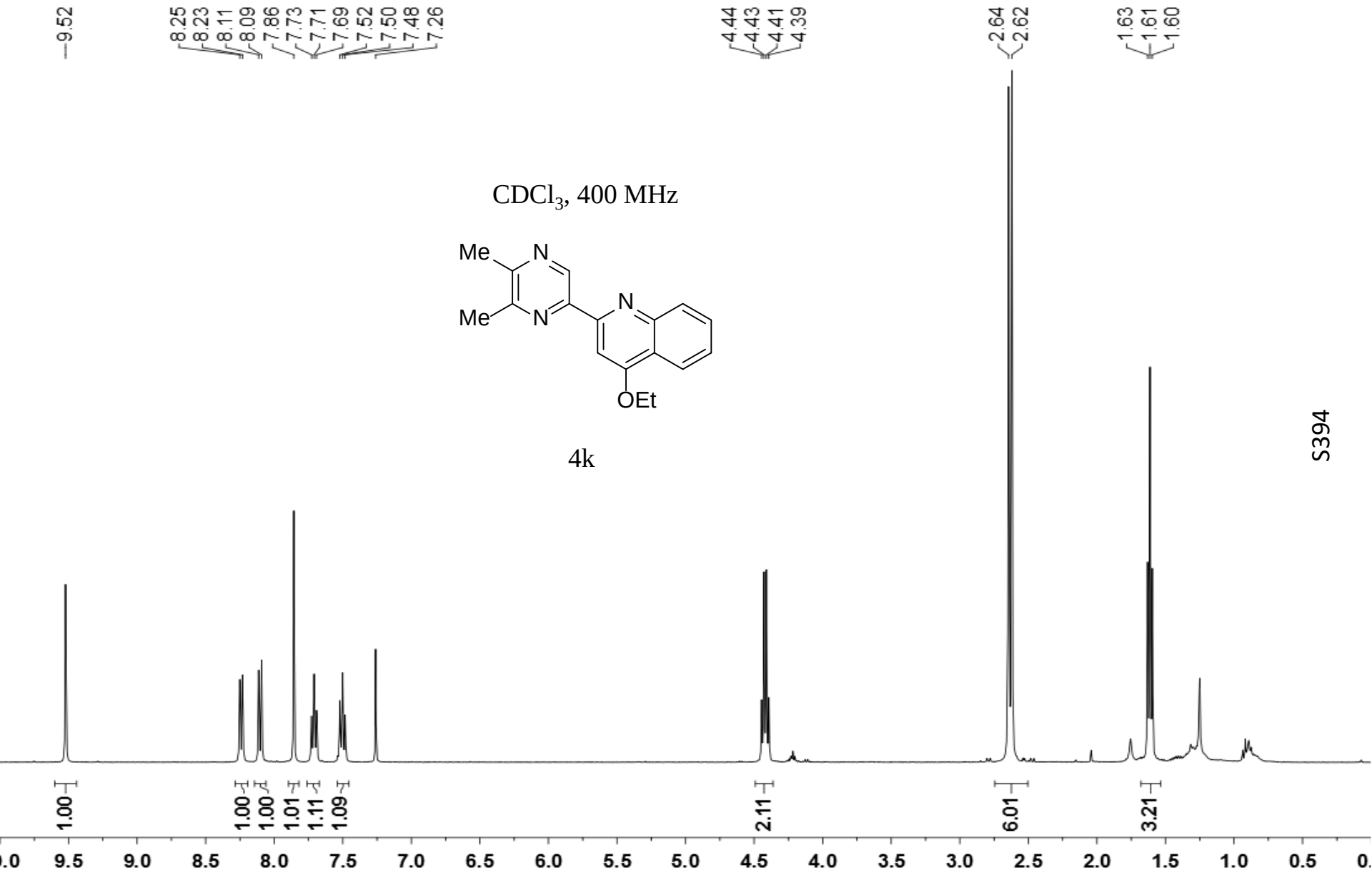

8.60
8.29
8.27
8.25
8.25
8.13
8.09
8.07
8.04
8.02
7.69
7.60
7.59
7.58
7.57
7.56
7.54
7.54
7.50
7.48
7.46
7.46
7.44
7.08
7.07
7.00
2.83
2.83
CDCl3, 400 MHz
O
F
Cl
N
N
Me
4i
S389
1.00
1.05
0.92
0.96
1.06
1.05
1.06
2.05
1.07
3.03
3.05
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

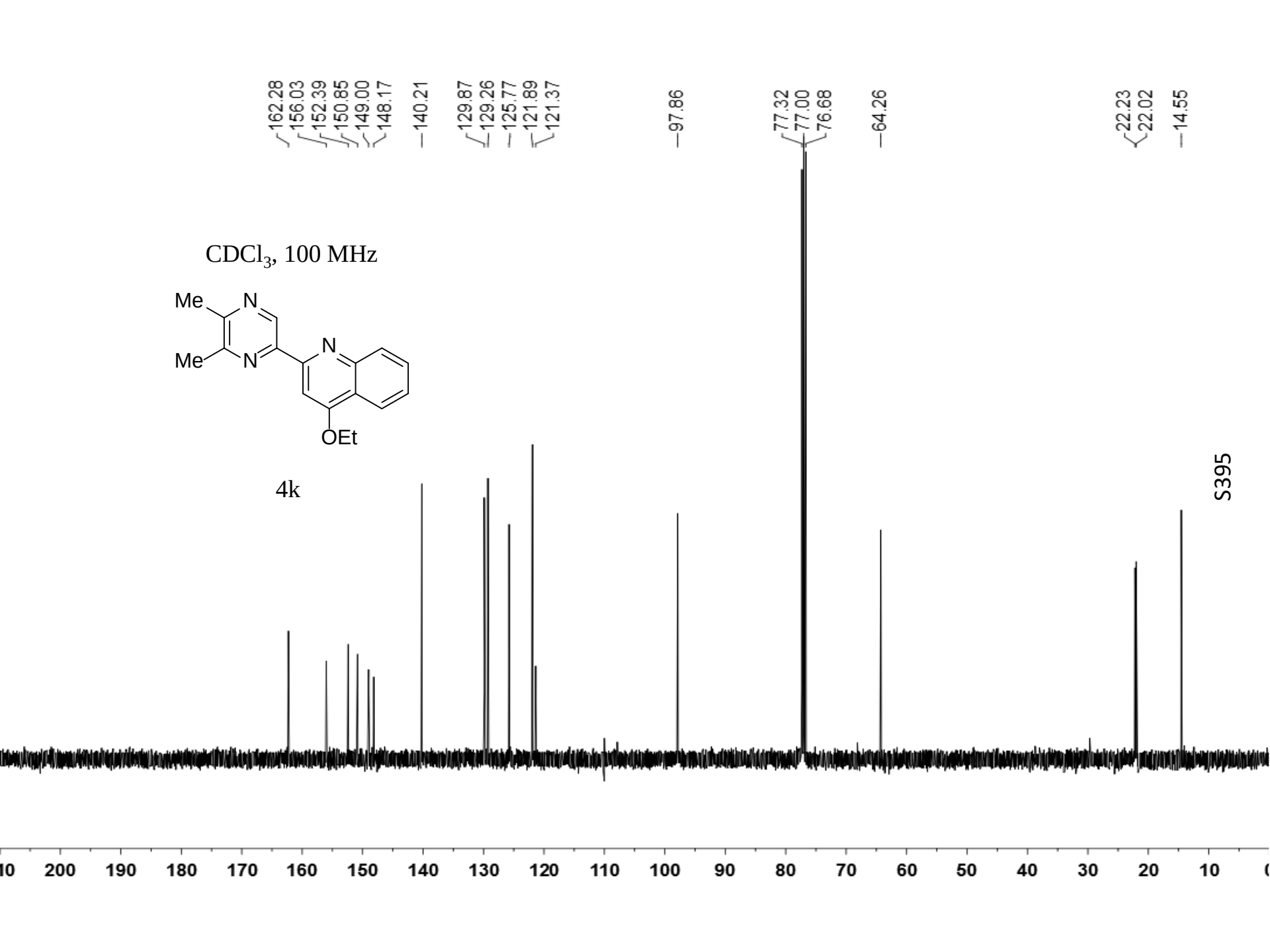

164.84
162.37
161.43
158.99
155.81
155.70
154.93
150.04
147.57
145.07
136.33
131.15
131.05
130.50
129.22
128.57
128.54
127.50
126.90
123.75
123.26
120.13
119.70
116.34
116.30
112.55
112.34
108.77
108.53
103.43
18.95
CDCl3, 100 MHz
O
F
Cl
N
N
Me
4i
S390
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 ppm

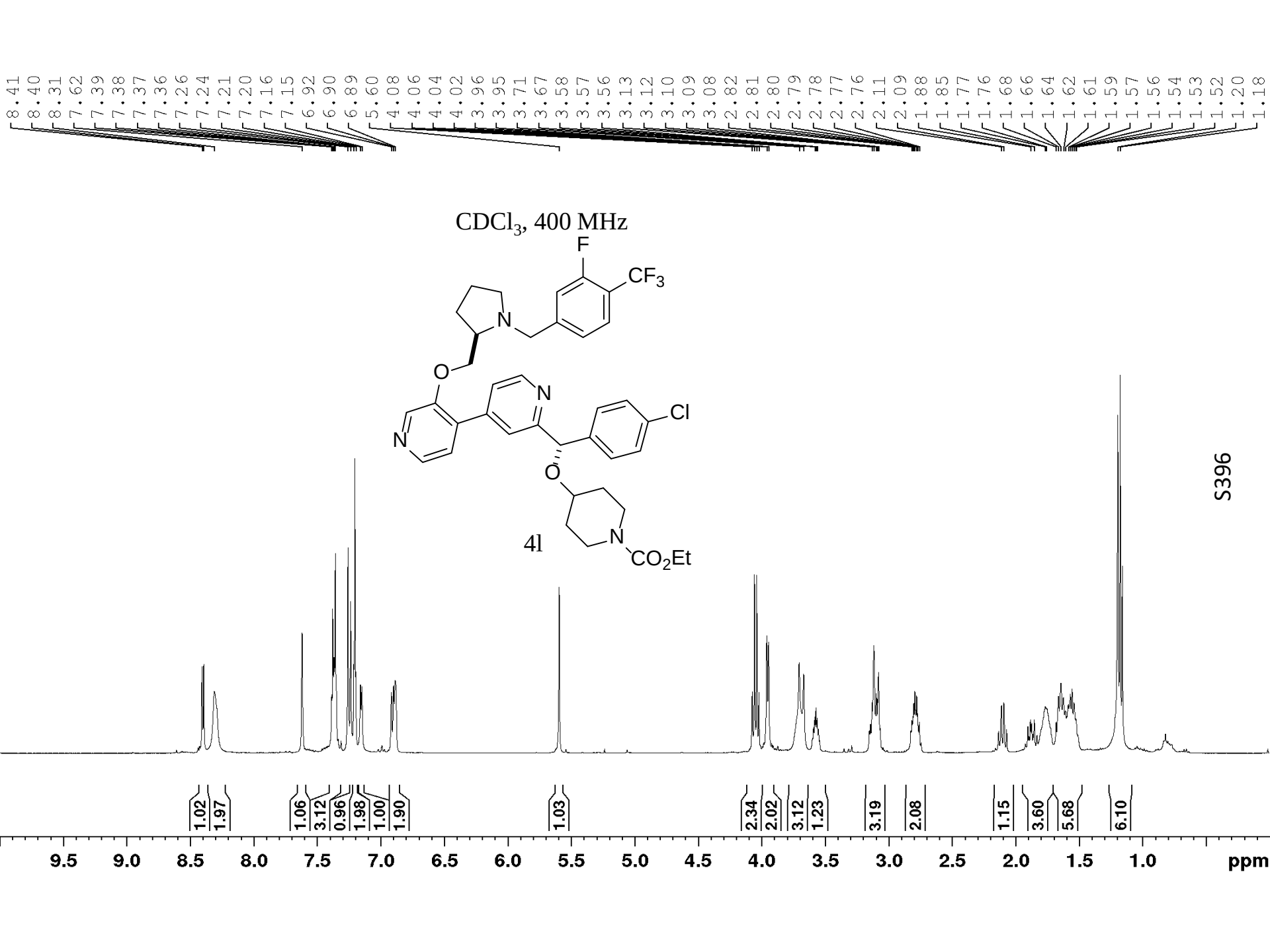

-109.72
-109.74
-109.74
-109.76
-109.77
-109.79
CDCl3, 365 MHz
O
F
Cl
N
N
Me
4i
S391
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
ppm

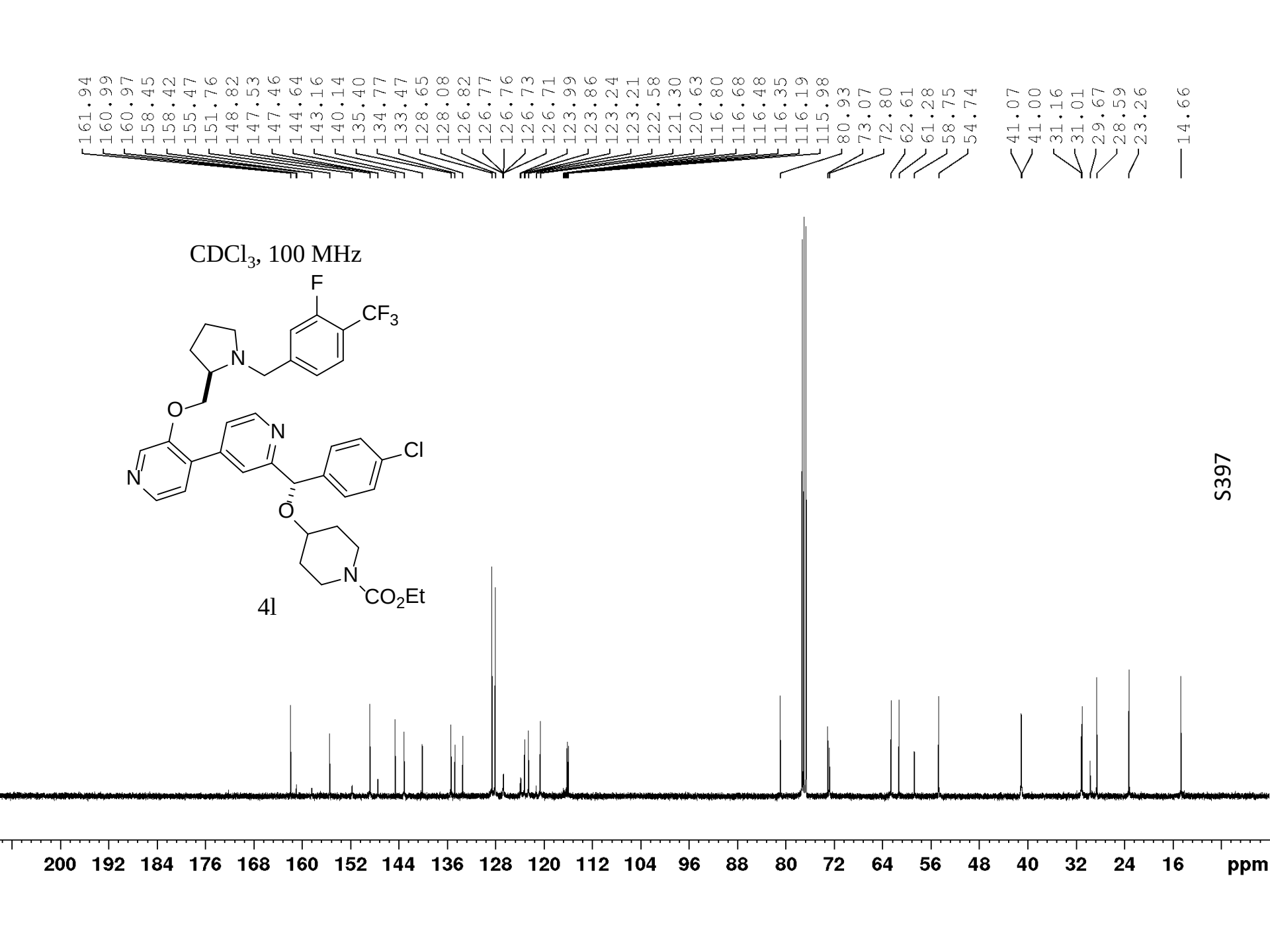

8.67
8.66
8.40
8.24
8.23
8.18
8.16
8.04
8.02
7.76
7.75
7.73
7.63
7.61
7.59
7.26
3.28
3.26
3.24
2.80
1.91
1.89
1.87
1.85
1.15
1.13
1.11
CDCl3, 400 MHz
N
SPr
N
N
Me
4j
S392
1.00
1.01
1.00
1.06
1.08
1.08
1.06
2.11
3.21
2.16
3.40
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

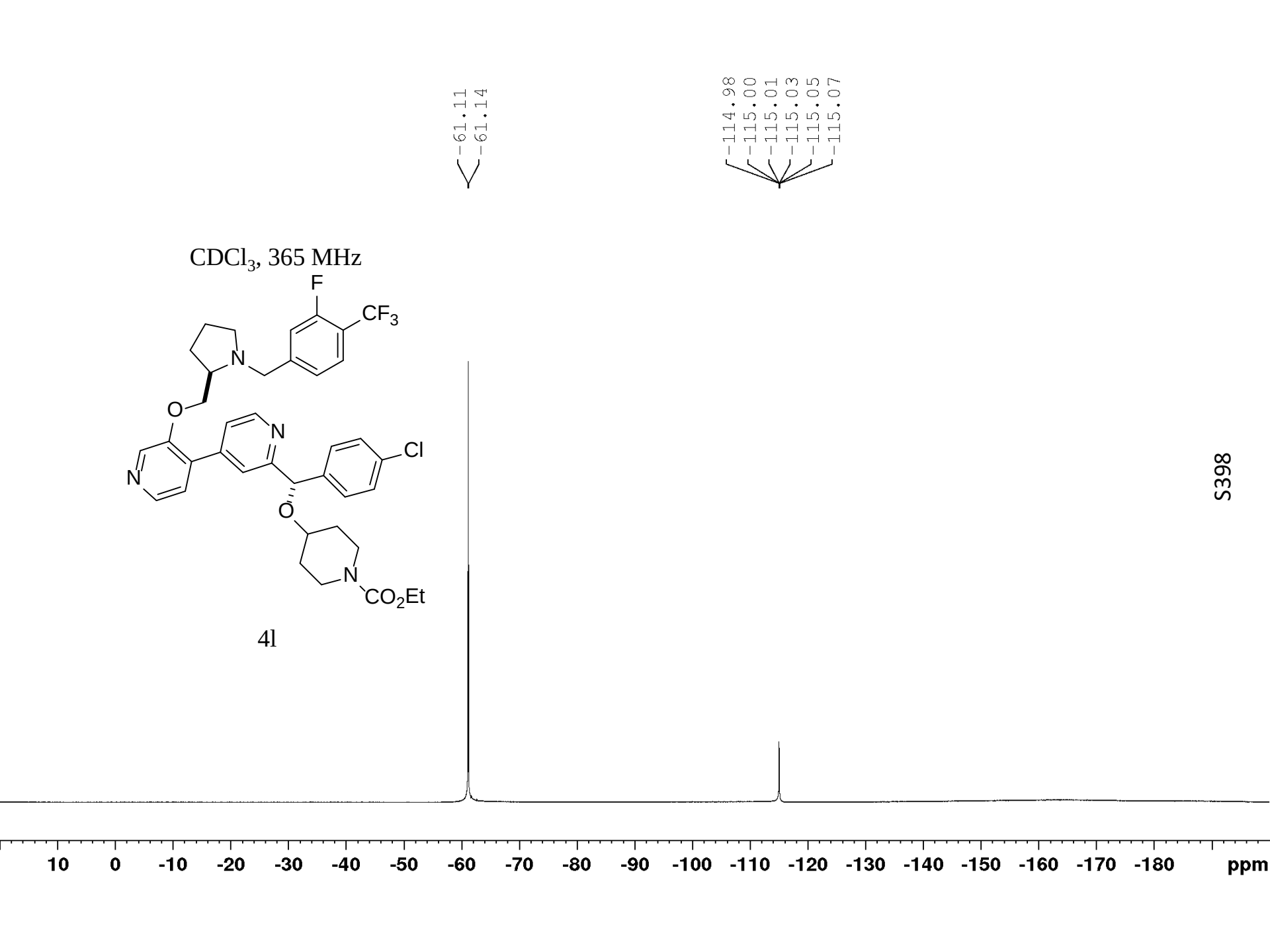

172.21
163.22
158.12
153.21
147.69
145.36
130.61
129.52
128.96
127.37
123.79
119.28
112.97
77.31
77.00
76.68
33.03
22.72
19.02
13.62
CDCl3, 100 MHz
N
SPr
N
N
Me
4j
S393
200
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)

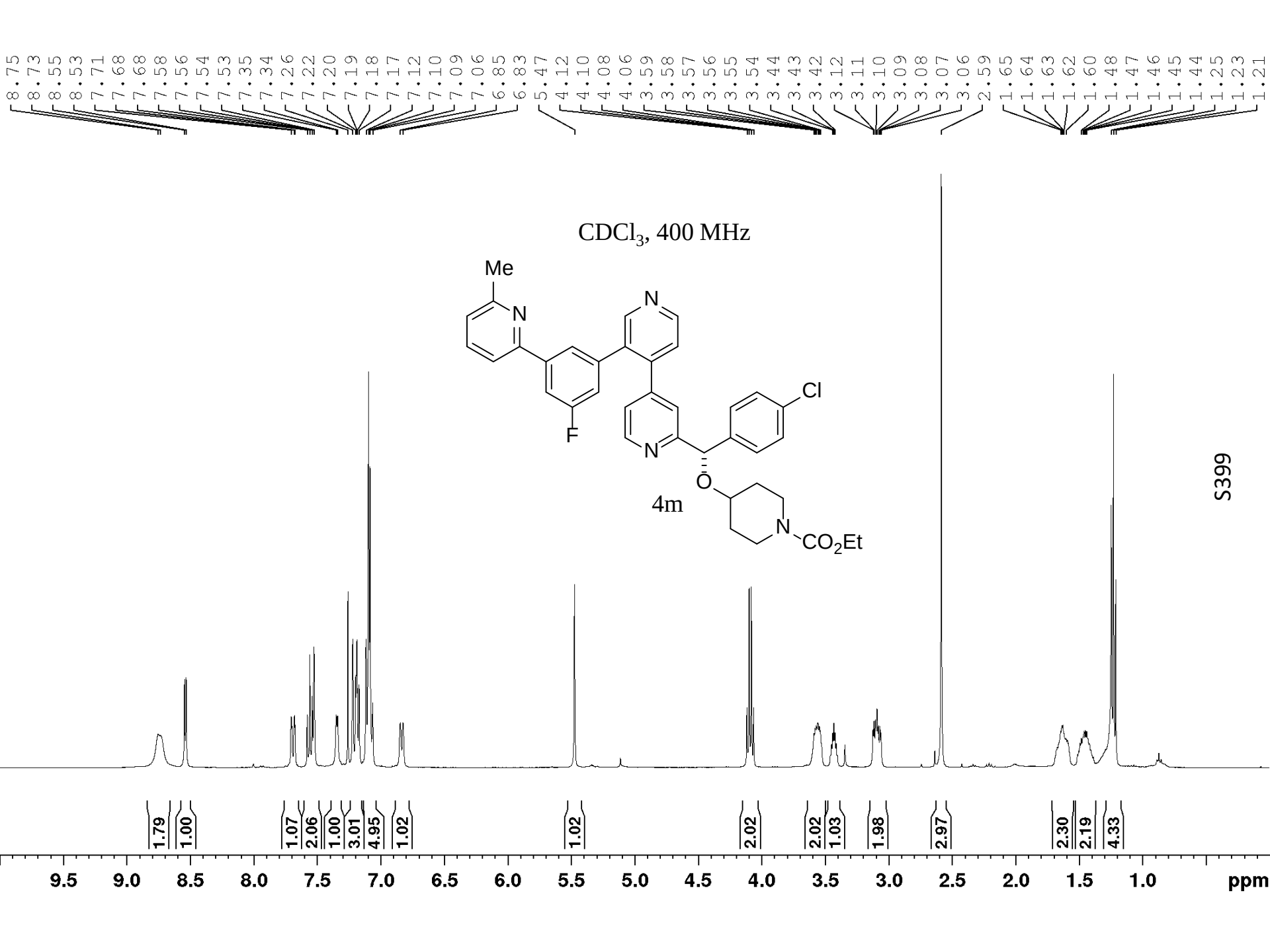

9.52
8.25
8.23
8.11
8.09
7.86
7.73
7.71
7.69
7.52
7.50
7.48
7.26
4.44
4.43
4.41
4.39
2.64
2.62
1.63
1.61
1.60
CDCl3, 400 MHz
Me
N
Me
N
N
OEt
4k
S394
1.00
1.00
1.00
1.01
1.11
1.09
2.11
6.01
3.21
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

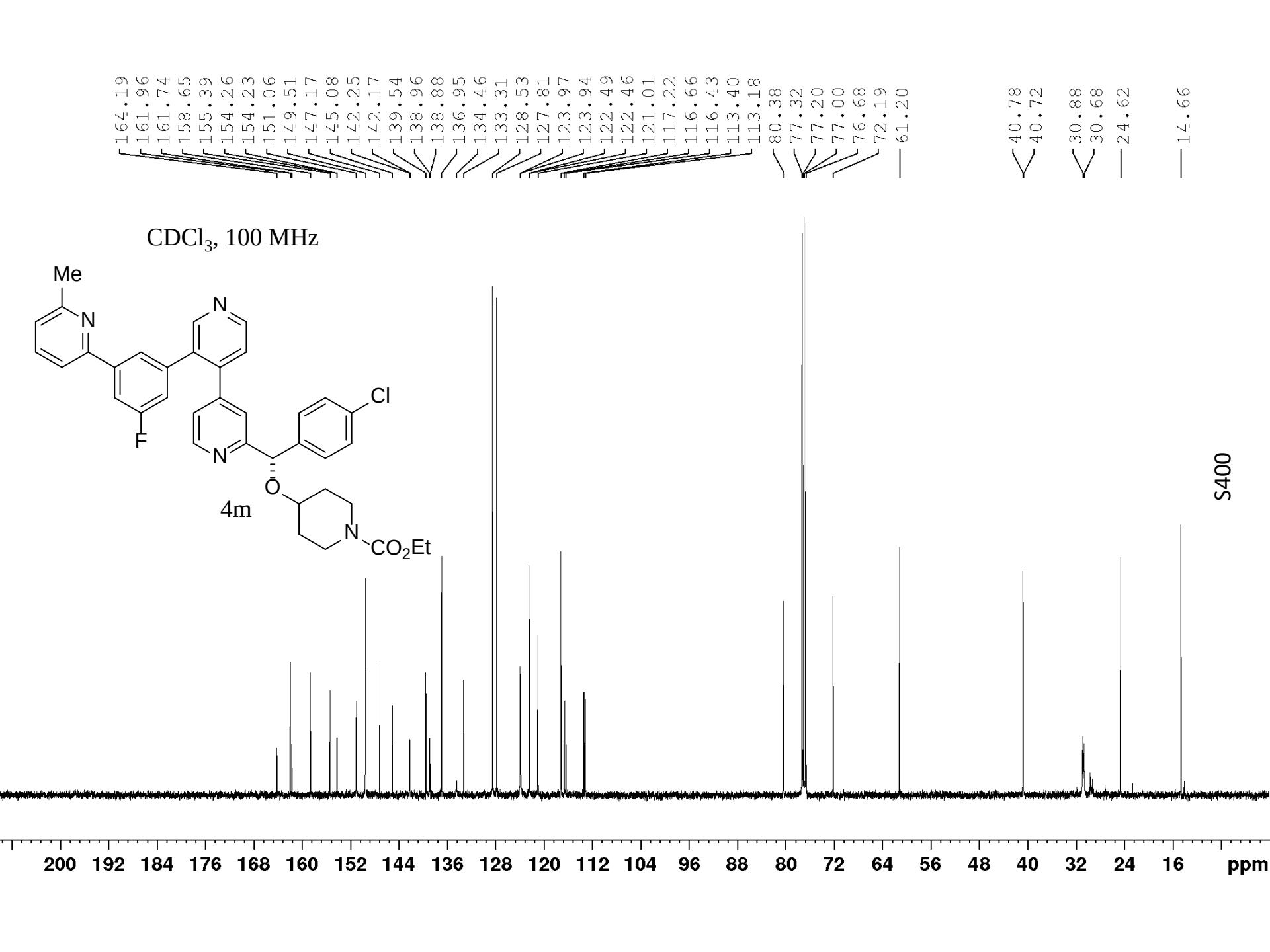

162.28
156.03
152.39
150.85
149.00
148.17
140.21
129.87
129.26
125.77
121.89
121.37
97.86
77.32
77.00
76.68
64.26
22.23
22.02
14.55
CDCl3, 100 MHz
Me
N
Me
N
N
OEt
4k
S395
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

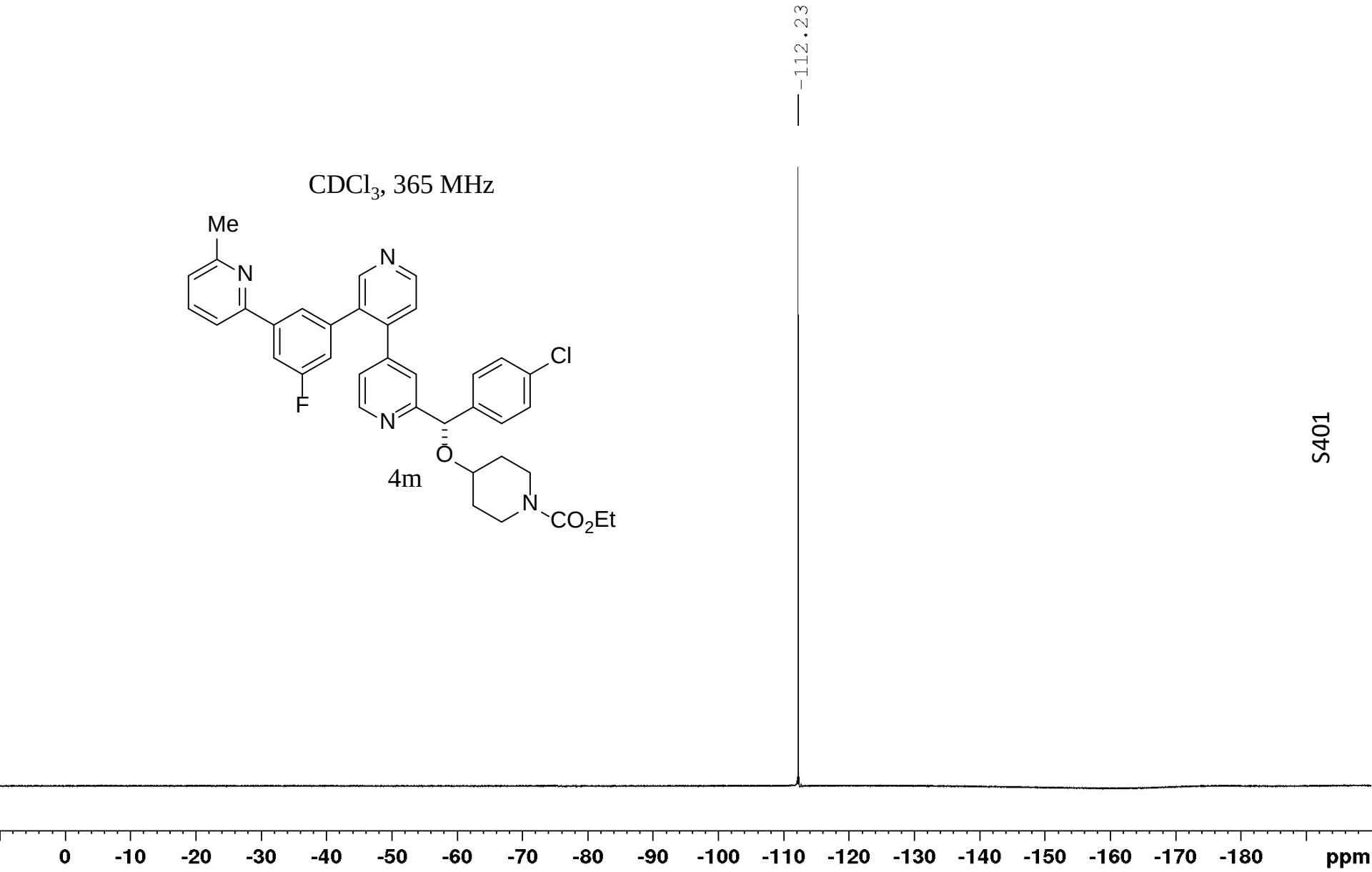

8.41
8.40
8.31
7.62
7.39
7.38
7.37
7.36
7.26
7.24
7.21
7.20
7.16
7.15
6.92
6.90
6.89
5.60
4.08
4.06
4.04
4.02
3.96
3.95
3.71
3.67
3.58
3.57
3.56
3.13
3.12
3.10
3.09
3.08
2.82
2.81
2.80
2.79
2.78
2.77
2.76
2.11
2.09
1.88
1.85
1.77
1.76
1.68
1.66
1.64
1.62
1.61
1.59
1.57
1.56
1.54
1.53
1.52
1.20
1.18
CDCl3, 400 MHz
F
CF3
N
O
N
N
Cl
O
N
CO2Et
4l
S396
1.02
1.97
1.06
3.12
0.96
1.98
1.00
1.90
1.03
2.34
2.02
3.12
1.23
3.19
2.08
1.15
3.60
5.68
6.10
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

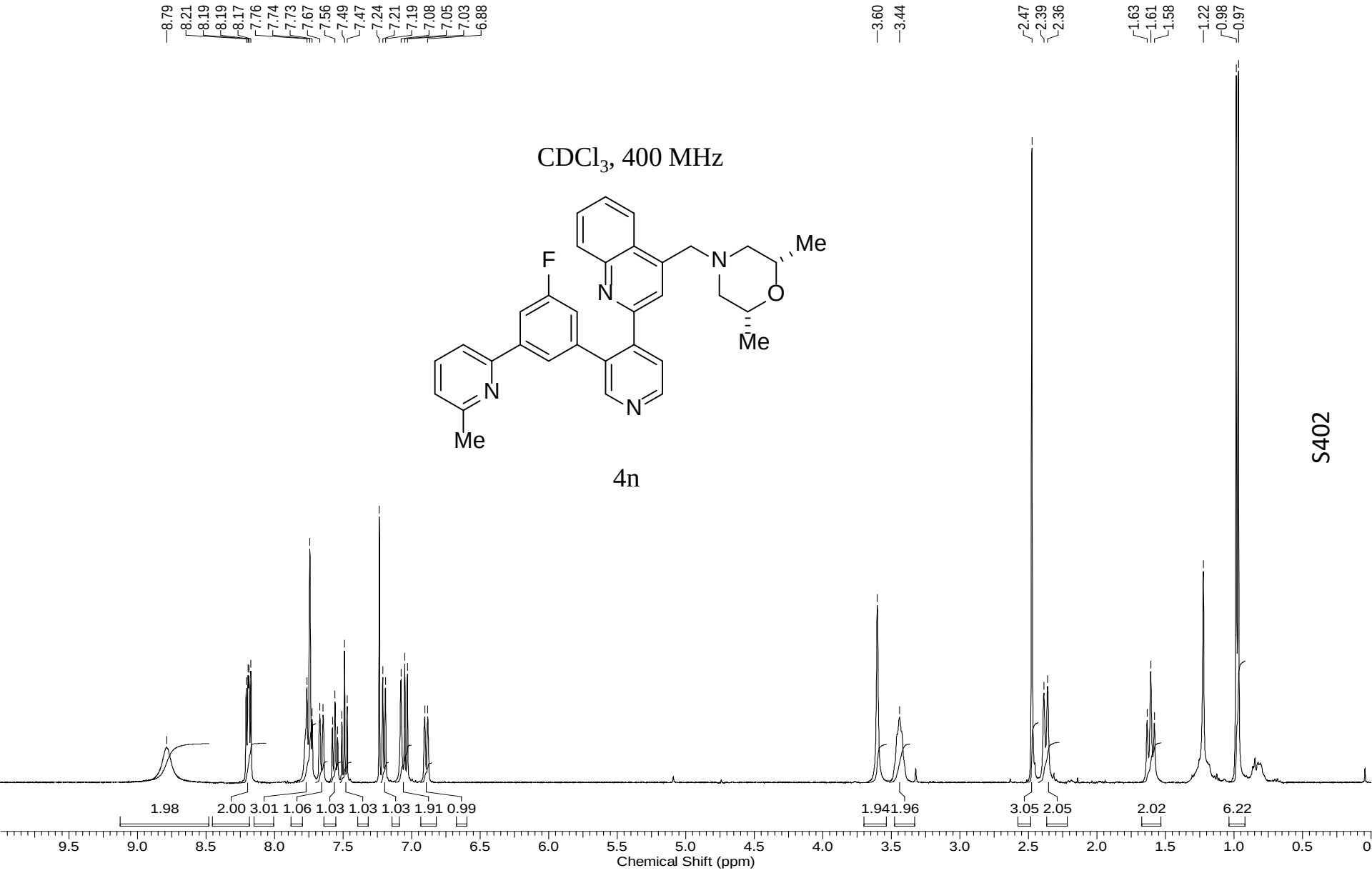

161.94
160.99
160.97
158.45
158.42
155.47
151.76
148.82
147.53
147.46
144.64
143.16
140.14
135.40
134.77
133.47
128.65
128.08
126.82
126.77
126.76
126.73
126.71
123.99
123.86
123.24
123.21
122.58
121.30
120.63
116.80
116.68
116.48
116.35
116.19
115.98
80.93
73.07
72.80
62.61
61.28
58.75
54.74
41.07
41.00
31.16
31.01
29.67
28.59
23.26
14.66
CDCl3, 100 MHz
F
CF3
N
O
N
N
Cl
O
N
CO2Et
4l
S397
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

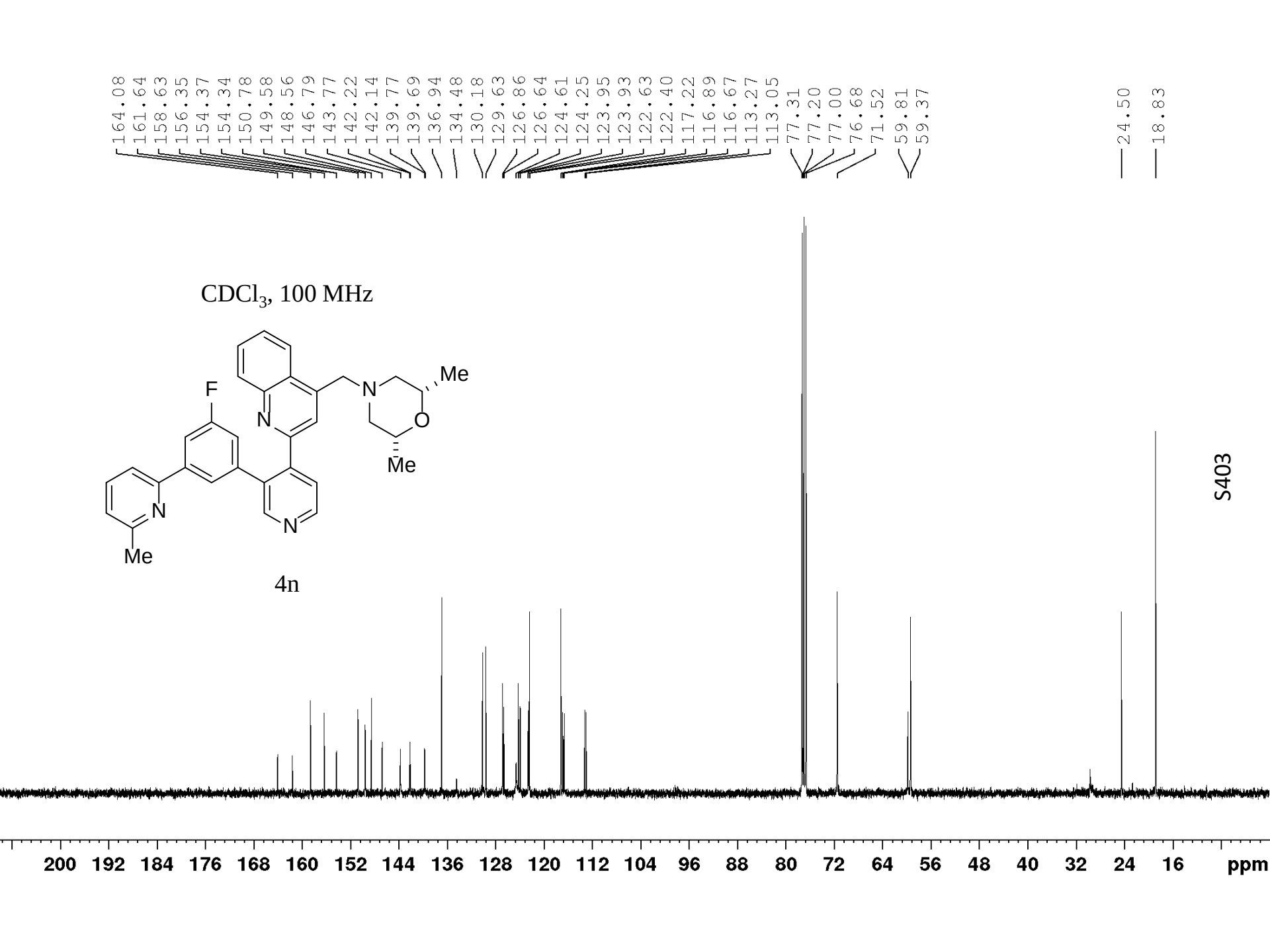

-61.11
-61.14
-114.98
-115.00
-115.01
-115.03
-115.05
-115.07
CDCl3, 365 MHz
F
CF3
N
O
N
N
Cl
O
N
CO2Et
4l
S398
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
ppm

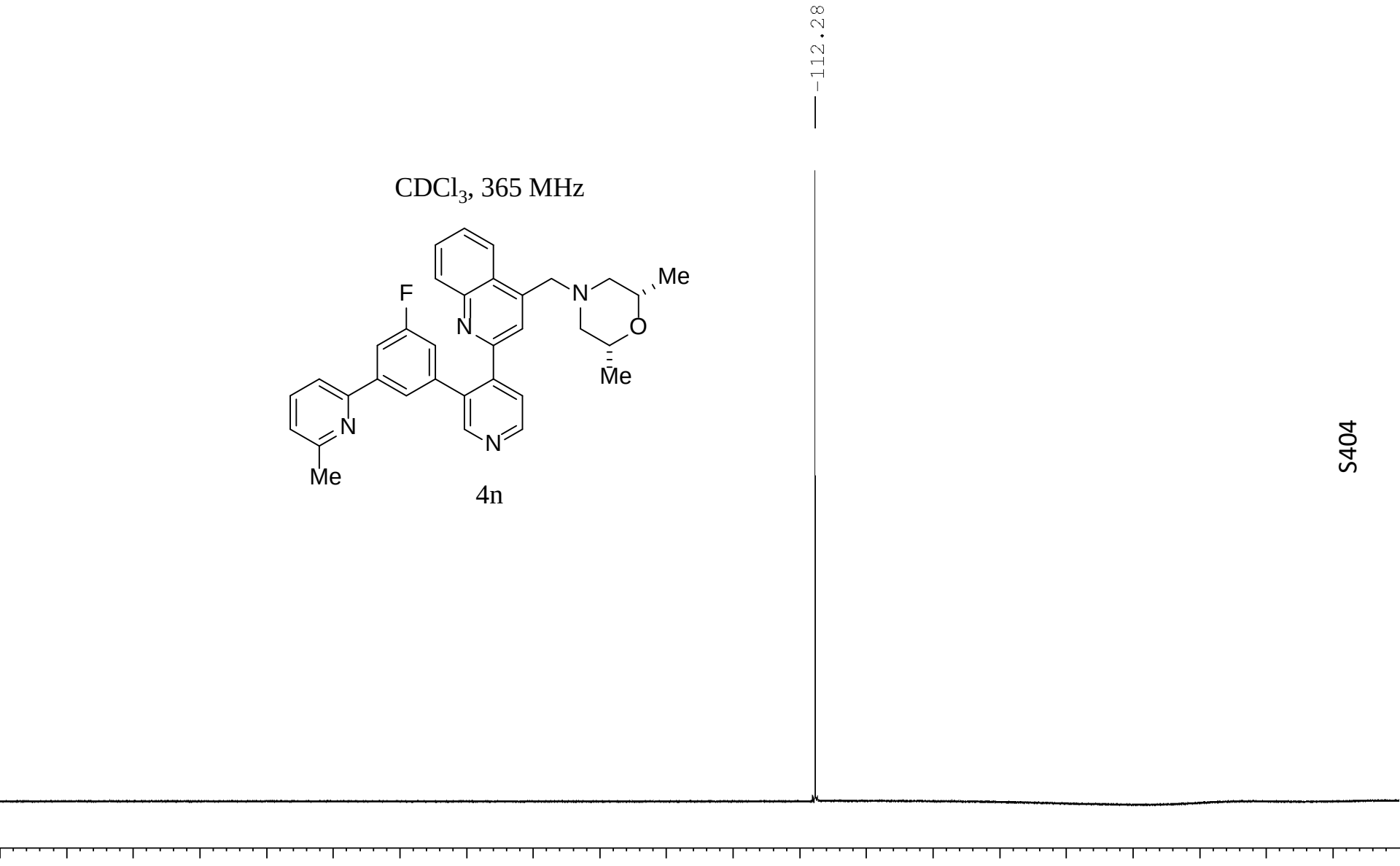

8.75
8.73
8.55
8.53
7.71
7.68
7.68
7.58
7.56
7.54
7.53
7.35
7.34
7.26
7.22
7.20
7.19
7.18
7.17
7.12
7.10
7.09
7.06
6.85
6.83
5.47
4.12
4.10
4.08
4.06
3.59
3.58
3.57
3.56
3.55
3.54
3.44
3.43
3.42
3.12
3.11
3.10
3.09
3.08
3.07
3.06
2.59
1.65
1.64
1.63
1.62
1.60
1.48
1.47
1.46
1.45
1.44
1.25
1.23
1.21
CDCl3, 400 MHz
Me
N
N
N
F
Cl
N
O
N
CO2Et
4m
S399
1.79
1.00
1.07
2.06
1.00
3.01
4.95
1.02
1.02
2.02
2.02
1.03
1.98
2.97
2.30
2.19
4.33
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

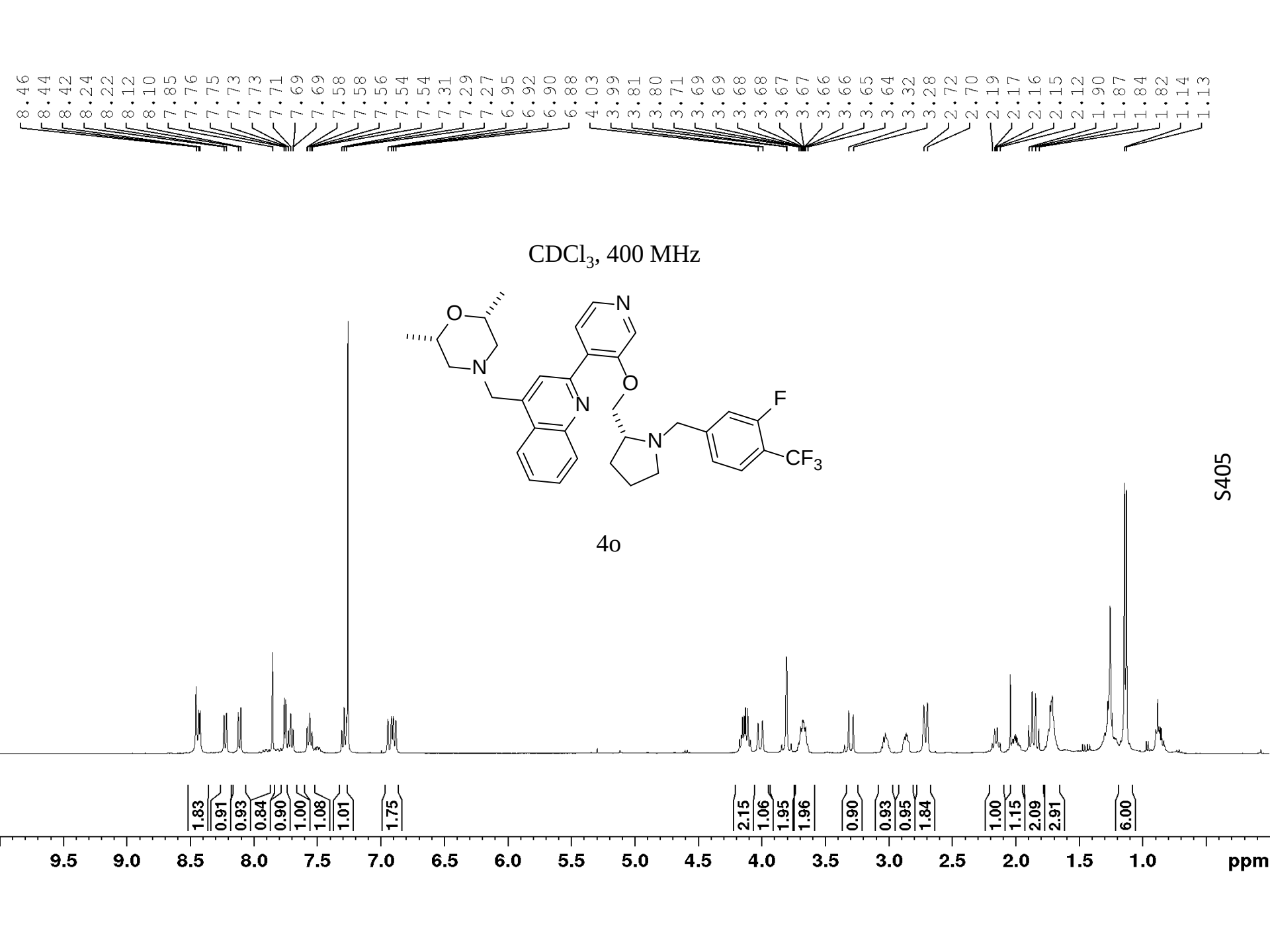

164.19
161.96
161.74
158.65
155.39
154.26
154.23
151.06
149.51
147.17
145.08
142.25
142.17
139.54
138.96
138.88
136.95
134.46
133.31
128.53
127.81
123.97
123.94
122.49
122.46
121.01
117.22
116.66
116.43
113.40
113.18
80.38
77.32
77.20
77.00
76.68
72.19
61.20
40.78
40.72
30.88
30.68
24.62
14.66
CDCl3, 100 MHz
Me
N
N
F
Cl
N
O
N
CO2Et
4m
S400
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

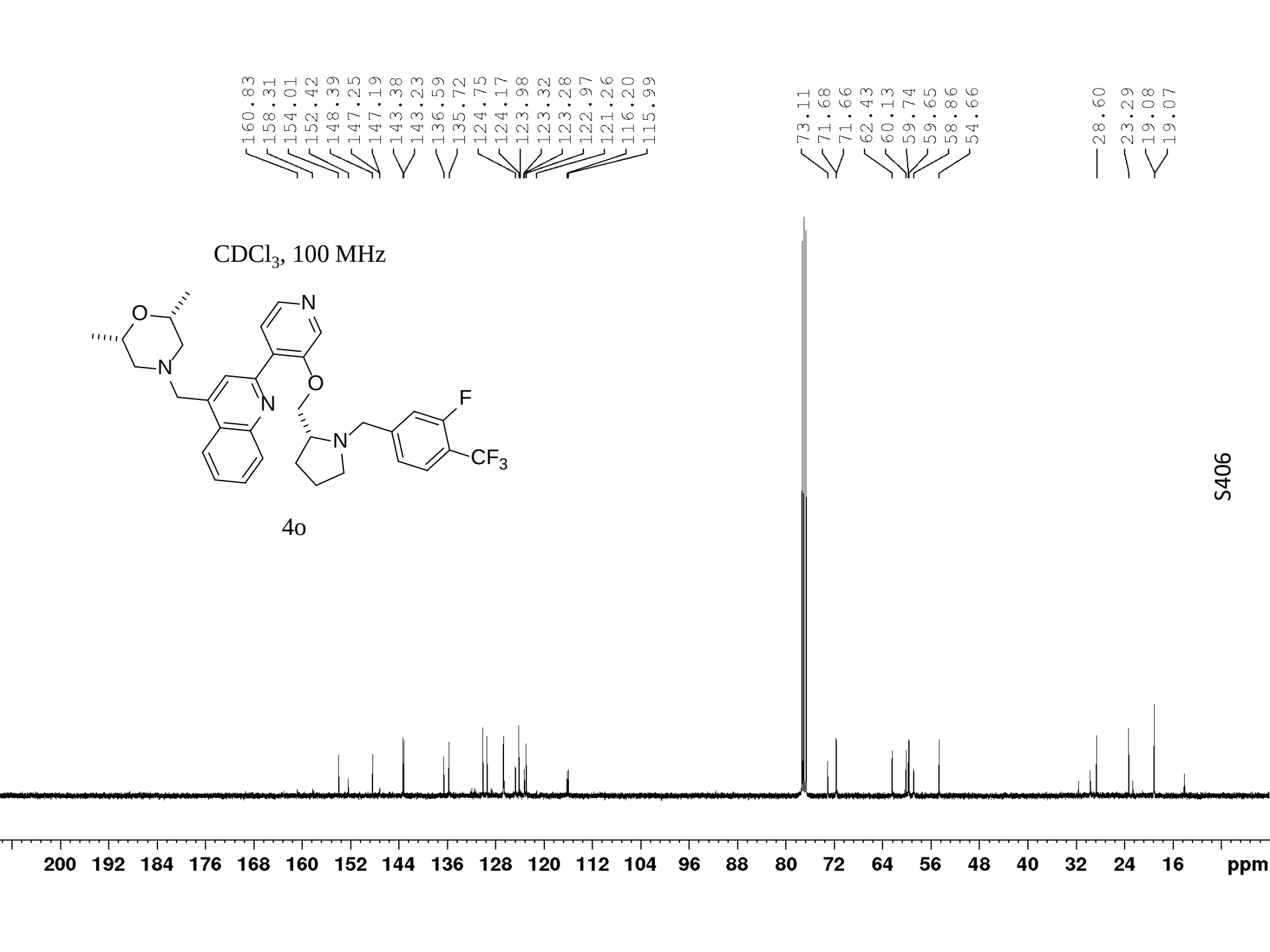

-112.23
CDCl3, 365 MHz
Me
N
N
F
Cl
N
O
4m
N
CO2Et
S401
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
ppm

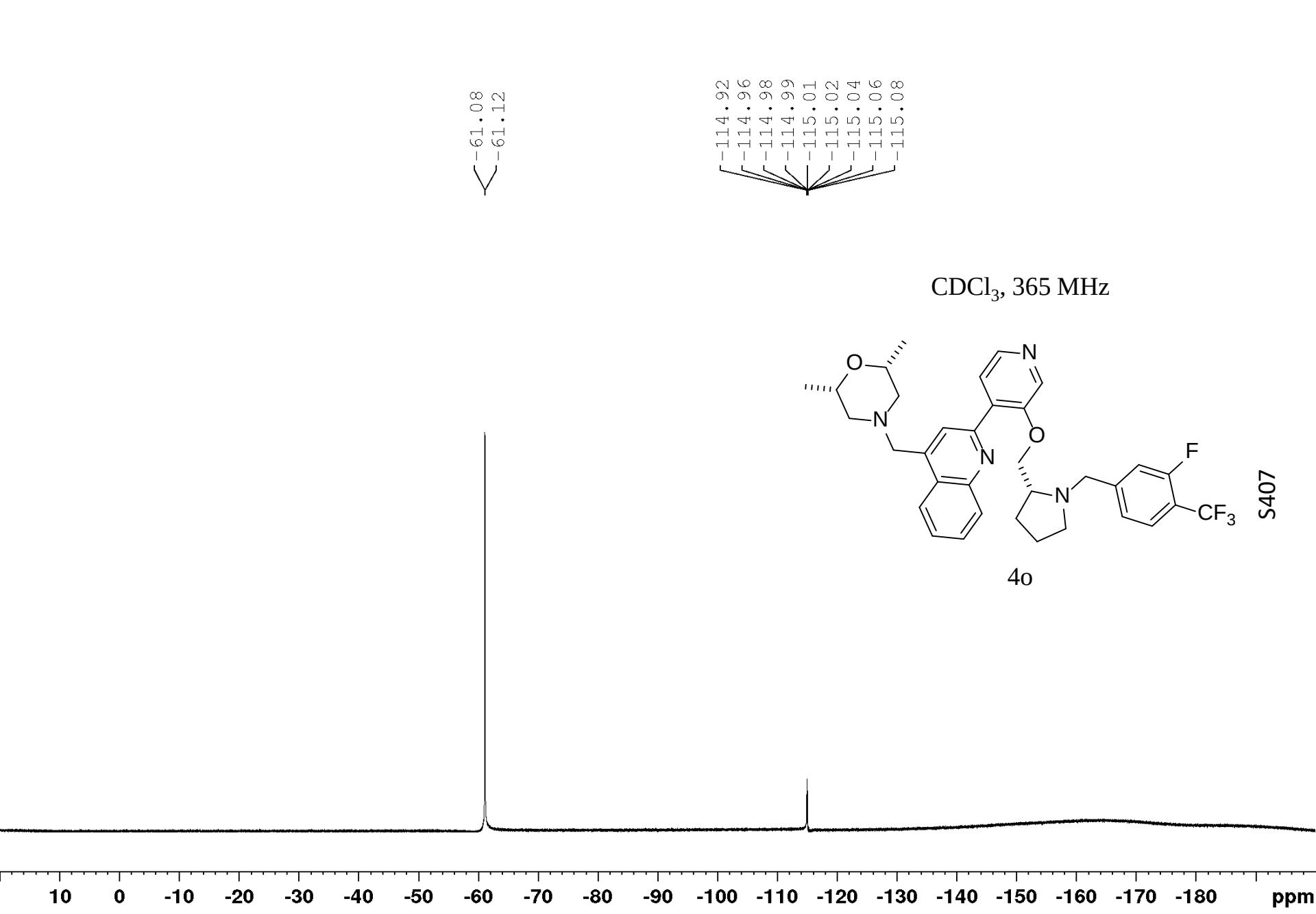

8.79
8.21
8.19
8.19
8.17
7.76
7.74
7.73
7.67
7.56
7.49
7.47
7.24
7.21
7.19
7.08
7.05
7.03
6.88
3.60
3.44
2.47
2.39
2.36
1.63
1.61
1.58
1.22
0.98
0.97
CDCl3, 400 MHz
F
N
N
N
N
O
Me
Me
Me
4n
S402
1.98
2.00
3.01
1.06
1.03
1.03
1.03
1.91
0.99
1.94
1.96
3.05
2.05
2.02
6.22
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

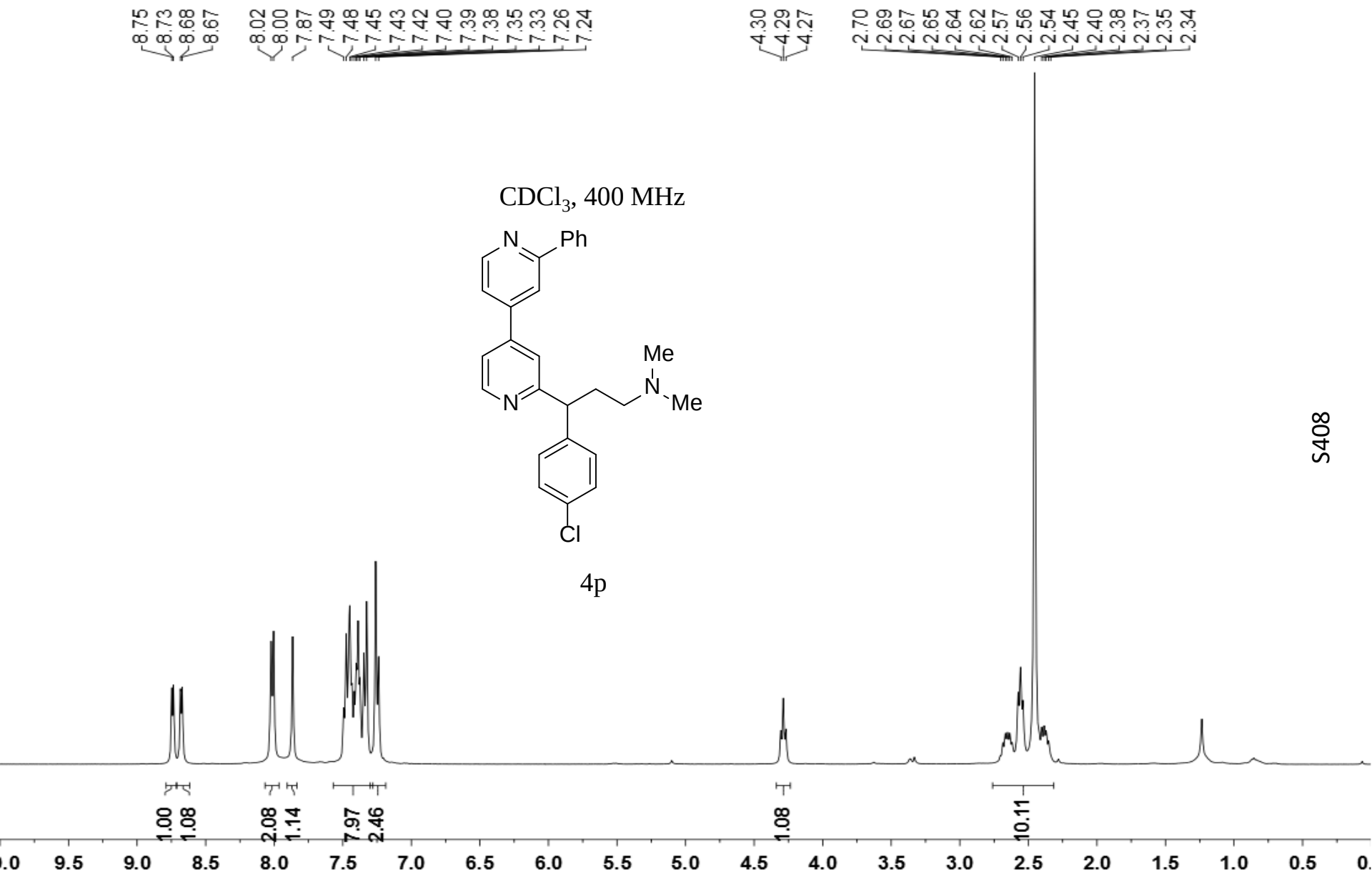

164.08
161.64
158.63
156.35
154.37
154.34
150.78
149.58
148.56
146.79
143.77
142.22
142.14
139.77
139.69
136.94
134.48
130.18
129.63
126.86
126.64
124.61
124.25
123.95
123.93
122.63
122.40
117.22
116.89
116.67
113.27
113.05
77.31
77.20
77.00
76.68
71.52
59.81
59.37
24.50
18.83
CDCl3, 100 MHz
F
N
N
N
N
O
Me
Me
Me
4n
S403
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

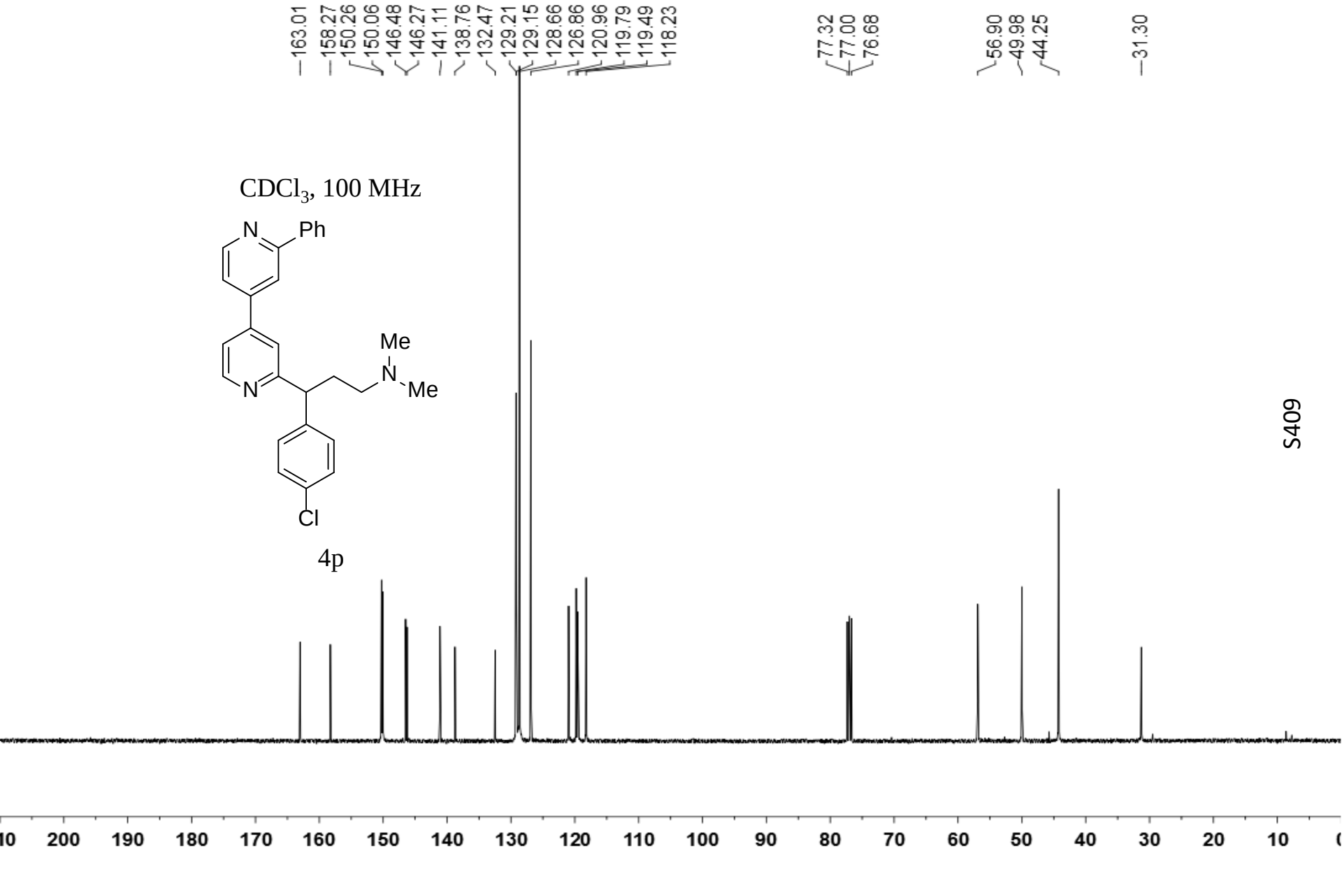

-112.28
CDCl3, 365 MHz
F
N
N
Me
N
O
Me
N
Me
4n
S404
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
ppm

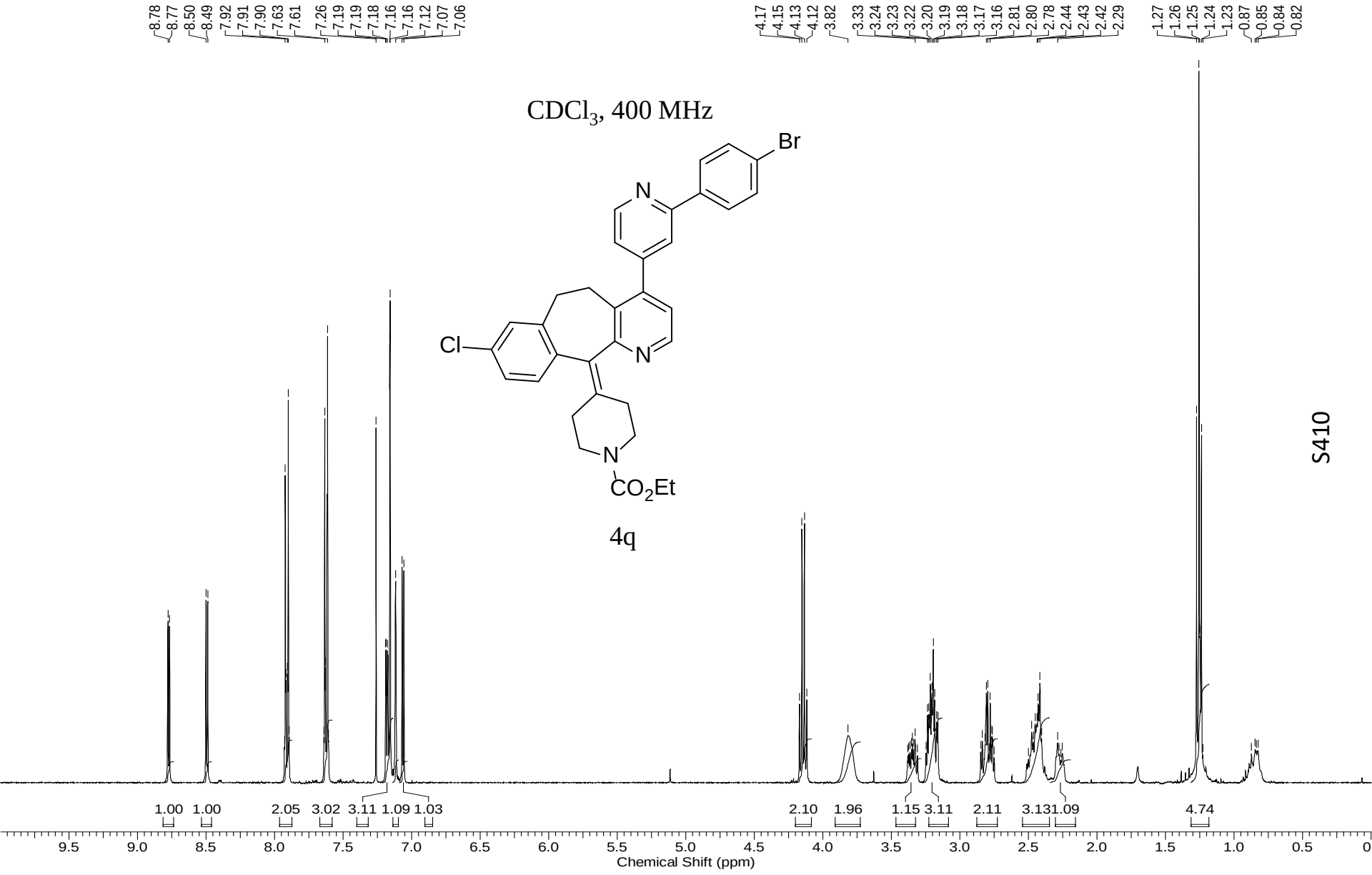

8.46
8.44
8.42
8.24
8.22
8.12
8.10
7.85
7.76
7.75
7.73
7.73
7.71
7.69
7.69
7.58
7.58
7.56
7.54
7.54
7.31
7.29
7.27
6.95
6.92
6.90
6.88
4.03
3.99
3.81
3.80
3.71
3.69
3.69
3.68
3.68
3.67
3.67
3.66
3.66
3.65
3.64
3.32
3.28
2.72
2.70
2.19
2.17
2.16
2.15
2.12
1.90
1.87
1.84
1.82
1.14
1.13
CDCl3, 400 MHz
O
N
N
O
N
F
CF3
4o
S405
1.83
0.91
0.93
0.84
0.90
1.00
1.08
1.01
1.75
2.15
1.06
1.95
1.96
0.90
0.93
0.95
1.84
1.00
1.15
2.09
2.91
6.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

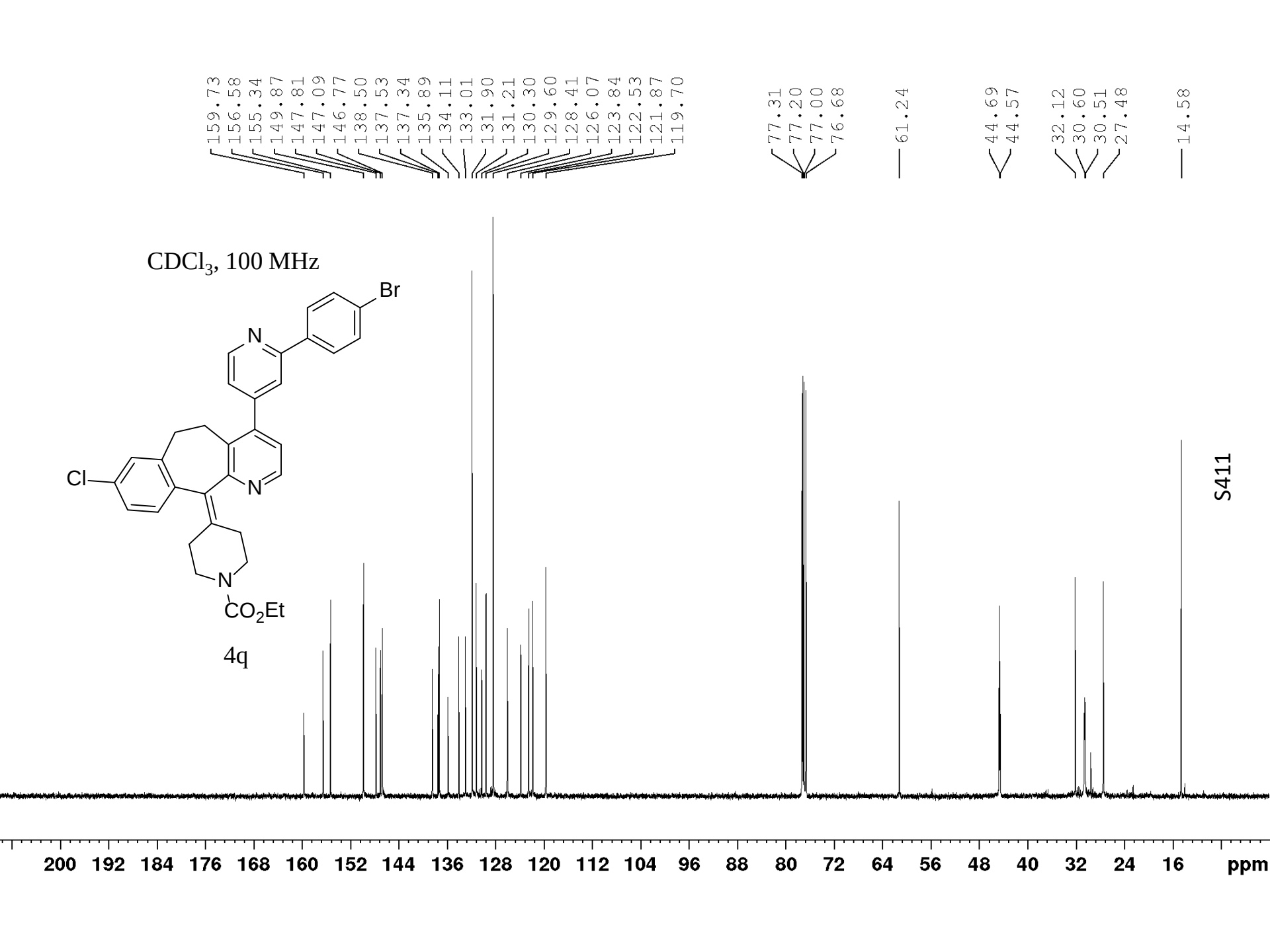

160.83
158.31
154.01
152.42
148.39
147.25
147.19
143.38
143.23
136.59
135.72
124.75
124.17
123.98
123.32
123.28
122.97
121.26
116.20
115.99
73.11
71.68
71.66
62.43
60.13
59.74
59.65
58.86
54.66
28.60
23.29
19.08
19.07
CDCl3, 100 MHz
O
N
N
O
N
F
CF3
4o
S406
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 ppm

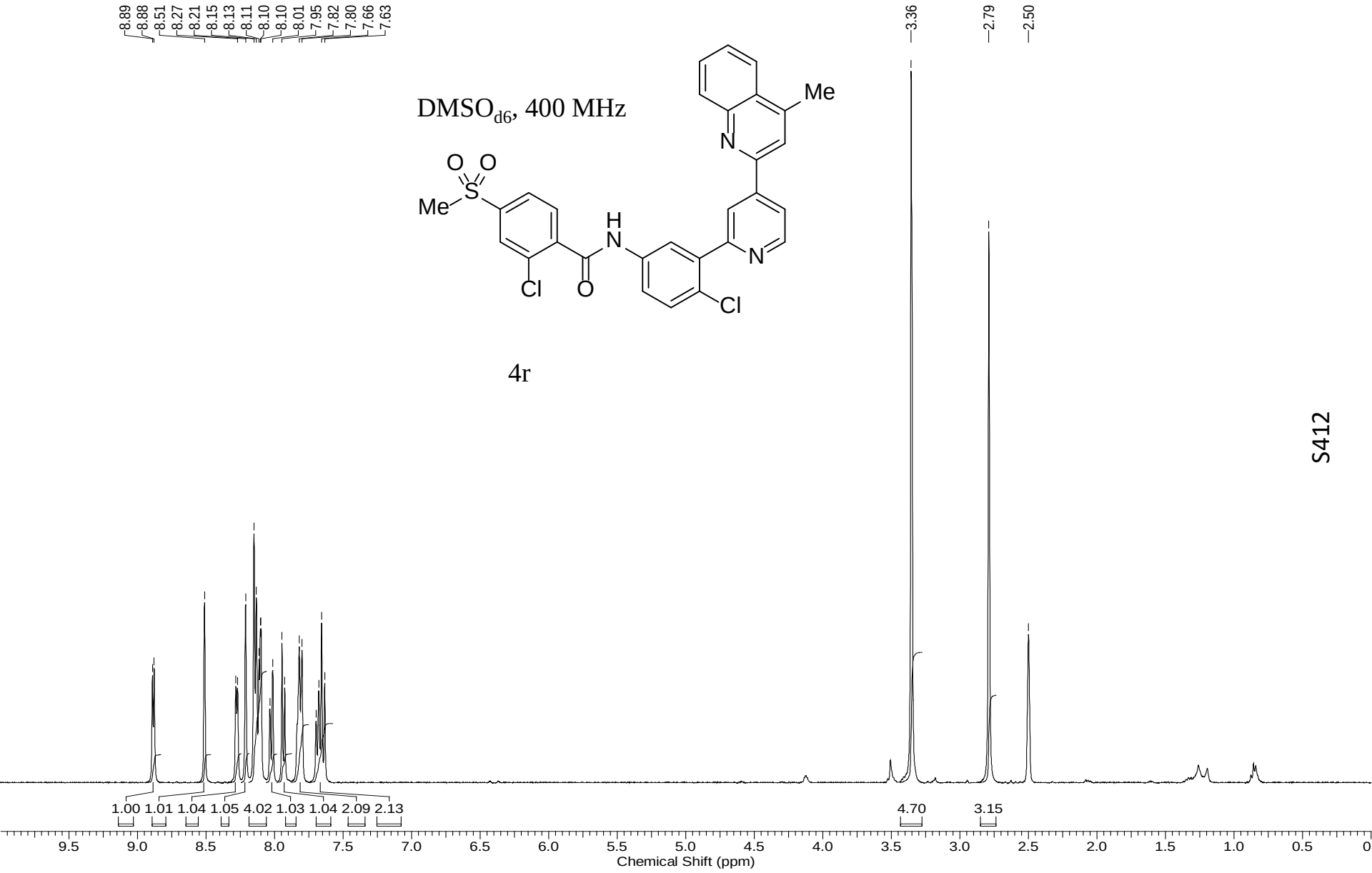

-61.08
-61.12
-114.92
-114.96
-114.98
-114.99
-115.01
-115.02
-115.04
-115.06
-115.08
CDCl3, 365 MHz
O
N
N
O
N
F
N
CF3
S407
4o
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
ppm

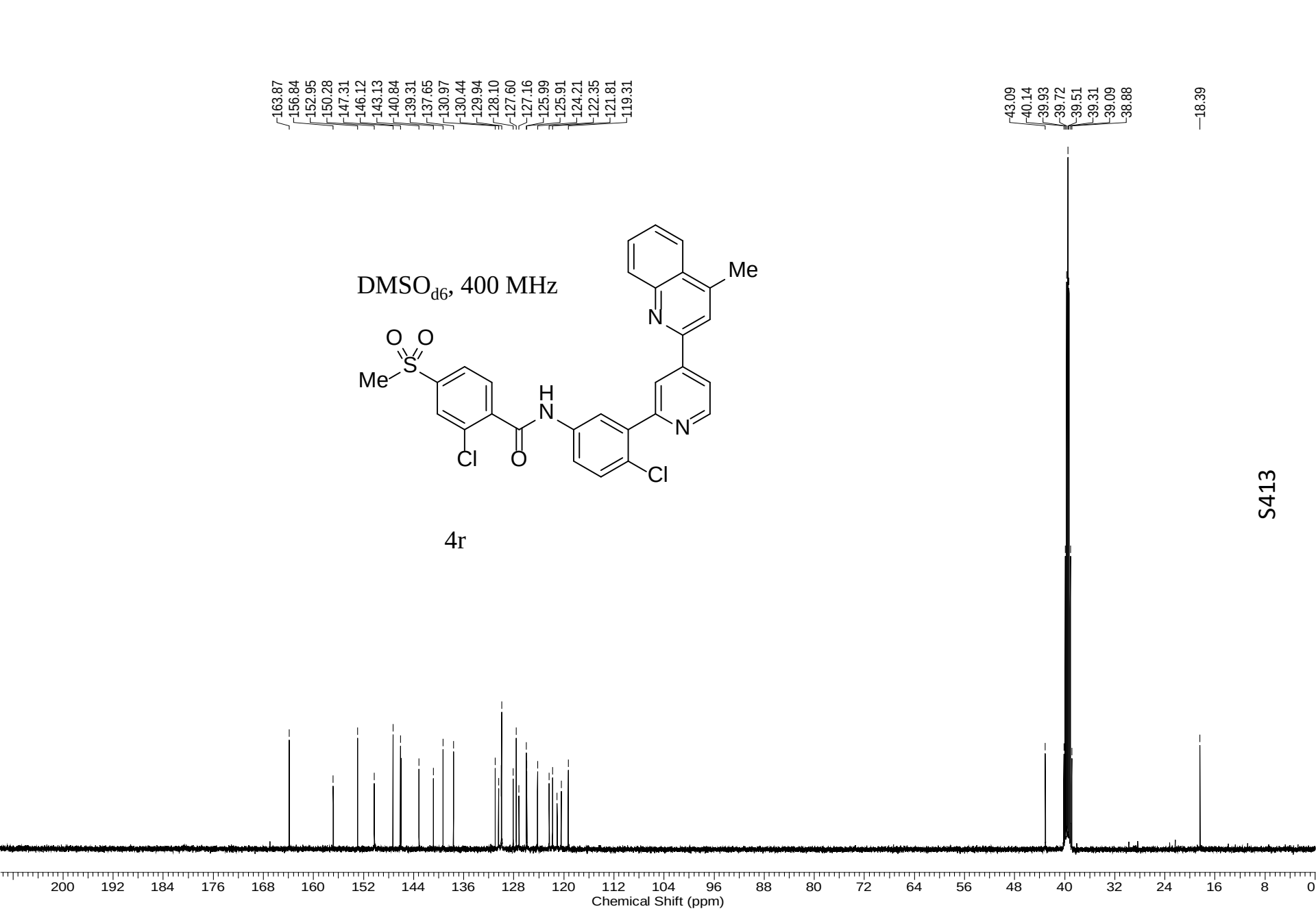

8.75
8.73
8.68
8.67
8.02
8.00
7.87
7.49
7.48
7.45
7.43
7.42
7.40
7.39
7.38
7.35
7.33
7.26
7.24
4.30
4.29
4.27
2.70
2.69
2.67
2.65
2.64
2.62
2.57
2.56
2.54
2.45
2.40
2.38
2.37
2.35
2.34
CDCl3, 400 MHz
N
Ph
Me
N
Me
N
Cl
4p
S408
1.00
1.08
2.08
1.14
7.97
2.46
1.08
10.11
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

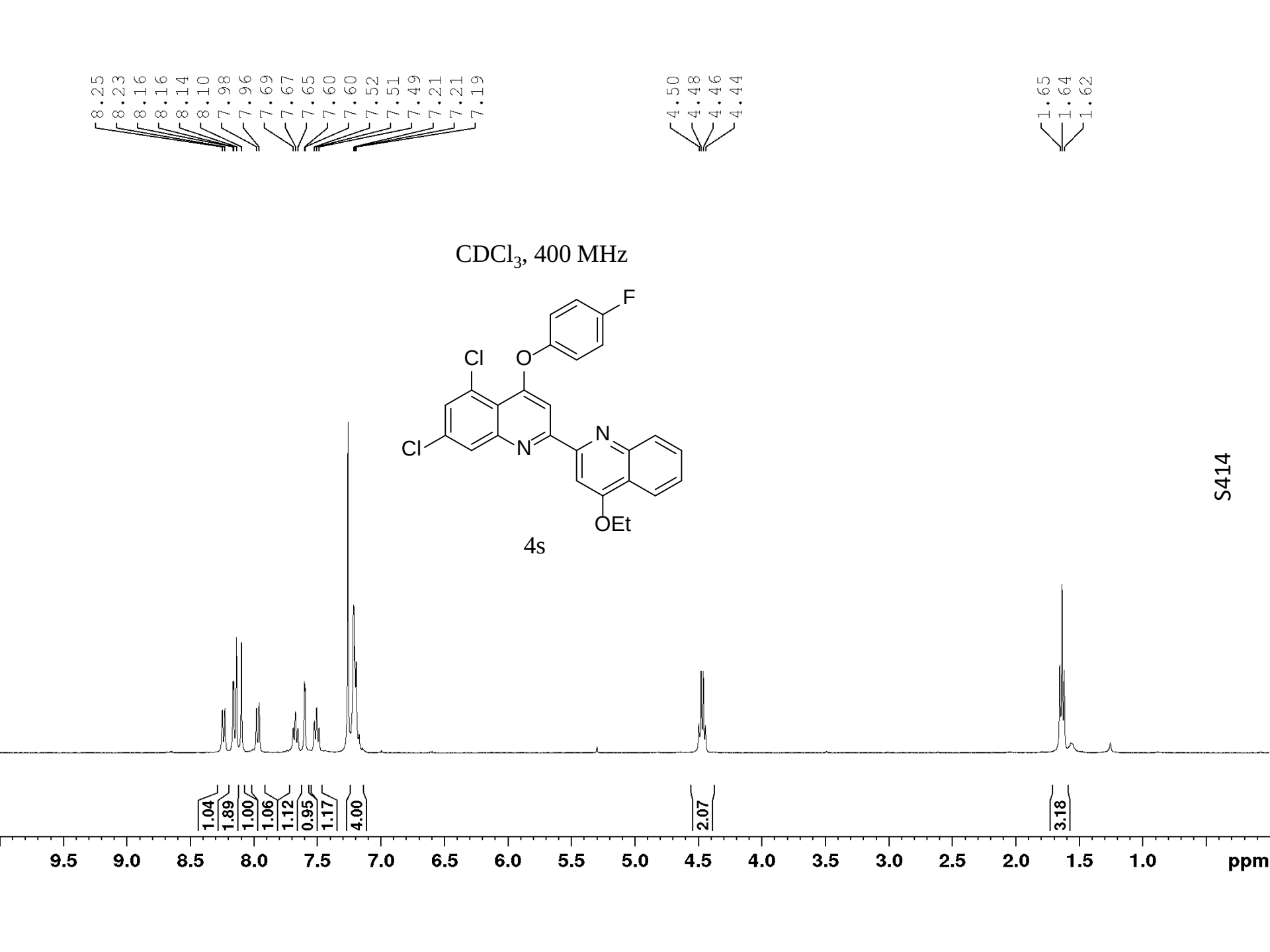

163.01
158.27
150.26
150.06
146.48
146.27
141.11
138.76
132.47
129.21
129.15
128.66
126.86
120.96
119.79
119.49
118.23
77.32
77.00
76.68
56.90
49.98
44.25
31.30
CDCl3, 100 MHz
N
Ph
Me
N
Me
N
Cl
4p
S409
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

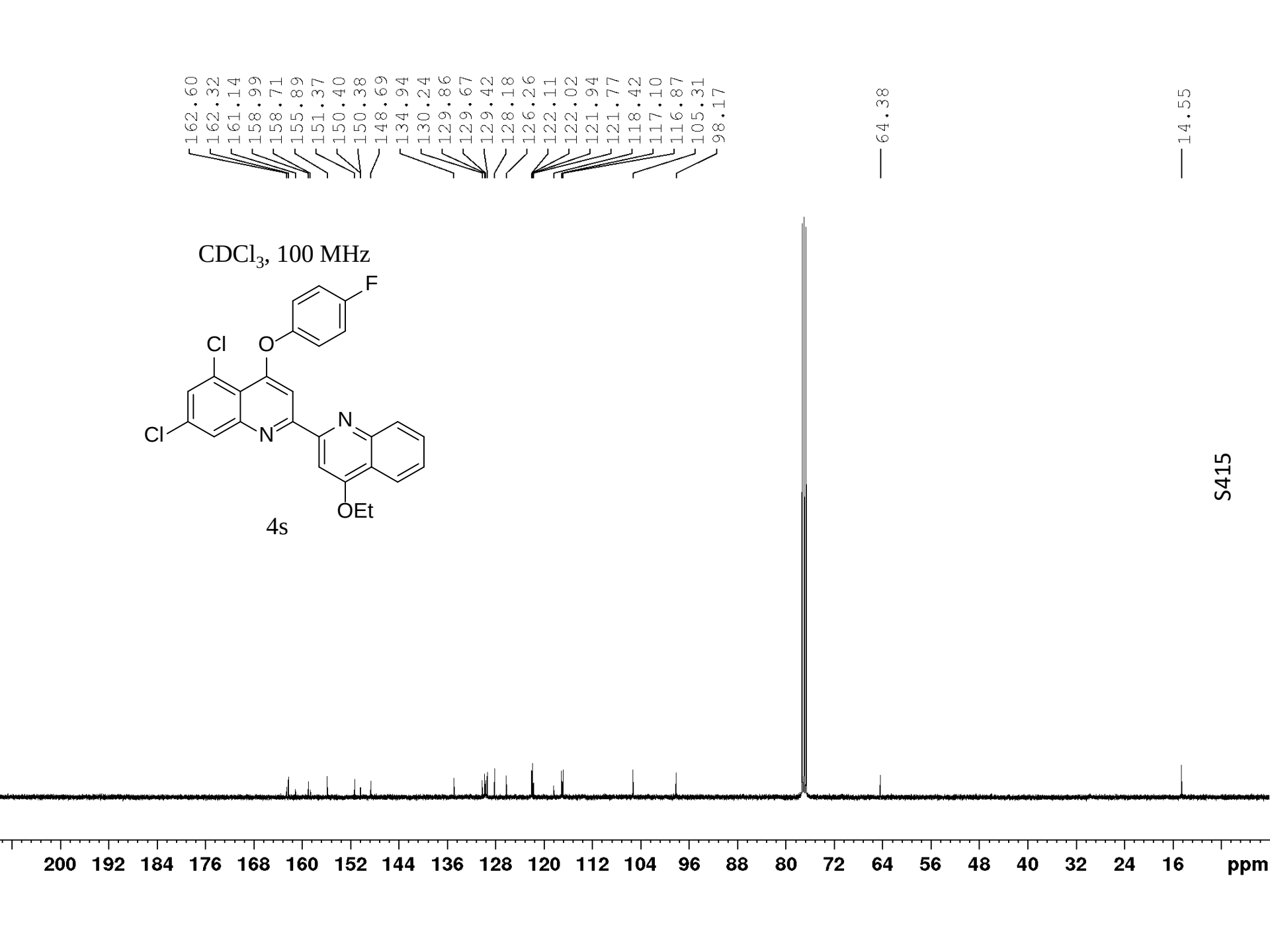

8.78
8.77
8.50
8.49
7.92
7.91
7.90
7.63
7.61
7.26
7.19
7.19
7.18
7.16
7.16
7.12
7.07
7.06
4.17
4.15
4.13
4.12
3.82
3.33
3.24
3.23
3.22
3.20
3.19
3.18
3.17
3.16
2.81
2.80
2.78
2.44
2.43
2.42
2.29
1.27
1.26
1.25
1.24
1.23
0.87
0.85
0.84
0.82
CDCl3, 400 MHz
Br
N
Cl
N
N
CO2Et
4q
S410
1.00
1.00
2.05
3.02
3.11
1.09
1.03
2.10
1.96
1.15
3.11
2.11
3.13
1.09
4.74
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)


159.73
156.58
155.34
149.87
147.81
147.09
146.77
138.50
137.53
137.34
135.89
134.11
133.01
131.90
131.21
130.30
129.60
128.41
126.07
123.84
122.53
121.87
119.70
77.31
77.20
77.00
76.68
61.24
44.69
44.57
32.12
30.60
30.51
27.48
14.58
CDCl3, 100 MHz
Br
N
Cl
N
N
CO2Et
4q
S411
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


8.89
8.88
8.51
8.27
8.21
8.15
8.13
8.11
8.10
8.10
8.01
7.95
7.82
7.80
7.66
7.63
3.36
2.79
2.50
DMSO$_{d6}$, 400 MHz
Me
N
O
O
S
Me
H
N
N
Cl
O
Cl
4r
S412
1.00 1.01 1.04 1.05 4.02 1.03 1.04 2.09 2.13
4.70
3.15
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
Chemical Shift (ppm)

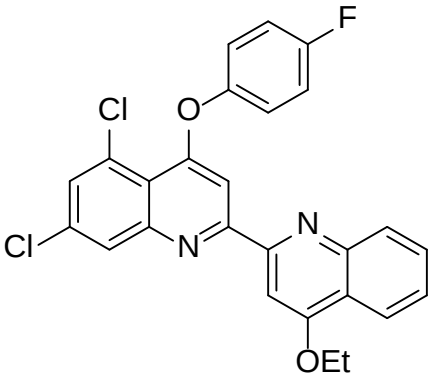

163.87
156.84
152.95
150.28
147.31
146.12
143.13
140.84
139.31
137.65
130.97
130.44
129.94
128.10
127.60
127.16
125.99
125.91
124.21
122.35
121.81
119.31
43.09
40.14
39.93
39.72
39.51
39.31
39.09
38.88
18.39
DMSO$_{d6}$, 400 MHz
Me
N
O
O
S
Me
H
N
N
Cl
O
Cl
4r
S413
200
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)


8.25
8.23
8.16
8.16
8.14
8.10
7.98
7.96
7.69
7.67
7.65
7.60
7.60
7.52
7.51
7.49
7.21
7.21
7.19
4.50
4.48
4.46
4.44
1.65
1.64
1.62
CDCl3, 400 MHz
F
Cl
O
Cl
N
N
OEt
4s
S414
1.04
1.89
1.00
1.06
1.12
0.95
1.17
4.00
2.07
3.18
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

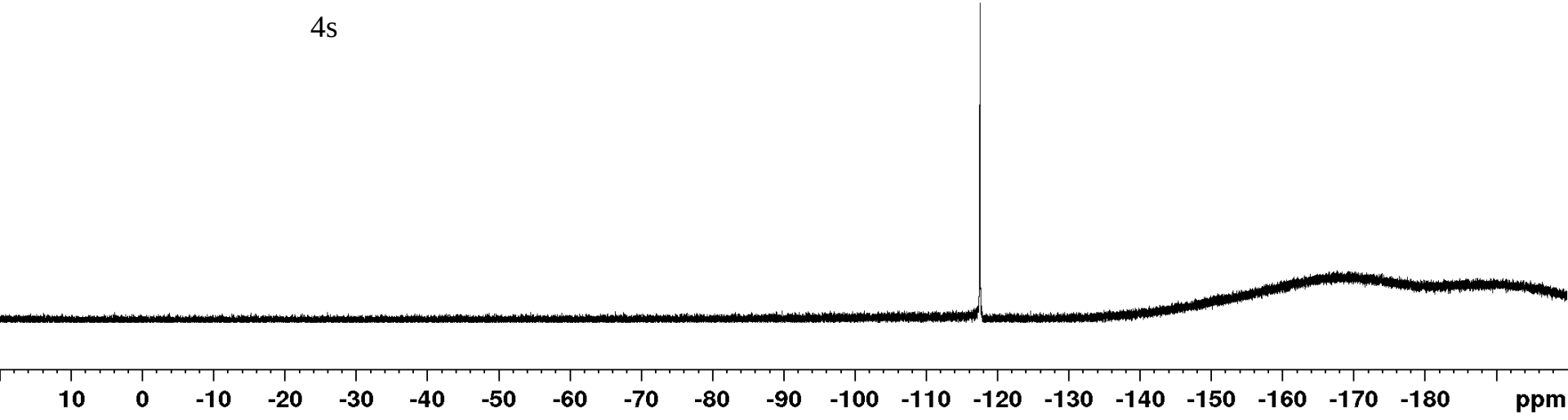

162.60
162.32
161.14
158.99
158.71
155.89
151.37
150.40
150.38
148.69
134.94
130.24
129.86
129.67
129.42
128.18
126.26
122.11
122.02
121.94
121.77
118.42
117.10
116.87
105.31
98.17
64.38
14.55
CDCl3, 100 MHz
F
Cl
O
Cl
N
N
OEt
4s
S415
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 ppm

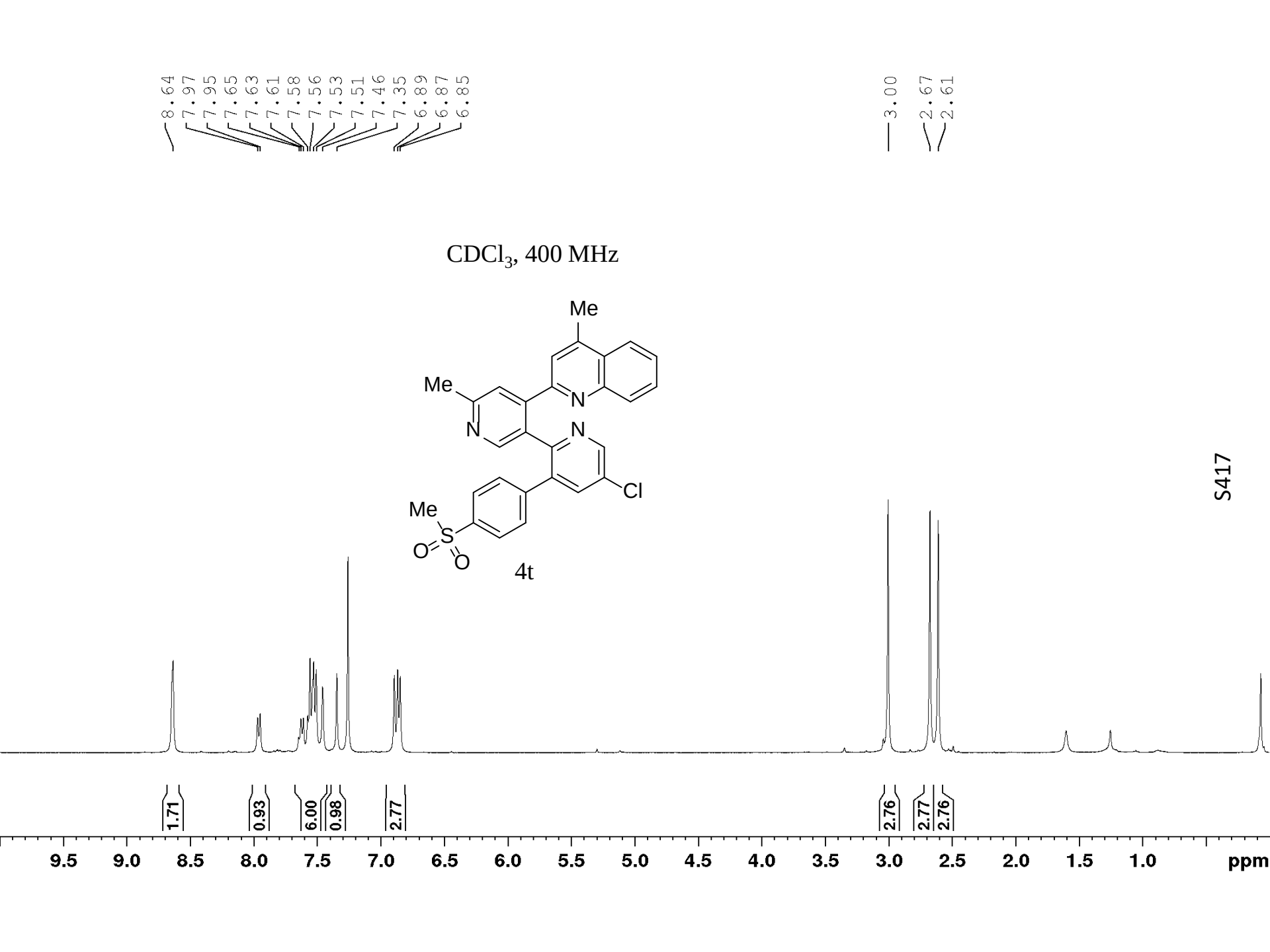
-117.54
-117.55
-117.56
-117.58
-117.58
-117.60

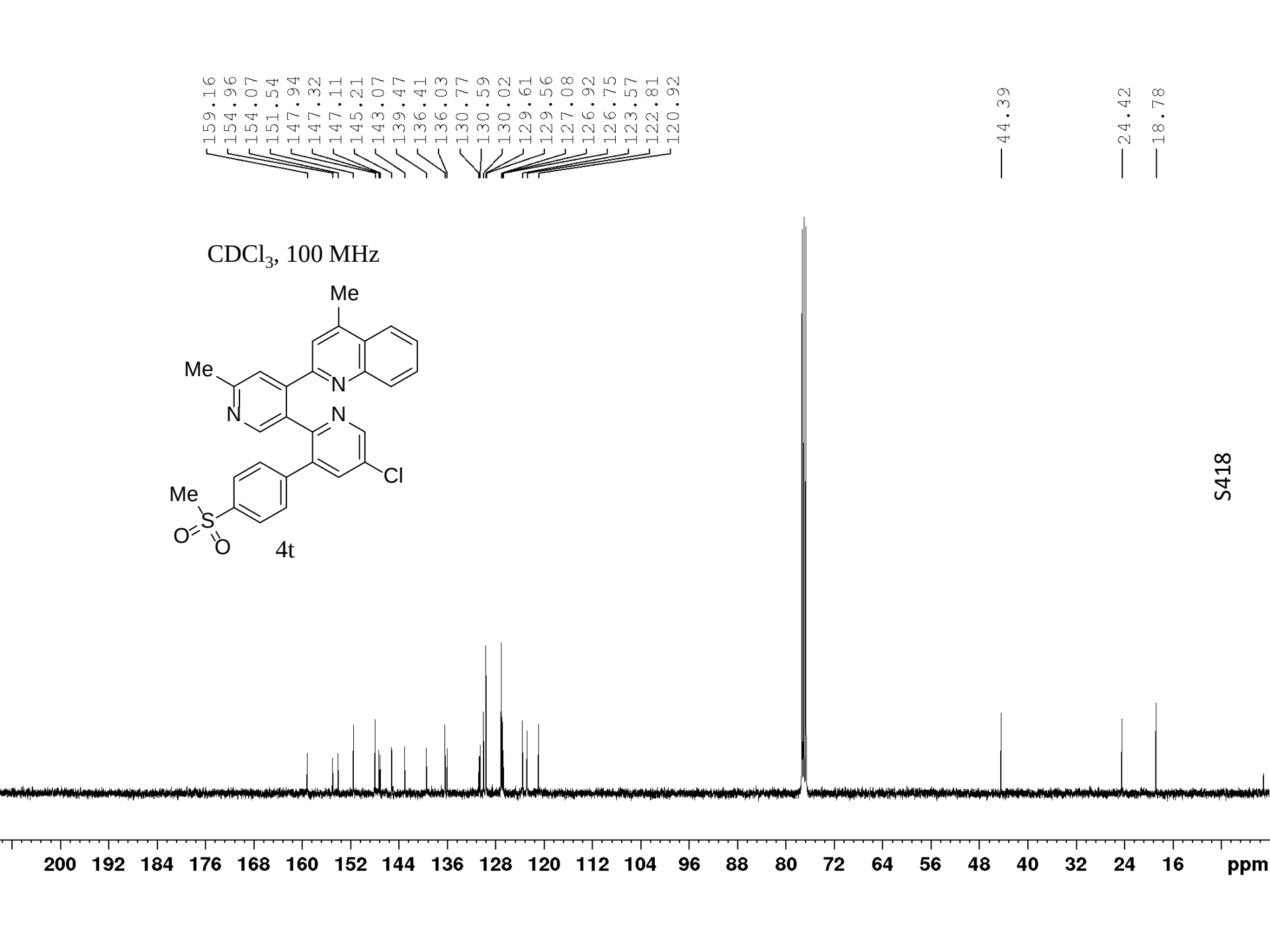
$CDCl_3$, 365 MHz

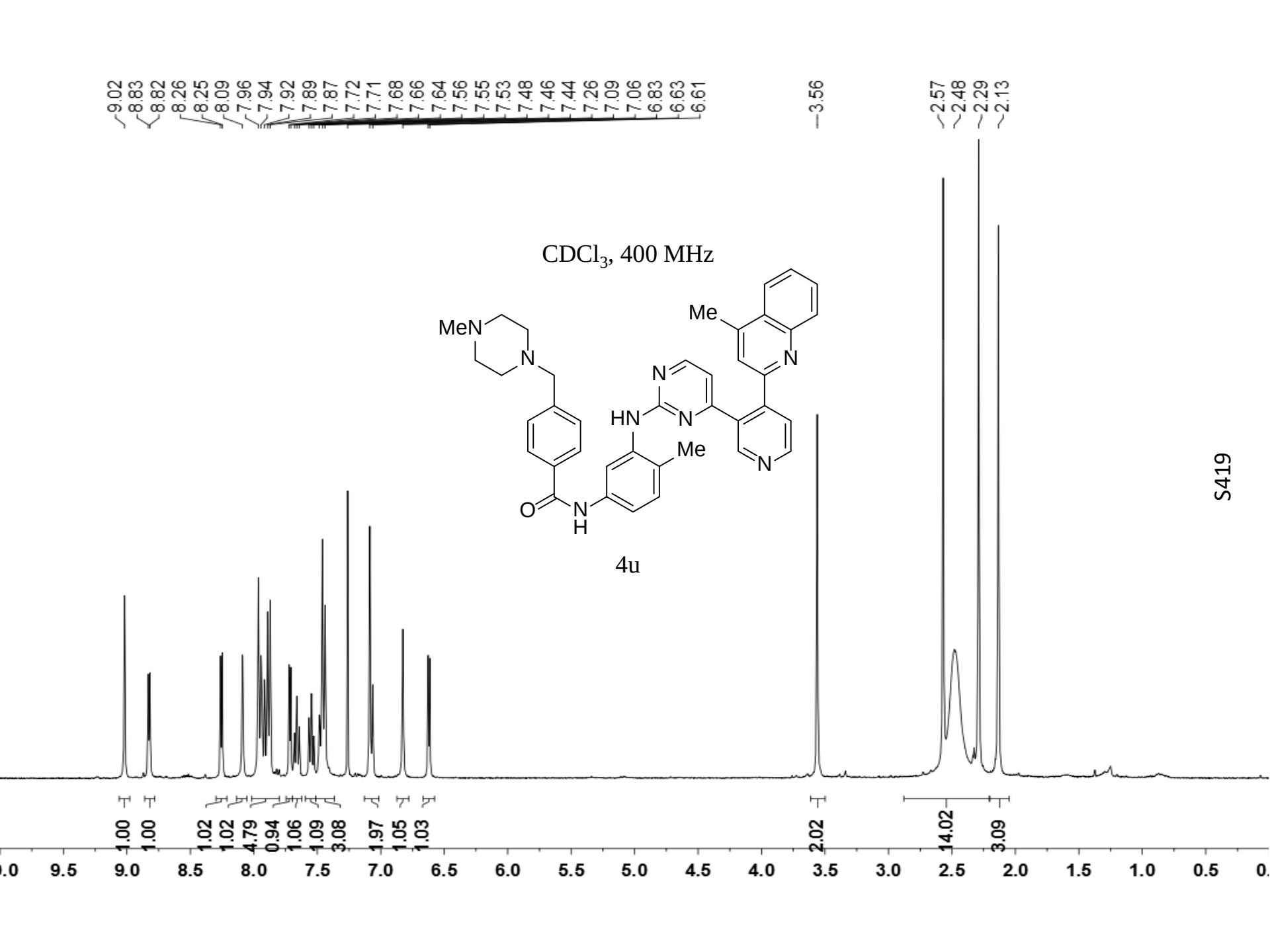


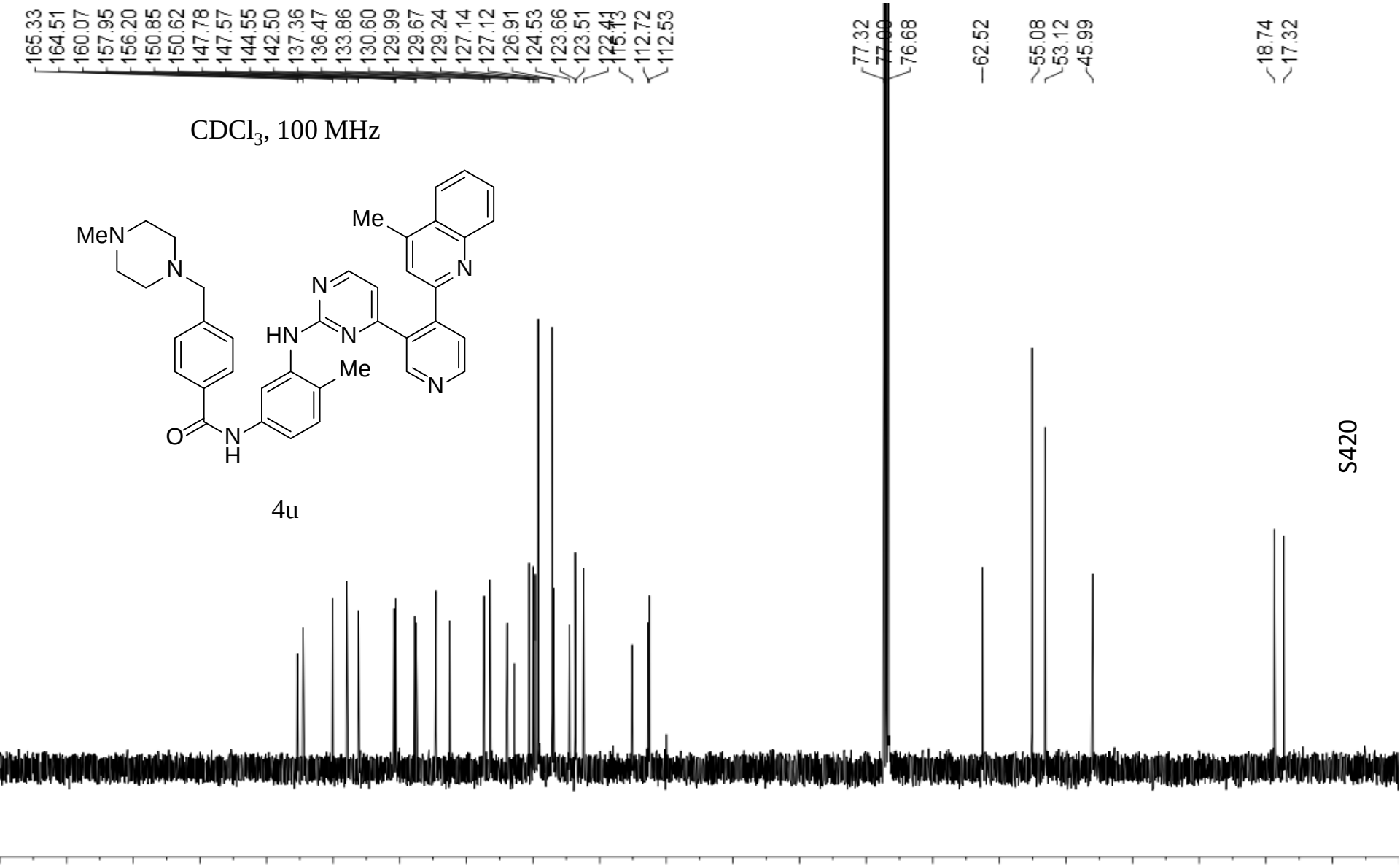
4s

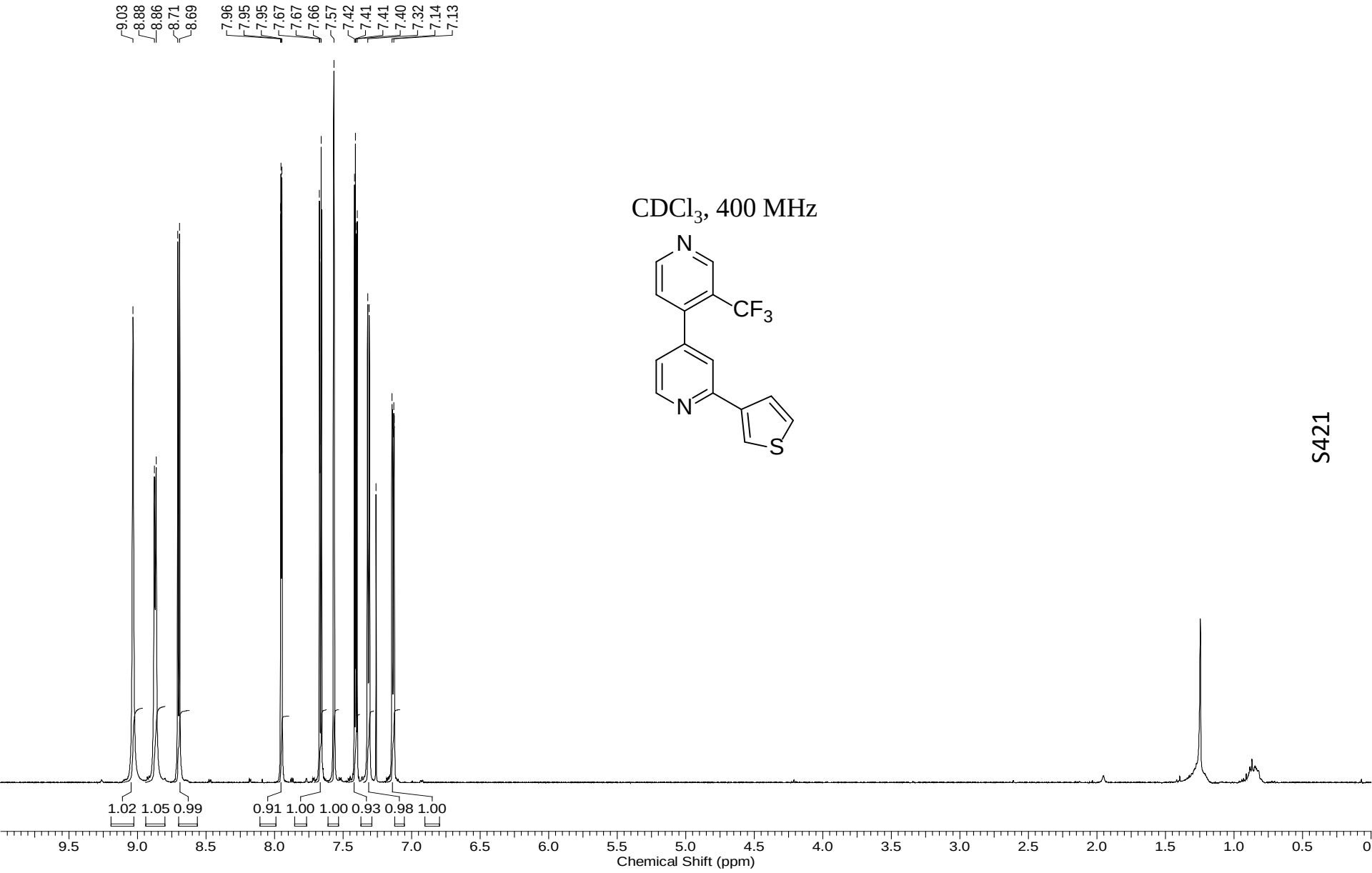



8.64
7.97
7.95
7.65
7.63
7.61
7.58
7.56
7.53
7.51
7.46
7.35
6.89
6.87
6.85
3.00
2.67
2.61
CDCl3, 400 MHz
Me
Me
N
N
N
Cl
Me
S
O
O
4t
S417
1.71
0.93
6.00
0.98
2.77
2.76
2.77
2.76
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

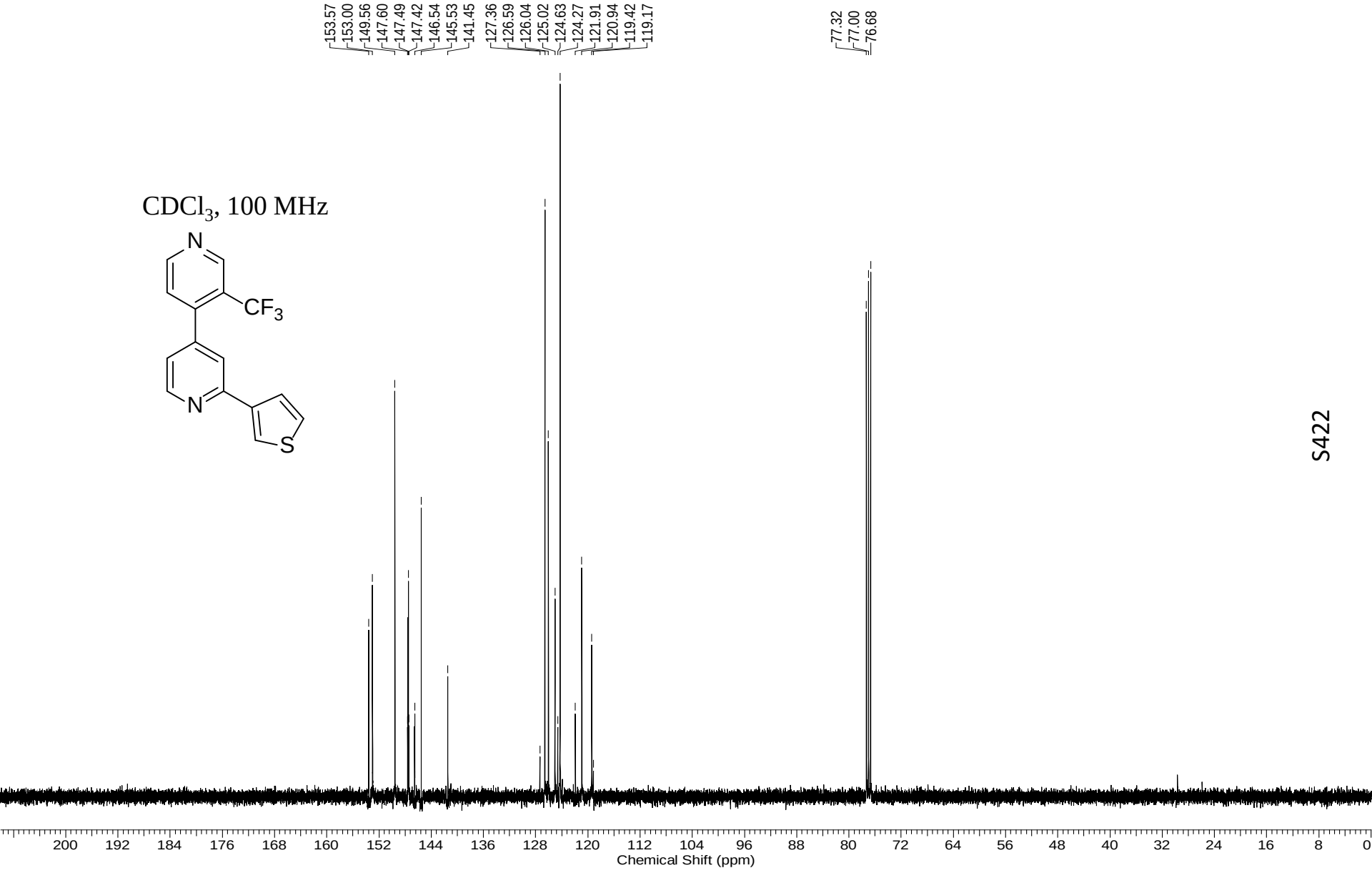

159.16
154.96
154.07
151.54
147.94
147.32
147.11
145.21
143.07
139.47
136.41
136.03
130.77
130.59
130.02
129.61
129.56
127.08
126.92
126.75
123.57
122.81
120.92
44.39
24.42
18.78
CDCl3, 100 MHz
Me
Me
N
N
N
Cl
Me
S
O
O
4t
S418
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 ppm

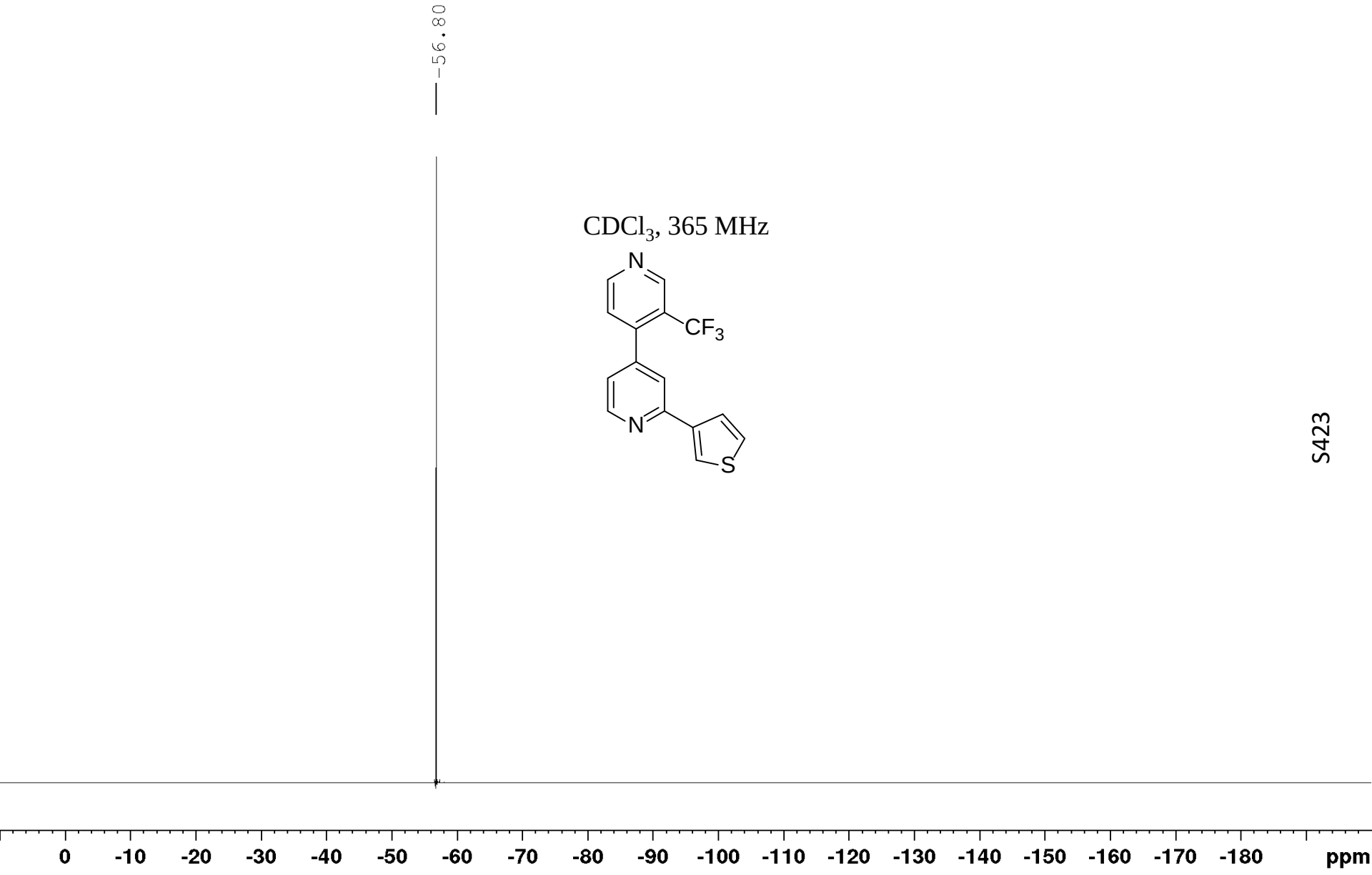

9.02
8.83
8.82
8.26
8.25
8.09
7.96
7.94
7.92
7.89
7.87
7.72
7.71
7.68
7.66
7.64
7.56
7.55
7.53
7.48
7.46
7.44
7.26
7.09
7.06
6.83
6.63
6.61
3.56
2.57
2.48
2.29
2.13
CDCl3, 400 MHz
MeN
N
HN
N
N
Me
Me
N
N
O
N
H
4u
1.00
1.00
1.02
1.02
4.79
0.94
1.06
1.09
3.08
1.97
1.05
1.03
2.02
14.02
3.09
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
S419

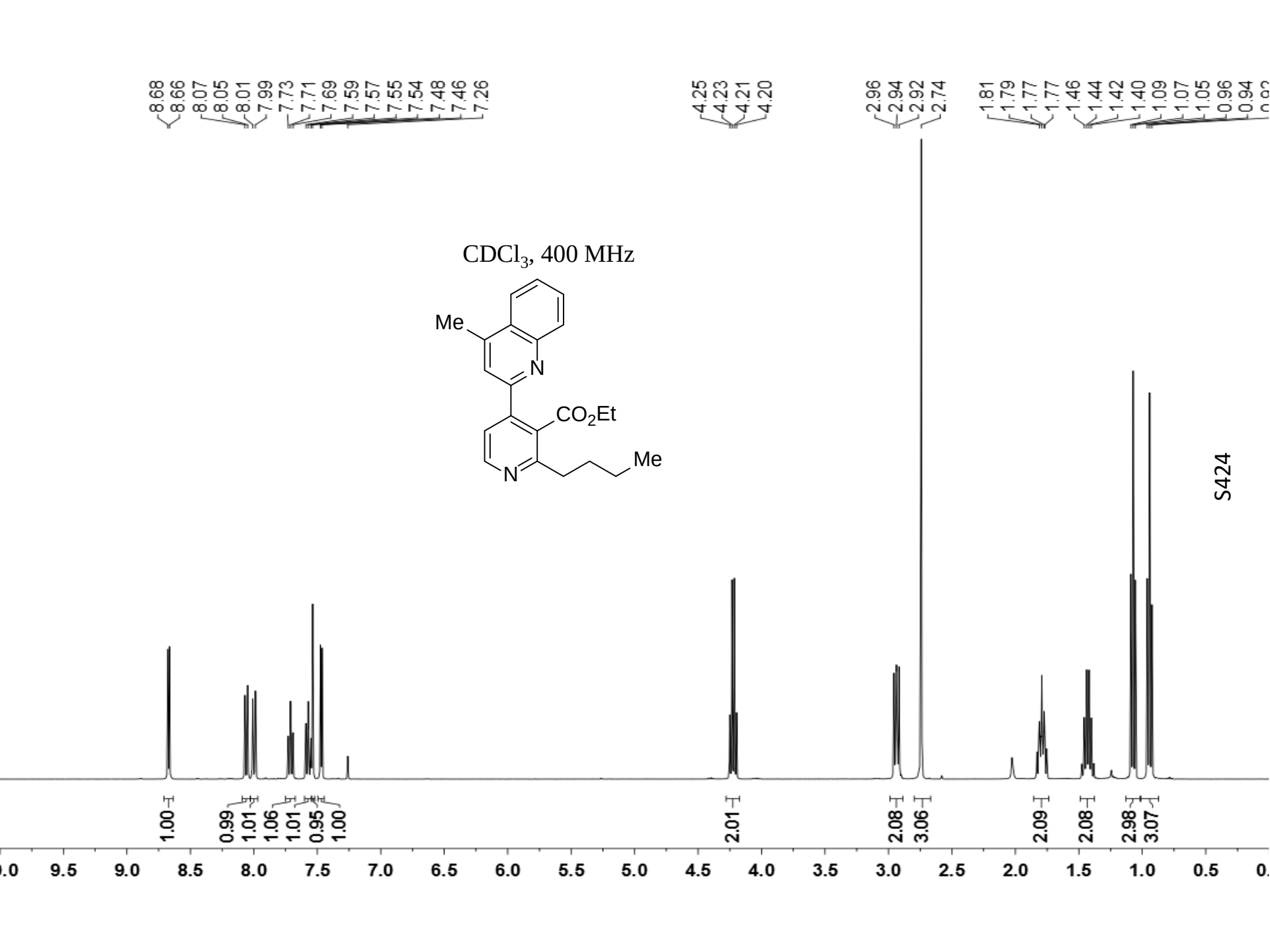

165.33
164.51
160.07
157.95
156.20
150.85
150.62
147.78
147.57
144.55
142.50
137.36
136.47
133.86
130.60
129.99
129.67
129.24
127.14
127.12
126.91
124.53
123.66
123.51
122.41
115.13
112.72
112.53
77.32
77.00
76.68
62.52
55.08
53.12
45.99
18.74
17.32
CDCl3, 100 MHz
MeN
N
O
N
H
HN
N
N
Me
Me
N
N
4u
S420
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

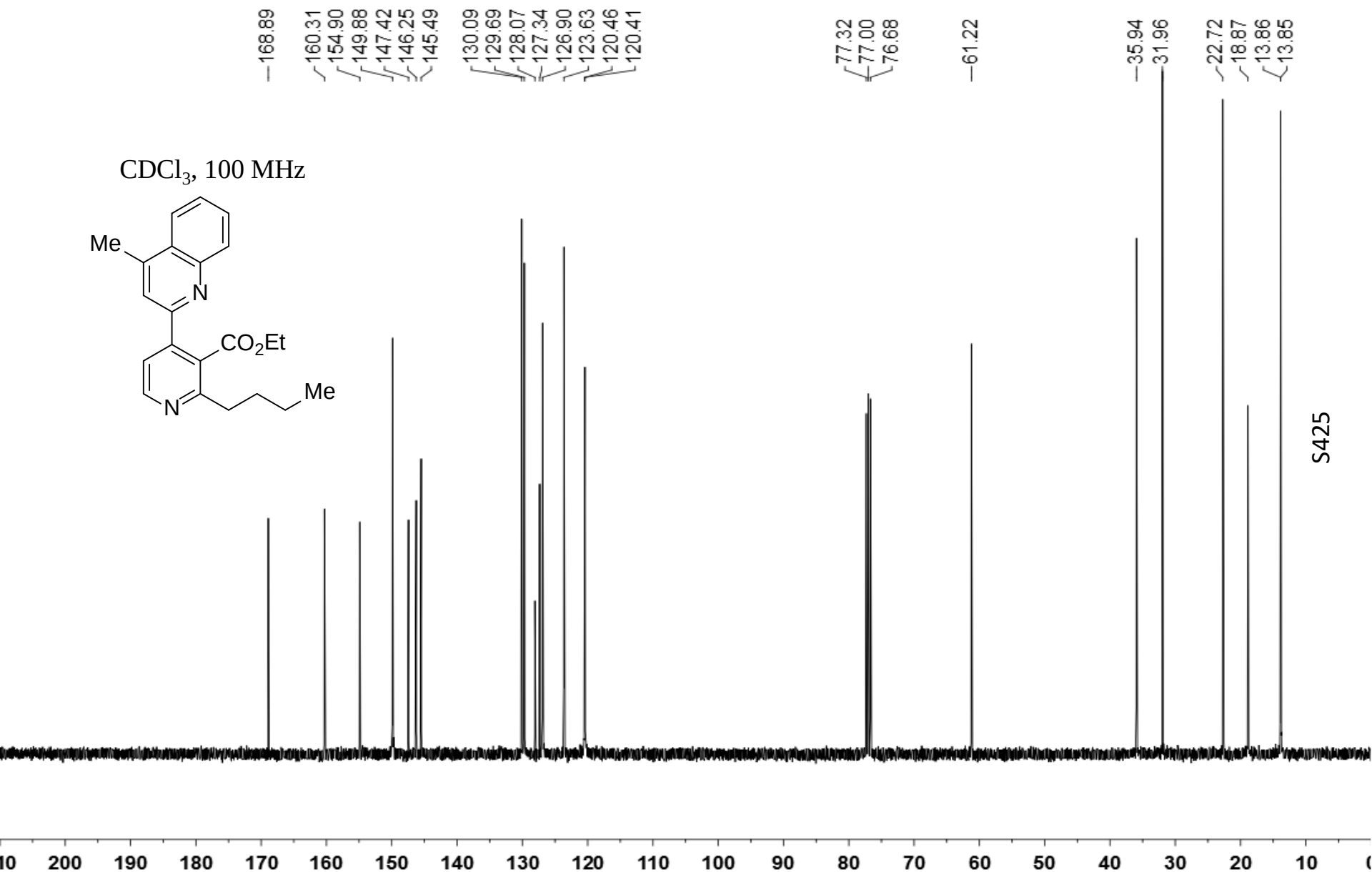

9.03
8.88
8.86
8.71
8.69
7.96
7.95
7.95
7.67
7.67
7.66
7.57
7.42
7.41
7.41
7.40
7.32
7.14
7.13
CDCl3, 400 MHz
N
CF3
N
S
1.02 1.05 0.99
0.91 1.00 1.00 0.93 0.98 1.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
Chemical Shift (ppm)

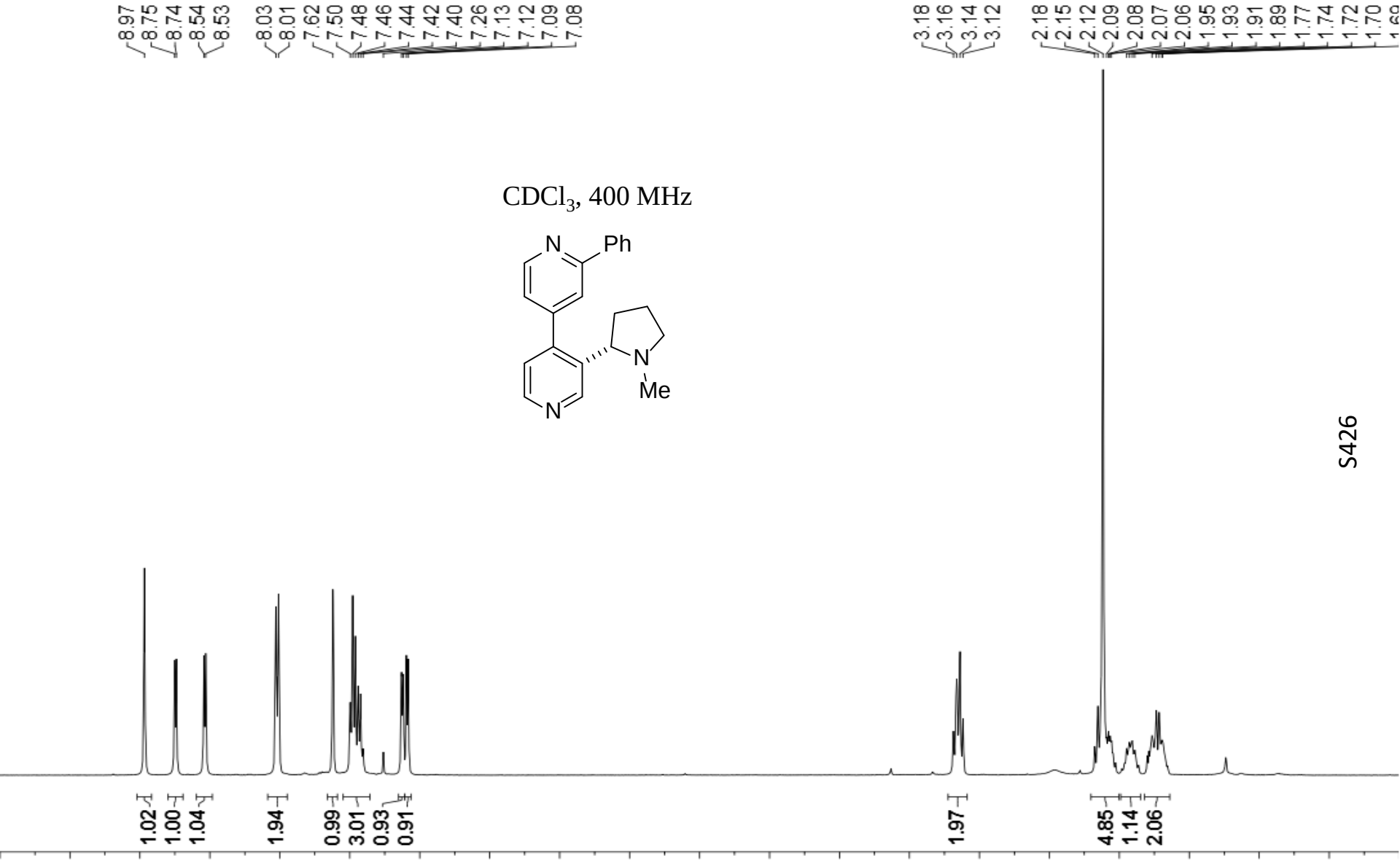
S421

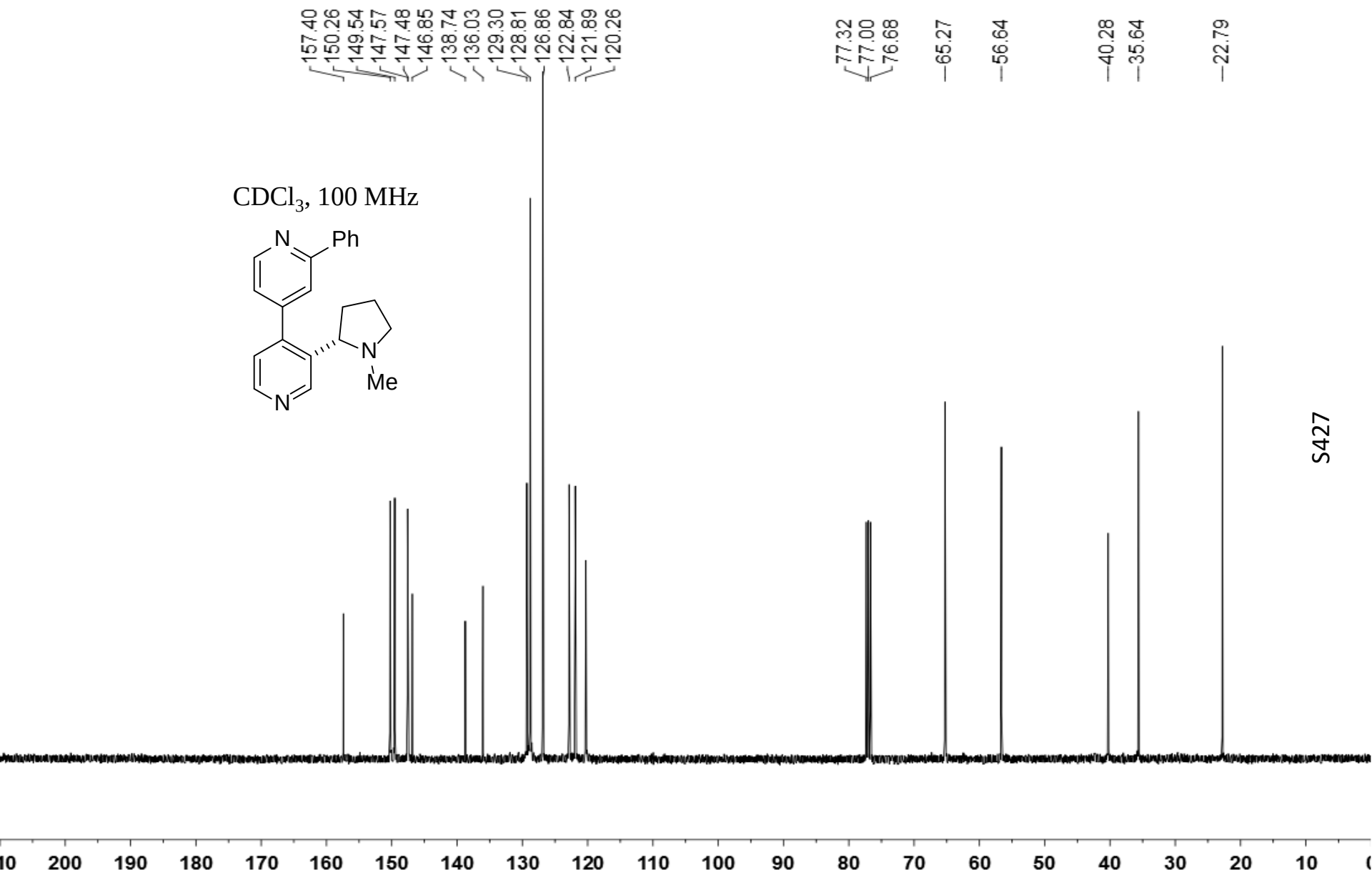

153.57
153.00
149.56
147.60
147.49
147.42
146.54
145.53
141.45
127.36
126.59
126.04
125.02
124.63
124.27
121.91
120.94
119.42
119.17
77.32
77.00
76.68
CDCl3, 100 MHz
N
CF3
N
S
S422
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 0
Chemical Shift (ppm)

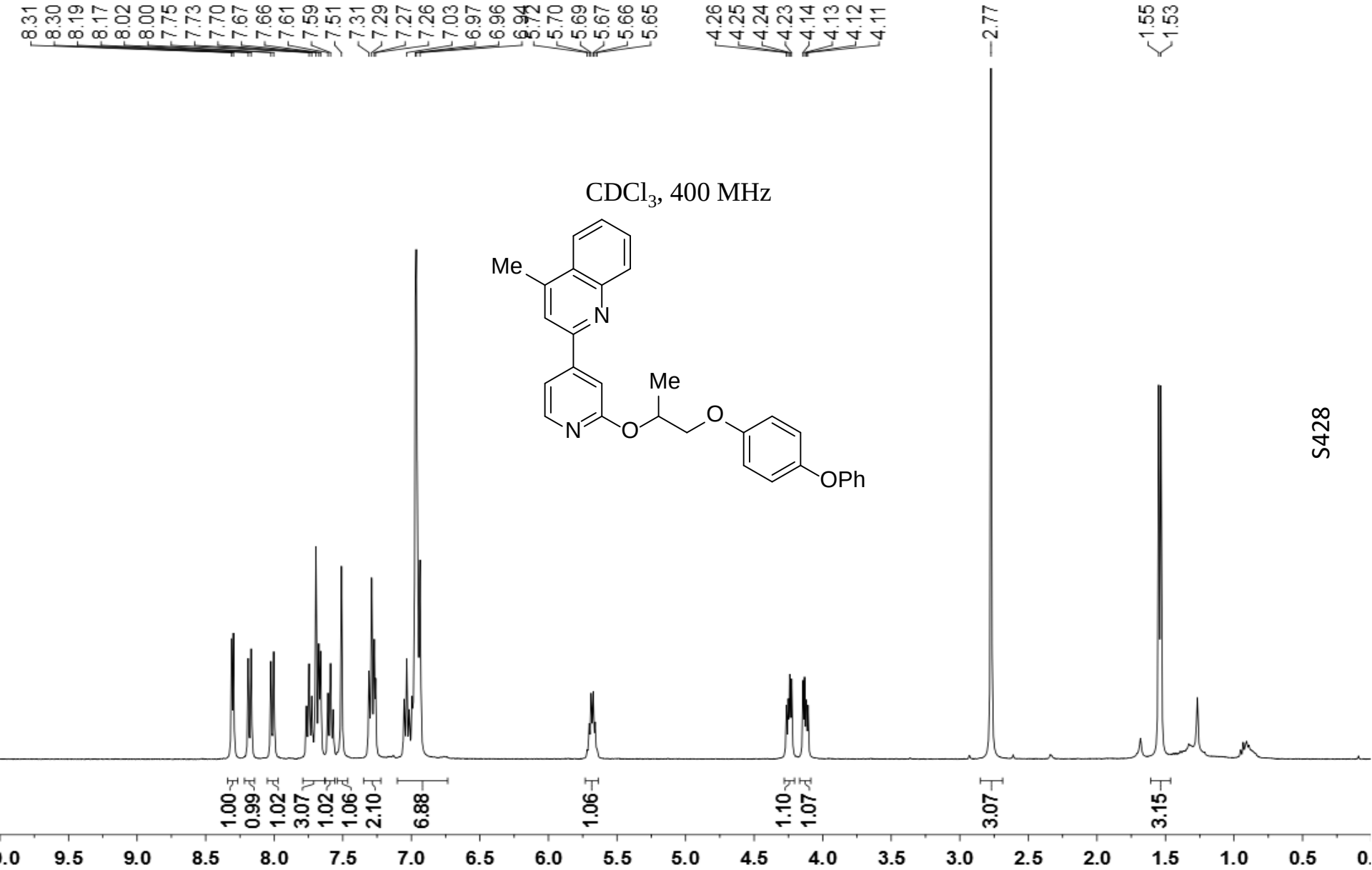

-56.80
CDCl3, 365 MHz
N
CF3
N
S
S423
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
ppm

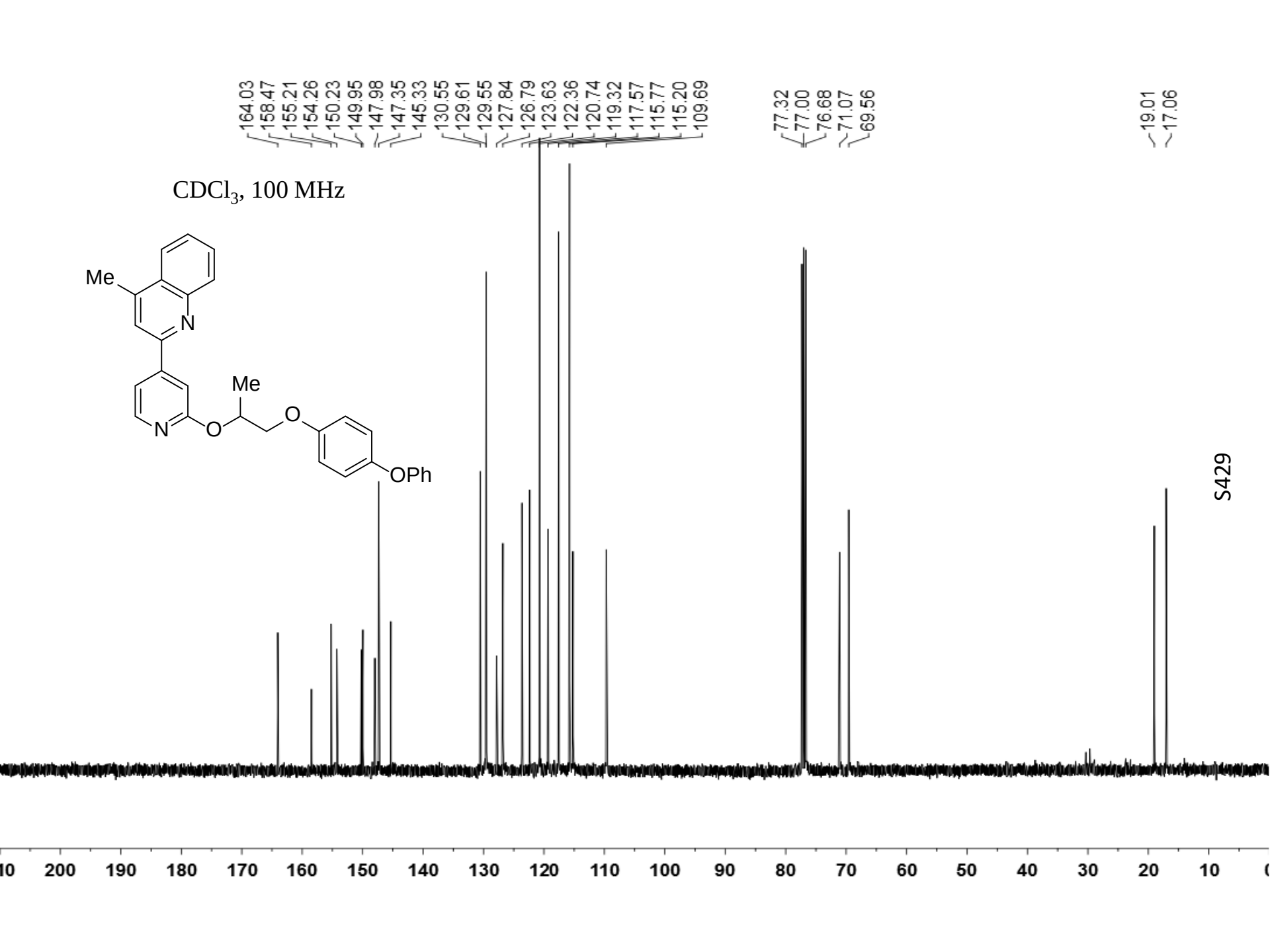

8.68
8.66
8.07
8.05
8.01
7.99
7.73
7.71
7.69
7.59
7.57
7.55
7.54
7.48
7.46
7.26
4.25
4.23
4.21
4.20
2.96
2.94
2.92
2.74
1.81
1.79
1.77
1.77
1.46
1.44
1.42
1.40
1.09
1.07
1.05
0.96
0.94
CDCl3, 400 MHz
Me
N
CO2Et
N
Me
S424
1.00
0.99
1.01
1.06
1.01
0.95
1.00
2.01
2.08
3.06
2.09
2.08
2.98
3.07
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

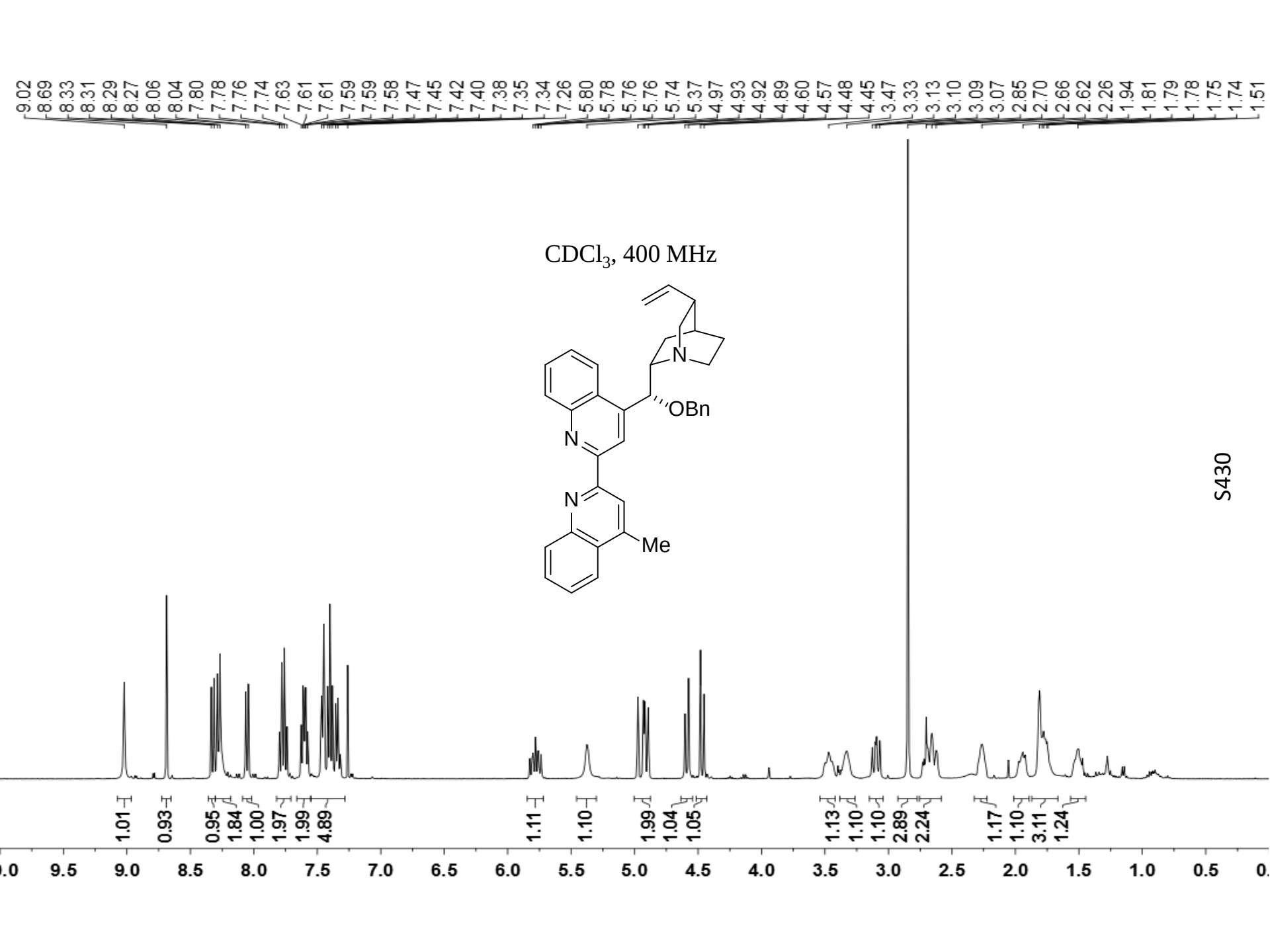

168.89
160.31
154.90
149.88
147.42
146.25
145.49
130.09
129.69
128.07
127.34
126.90
123.63
120.46
120.41
77.32
77.00
76.68
61.22
35.94
31.96
22.72
18.87
13.86
13.85
CDCl3, 100 MHz
Me
N
CO2Et
N
Me
S425
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

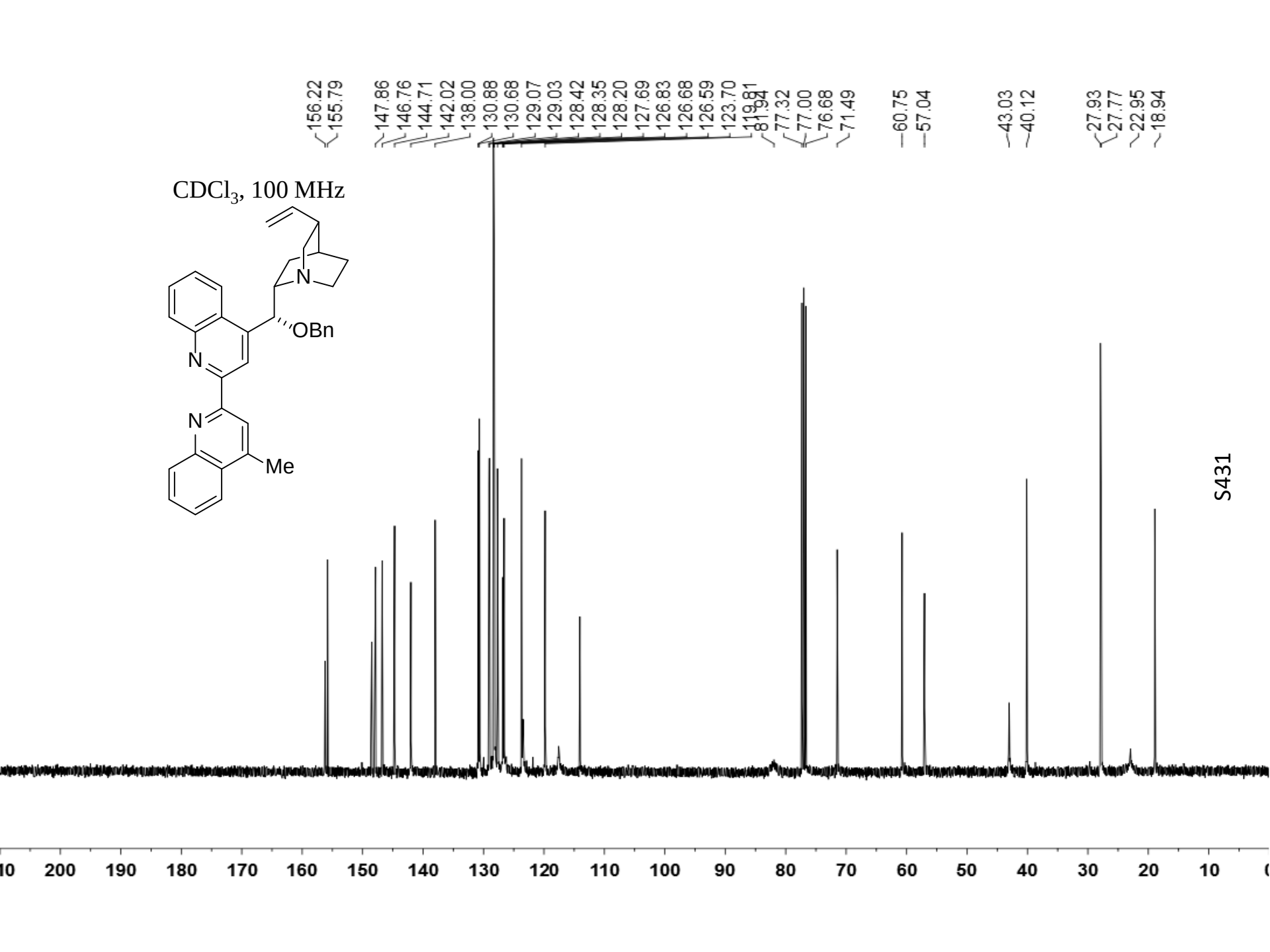

8.97
8.75
8.74
8.54
8.53
8.03
8.01
7.62
7.50
7.48
7.46
7.44
7.42
7.40
7.26
7.13
7.12
7.09
7.08
3.18
3.16
3.14
3.12
2.18
2.15
2.12
2.09
2.08
2.07
2.06
1.95
1.93
1.91
1.89
1.77
1.74
1.72
1.70
CDCl3, 400 MHz
N
Ph
N
Me
N
S426
1.02
1.00
1.04
1.94
0.99
3.01
0.93
0.91
1.97
4.85
1.14
2.06
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5


157.40
150.26
149.54
147.57
147.48
146.85
138.74
136.03
129.30
128.81
126.86
122.84
121.89
120.26
77.32
77.00
76.68
65.27
56.64
40.28
35.64
22.79
CDCl3, 100 MHz
N
Ph
N
Me
N
S427
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10


8.31
8.30
8.19
8.17
8.02
8.00
7.75
7.73
7.70
7.67
7.66
7.61
7.59
7.51
7.31
7.29
7.27
7.26
7.03
6.97
6.96
6.94
6.92
5.70
5.69
5.67
5.66
5.65
4.26
4.25
4.24
4.23
4.14
4.13
4.12
4.11
2.77
1.55
1.53
CDCl3, 400 MHz
Me
N
Me
N
O
O
OPh
S428
1.00
0.99
1.02
3.07
1.02
1.06
2.10
6.88
1.06
1.10
1.07
3.07
3.15
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5


164.03
158.47
155.21
154.26
150.23
149.95
147.98
147.35
145.33
130.55
129.61
129.55
127.84
126.79
123.63
122.36
120.74
119.32
117.57
115.77
115.20
109.69
77.32
77.00
76.68
71.07
69.56
19.01
17.06
CDCl3, 100 MHz
Me
N
Me
N
O
O
OPh
S429
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10


9.02
8.69
8.33
8.31
8.29
8.27
8.06
8.04
7.80
7.78
7.76
7.74
7.63
7.61
7.61
7.59
7.59
7.58
7.47
7.45
7.42
7.40
7.38
7.35
7.34
7.26
5.80
5.78
5.76
5.76
5.74
5.37
4.97
4.93
4.92
4.89
4.60
4.57
4.48
4.45
3.47
3.33
3.13
3.10
3.09
3.07
2.85
2.70
2.66
2.62
2.26
1.94
1.81
1.79
1.78
1.75
1.74
1.51
CDCl3, 400 MHz
N
OBn
N
N
Me
S430
1.01
0.93
0.95
1.84
1.00
1.97
1.99
4.89
1.11
1.10
1.99
1.04
1.05
1.13
1.10
1.10
2.89
2.24
1.17
1.10
3.11
1.24
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5


156.22
155.79
147.86
146.76
144.71
142.02
138.00
130.88
130.68
129.07
129.03
128.42
128.35
128.20
127.69
126.83
126.68
126.59
123.70
119.81
81.94
77.32
77.00
76.68
71.49
60.75
57.04
43.03
40.12
27.93
27.77
22.95
18.94
CDCl3, 100 MHz
N
OBn
N
N
Me
S431
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

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