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Facile Pyridine S$_N$Ar Reactions via *N*-Phosphonium Pyridinium Intermediates

Benjamin T. Boyle, J. Luke Koniarczyk and Andrew McNally*

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

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1. General Information

Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded at ambient temperature on either a Bruker Ultrashield–400 (400 MHz) spectrometer, a Varian 400 MR (400 MHz) spectrometer or an Agilent Inova 400 (400 MHz) spectrometer. Chemical shifts (δ) are reported in ppm and quoted to the nearest 0.01 ppm relative to the residual protons in $CDCl_3$ (7.26 ppm), C_6D_6 (7.16 ppm), $(CD_3)_2SO$ (2.50 ppm), CD_3OD (3.31 ppm) or CD_3CN (1.94 ppm) and coupling constants (*J*) are quoted in Hertz (Hz). Data are reported as follows: Chemical shift (multiplicity, coupling constants, number of protons). 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. Carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded at ambient temperature on either a Bruker Ultrashield–400 (400 MHz) spectrometer, a Varian 400 MR spectrometer (100 MHz) or an Agilent Inova 400 (100 MHz) spectrometer. Chemical shift (δ) was measured in ppm and quoted to the nearest 0.1 ppm relative to the residual solvent peaks in $CDCl_3$ (77.16 ppm), C_6D_6 (128.06 ppm), $(CD_3)_2SO$ (39.51 ppm), CD_3OD (49.00 ppm) or CD_3CN (1.32 ppm). DEPT135, NOE experiments and 2–dimensional experiments (COSY, HMBC, and HSQC) were used to support assignments where appropriate.

Low–resolution mass spectra (LRMS) were measured on an Agilent 6310 Quadrupole Mass Spectrometer.

Analytical thin layer chromatography (TLC) was performed using pre–coated Merck glass backed silica gel plates (Silicagel 60 F254). Flash column chromatography was undertaken on Fluka or Material Harvest silica gel (230–400 mesh) under a positive pressure of air. Visualization was achieved using ultraviolet light (254 nm) and chemical staining with ceric ammonium molybdate or basic potassium permanganate solutions as appropriate.

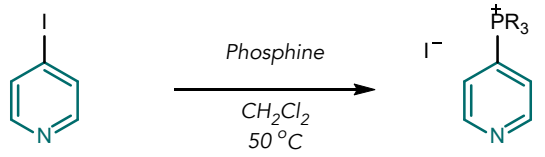
Tetrahydrofuran (THF), toluene, hexane, diethyl ether and dichloromethane were dried and distilled using standard methods.[1] Chloroform ($CHCl_3$) was purchased anhydrous from Sigma Aldrich chemical company. All reagents were purchased at the highest commercial quality and used without further purification. Reactions were carried out under an atmosphere of air unless otherwise stated. All reactions were monitored by TLC, ^{1}H NMR spectra taken from reaction

samples, gas chromatography (GC) and gas chromatography–mass spectrometry (GCMS) using an Agilent 5977A fitted with an Agilent J&W HP–5ms Ultra Inert Column (30 m, 0.25 mm, 0.25 μm film) for MS analysis and an Agilent J&W VF–5ms column (10 m, 0.15 mm, 0.15 μm film) for FID analysis or liquid chromatography mass spectrometry (LCMS) using an Agilent 6310 Quadrupole Mass Spectrometer. Melting points (mp) were recorded using a Büchi B–450 melting point apparatus and are reported uncorrected.

Tri-p-anisole phosphine (99%) was purchased from Oakwood Chemicals and stored in a glovebox. Tri-p-anisole phosphine was commonly dispensed into vials for use in the reaction and stored under air on a benchtop prior to use. Anhydrous chloroform (0.05-0.1% EtOH as stabilizer) was purchased from Sigma Aldrich chemical company and used without further purification

2. Optimization Studies

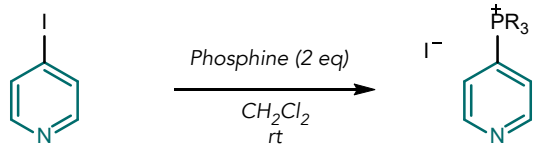
Table S1: Phosphine Screen at 50 °C



Entry	Phosphine	Yield (%)*
1	PPh_3	79
2	(p-Cl)Ph_3P	4
3	(thienyl)$_3P$	15
4	(p-tol)$_3P$	97
5	(o-tol)$_3P$	2
6	nBu_3P	56
7	(p-OMe)Ph_3P	97
8	Ph_2PEt	99

*^{1}H NMR yields shown using triphenylmethane as an internal standard.

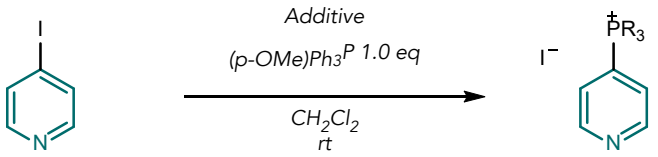
Table S2: Phosphine Screen: Room Temperature



Entry	Phosphine	Yield (%)*
1	Ph_3P	6
2	nBu_3P	5
3	PEt_3	8
4	$PhPEt_2$	79
5	Ph_2PEt	86
6	(p-tol)$_3P$	78
8	(p-OMe)Ph_3P	86

*^{1}H NMR yields shown using triphenylmethane as an internal standard.

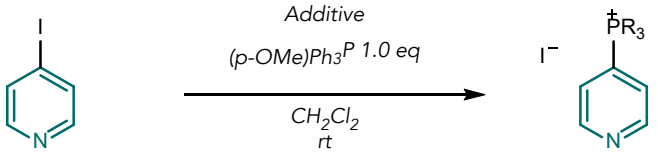
Table S3: Phosphonium Formation Additive Screen



Entry	Conditions/Additive	Yield (%)*
1	H_2O (10 eq)	83
2	Cs_2CO_3	n.d.†
3	MeOH‡	n.d.†
4	Light excluded	83
5	Sublimed Iodopyridine	66
6	Standard	87

*^{1}H NMR yields shown using triphenylmethane an internal standard. †Products were not detected by LCMS or ^{1}H NMR. ‡MeOH was used as the solvent instead of CH_2Cl_2.

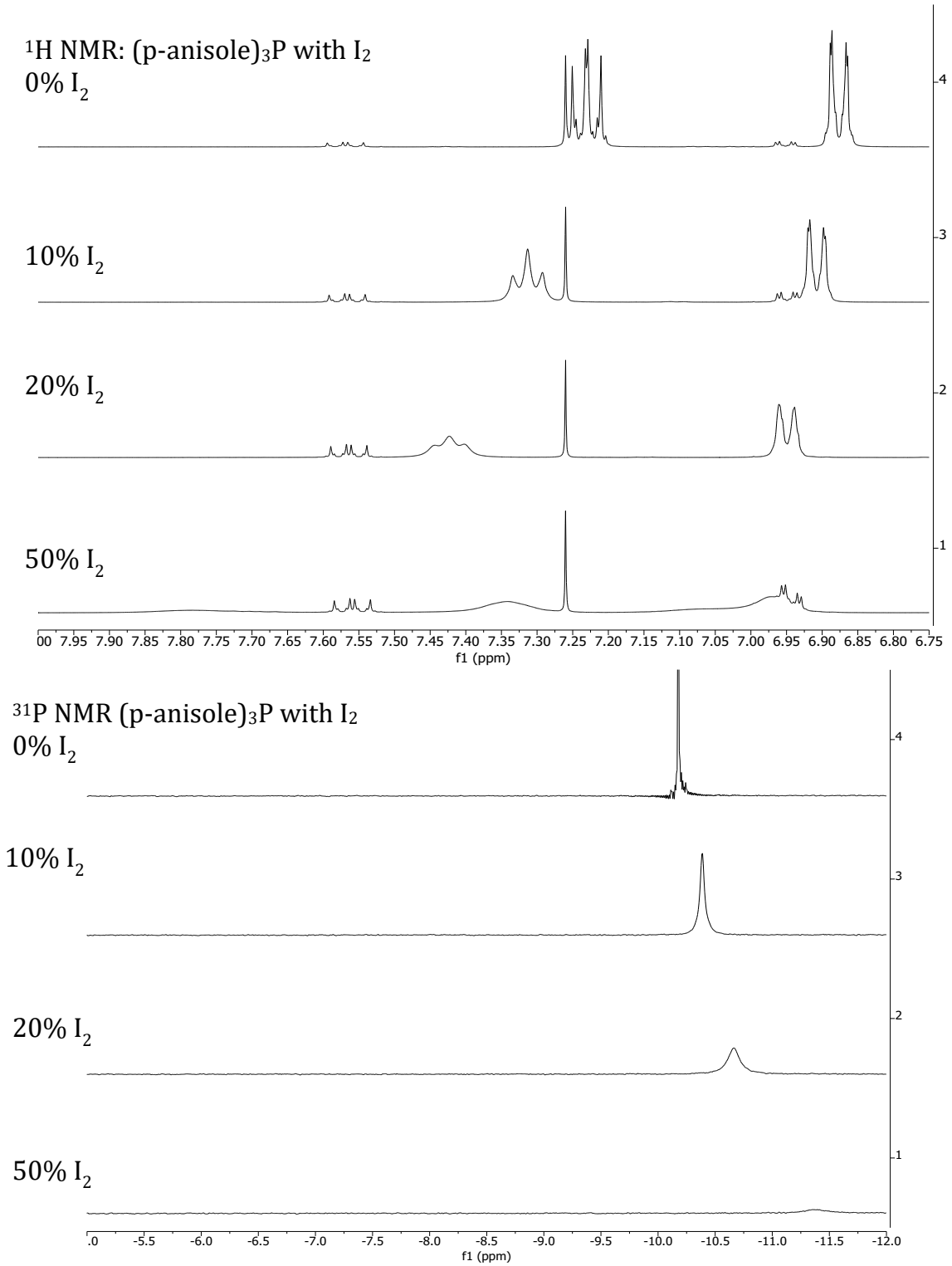
Table S4: AIBN Study: Radical Initiator -Shortened Reaction Times



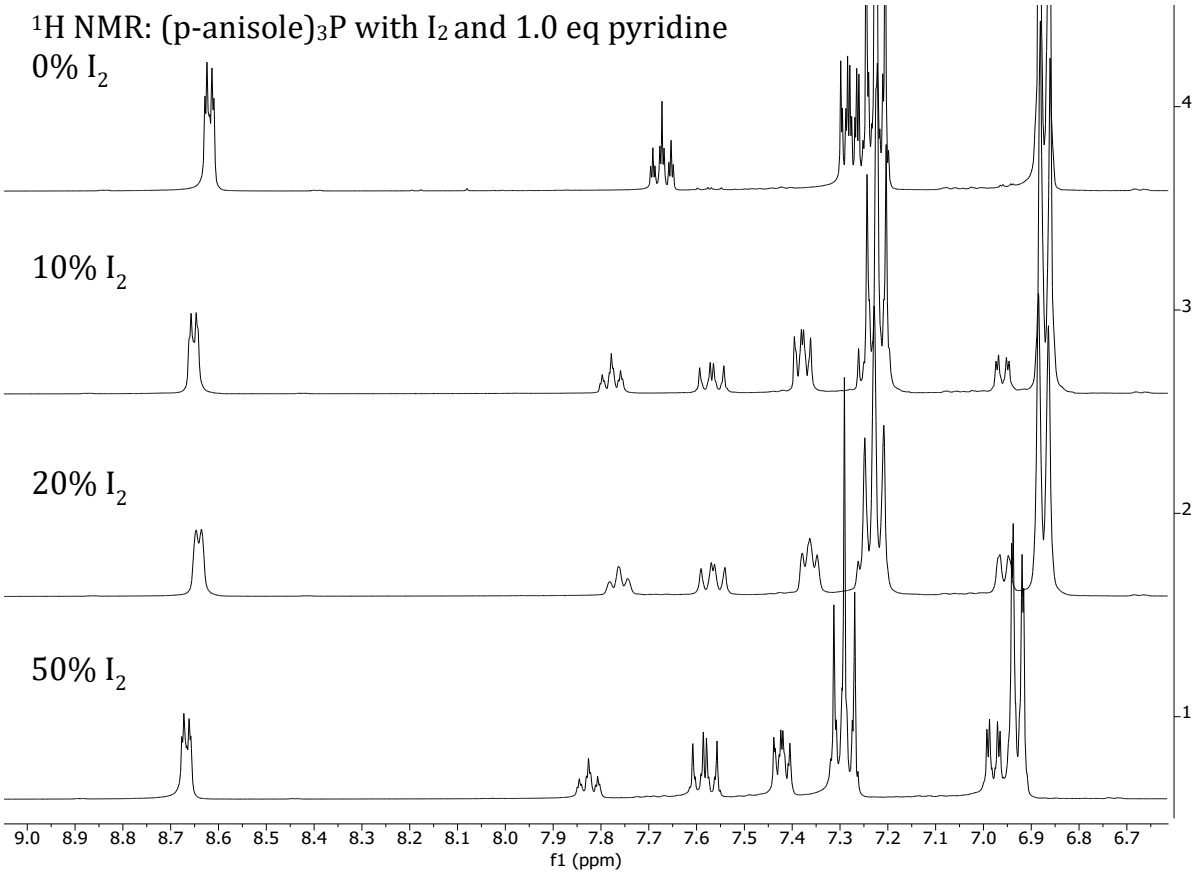
Entry	Additive	Yield (%)*
1	None	23
2	AIBN (5 mol%)	22
3	AIBN (10 mol%)	24
4	AIBN (25 mol%)	24

*^{1}H NMR yields shown using triphenylmethane as an internal standard. No increase in reaction rate was observed using AIBN as a radical initiator, this experiment was ran at 50 °C and 80 °C with no observable increase in reaction rate.

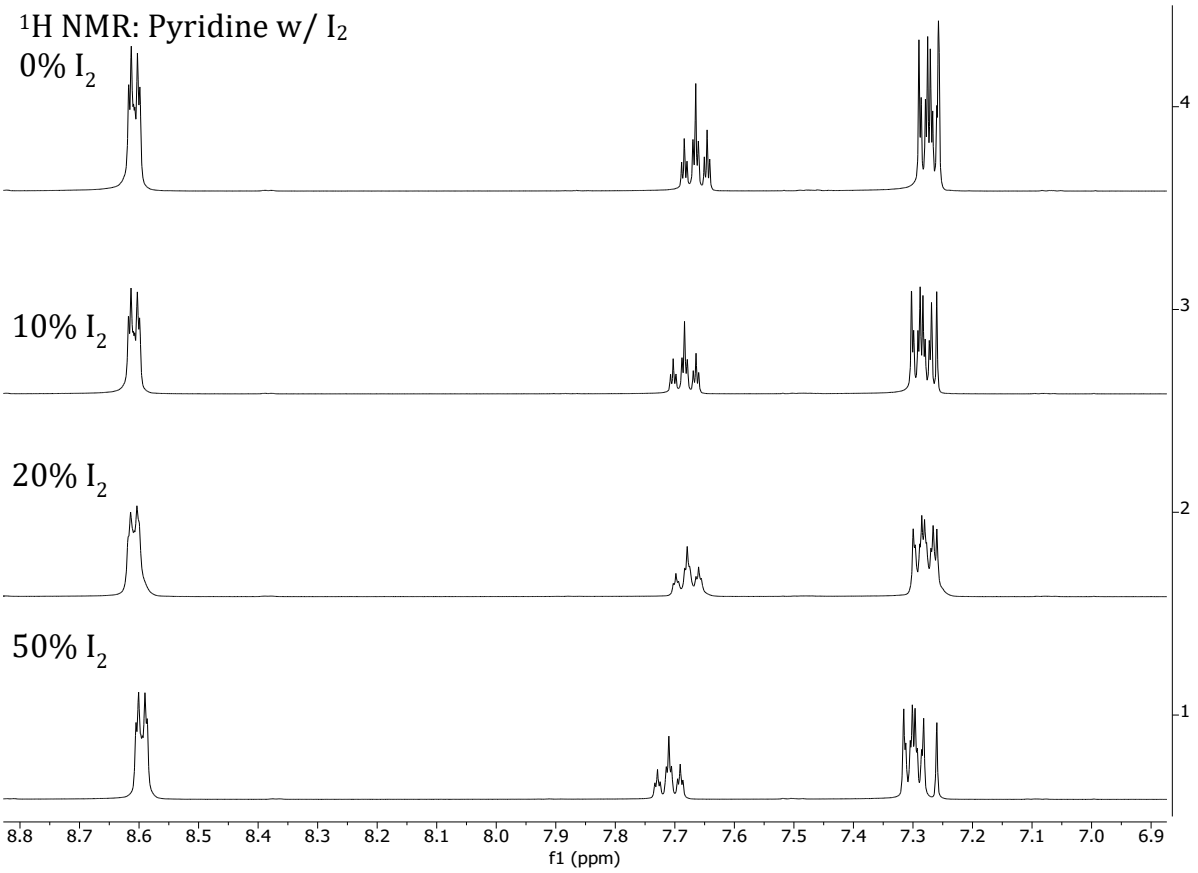
3. Iodine Spiking Studies



Scheme S1: ^{1}H NMR and ^{31}P NMR: I$_2$ addition to (p-anisole)Ph$_3$P. Show reaction and shifting of phosphine peaks as iodine concentration increase. Consistent with reports of I-$^{+}$PAr3 formation.

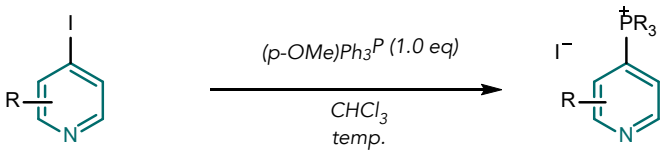


Scheme S2: ^{1}H NMR: I_2 addition to (p-anisole)Ph_3P with 1 equivalent of pyridine. Show reaction and shifting of phosphine peaks as iodine concentration increase. Consistent with formation of an activated pyridinium species, in particular meta position proton shift 7.3 to 7.5 ppm and para position shift from 7.7 to 7.85 ppm.

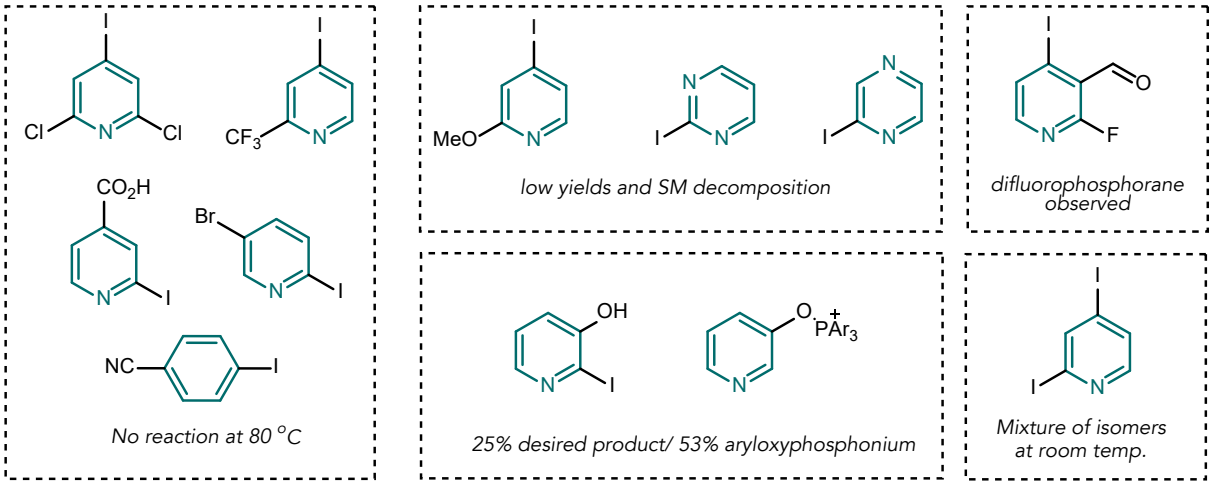


Scheme S3: ^{1}H NMR: I_2 addition to pyridine. Known reactivity to form activated pyridines. Shows distinct peaks when compared to Scheme S3 indicating species observed under reaction conditions are not associated with an iodo-pyridinium.

4. Challenges and Limitations

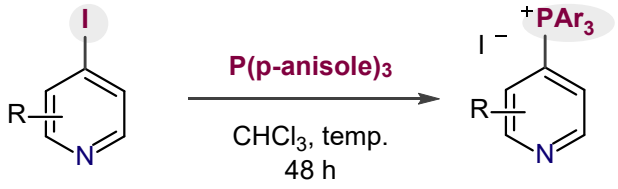


What doesn't work:



5. Preparation of Heteroaryl Phosphonium Salts

General Procedure A:

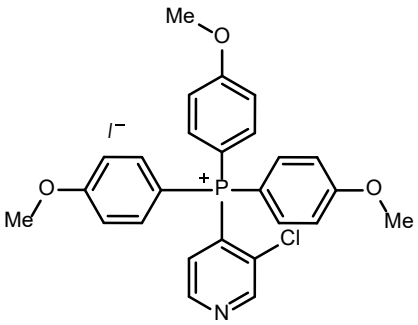


An oven dried 8 mL vial (< 1.0 mmol) or 16 mL vial (1.0-4.0 mmol) equipped with a stir bar was charged with the iodopyridine (1.0 equiv) and (p-anisole)$_3$P (1.0 equiv) and $CHCl_3$ (0.5 M). The reaction was then stirred at the temperature indicated (rt, 50 °C or 80 °C) for the stated time. The reaction was then purified by diluting the crude reaction with $CHCl_3$ and by crashing out in Et_2O (100 mL per 1.0 mmol) at room temperature.

Notes:

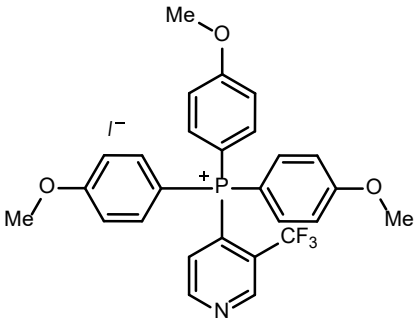
1. Reaction was ran under air and N_2 atmospheres and no notable differences in yields were observed.
2. Additional phosphine can be used to increase the reaction rate (1st order in phosphine)
3. In general the reaction does not product by-products besides trace phosphine oxide.

(3-Chloropyridin-4-yl)tris(4-methoxyphenyl)phosphonium iodide (1b)



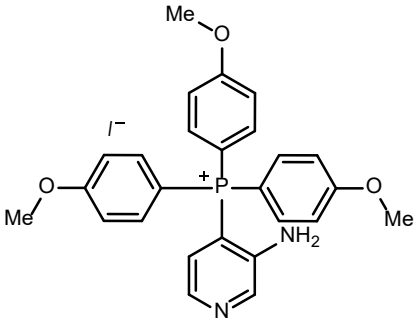
Prepared according to general procedure A using 3-chloro-4-iodopyridine (72 mg, 0.30 mmol), tris(4-methoxyphenyl)phosphane (106 mg, 0.30 mmol), and chloroform (0.6 mL) at room temperature for 36 hours. After purification procedure, the title compound was isolated as a light brown solid (174 mg, 0.3 mmol, 98% yield). mp 91-93 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.12 – 8.59 (m, 2H), 7.58 (dd, *J*=12.7, 8.9, 6H), 7.48 – 7.10 (m, 7H), 3.95 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 165.40 (d, *J*=3.0), 151.98 (d, *J*=5.0), 150.11 (d, *J*=9.8), 136.35 (d, *J*=12.4), 134.75 (d, *J*=2.2), 130.32 (d, *J*=8.4), 129.29 (d, *J*=88.3), 117.02 (d, *J*=14.5), 105.78 (d, *J*=100.0), 56.51; ^{31}P NMR (162 MHz, $CDCl_3$) δ: 21.08; *m/z* LRMS (ESI + APCI) found $[M-I]^+$ 464.2, $C_{26}H_{24}ClNO_3P^+$ requires 464.1.

Tris(4-methoxyphenyl)(3-(trifluoromethyl)pyridin-4-yl)phosphonium iodide (1c)



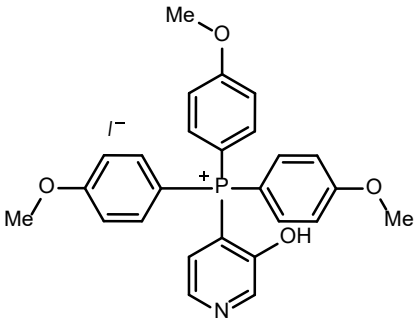
Prepared according to general procedure A using 4-iodo-3-(trifluoromethyl)pyridine (27 mg, 0.10 mmol), tris(4-methoxyphenyl)phosphane (35 mg, 0.10 mmol), and chloroform (0.2 mL) at room temperature for 37 hours. After purification procedure, the title compound was isolated as a yellow solid (53 mg, 0.09 mmol, 85% yield). mp 93-96 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.26 (m, 2H), 7.72 – 7.56 (m, 7H), 7.26 (m, 6H), 3.97 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 165.41 (d, *J*=3.0), 156.20 (d, *J*=9.5), 150.29, 150.21 (d, *J*=5.2), 136.67 (d, *J*=12.3), 131.24 (d, *J*=8.9), 122.51 (qd, *J*=273.2, 2.7), 116.80 (d, *J*=14.6), 106.96 (d, *J*=99.9), 56.4; ^{19}F NMR (365 MHz, $CDCl_3$) δ: –54.14 (d, J=2.1); ^{31}P NMR (162 MHz, $CDCl_3$) δ: 25.27; *m/z* LRMS (ESI + APCI) found $[M\text{-}I]^+$ 498.2, $C_{27}H_{24}F_3NO_3P^+$ requires 498.1.

(3-Aminopyridin-4-yl)tris(4-methoxyphenyl)phosphonium iodide (1d)



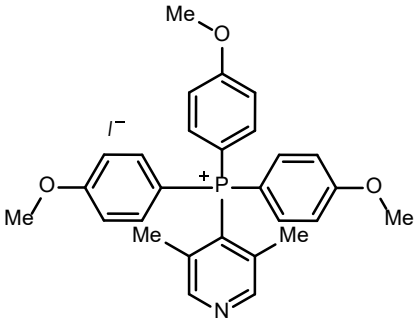
Prepared according to general procedure A using 4-iodopyridin-3-amine (66 mg, 0.30 mmol), tris(4-methoxyphenyl)phosphane (106 mg, 0.30 mmol), and chloroform (0.6 mL) at 50 ºC for 19 hours. After purification procedure, the title compound was isolated as a dark red crystalline solid (163 mg, 0.29 mmol, 95% yield). mp 148-151 ºC; IR ν_{max}/cm^{-1} (film): 3048, 3001, 2961, 1576, 1555, 1443, 1433, 1094, 796, 754, 698; ^{1}H NMR (400 MHz, CD_3CN) δ: 8.46 (d, *J*=7.3, 1H), 7.99 (dd, *J*=5.3, 3.4, 1H), 7.74 – 7.48 (m, 6H), 7.24 (dd, *J*=9.0, 2.7, 6H), 6.76 (dd, *J*=15.4, 5.4, 1H), 4.85 (s, 2H), 3.92 (s, 9H).; ^{13}C NMR (100 MHz, CD_3CN) δ: 166.18 (d, *J*=2.9), 147.39 (d, *J*=3.5), 141.32 (d, *J*=5.9), 138.31 (d, *J*=10.8), 137.39 (d, *J*=12.4), 134.47 (d, *J*=11.1), 128.00 (d, *J*=8.6), 117.20 (d, *J*=14.2), 107.65 (d, *J*=98.0), 56.8; ^{31}P NMR (162 MHz, $CDCl_3$) δ: 17.57; *m/z* LRMS (ESI + APCI) found $[M\text{-}I]^+$ 445.3, $C_{26}H_{26}N_2O_3P^+$ requires 445.2.

(3-Hydroxypyridin-4-yl)tris(4-methoxyphenyl)phosphonium iodide (1e)



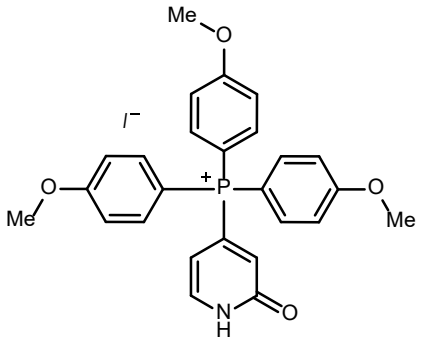
Prepared according to general procedure A using 4-iodopyridin-3-ol (66 mg, 0.30 mmol), tris(4-methoxyphenyl)phosphane (106 mg, 0.30 mmol), and chloroform (0.6 mL) at 50 ºC for 19 hours. After purification procedure, the title compound was isolated as a yellow solid (169 mg, 0.29 mmol, 99% yield). mp 123 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.79 (d, *J*=6.5, 1H), 8.09 (dd, *J*=5.2, 3.7, 1H), 7.50 (dd, *J*=12.7, 8.9, 6H), 7.15 (dd, *J*=9.0, 2.7, 6H), 6.90 (dd, *J*=14.6, 5.2, 1H), 3.91 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 164.81 (d, *J*=2.9), 159.17, 140.97, 136.05 (d, *J*=12.4), 133.87 (d, *J*=11.8), 127.72 (d, *J*=8.0), 116.24 (d, *J*=14.5), 114.31 (d, *J*=13.5), 108.13 (d, *J*=100.0), 56.2; ^{31}P NMR (162 MHz, $CDCl_3$) δ: 19.74; *m/z* LRMS (ESI + APCI) found $[M\text{-}I]^+$ 446.2, $C_{26}H_{25}NO_4P^+$ requires 446.2

(3,5-Dimethylpyridin-4-yl)tris(4-methoxyphenyl)phosphonium iodide (1f)



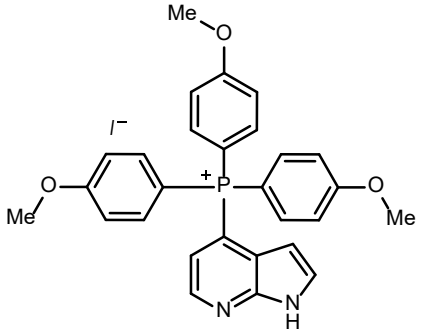
Prepared according to general procedure A using 4-iodo-3,5-dimethylpyridine (70 mg, 0.30 mmol), tris(4-methoxyphenyl)phosphane (106 mg, 0.30 mmol), and chloroform (0.6 mL) at 80 ºC for 19 hours. After purification procedure, the title compound was isolated as a red crystalline solid (175 mg, 0.3 mmol, 99% yield). mp 122-124 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.50 (d, *J*=6.0, 2H), 7.68 – 7.55 (m, 6H), 7.28 – 7.23 (m, 7H), 3.94 (s, 9H), 1.83 (d, *J*=1.1, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 165.16 (d, *J*=3.0), 152.49 (d, *J*=8.5), 137.55 (d, *J*=7.6), 136.14 (d, *J*=12.2), 126.41 (d, *J*=81.8), 117.09 (d, *J*=14.2), 109.34 (d, *J*=95.7), 56.51, 21.08 (d, *J*=5.2); ^{31}P NMR (162 MHz, $CDCl_3$) δ: 15.33; *m/z* LRMS (ESI + APCI) found $[M\text{-}I]^+$ 458.3, $C_{28}H_{29}NO_3P^+$ requires 458.2.

Tris(4-methoxyphenyl)(2-oxo-1,2-dihydropyridin-4-yl)phosphonium iodide (1g)



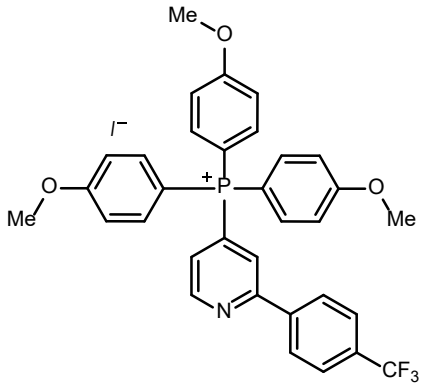
Prepared according to general procedure A using 4-iodopyridin-2-ol (66 mg, 0.30 mmol), tris(4-methoxyphenyl)phosphane (106 mg, 0.30 mmol), and chloroform (0.6 mL) at 50 ºC for 19 hours. After purification procedure, the title compound was isolated as a brown solid (160 mg, 0.29 mmol, 98% yield). mp 78-80 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.13 (s, 1H), 7.54 (dd, *J*=12.5, 8.5, 6H), 7.25 – 7.18 (m, 6H), 7.13 (d, *J*=6.7, 1H), 7.08 (d, *J*=1.6, 1H), 6.67 – 6.55 (m, 2H), 6.30 (s, 1H), 3.95 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 165.53 (d, *J*=2.9), 139.50 (d, *J*=14.1), 136.44 (d, *J*=12.0), 135.43 (d, *J*=79.6), 134.30, 129.62 (d, *J*=8.1), 116.87 (d, *J*=14.2), 105.81 (d, *J*=10.3), 105.80, 56.4; ^{31}P NMR (162 MHz, $CDCl_3$) δ: 20.74; *m/z* LRMS (ESI + APCI) found $[M\text{-}I]^+$ 446.2, $C_{26}H_{25}NO_4P^+$ requires 446.2.

Tris(4-methoxyphenyl)(1H-pyrrolo[2,3-b]pyridin-4-yl)phosphonium iodide (1h)



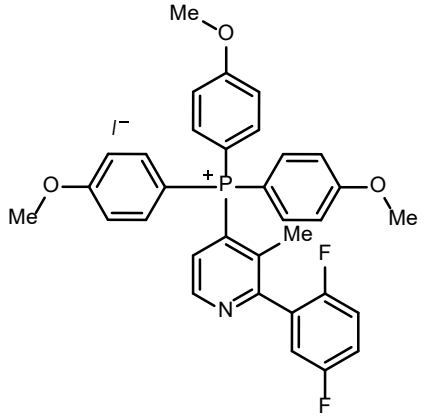
Prepared according to general procedure A using 4-iodo-1H-pyrrolo[2,3-b]pyridine (73 mg, 0.30 mmol), tris(4-methoxyphenyl)phosphane (106 mg, 0.30 mmol), and chloroform (0.6 mL) at 50 ºC for 19 hours. After purification procedure, the title compound was isolated as a yellow solid (156 mg, 0.26 mmol, 87% yield). mp 131 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 11.66 (s, 1H), 8.55 (t, *J*=4.7, 1H), 7.85 (t, *J*=2.9, 1H), 7.50 (dd, *J*=12.5, 8.9, 6H), 7.18 (dd, *J*=9.0, 2.7, 6H), 6.98 (dd, *J*=14.8, 4.9, 1H), 5.63 (d, *J*=3.5, 1H), 3.92 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 165.15 (d, *J*=2.9), 148.35 (d, *J*=11.6), 142.84 (d, *J*=11.4), 136.20 (d, *J*=12.1), 131.61, 121.71 (d, *J*=8.8), 120.82 (d, *J*=9.1), 118.42 (d, *J*=88.1), 116.60 (d, *J*=14.2), 107.66 (d, *J*=98.1), 100.09 (d, *J*=3.0), 56.37; ^{31}P NMR (162 MHz, $CDCl_3$) δ: 18.33; *m/z* LRMS (ESI + APCI) found $[M\text{-}I]^+$ 469.3, $C_{28}H_{26}N_2O_3P^+$ requires 469.2.

Tris(4-methoxyphenyl)(2-(4-(trifluoromethyl)phenyl)pyridin-4-yl)phosphonium iodide (1i)



Prepared according to general procedure A using 4-iodo-2-(4-(trifluoromethyl)phenyl)pyridine (35 mg, 0.10 mmol), tris(4-methoxyphenyl)phosphane (35 mg, 0.10 mmol), and chloroform (0.2 mL) at 50 ºC for 18 hours. After purification procedure, the title compound was isolated as a yellow amorphous solid (62 mg, 0.09 mmol, 89% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.08 (td, *J*=5.0, 0.9, 1H), 8.10 – 8.04 (m, 2H), 7.83 (ddd, *J*=13.6, 1.6, 0.9, 1H), 7.74 – 7.66 (m, 2H), 7.58 (dd, *J*=12.4, 8.9, 7H), 7.29 (dd, *J*=9.0, 2.8, 6H), 3.95 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 165.52 (d, *J*=2.9), 157.68 (d, *J*=10.2), 151.84 (d, *J*=10.6), 140.44, 136.50 (d, *J*=12.1), 132.10 (d, *J*=85.2), 131.95 (d, *J*=32.7), 127.86, 126.23 (d, *J*=8.1), 126.09 (q, *J*=3.8), 123.90 (q, *J*=272.5), 123.52 (d, *J*=8.8), 117.04 (d, *J*=14.2), 106.13 (d, *J*=98.6), 56.52; ^{19}F NMR (365 MHz, $CDCl_3$) δ: –62.76; ^{31}P NMR (162 MHz, $CDCl_3$) δ: 20.80; *m/z* LRMS (ESI + APCI) found $[M-I]^+$ 574.3, $C_{33}H_{28}F_3NO_3P^+$ requires 574.2.

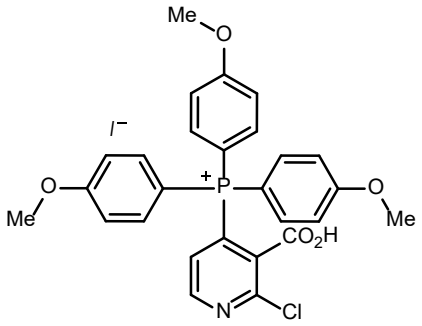
(2-(2,5-Difluorophenyl)-3-methylpyridin-4-yl)tris(4-methoxyphenyl)phosphonium iodide (1j)



Prepared according to general procedure A using 2-(2,5-difluorophenyl)-4-iodo-3-methylpyridine (99 mg, 0.30 mmol), tris(4-methoxyphenyl)phosphane (106 mg, 0.30 mmol), and chloroform (0.6 mL) at 50 ºC for 21 hours. After purification procedure, the title compound was isolated as a white solid (171 mg, 0.25 mmol, 83% yield). mp 112 ºC; ^{1}H NMR (400 MHz, $CDCl_3$)

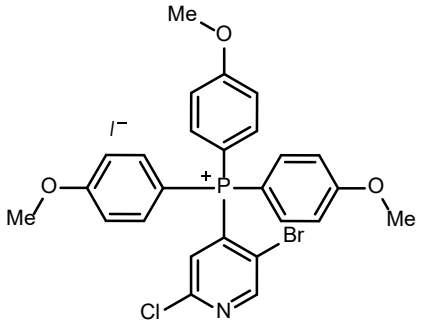
δ: 8.82 (t, *J*=4.5, 1H), 7.59 (dd, *J*=12.5, 8.9, 6H), 7.40 – 7.25 (m, 7H), 7.21 – 7.03 (m, 3H), 3.94 (s, 9H), 1.91 (s, 3zH); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 165.30 (d, *J*=3.0), 158.86 (dd, *J*=244.9, 2.2), 156.54 (d, *J*=2.4), 156.60 – 156.33 (m), 154.13 (d, *J*=2.6), 148.96 (d, *J*=11.6), 136.14 (d, *J*=12.1), 130.02 (d, *J*=84.0), 128.48 (d, *J*=10.5), 127.95 (ddd, *J*=18.4, 8.0, 2.4), 118.25 – 117.76 (m), 117.88 (d, *J*=24.1), 117.14 (d, *J*=14.2), 116.90 (d, *J*=8.6), 106.84 (d, *J*=97.9), 56.52, 19.93; ^{19}F NMR (365 MHz, $CDCl_3$) δ: −116.86 – −117.90 (m), −120.61 – −122.10 (m); ^{31}P NMR (162 MHz, $CDCl_3$) δ: 20.32; *m/z* LRMS (ESI + APCI) found $[M\text{-}I]^+$ 556.3, $C_{33}H_{29}F_2NO_3P^+$ requires 556.2.

(3-Carboxy-2-chloropyridin-4-yl)tris(4-methoxyphenyl)phosphonium iodide (1k)



Prepared according to general procedure A using 2-chloro-4-iodonicotinic acid (85 mg, 0.30 mmol), tris(4-methoxyphenyl)phosphane (106 mg, 0.30 mmol), and chloroform (0.6 mL) at 50 ºC for 19 hours. After purification procedure, the title compound was isolated as a yellow solid (136 mg, 0.27 mmol, 89% yield). mp 95-98 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.61 – 8.57 (m, 1H), 7.58 (dd, *J*=12.5, 9.0, 6H), 7.25 – 7.21 (m, 1H), 7.15 (dd, *J*=9.0, 2.9, 6H), 3.91 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 165.05 (d, *J*=3.7), 164.88 (d, *J*=3.0), 162.59 (d, *J*=2.8), 151.07 (d, *J*=12.5), 149.73 (d, *J*=11.9), 136.88 (d, *J*=12.1), 130.92 (d, *J*=86.4), 126.90 (d, *J*=9.9), 116.08 (d, *J*=14.5), 108.06 (d, *J*=100.0), 56.21; ^{31}P NMR (162 MHz, $CDCl_3$) δ: 22.97; *m/z* LRMS (ESI + APCI) found $[M\text{-}I]^+$ 508.2, $C_{27}H_{24}ClNO_5P^+$ requires 508.1.

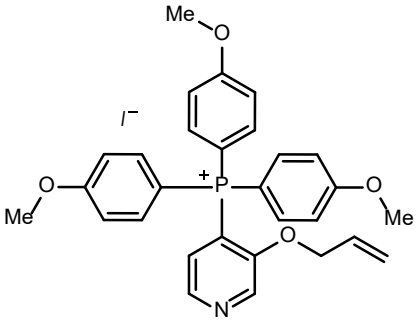
(5-Bromo-2-chloropyridin-4-yl)tris(4-methoxyphenyl)phosphonium iodide (1l)



Prepared according to general procedure A using 5-bromo-2-chloro-4-iodopyridine (96 mg, 0.30 mmol), tris(4-methoxyphenyl)phosphane (106 mg, 0.30 mmol), and chloroform (0.6 mL) at 80 ºC for 19 hours. After purification procedure, the title compound was isolated as a golden

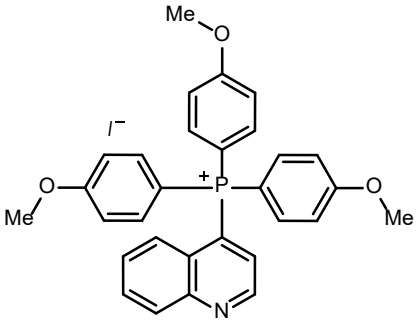
yellow solid (201 mg, 0.3 mmol, 99% yield). mp 111-114 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.75 (d, *J*=5.7, 1H), 7.61 (dd, *J*=12.8, 8.9, 6H), 7.30 – 7.24 (m, 6H), 7.12 (d, *J*=14.1, 1H), 3.95 (s, 10H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 165.56 (d, *J*=3.0), 154.76 (d, *J*=6.7), 152.76 (d, *J*=13.7), 136.61 (d, *J*=12.4), 134.49 (d, *J*=87.9), 131.87 (d, *J*=10.5), 123.00 (d, *J*=3.5), 117.16 (d, *J*=14.5), 105.14 (d, *J*=100.1), 56.5: ^{31}P NMR (162 MHz, $CDCl_3$) δ: 23.14; *m/z* LRMS (ESI + APCI) found $[M-I]^+$ 542.1, $C_{26}H_{23}BrClNO_3P^+$ requires 542.0.

Tris(4-methoxyphenyl)(2-oxo-1,2-dihydropyridin-4-yl)phosphonium iodide (1m)



Prepared according to general procedure A using 3-(allyloxy)-4-iodopyridine (78 mg, 0.30 mmol), tris(4-methoxyphenyl)phosphane (106 mg, 0.30 mmol), and chloroform (0.6 mL) at room temperature for 36 hours. After purification procedure, the title compound was isolated as a yellow solid (160 mg, 0.30 mmol, 99% yield). mp 71 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.66 (d, *J*=6.5, 1H), 8.53 (dd, *J*=4.9, 3.6, 1H), 7.54 (dd, *J*=12.8, 8.9, 6H), 7.26 – 7.16 (m, 6H), 7.08 (dd, *J*=14.8, 4.9, 1H), 5.40 (ddd, *J*=16.2, 10.7, 5.4, 1H), 5.09 (dd, *J*=10.5, 1.2, 1H), 5.00 (dd, *J*=17.2, 1.4, 1H), 4.59 (d, *J*=5.5, 2H), 3.96 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 165.02 (d, *J*=3.0), 154.93, 143.88 (d, *J*=11.0), 137.18 (d, *J*=4.5), 135.95 (d, *J*=12.5), 130.09, 128.12 (d, *J*=7.2), 119.85, 117.55 (d, *J*=87.3), 116.54 (d, *J*=14.5), 107.11 (d, *J*=100.3), 70.98, 56.4; ^{31}P NMR (162 MHz, $CDCl_3$) δ: 19.64; *m/z* LRMS (ESI + APCI) found $[M-I]^+$ 486.3, $C_{29}H_{29}NO_4P^+$ requires 486.2.

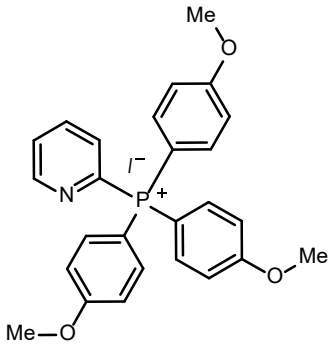
Tris(4-methoxyphenyl)(quinolin-4-yl)phosphonium iodide (1n)



Prepared according to general procedure A using 4-iodoquinoline (78 mg, 0.30 mmol), tris(4-methoxyphenyl)phosphane (106 mg, 0.30 mmol), and chloroform (0.6 mL) at room temperature for 39 hours. After purification procedure, the title compound was isolated as a yellow solid (147 mg, 0.24 mmol, 81% yield). mp 112-113 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.10 (t, *J*=4.1, 1H),

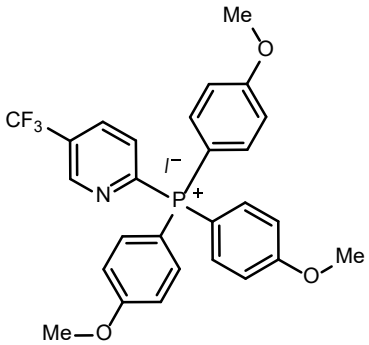
8.23 (d, *J*=8.2, 1H), 7.79 (t, *J*=7.7, 1H), 7.54 – 7.29 (m, 9H), 7.18 (dd, *J*=8.9, 2.6, 6H), 3.88 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 165.24 (d, *J*=3.0), 150.10 (d, *J*=12.2), 148.72 (d, *J*=6.9), 136.23 (d, *J*=12.3), 131.72 (d, *J*=2.3), 131.15, 130.11 (d, *J*=9.0), 129.31, 126.59 (d, *J*=74.2), 126.15 (d, *J*=2.7), 125.92 (d, *J*=6.4), 116.95 (d, *J*=14.3), 107.15 (d, *J*=98.0), 56.46; ^{31}P NMR (162 MHz, $CDCl_3$) δ: 19.60; *m/z* LRMS (ESI + APCI) found $[M-I]^+$ 480.2, $C_{30}H_{27}NO_3P^+$ requires 480.2.

Tris(4-methoxyphenyl)(pyridin-2-yl)phosphonium iodide (1o)



Prepared according to general procedure A using 2-iodopyridine (32 µL, 0.30 mmol), tris(4-methoxyphenyl)phosphane (106 mg, 0.30 mmol), and chloroform (0.6 mL) at 50 ºC for 19 hours. After purification procedure, the title compound was isolated as a yellow solid (114 mg, 0.20 mmol, 63% yield). mp 75-76 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.96 (dt, *J*=4.7, 1.4, 1H), 8.20 (tdd, *J*=7.9, 5.0, 1.7, 1H), 7.86 (ddt, *J*=7.6, 6.4, 1.2, 1H), 7.73 (dddd, *J*=7.8, 4.7, 2.8, 1.1, 1H), 7.58 (dd, *J*=12.3, 8.9, 6H), 7.21 (dd, *J*=9.0, 2.7, 6H), 3.95 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 165.21 (d, *J*=2.9), 152.29 (d, *J*=19.4), 147.10, 145.89, 138.90 (d, *J*=10.4), 136.70 (d, *J*=11.8), 131.73 (d, *J*=24.5), 128.13, 116.53 (d, *J*=14.0), 107.85 (d, *J*=97.7), 56.36; ^{31}P NMR (162 MHz, $CDCl_3$) δ: 13.80; *m/z* LRMS (ESI + APCI) found $[M-I]^+$ 430.2, $C_{26}H_{25}NO_3P^+$ requires 430.2.

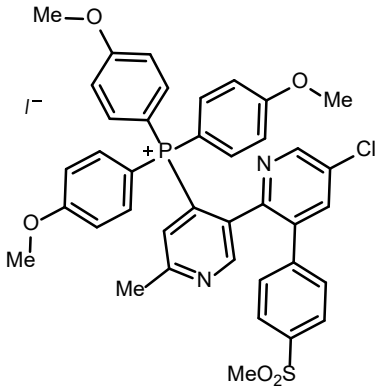
Tris(4-methoxyphenyl)(5-(trifluoromethyl)pyridin-2-yl)phosphonium iodide (1p)



Prepared according to general procedure A using 2-iodo-5-(trifluoromethyl)pyridine (82 mg, 0.30 mmol), tris(4-methoxyphenyl)phosphane (106 mg, 0.30 mmol), and chloroform (0.6 mL) at 80 ºC for 19 hours. After purification procedure, the title compound was isolated as a golden solid (174 mg, 0.28 mmol, 93% yield). mp 87 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.11 (s, 1H), 8.65 –

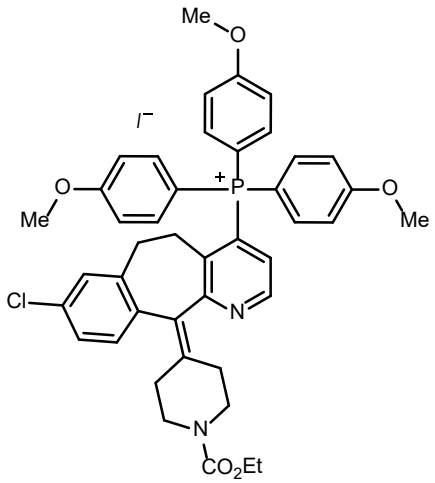
8.41 (m, 1H), 8.31 (dd, *J*=8.1, 5.9, 2H), 7.58 (dd, *J*=12.4, 8.9, 6H), 7.21 (dd, *J*=9.0, 2.8, 6H), 3.92 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 165.37 (d, *J*=3.0), 150.84 (d, *J*=118.7), 148.36 (dd, *J*=19.7, 3.8), 136.74 (d, *J*=12.0), 136.33 (dd, *J*=10.4, 3.6), 131.98 (d, *J*=24.6), 129.81 (d, *J*=31.0), 122.44 (qd, *J*=275.3, 1.7), 116.67 (d, *J*=14.2), 106.65 (d, *J*=98.3), 56.34; ^{19}F NMR (365 MHz, $CDCl_3$) δ: –62.82; ^{31}P NMR (162 MHz, $CDCl_3$) δ: 15.08; *m/z* LRMS (ESI + APCI) found $[M\text{-}I]^+$ 498.2, $C_{27}H_{24}F_3NO_3P^+$ requires 498.1.

(5-chloro-6'-methyl-3-(4-(methylsulfonyl)phenyl)-[2,3'-bipyridin]-4'-yl)tris(4-methoxyphenyl)phosphonium iodide (1q)



Prepared according to general procedure A using 5-chloro-4'-iodo-6'-methyl-3-(4-(methylsulfonyl)phenyl)-2,3'-bipyridine (48 mg, 0.10 mmol), tris(4-methoxyphenyl)phosphane (35 mg, 0.10 mmol), and chloroform (0.2 mL) at room temperature for 34 hours. After purification procedure, the title compound was isolated as a yellow solid (76 mg, 0.09 mmol, 92% yield). mp 180 ºC (decomposition); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.23 (d, *J*=6.9, 1H), 8.10 (d, *J*=8.4, 2H), 7.82 (d, *J*=2.3, 1H), 7.63 (dd, *J*=12.3, 9.0, 6H), 7.51 (d, *J*=2.3, 1H), 7.44 (d, *J*=8.5, 2H), 7.22 (d, *J*=16.1, 1H), 7.14 (dd, *J*=9.0, 2.8, 6H), 3.89 (s, 9H), 3.12 (s, 3H), 2.55 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 164.54 (d, *J*=3.0), 160.57 (d, *J*=10.9), 152.82 (d, *J*=7.3), 148.29 (d, *J*=2.7), 146.71, 141.56, 140.92, 138.61, 135.82, 133.76 (d, *J*=4.0), 132.12, 130.65, 130.30, 130.01 (d, *J*=43.3), 128.90, 116.01 (d, *J*=14.3), 109.34 (d, *J*=100.2), 56.36, 44.39, 25.00; ^{31}P NMR (162 MHz, $CDCl_3$) δ: 23.46; *m/z* LRMS (ESI + APCI) found $[M\text{-}I]^+$ 709.3, $C_{39}H_{35}ClN_2O_5PS^+$ requires 709.2.

(8-chloro-11-(1-(ethoxycarbonyl)piperidin-4-ylidene)-6,11-dihydro-5H-benzo[5,6]cyclohepta[1,2-b]pyridin-4-yl)tris(4-methoxyphenyl)phosphonium iodide (1r)

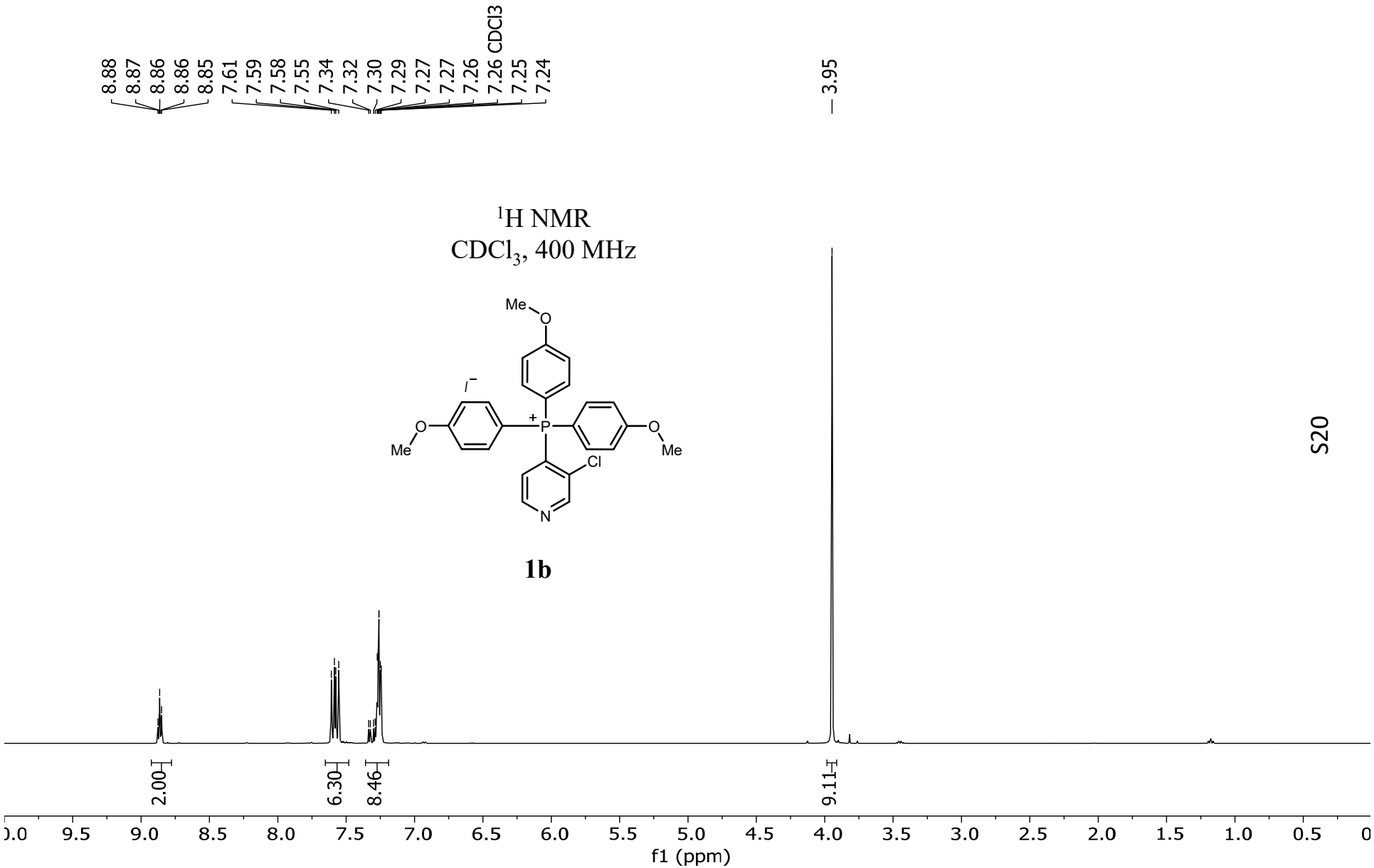


Prepared according to general procedure A using ethyl 4-(8-chloro-4-iodo-5,6-dihydro-11H-benzo[5,6]cyclohepta[1,2-b]pyridin-11-ylidene)piperidine-1-carboxylate (51 mg, 0.10 mmol), tris(4-methoxyphenyl)phosphane (35 mg, 0.10 mmol), and chloroform (0.2 mL) at 50 ºC for 19 hours. After purification procedure, the title compound was isolated as a yellow solid (83 mg, 0.1 mmol, 96% yield). mp 153 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.69 (dd, *J*=5.1, 4.2, 1H), 7.56 (dd, *J*=12.5, 8.9, 6H), 7.28 (dd, *J*=9.0, 2.8, 6H), 7.22 – 7.06 (m, 2H), 7.00 (dd, *J*=14.8, 5.1, 1H), 6.78 (d, *J*=2.0, 1H), 4.13 (q, *J*=7.1, 2H), 3.97 (s, 9H), 3.73 (ddd, *J*=22.4, 12.2, 5.8, 2H), 3.37 (ddd, *J*=12.7, 8.2, 4.1, 2H), 3.28 (ddd, *J*=14.8, 11.6, 5.7, 1H), 2.83 (dt, *J*=17.4, 5.2, 1H), 2.63 (dt, *J*=15.0, 4.8, 1H), 2.53 – 2.32 (m, 2H), 2.21 (s, 1H), 1.72 (ddd, *J*=17.2, 11.8, 5.3, 2H), 1.25 (t, *J*=7.1, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 165.34 (d, *J*=3.0), 163.60 (d, *J*=8.2), 155.55, 148.92 (d, *J*=11.4), 139.15, 137.23, 136.80 (d, *J*=6.5), 136.28 (d, *J*=12.0), 133.66, 132.73, 131.66, 130.01, 129.15 (d, *J*=83.0), 127.18 (d, *J*=10.3), 126.58, 117.12 (d, *J*=14.2), 107.04 (d, *J*=97.8), 61.57, 56.54, 44.82, 44.61, 31.01, 30.54, 29.88, 14.7; ^{31}P NMR (162 MHz, $CDCl_3$) δ: 19.39; *m/z* LRMS (ESI + APCI) found $[M-I]^+$ 733.3, $C_{43}H_{43}ClN_2O_5P^+$ requires 733.3.

6. References

1. D. D. Perrin, W. L. F. Amerego, Purification of Laboratory Chemicals (Pergamon, ed. 3, 1988).

7. ^{1}H, ^{13}C, ^{19}F and ^{31}P Spectra


8.88
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7.58
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7.34
7.32
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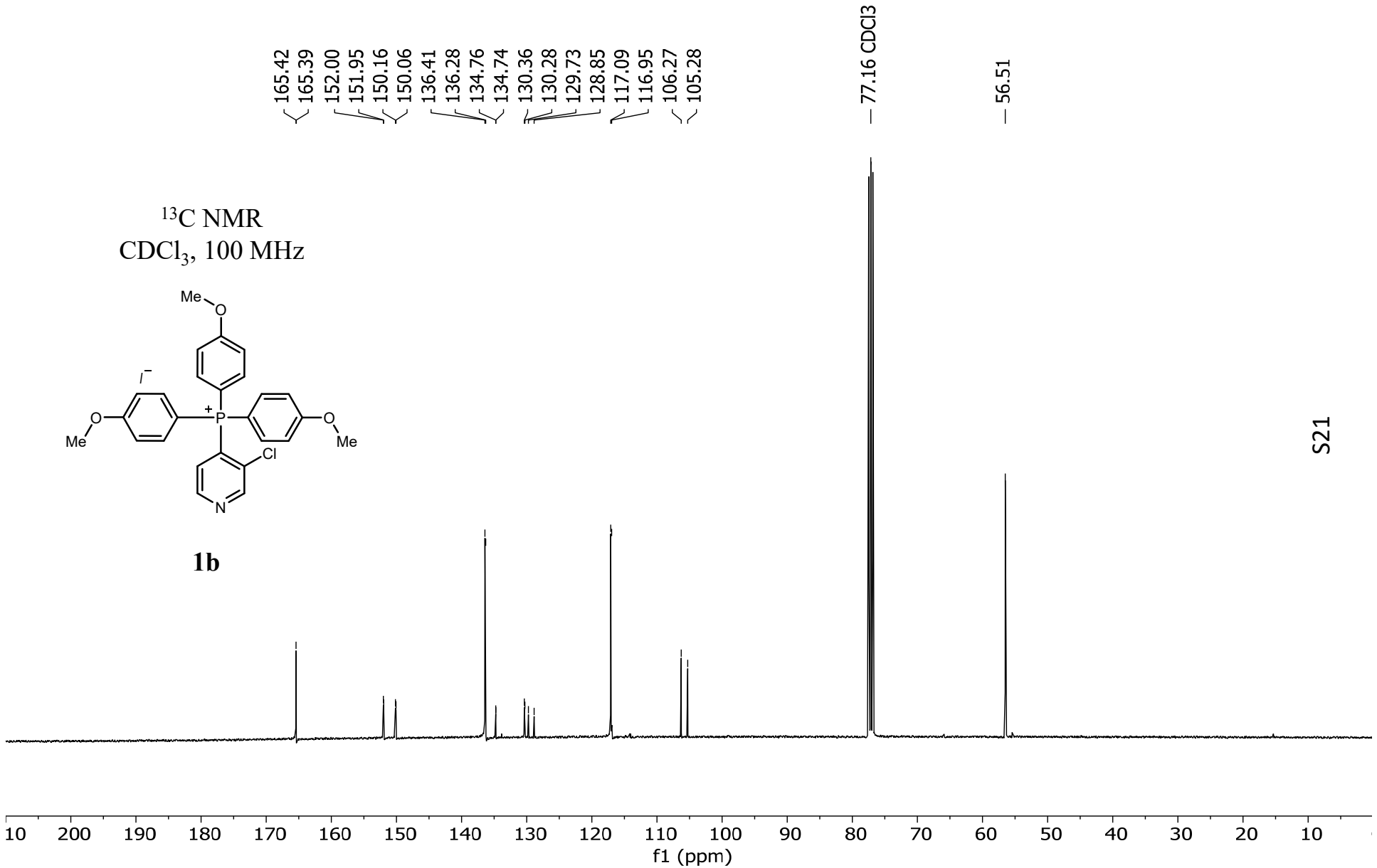
7.27
7.27
7.26
7.26 CDCl3
7.25
7.24
3.95
1H NMR
CDCl3, 400 MHz
Me
O
I−
O
Me
+
P
O
Me
Cl
N
1b
S20
2.00
6.30
8.46
9.11
f1 (ppm)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128.85
117.09
116.95
106.27
105.28
77.16 CDCl3
56.51
13C NMR
CDCl3, 100 MHz
Me
O
I−
+
P
O
Me
O
Me
Cl
N
1b
S21
10
200
190
180
170
160
150
140
130
120
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80
70
60
50
40
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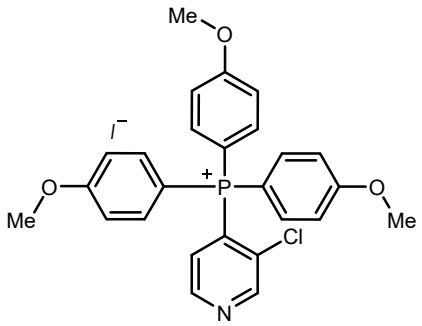
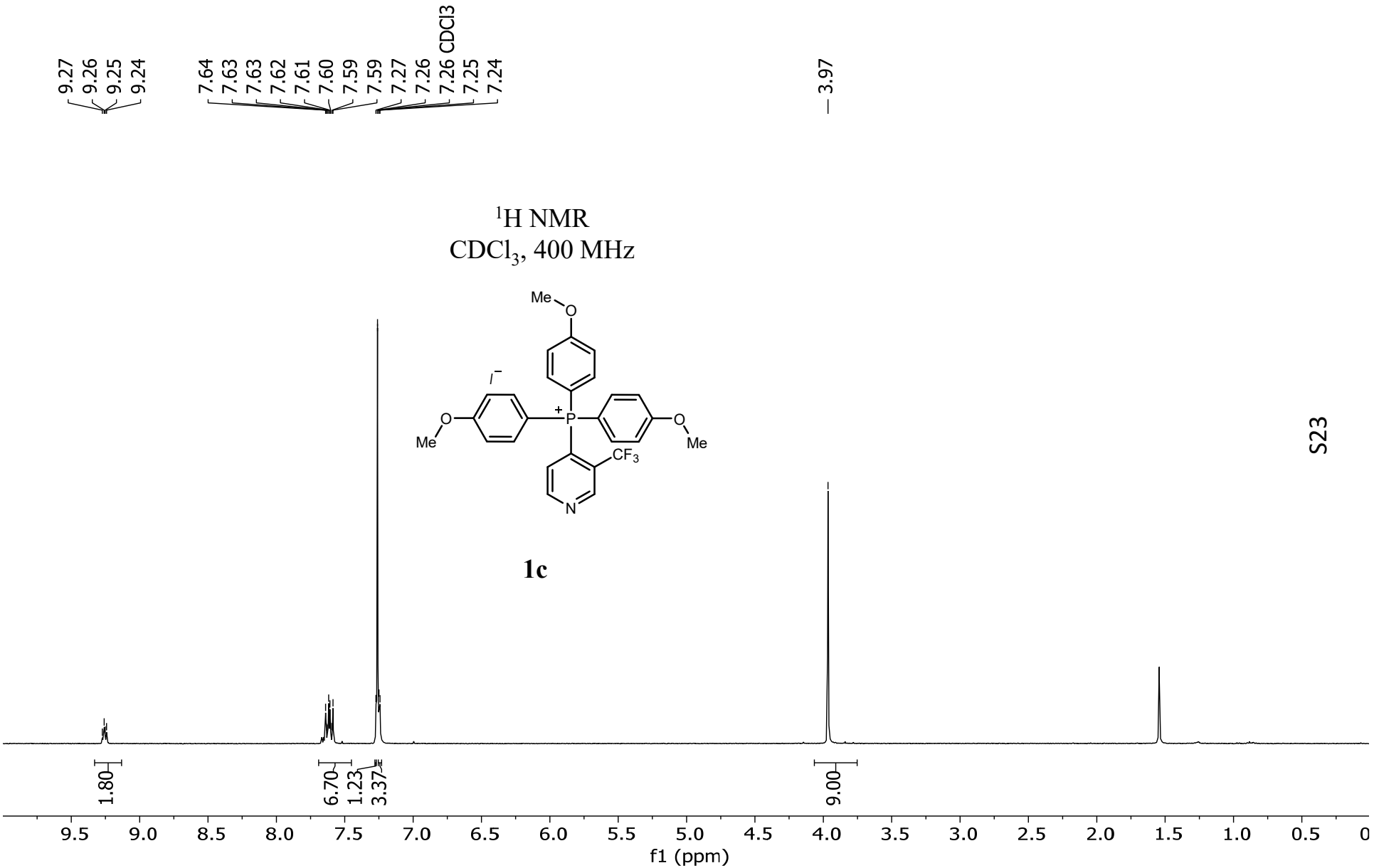
20
10
f1 (ppm)

^{31}P NMR
$CDCl_3$, 162 MHz



1b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7.59
7.27
7.26
7.26 CDCl3
7.25
7.24
3.97
1H NMR
CDCl3, 400 MHz
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O
I−
O
Me
P+
O
Me
CF3
N
1c
S23
1.80
6.70
1.23
3.37
9.00
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8.5
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6.0
5.5
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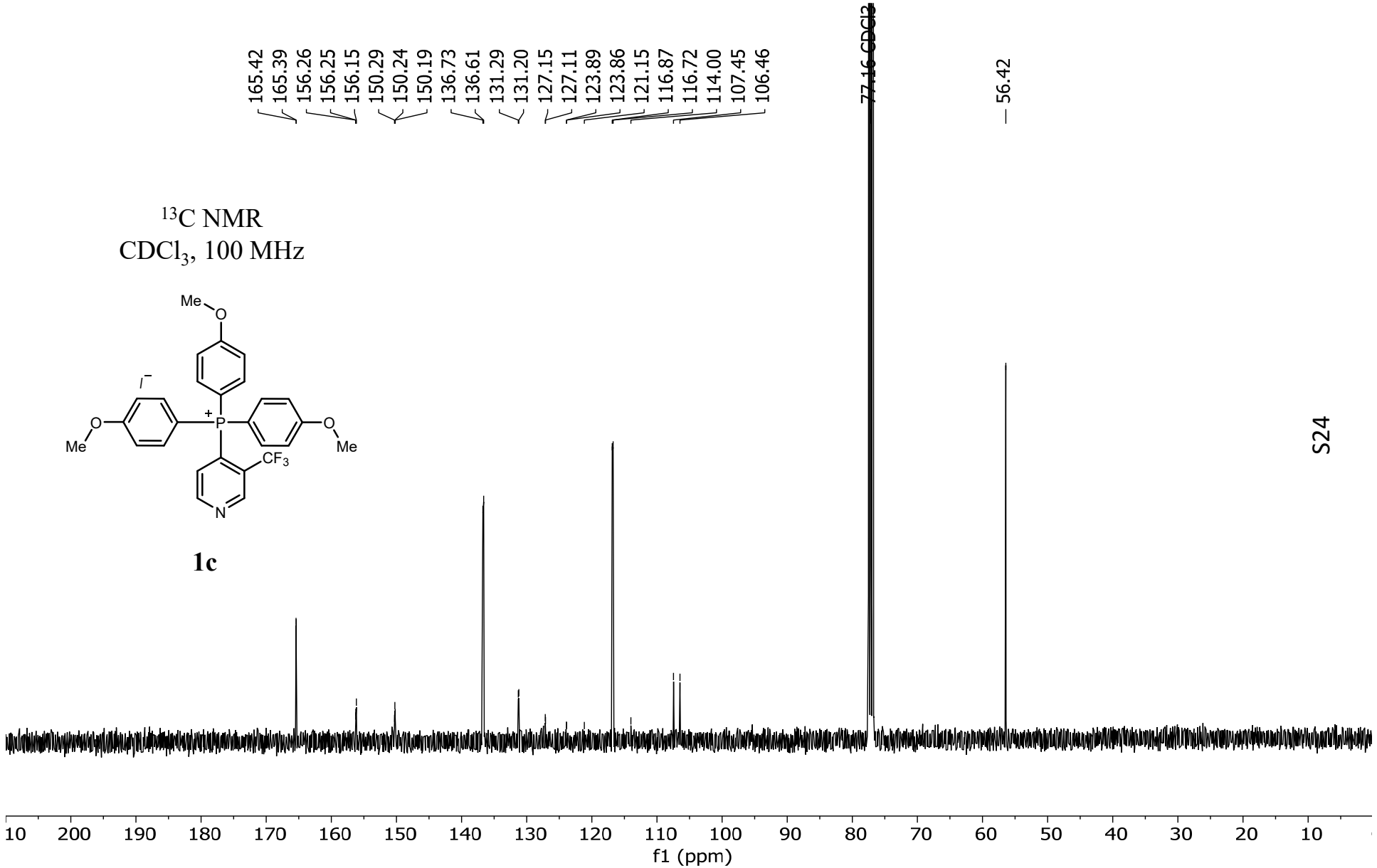
0
f1 (ppm)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127.11
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121.15
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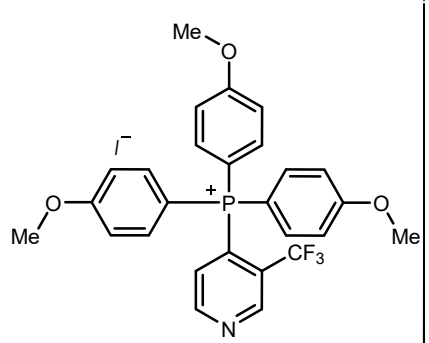
116.72
114.00
107.45
106.46
77.16 CDCl3
56.42
13C NMR
CDCl3, 100 MHz
Me
O
I−
+
P
O
Me
O
Me
CF3
N
1c
S24
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

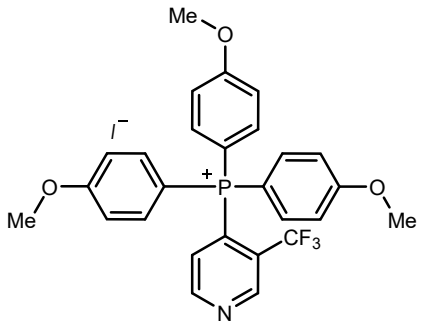
-54.14
-54.14

^{19}F NMR
CD_3CN, 365 MHz

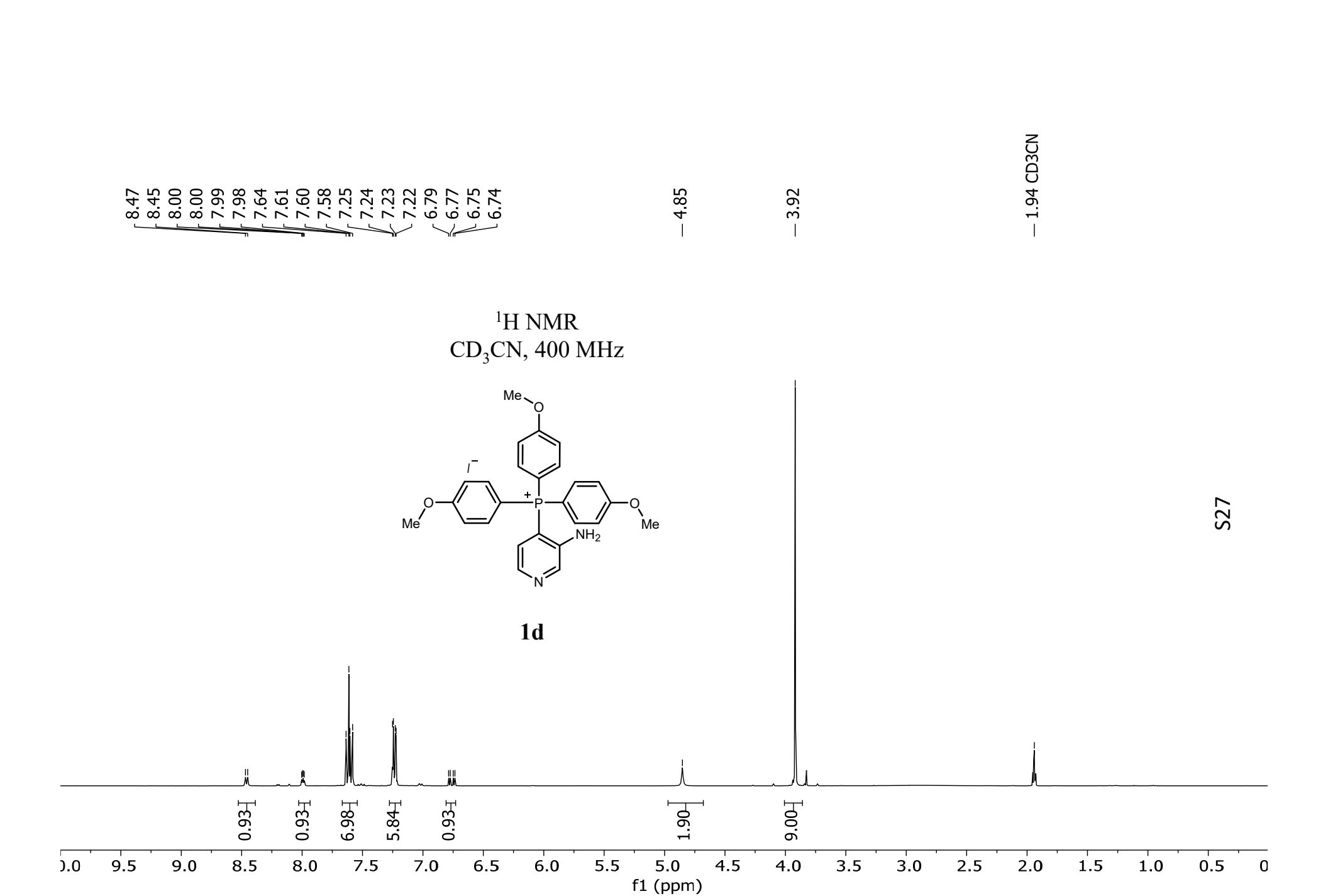


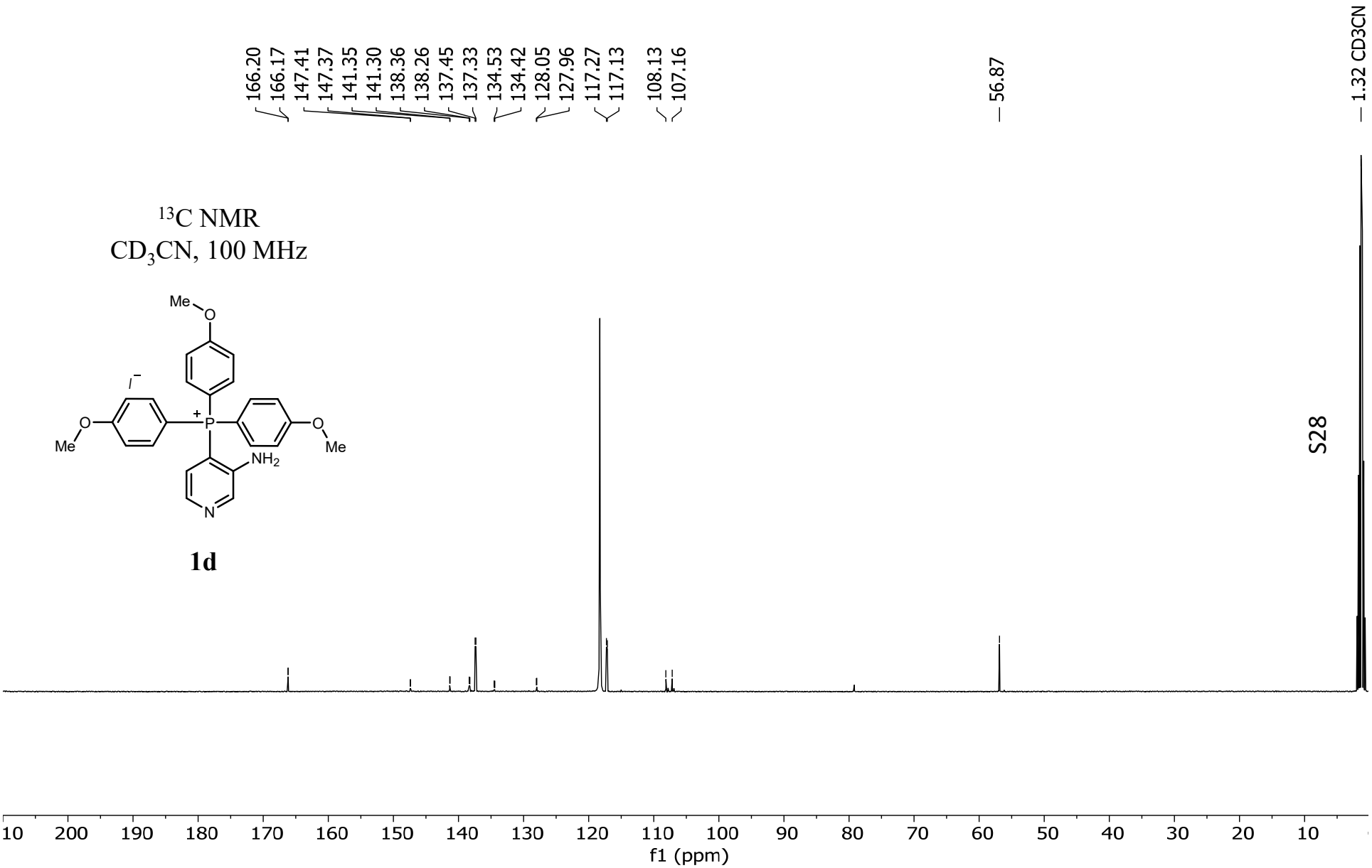
1c

^{31}P NMR
$CDCl_3$, 162 MHz

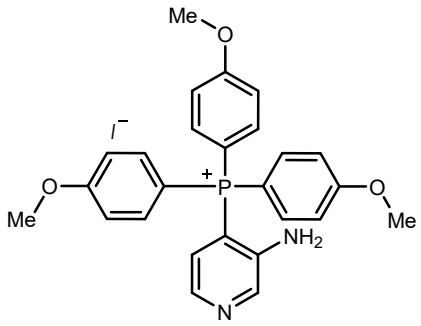


1c


8.47
8.45
8.00
8.00
7.99
7.98
7.64
7.61
7.60
7.58
7.25
7.24
7.23
7.22
6.79
6.77
6.75
6.74
4.85
3.92
1.94 CD3CN
^{1}H NMR
CD_3CN, 400 MHz
Me
O
I^-
O
Me
P
+
O
Me
NH_2
N
1d
S27
0.93
0.93
6.98
5.84
0.93
1.90
9.00
f1 (ppm)

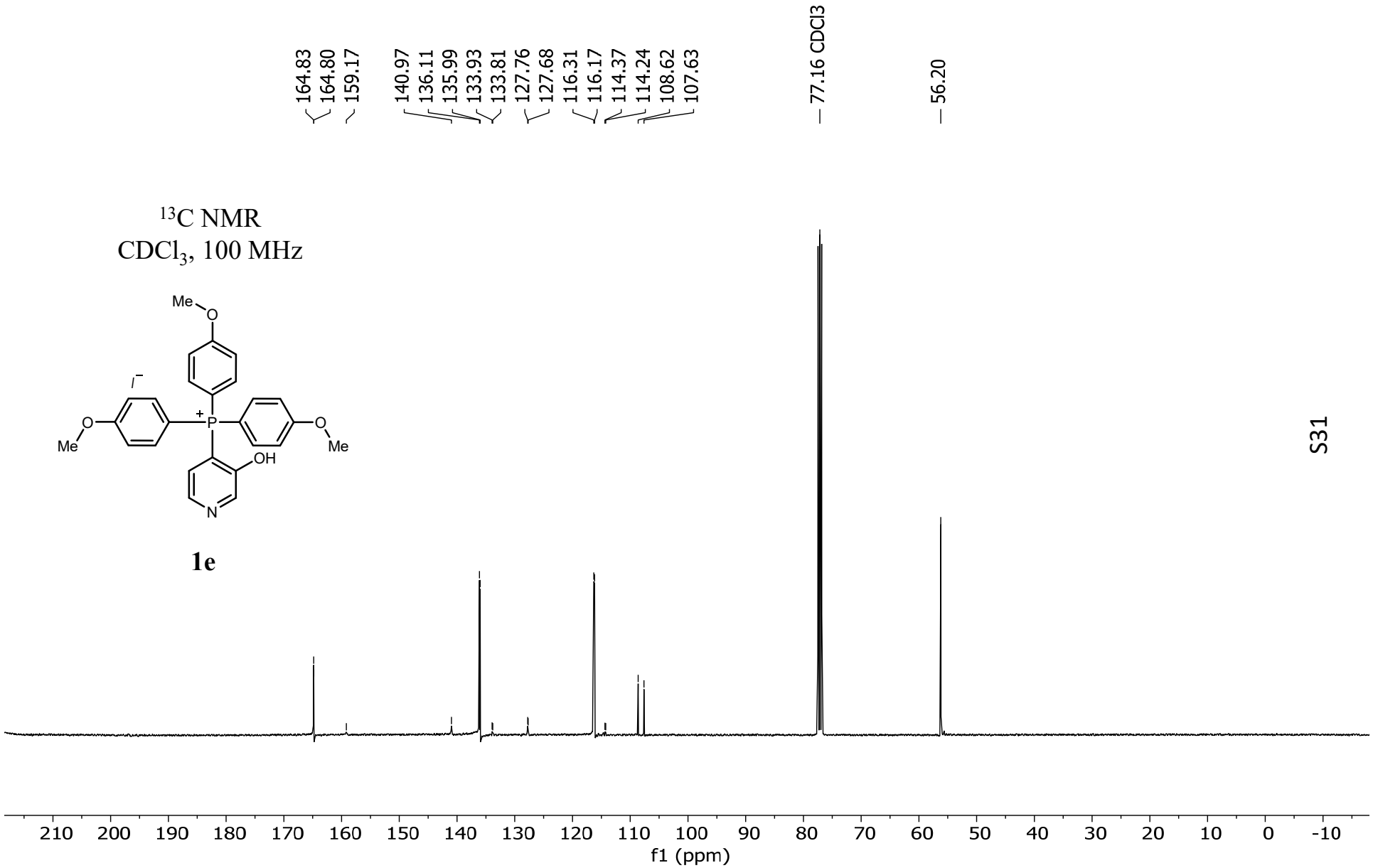

166.20
166.17
147.41
147.37
141.35
141.30
138.36
138.26
137.45
137.33
134.53
134.42
128.05
127.96
117.27
117.13
108.13
107.16
56.87
1.32 CD3CN
S28
13C NMR
CD3CN, 100 MHz
Me
O
I−
O
Me
+
P
O
Me
NH2
N
1d
f1 (ppm)

^{31}P NMR
$CDCl_3$, 162 MHz

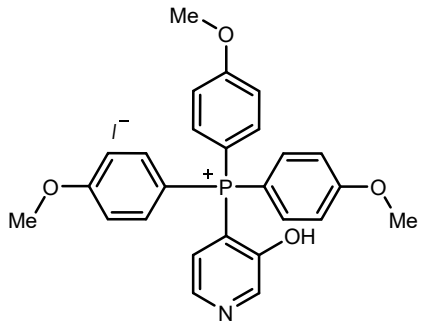


1d

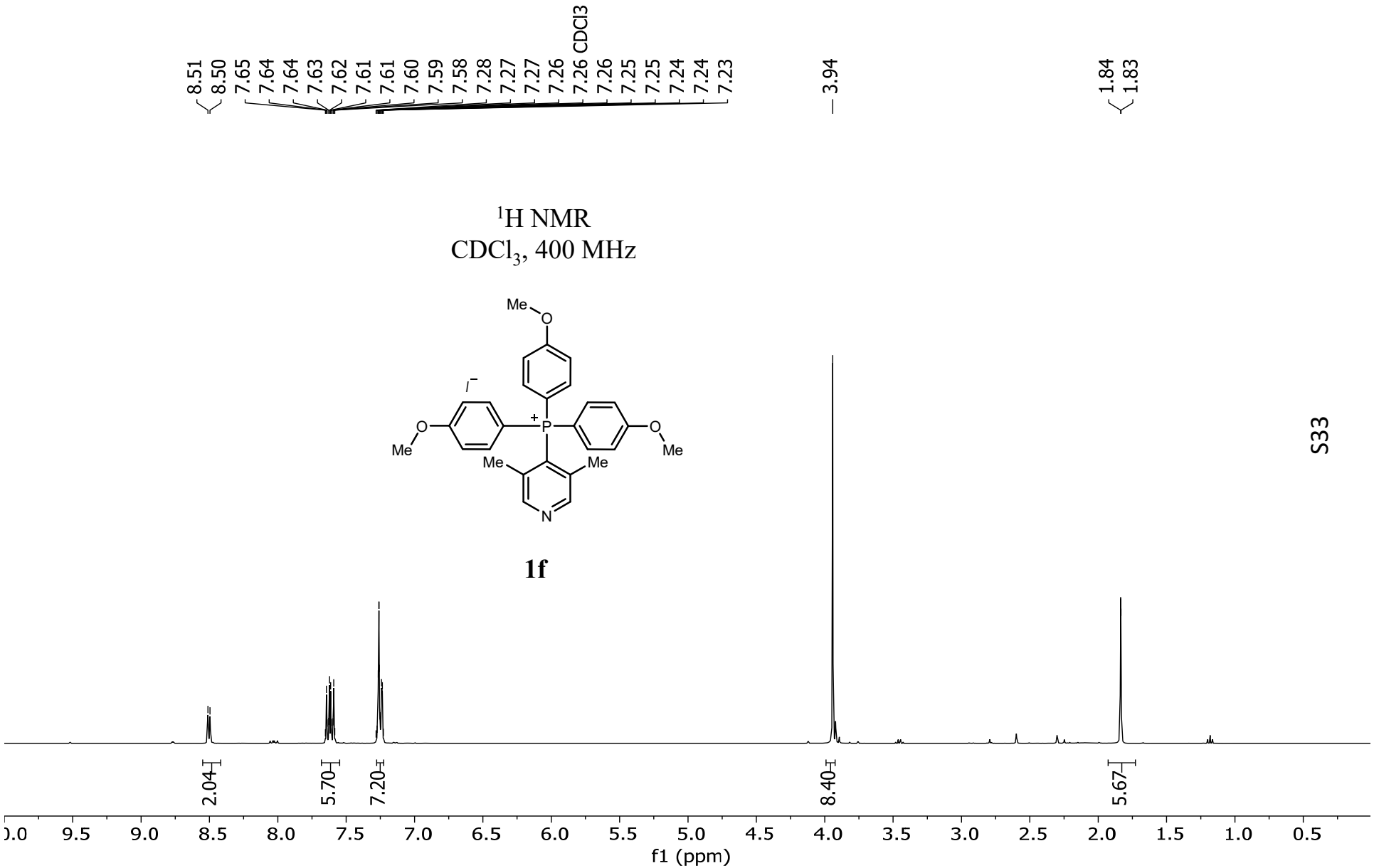
8.80
8.78
8.10
8.09
8.09
8.08
7.53
7.51
7.50
7.48
7.26 CDCl3
7.16
7.15
7.14
7.13
6.93
6.91
6.89
6.88
3.91
1H NMR
CDCl3, 400 MHz
Me
O
I−
O
Me
+
P
O
Me
OH
N
1e
S30
1.00
1.08
6.76
6.48
1.18
9.80
f1 (ppm)


164.83
164.80
159.17
140.97
136.11
135.99
133.93
133.81
127.76
127.68
116.31
116.17
114.37
114.24
108.62
107.63
77.16 CDCl3
56.20
13C NMR
CDCl3, 100 MHz
Me
O
I−
O
Me
P+
O
Me
OH
N
1e
S31
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)

^{31}P NMR
$CDCl_3$, 162 MHz

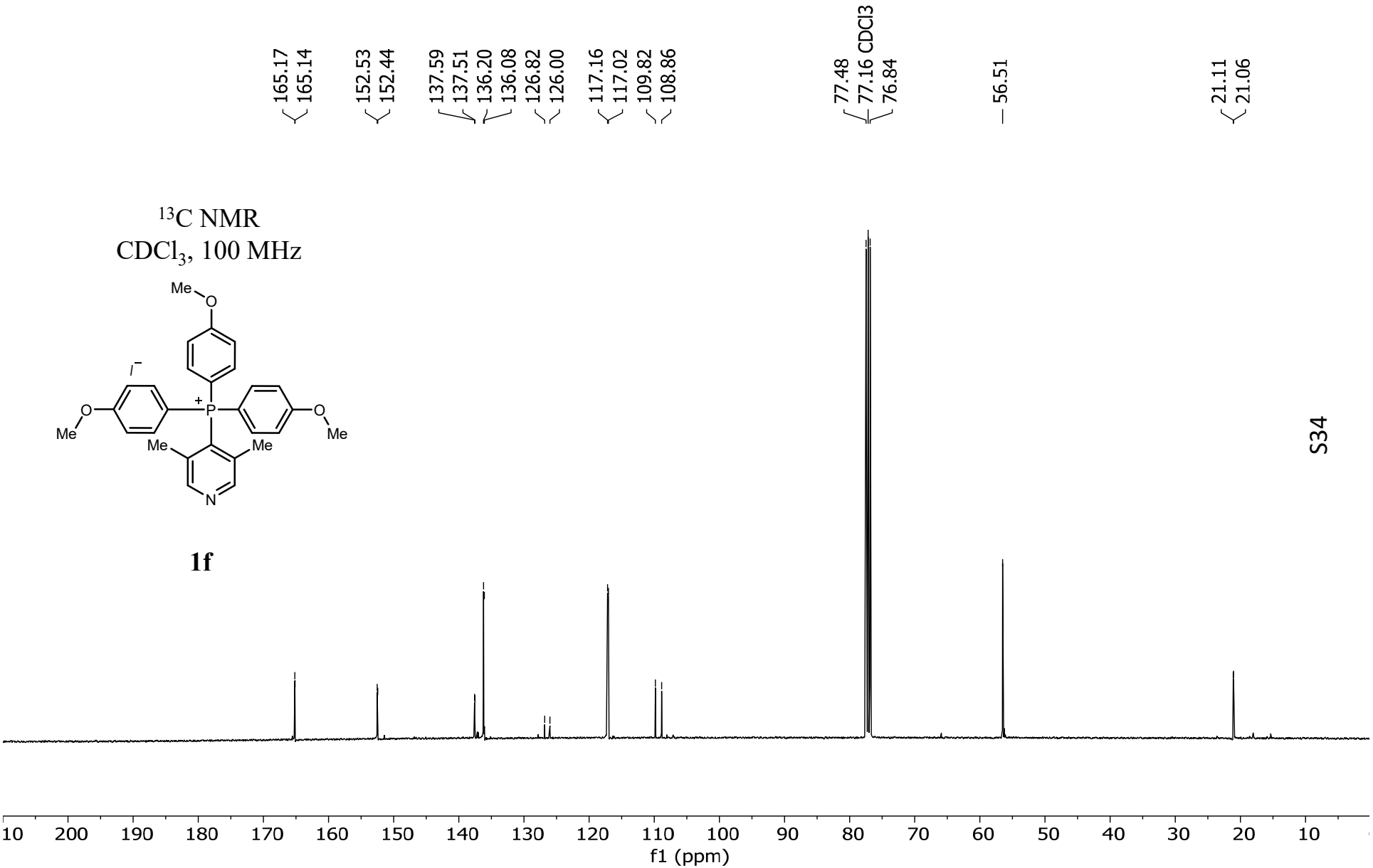


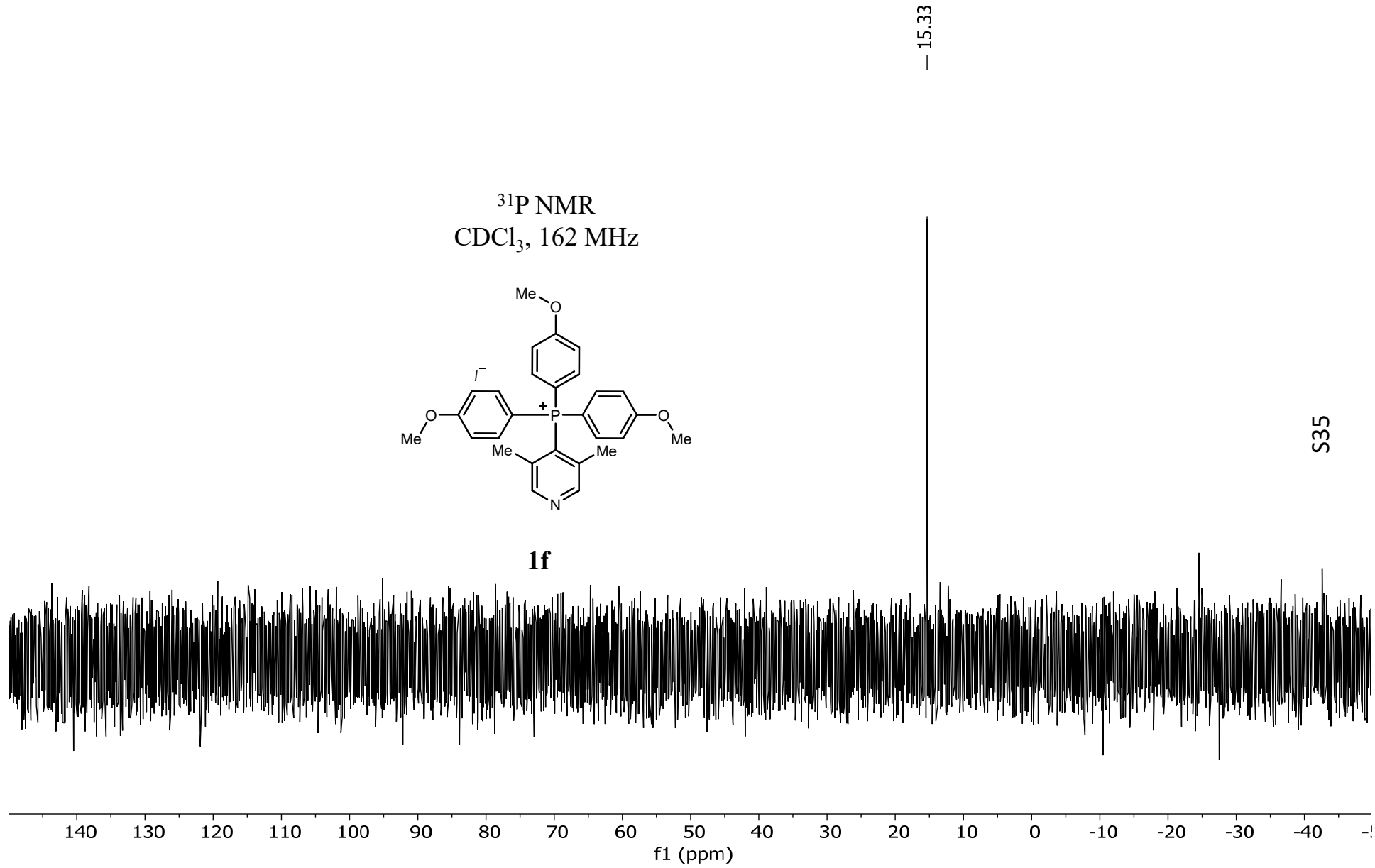
1e

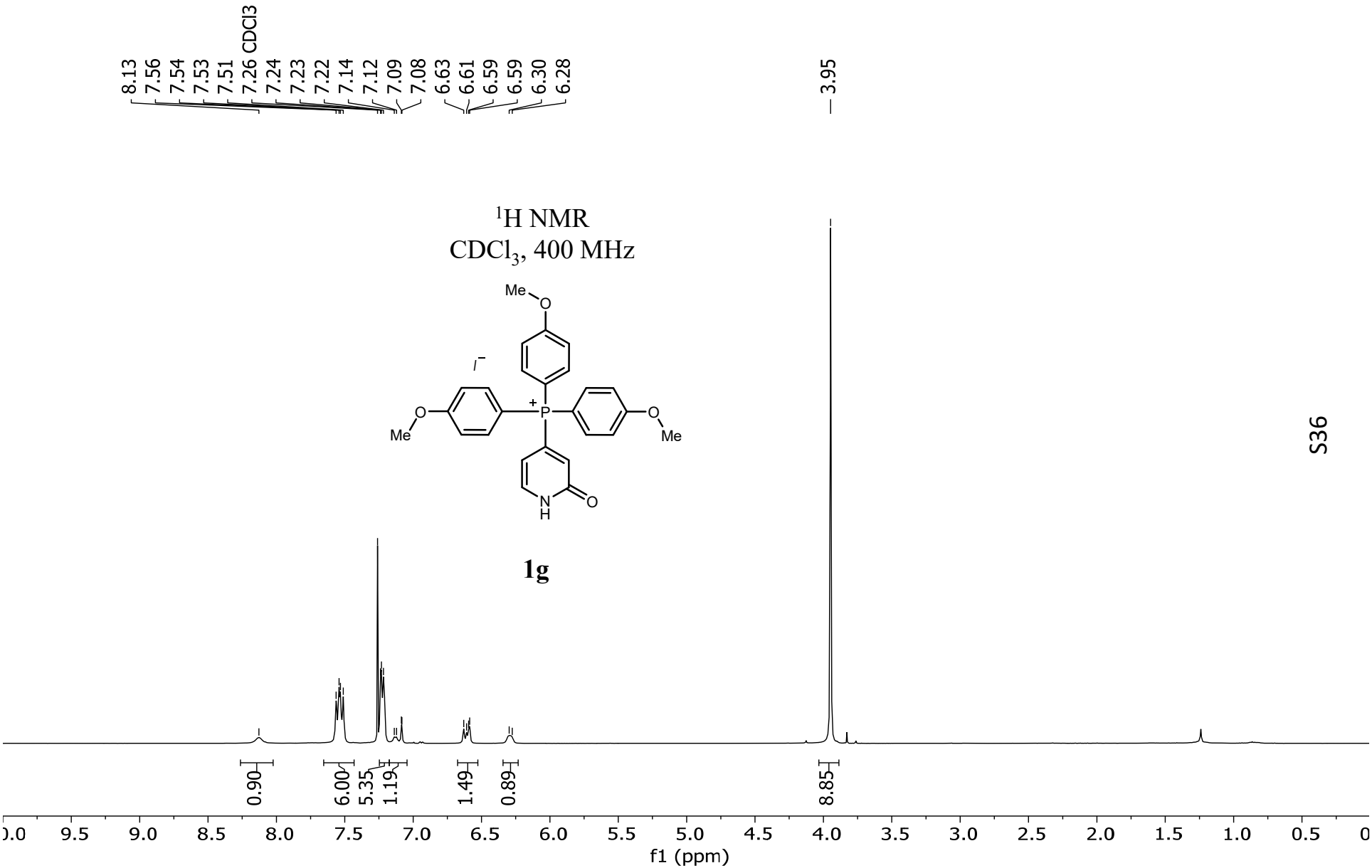


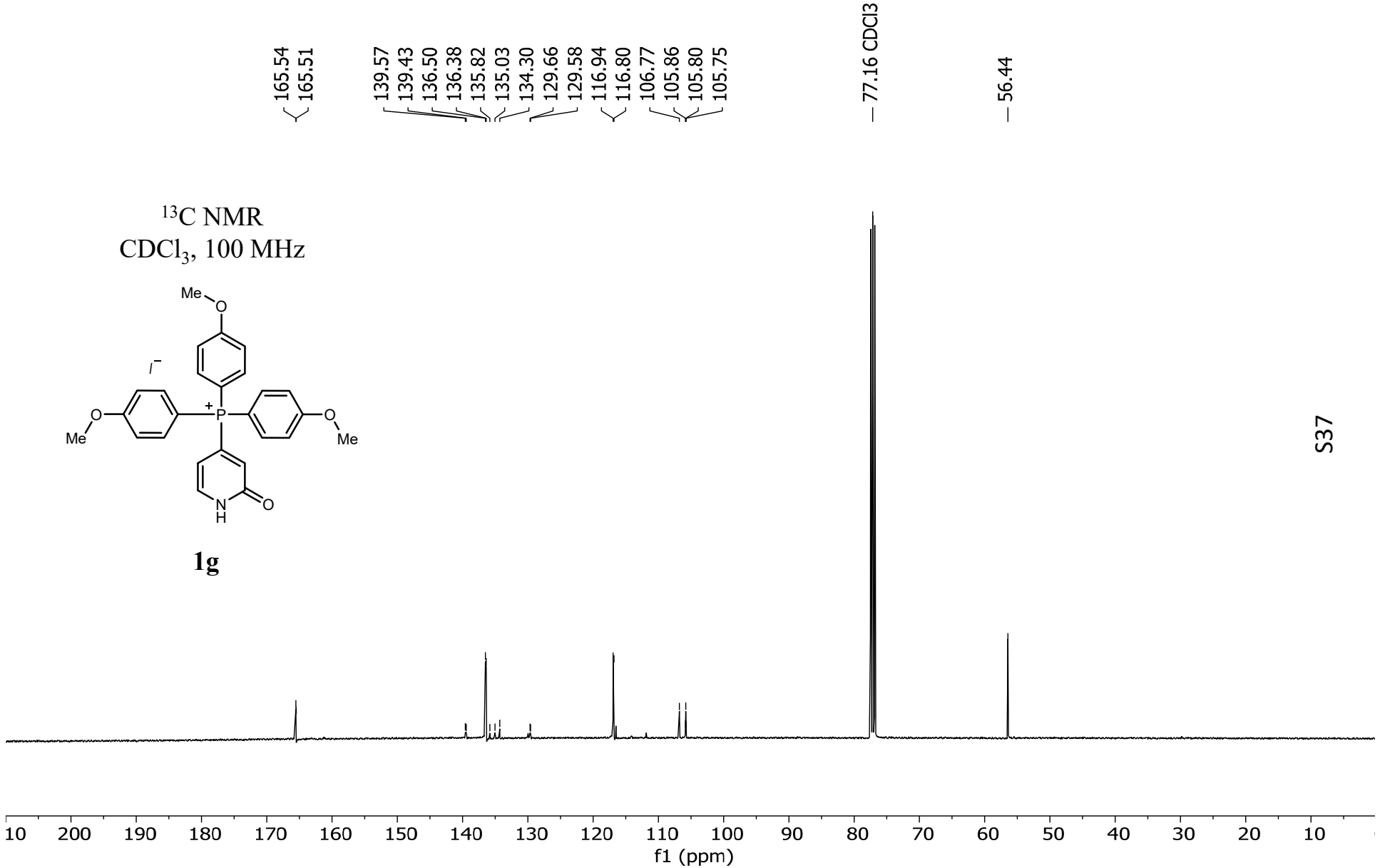
^{1}H NMR
$CDCl_3$, 400 MHz

1f

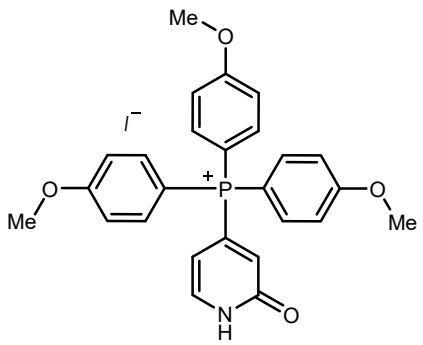

165.17
165.14
152.53
152.44
137.59
137.51
136.20
136.08
126.82
126.00
117.16
117.02
109.82
108.86
77.48
77.16 CDCl3
76.84
56.51
21.11
21.06
13C NMR
CDCl3, 100 MHz
Me
O
I−
+
P
O
Me
O
Me
Me
Me
N
1f
S34
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


15.33
31P NMR
CDCl3, 162 MHz
Me
O
I−
+
P
O
Me
O
Me
Me
Me
N
1f
S35
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
f1 (ppm)

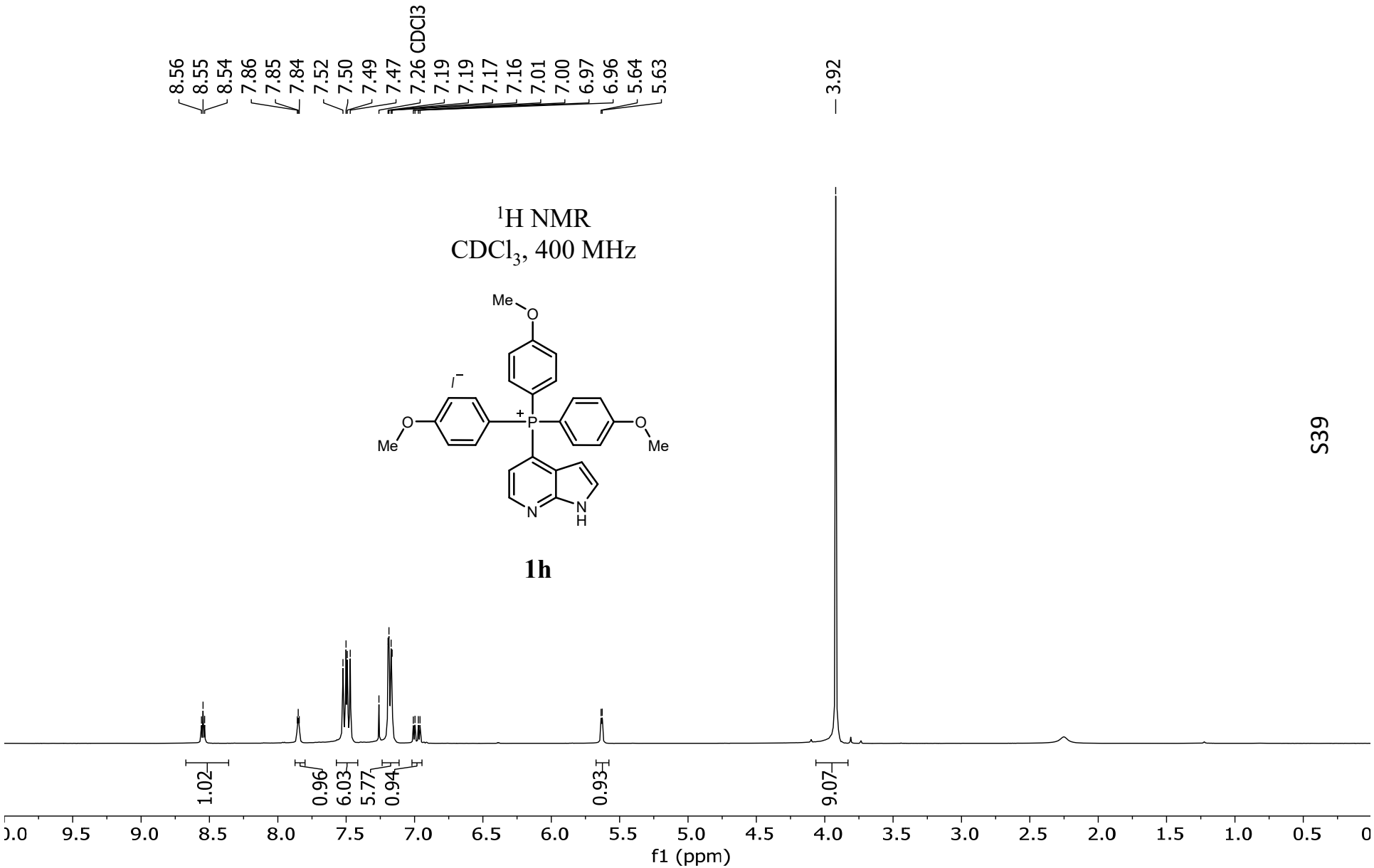

8.13
7.56
7.54
7.53
7.51
7.26 CDCl3
7.24
7.23
7.22
7.14
7.12
7.09
7.08
6.63
6.61
6.59
6.59
6.30
6.28
3.95
^{1}H NMR
$CDCl_3$, 400 MHz
Me
O
I⁻
O
Me
+
P
O
Me
N
H
O
1g
S36
0.90
6.00
5.35
1.19
1.49
0.89
8.85
f1 (ppm)

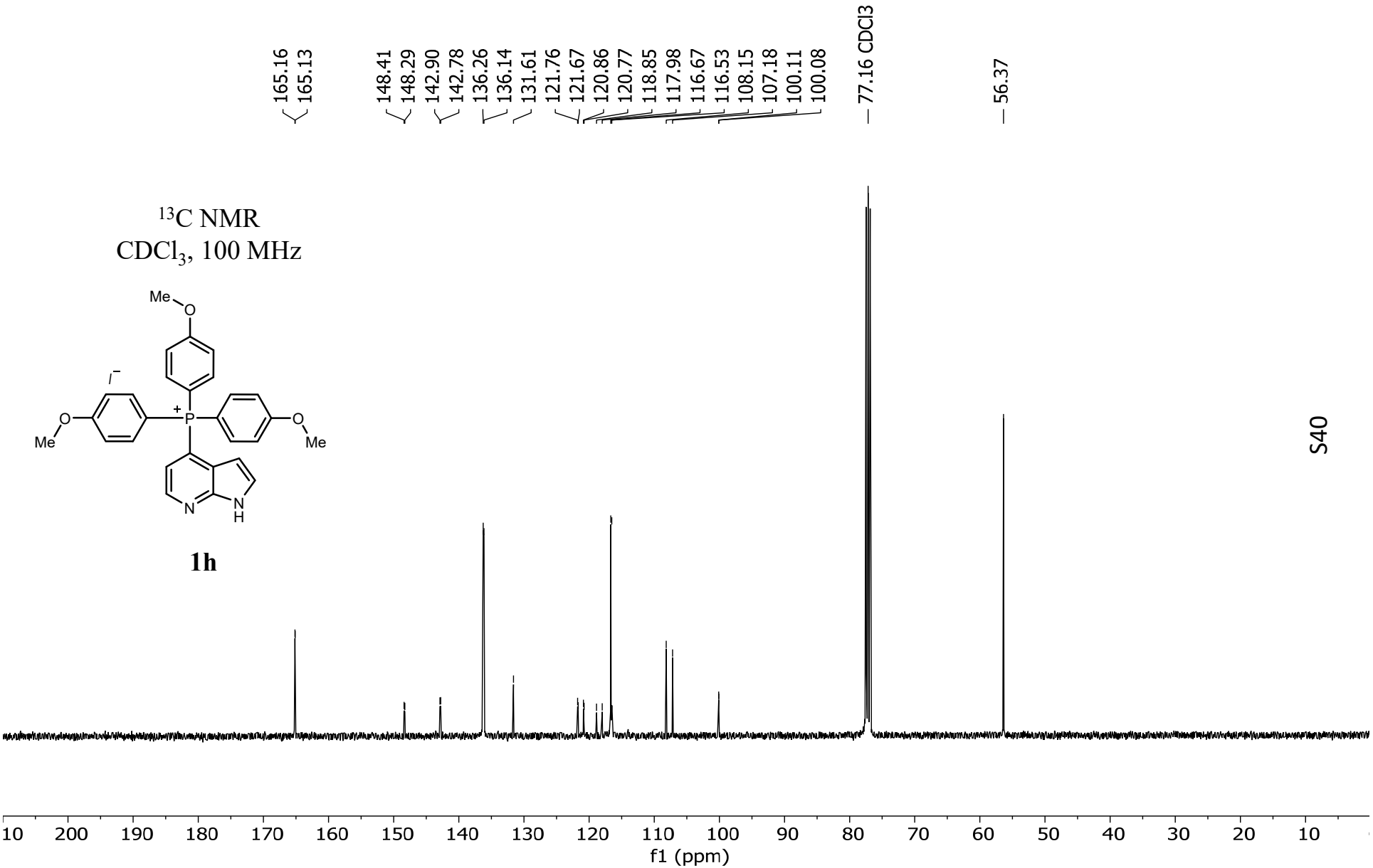

165.54
165.51
139.57
139.43
136.50
136.38
135.82
135.03
134.30
129.66
129.58
116.94
116.80
106.77
105.86
105.80
105.75
77.16 CDCl3
56.44
13C NMR
CDCl3, 100 MHz
Me
O
I−
+
P
O
Me
O
Me
N
H
O
1g
S37
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

^{31}P NMR
$CDCl_3$, 162 MHz

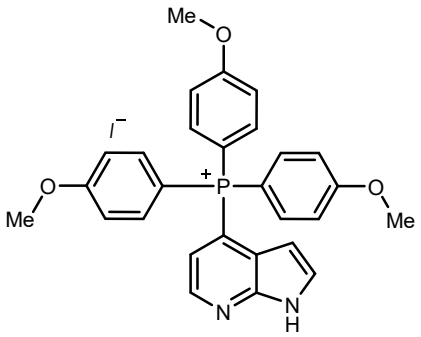


1g

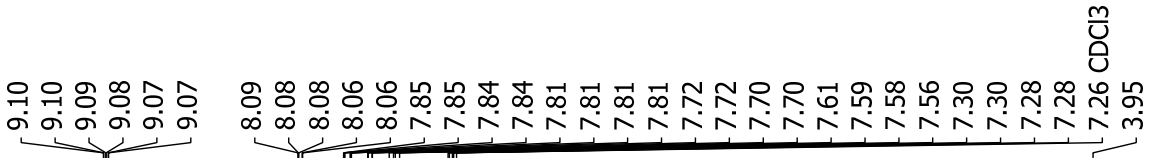

8.56
8.55
8.54
7.86
7.85
7.84
7.52
7.50
7.49
7.47
7.26 CDCl3
7.19
7.19
7.17
7.16
7.01
7.00
6.97
6.96
5.64
5.63
3.92
1H NMR
CDCl3, 400 MHz
Me
O
I−
O
Me
P+
O
Me
N
N
H
1h
S39
1.02
0.96
6.03
5.77
0.94
0.93
9.07
f1 (ppm)


165.16
165.13
148.41
148.29
142.90
142.78
136.26
136.14
131.61
121.76
121.67
120.86
120.77
118.85
117.98
116.67
116.53
108.15
107.18
100.11
100.08
77.16 CDCl3
56.37
13C NMR
CDCl3, 100 MHz
Me
O
I−
+
P
O
Me
O
Me
N
N
H
1h
S40
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

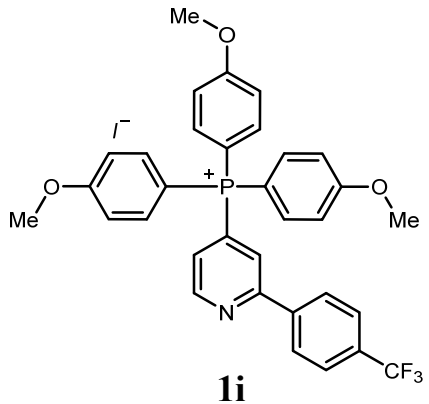
^{31}P NMR
$CDCl_3$, 162 MHz



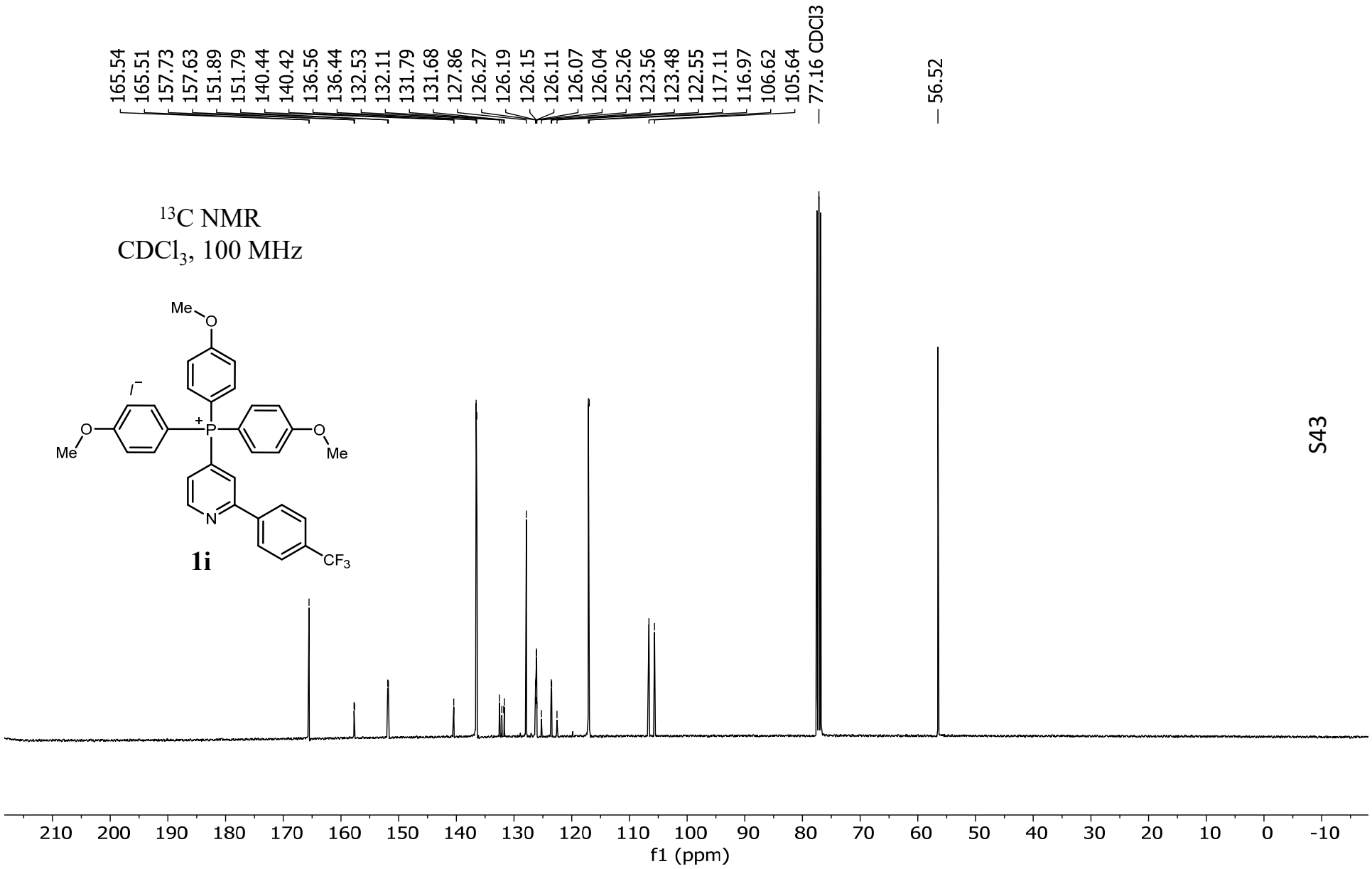
1h

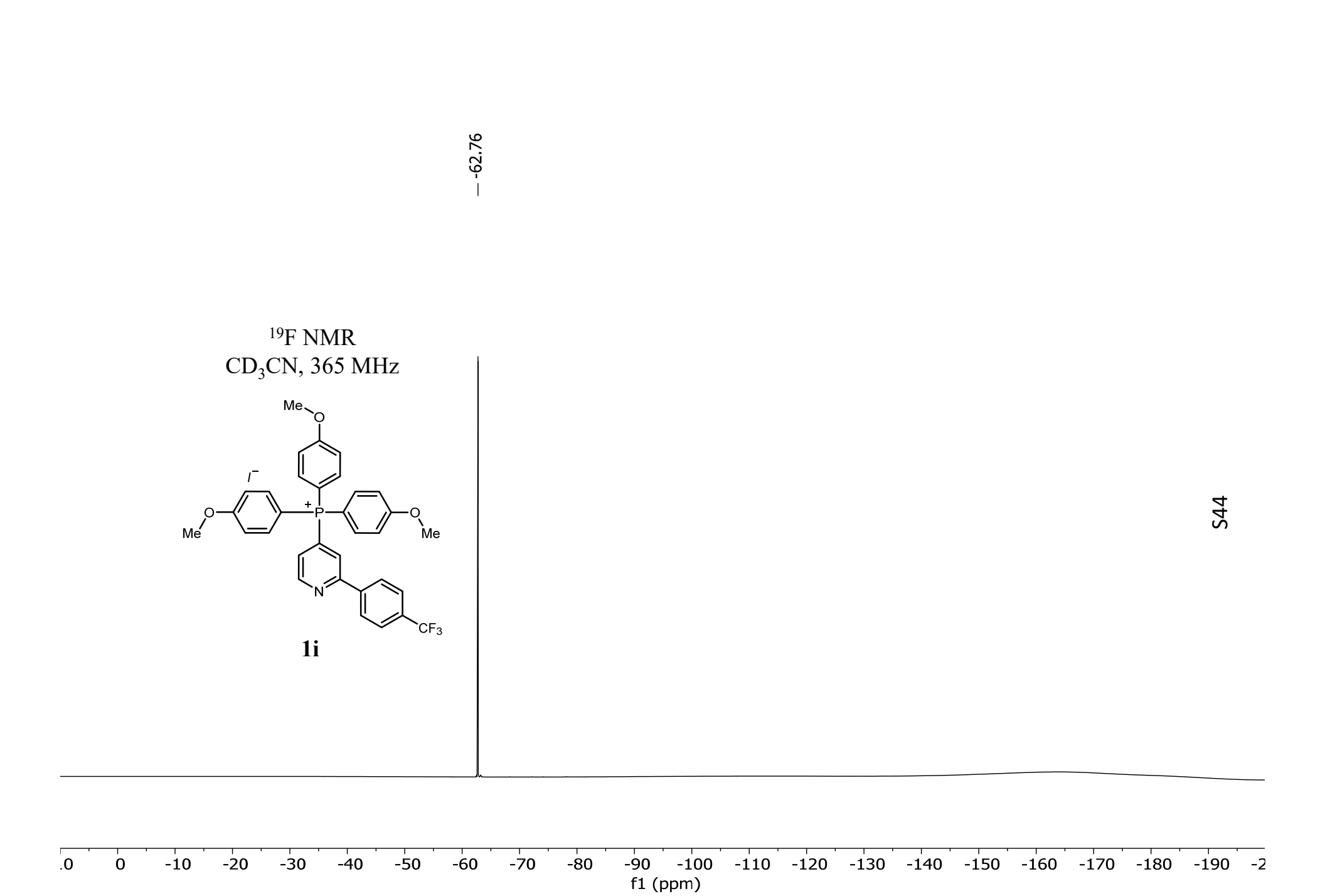


^{1}H NMR
$CDCl_3$, 400 MHz

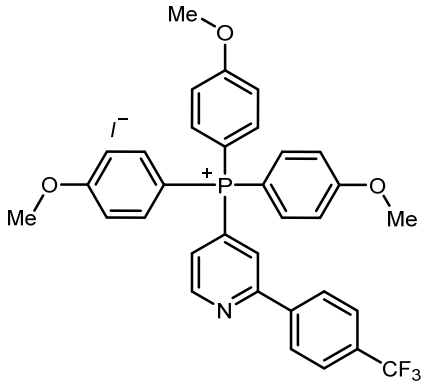


1i

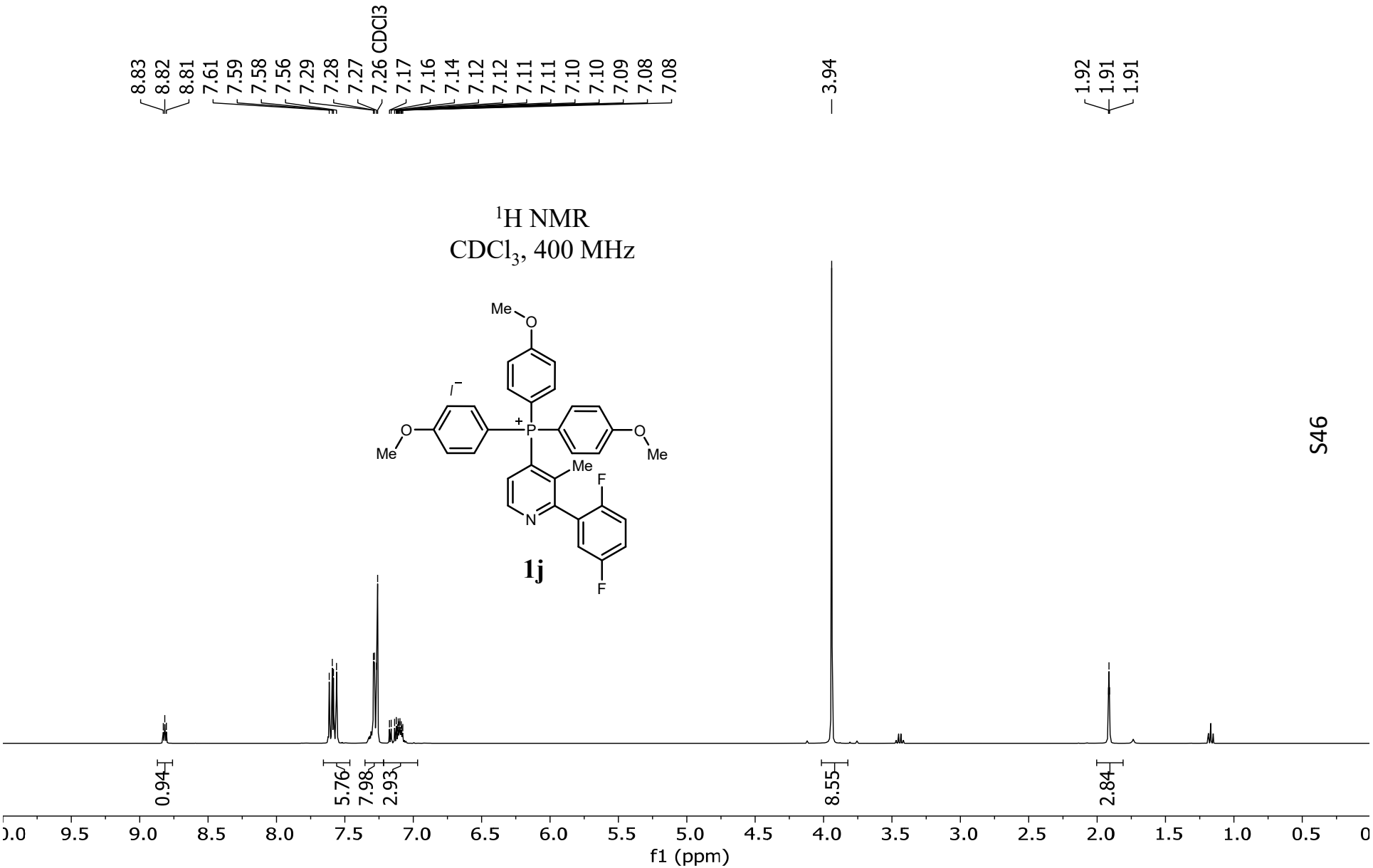

165.54
165.51
157.73
157.63
151.89
151.79
140.44
140.42
136.56
136.44
132.53
132.11
131.79
131.68
127.86
126.27
126.19
126.15
126.11
126.07
126.04
125.26
123.56
123.48
122.55
117.11
116.97
106.62
105.64
77.16 CDCl3
56.52
13C NMR
CDCl3, 100 MHz
Me
O
I−
+
P
O
Me
O
Me
N
CF3
1i
S43
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

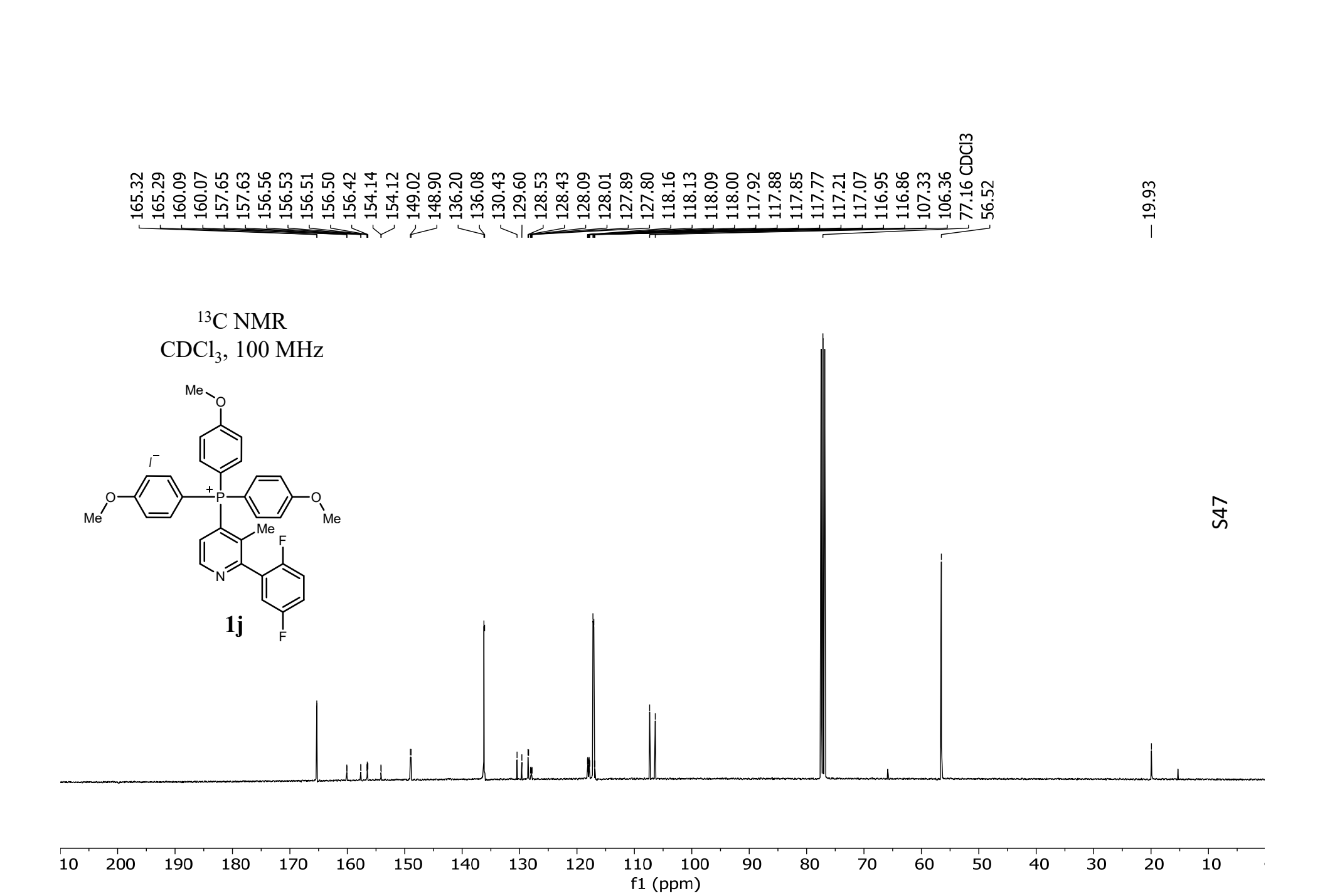

-62.76
19F NMR
CD3CN, 365 MHz
Me
O
I−
+
P
O
Me
O
Me
N
CF3
1i
S44
.0
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-2
f1 (ppm)

^{31}P NMR
$CDCl_3$, 162 MHz

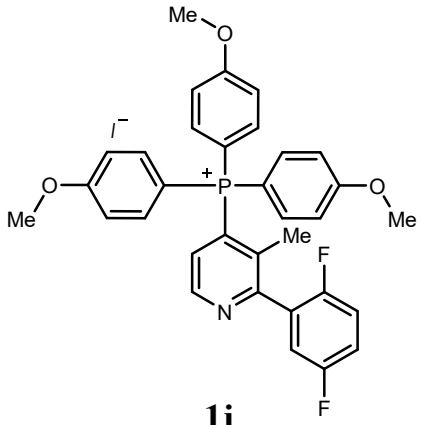


1i


8.83
8.82
8.81
7.61
7.59
7.58
7.56
7.29
7.28
7.27
7.26 CDCl3
7.17
7.16
7.14
7.12
7.12
7.11
7.11
7.10
7.10
7.09
7.08
7.08
3.94
1.92
1.91
1.91
^{1}H NMR
$CDCl_3$, 400 MHz
Me
O
I^-
O
Me
+
P
O
Me
Me
F
N
F
1j
S46
0.94
5.76
7.98
2.93
8.55
2.84
f1 (ppm)

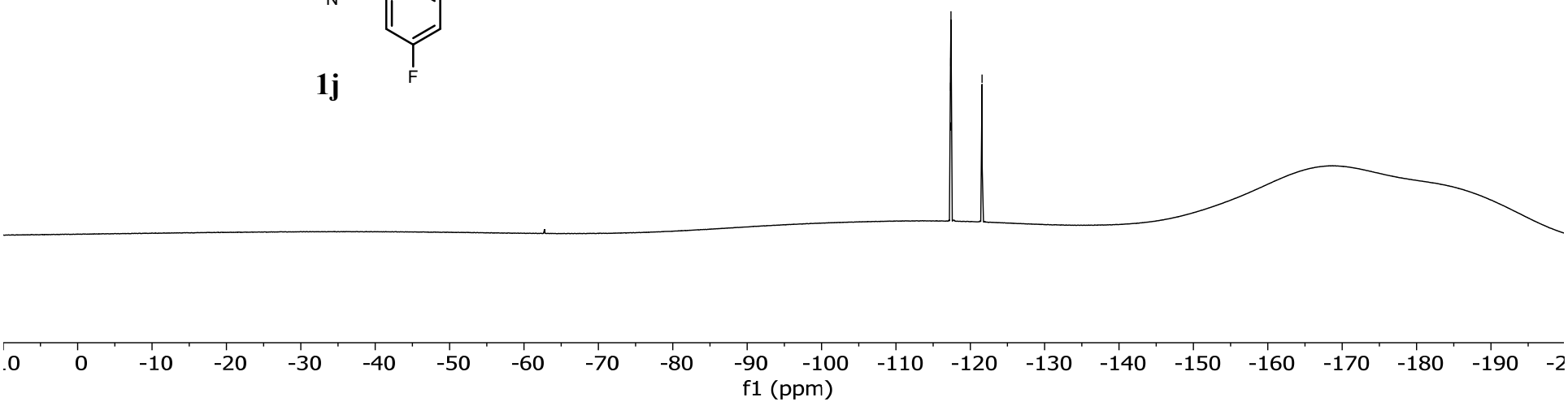

165.32
165.29
160.09
160.07
157.65
157.63
156.56
156.53
156.51
156.50
156.42
154.14
154.12
149.02
148.90
136.20
136.08
130.43
129.60
128.53
128.43
128.09
128.01
127.89
127.80
118.16
118.13
118.09
118.00
117.92
117.88
117.85
117.77
117.21
117.07
116.95
116.86
107.33
106.36
77.16 CDCl3
56.52
19.93
13C NMR
CDCl3, 100 MHz
Me
O
I−
+
P
O
Me
O
Me
Me
F
N
F
1j
S47
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

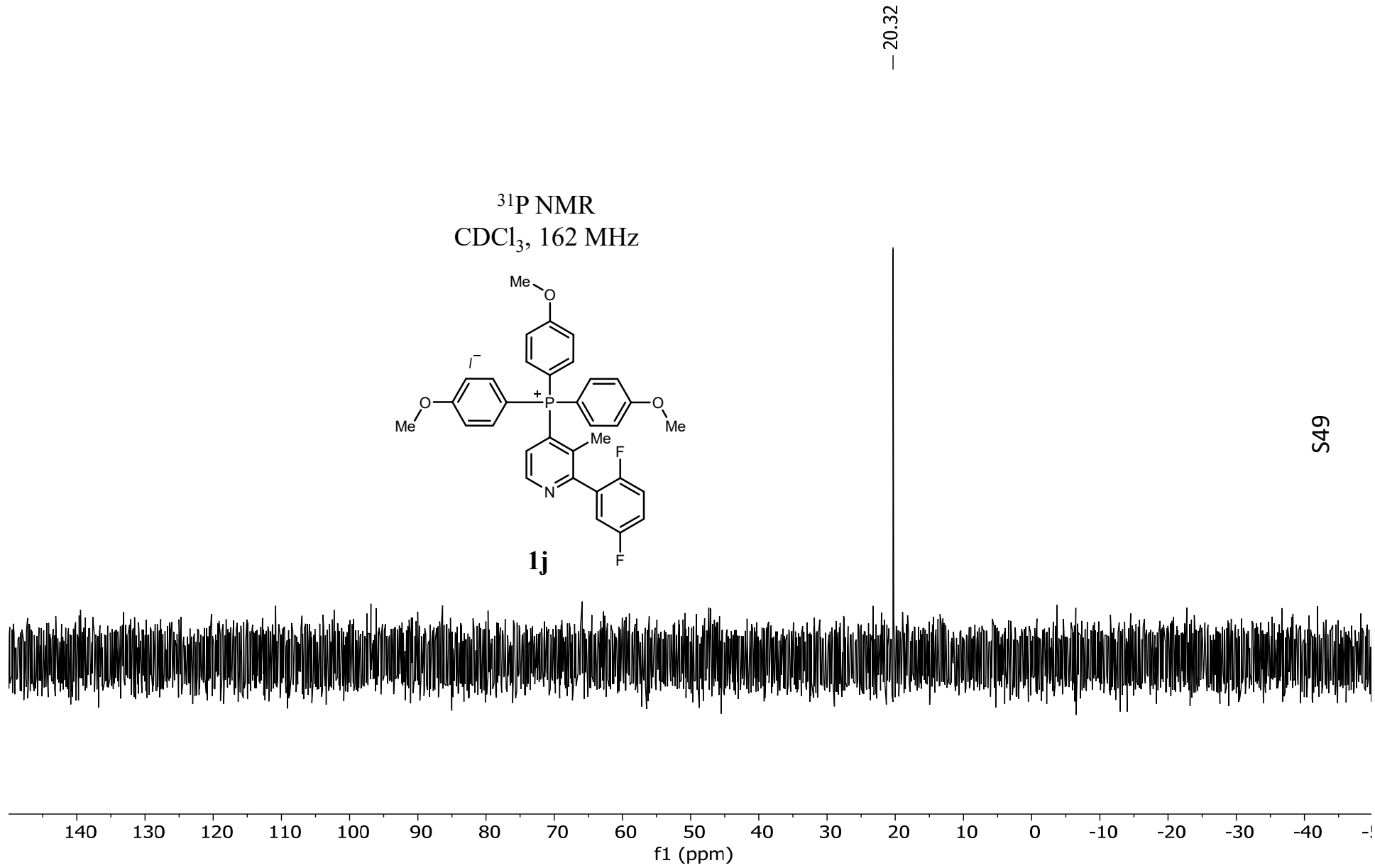
^{19}F NMR
CD_3CN, 365 MHz

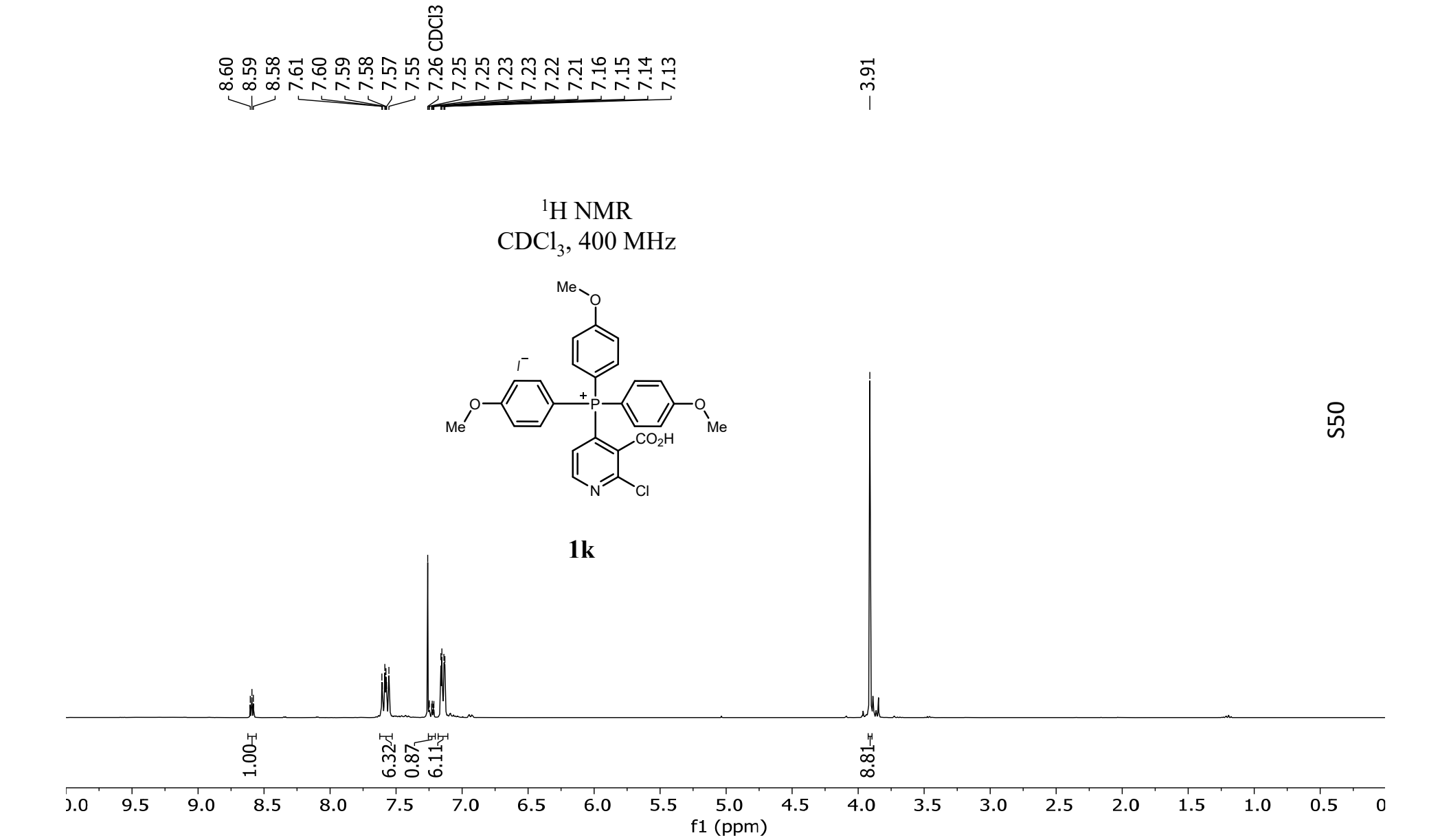


1j

-117.35
-117.36
-117.38
-117.39
-117.41
-117.42
-121.53
-121.56
-121.58

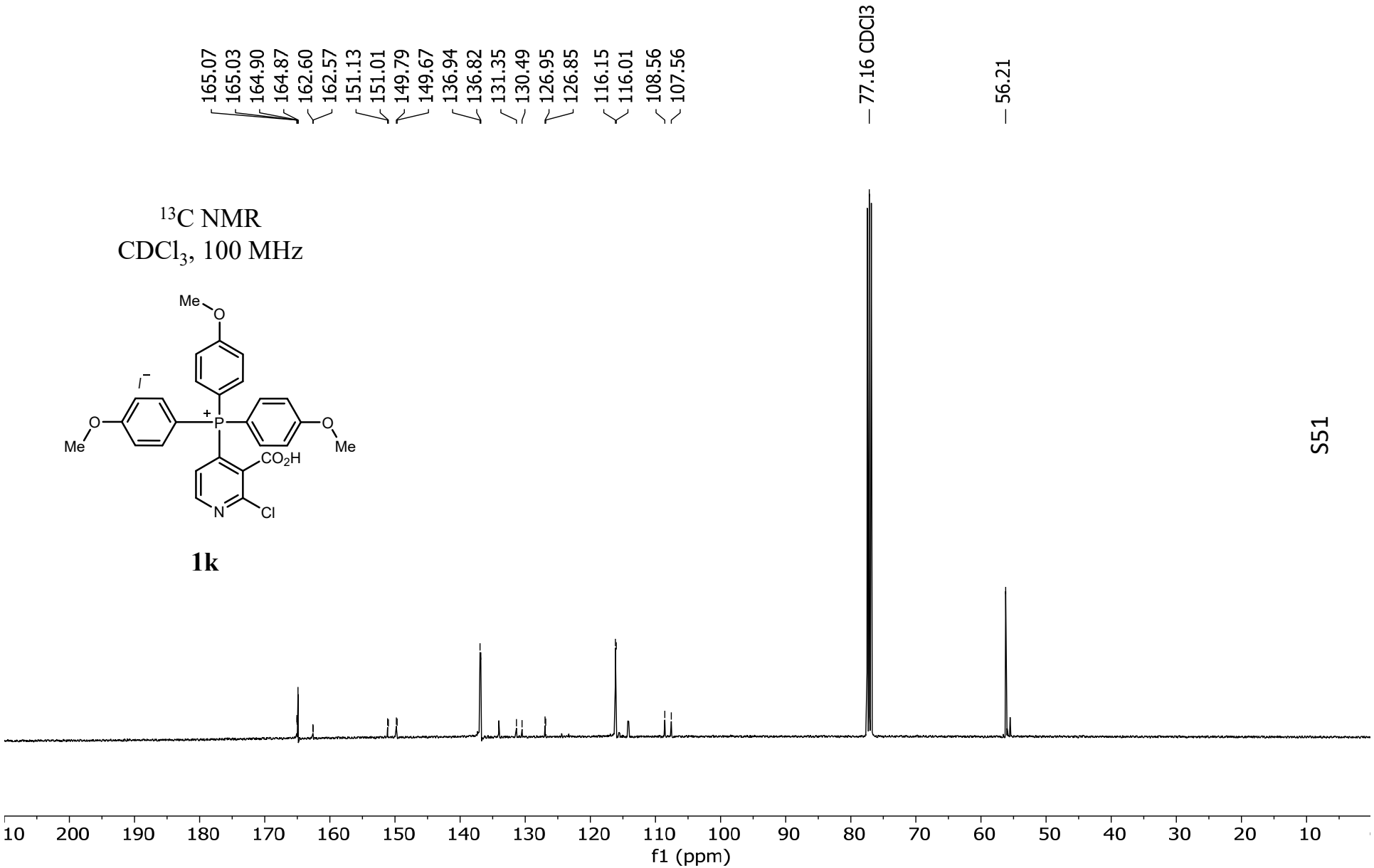



20.32
31P NMR
CDCl3, 162 MHz
Me
O
I−
O
Me
P+
O
Me
Me
F
N
F
1j
S49
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
f1 (ppm)

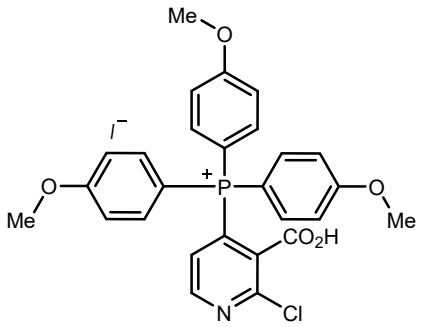


^{1}H NMR
$CDCl_3$, 400 MHz

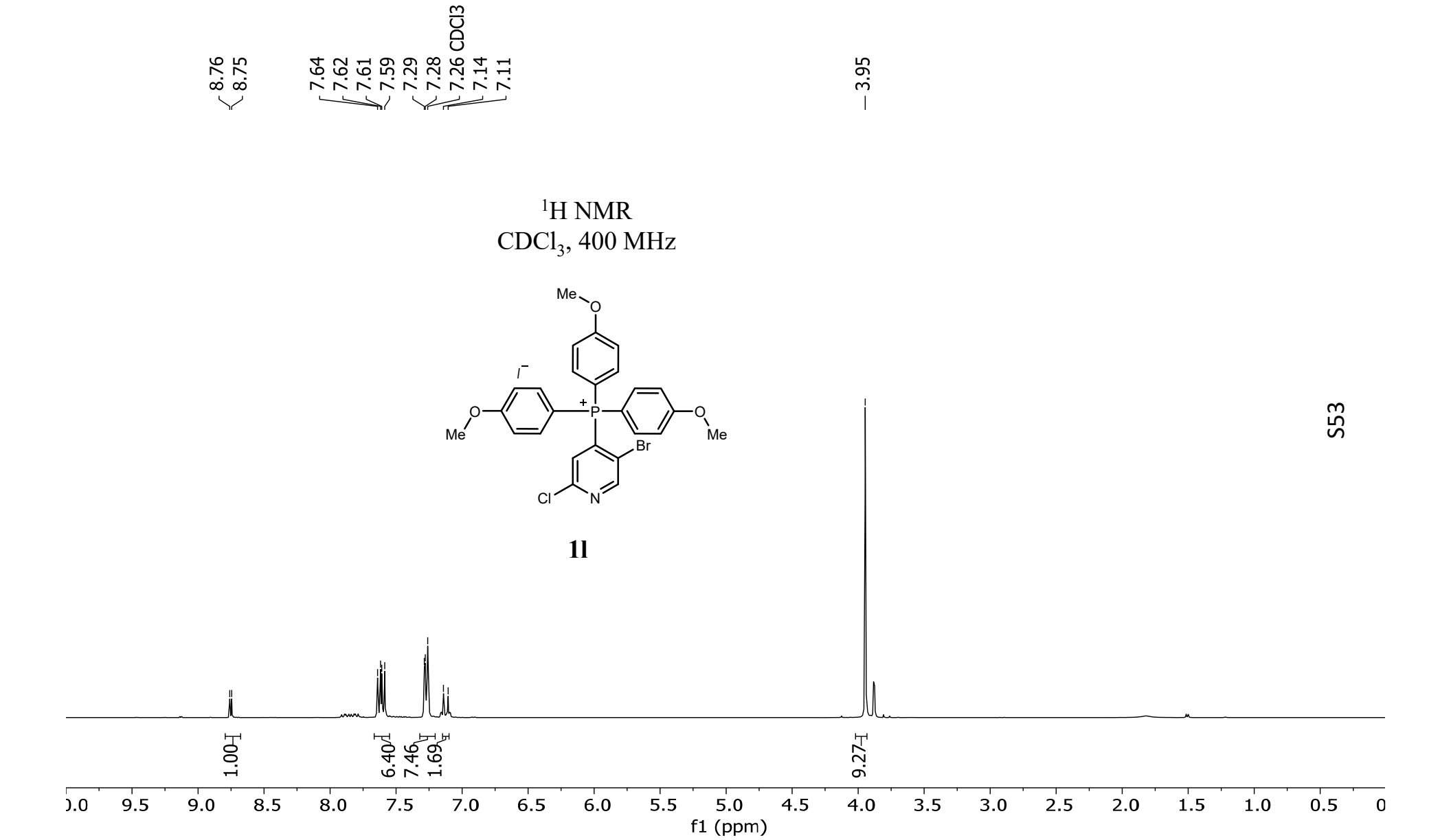
1k


165.07
165.03
164.90
164.87
162.60
162.57
151.13
151.01
149.79
149.67
136.94
136.82
131.35
130.49
126.95
126.85
116.15
116.01
108.56
107.56
77.16 CDCl3
56.21
13C NMR
CDCl3, 100 MHz
Me
O
I−
O
Me
+
P
O
Me
CO2H
N
Cl
1k
S51
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

^{31}P NMR
$CDCl_3$, 162 MHz

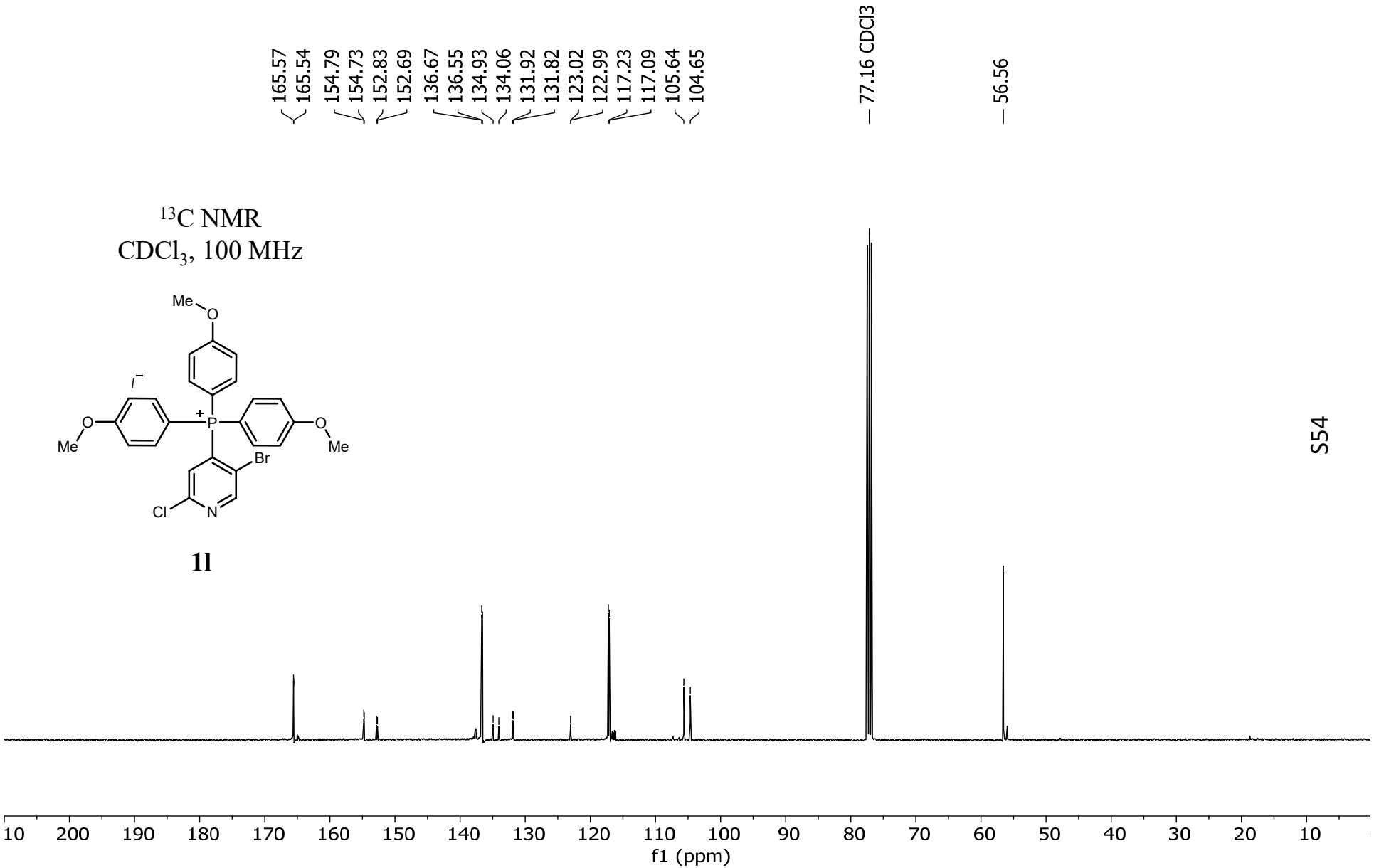


1k

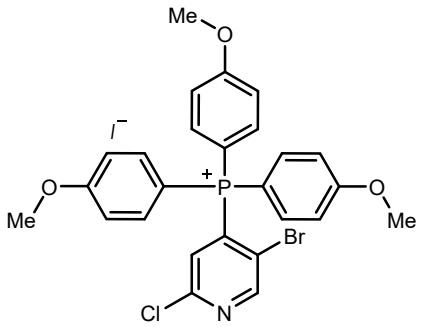


^{1}H NMR
$CDCl_3$, 400 MHz

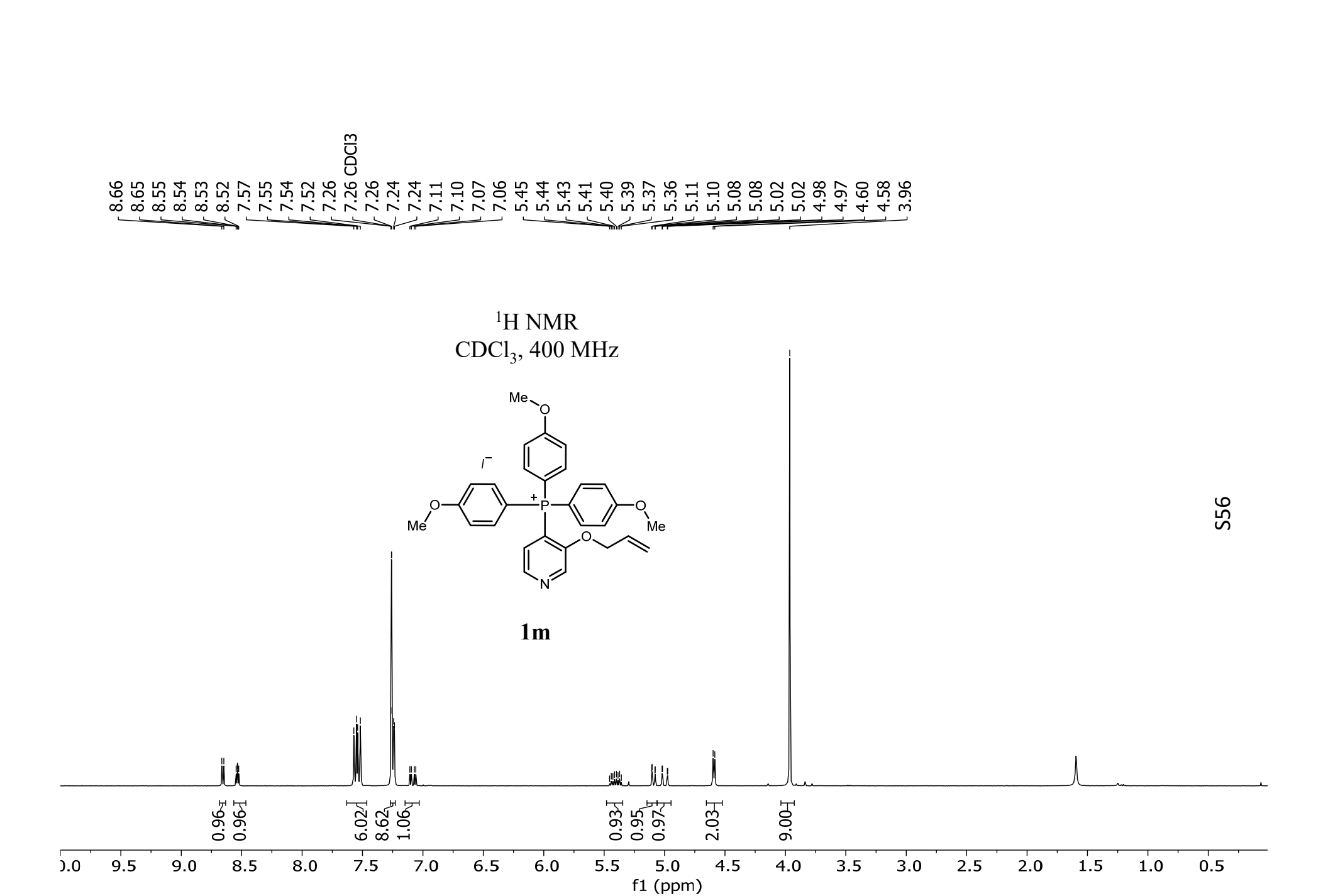
1l

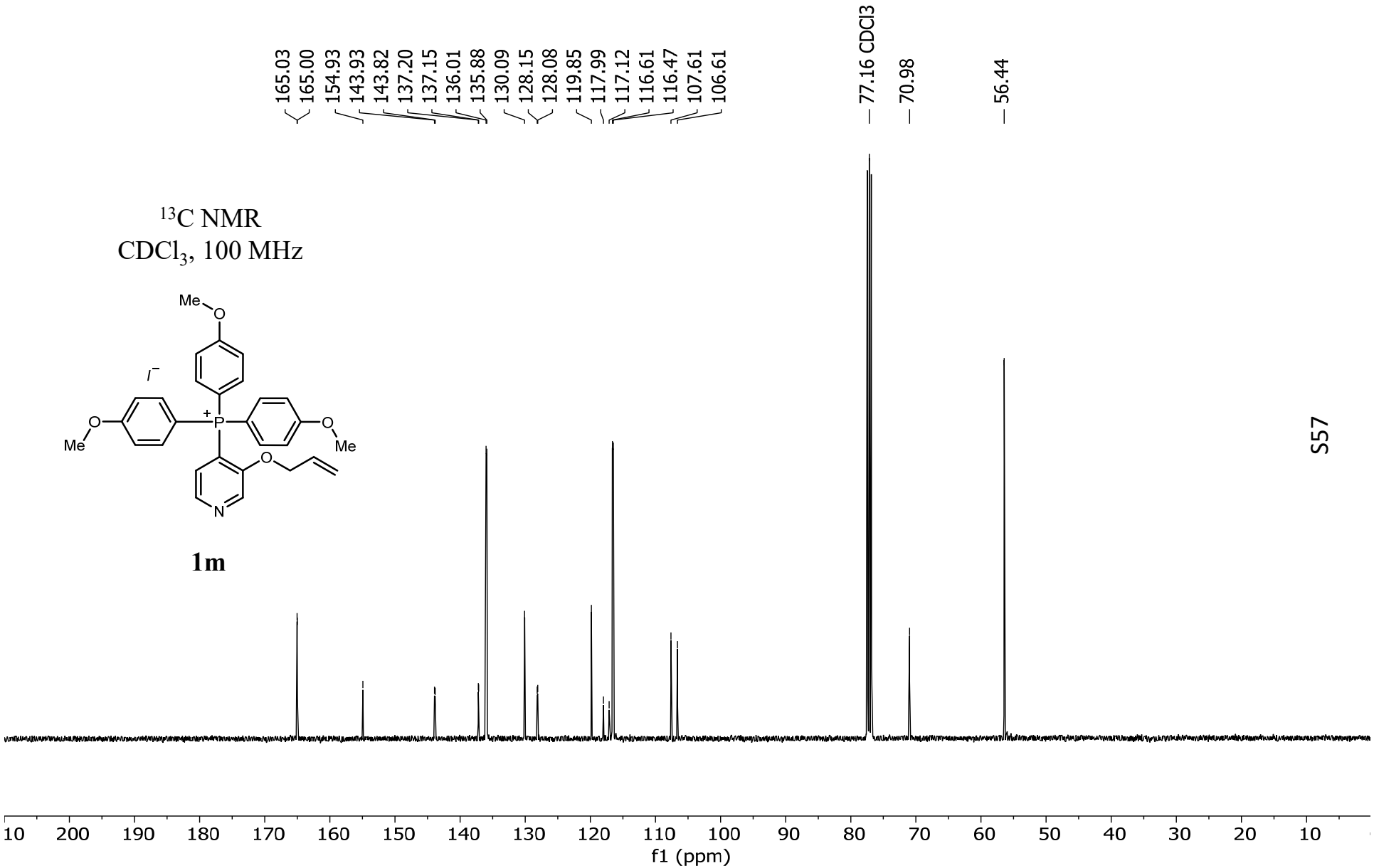

165.57
165.54
154.79
154.73
152.83
152.69
136.67
136.55
134.93
134.06
131.92
131.82
123.02
122.99
117.23
117.09
105.64
104.65
77.16 CDCl3
56.56
13C NMR
CDCl3, 100 MHz
Me
O
I−
O
Me
P+
O
Me
Br
Cl
N
1l
S54
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

^{31}P NMR
$CDCl_3$, 162 MHz

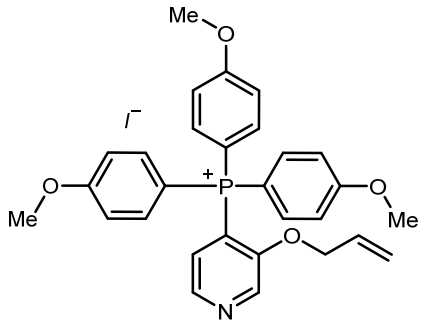


1l

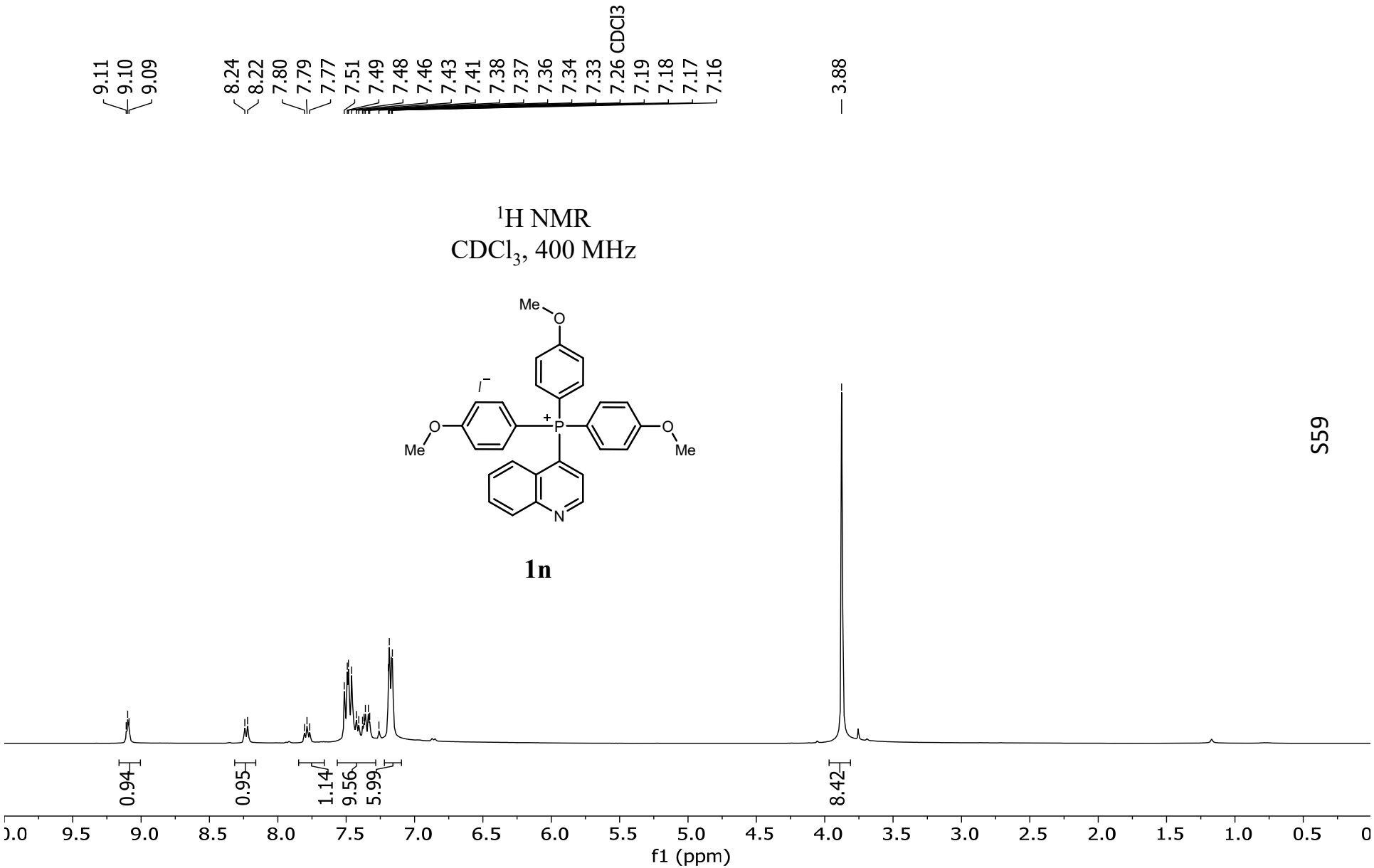

8.66
8.65
8.55
8.54
8.53
8.52
7.57
7.55
7.54
7.52
7.26
7.26 CDCl3
7.26
7.24
7.24
7.11
7.10
7.07
7.06
5.45
5.44
5.43
5.41
5.40
5.39
5.37
5.36
5.11
5.10
5.08
5.08
5.02
5.02
4.98
4.97
4.60
4.58
3.96
1H NMR
CDCl3, 400 MHz
Me
O
I−
P+
O
Me
O
Me
O
N
1m
S56
0.96
0.96
6.02
8.62
1.06
0.93
0.95
0.97
2.03
9.00
f1 (ppm)


165.03
165.00
154.93
143.93
143.82
137.20
137.15
136.01
135.88
130.09
128.15
128.08
119.85
117.99
117.12
116.61
116.47
107.61
106.61
77.16 CDCl3
70.98
56.44
13C NMR
CDCl3, 100 MHz
Me
O
I−
+
P
O
Me
O
Me
O
N
1m
S57
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

^{31}P NMR
$CDCl_3$, 162 MHz



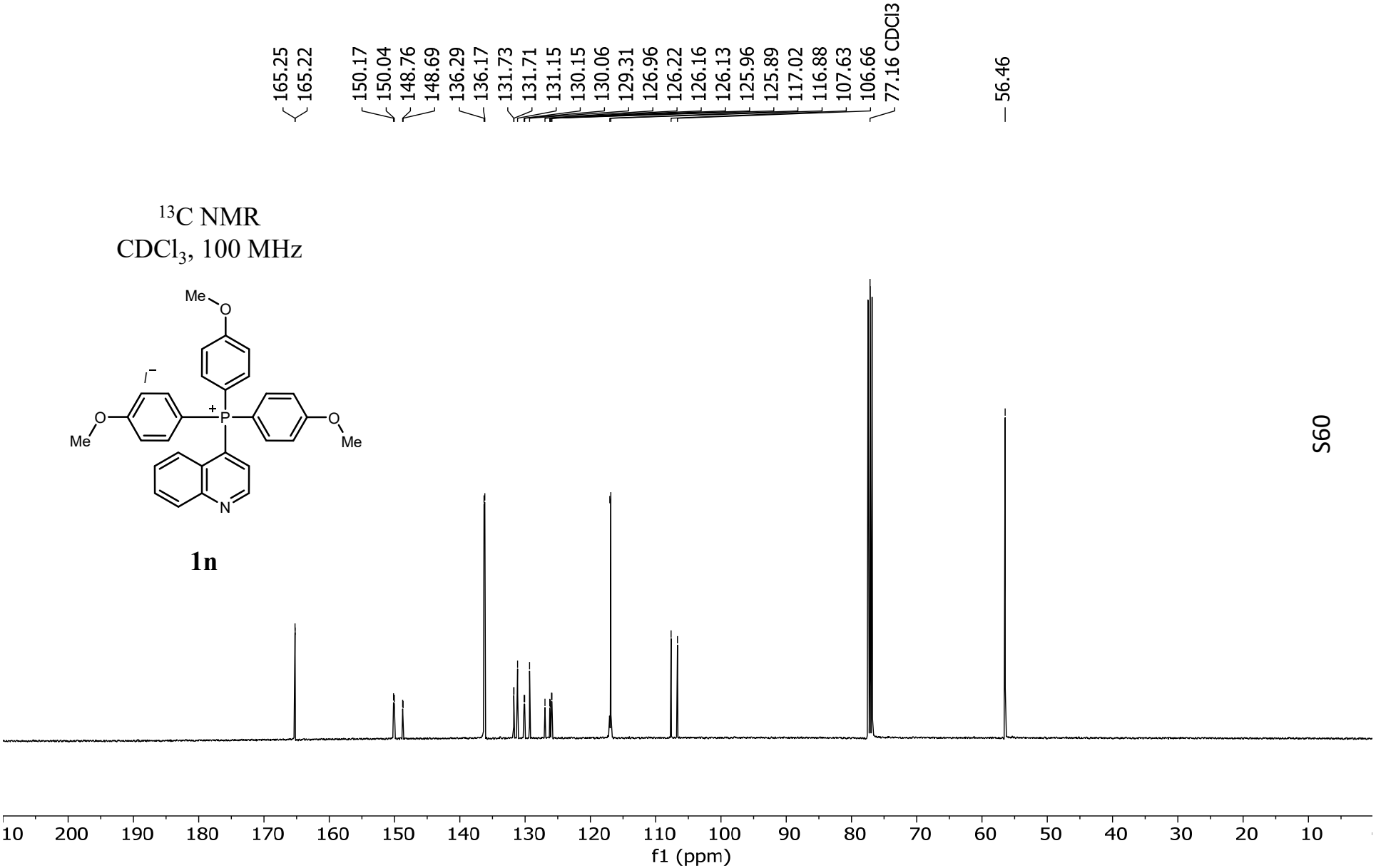
1m



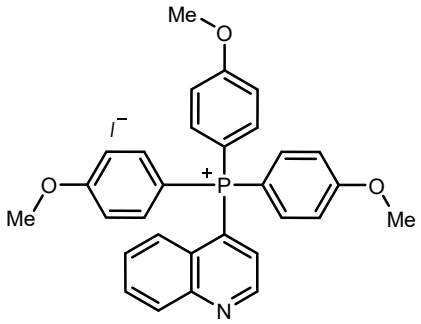
^{1}H NMR
$CDCl_3$, 400 MHz

1n

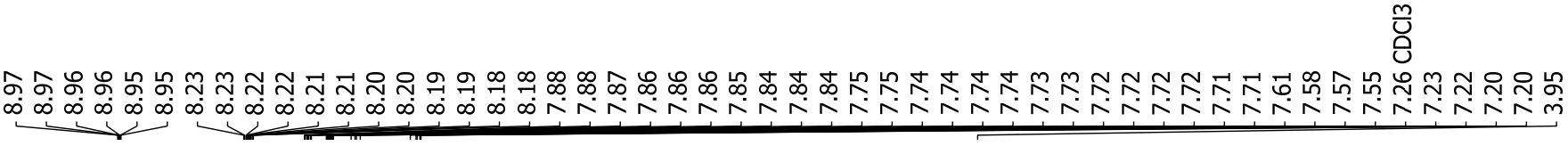
S59


165.25
165.22
150.17
150.04
148.76
148.69
136.29
136.17
131.73
131.71
131.15
130.15
130.06
129.31
126.96
126.22
126.16
126.13
125.96
125.89
117.02
116.88
107.63
106.66
77.16 CDCl3
56.46
13C NMR
CDCl3, 100 MHz
Me
O
I−
+
P
O
Me
O
Me
N
1n
S60
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

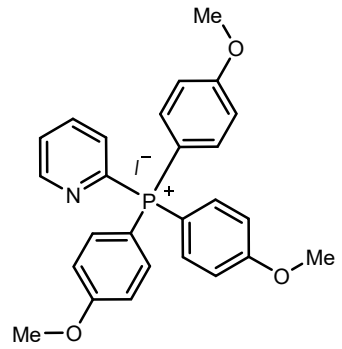
^{31}P NMR
$CDCl_3$, 162 MHz



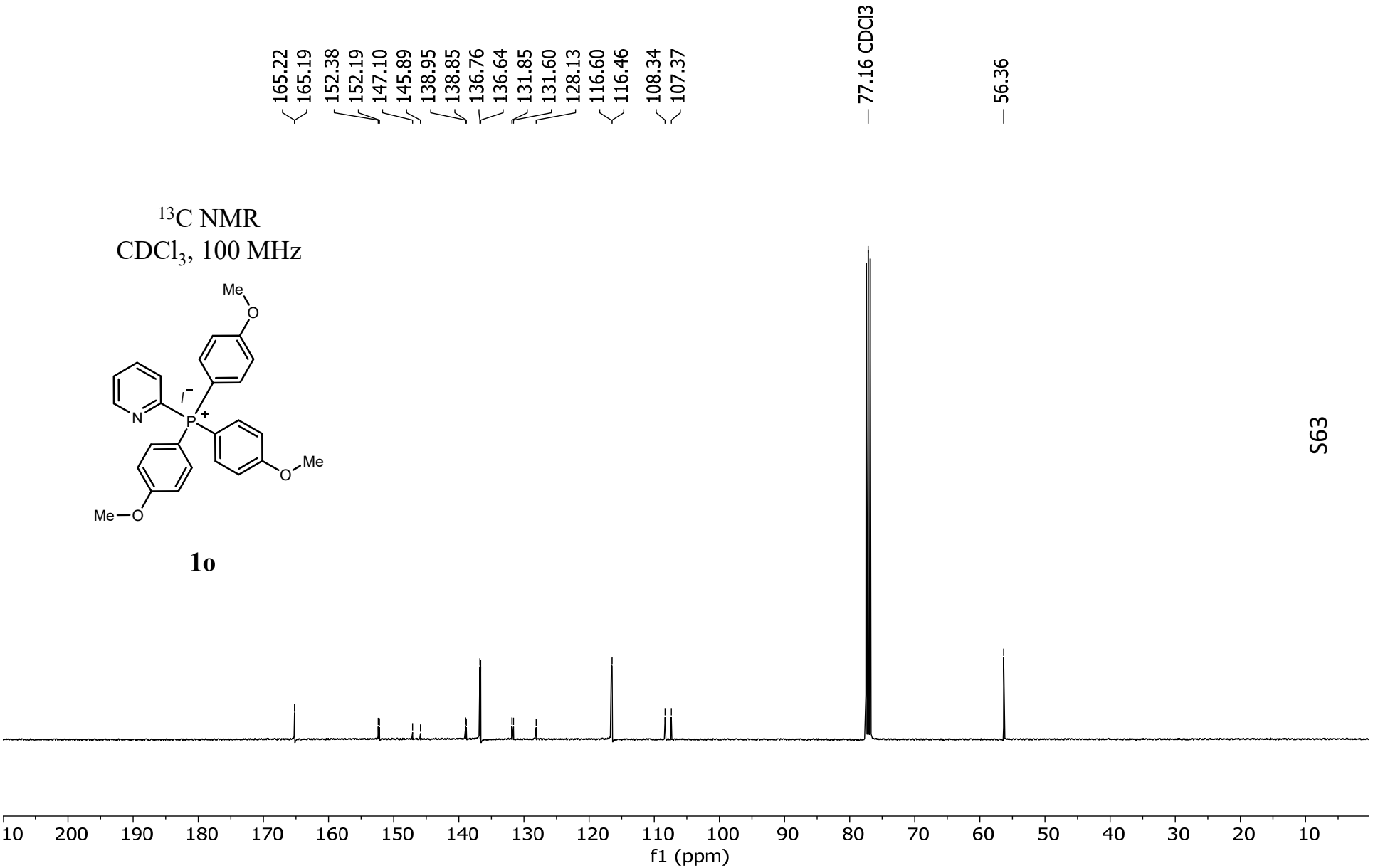
1n



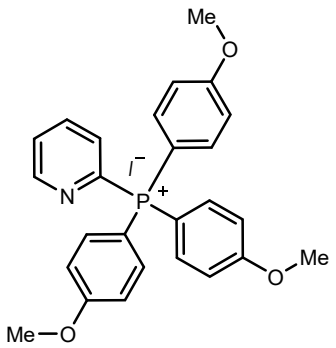
^{1}H NMR
$CDCl_3$, 400 MHz



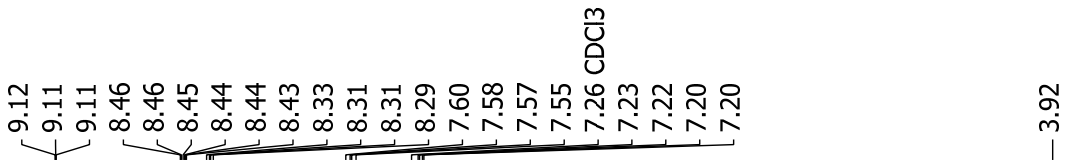
1o


165.22
165.19
152.38
152.19
147.10
145.89
138.95
138.85
136.76
136.64
131.85
131.60
128.13
116.60
116.46
108.34
107.37
77.16 CDCl3
56.36
13C NMR
CDCl3, 100 MHz
Me
O
I−
N
P+
Me
O
Me
O
1o
S63
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

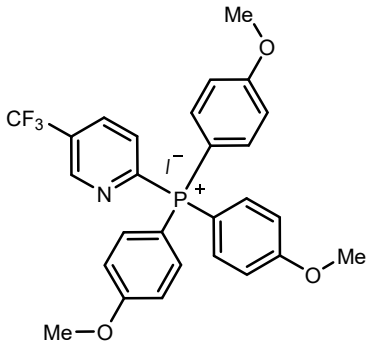
^{31}P NMR
$CDCl_3$, 162 MHz



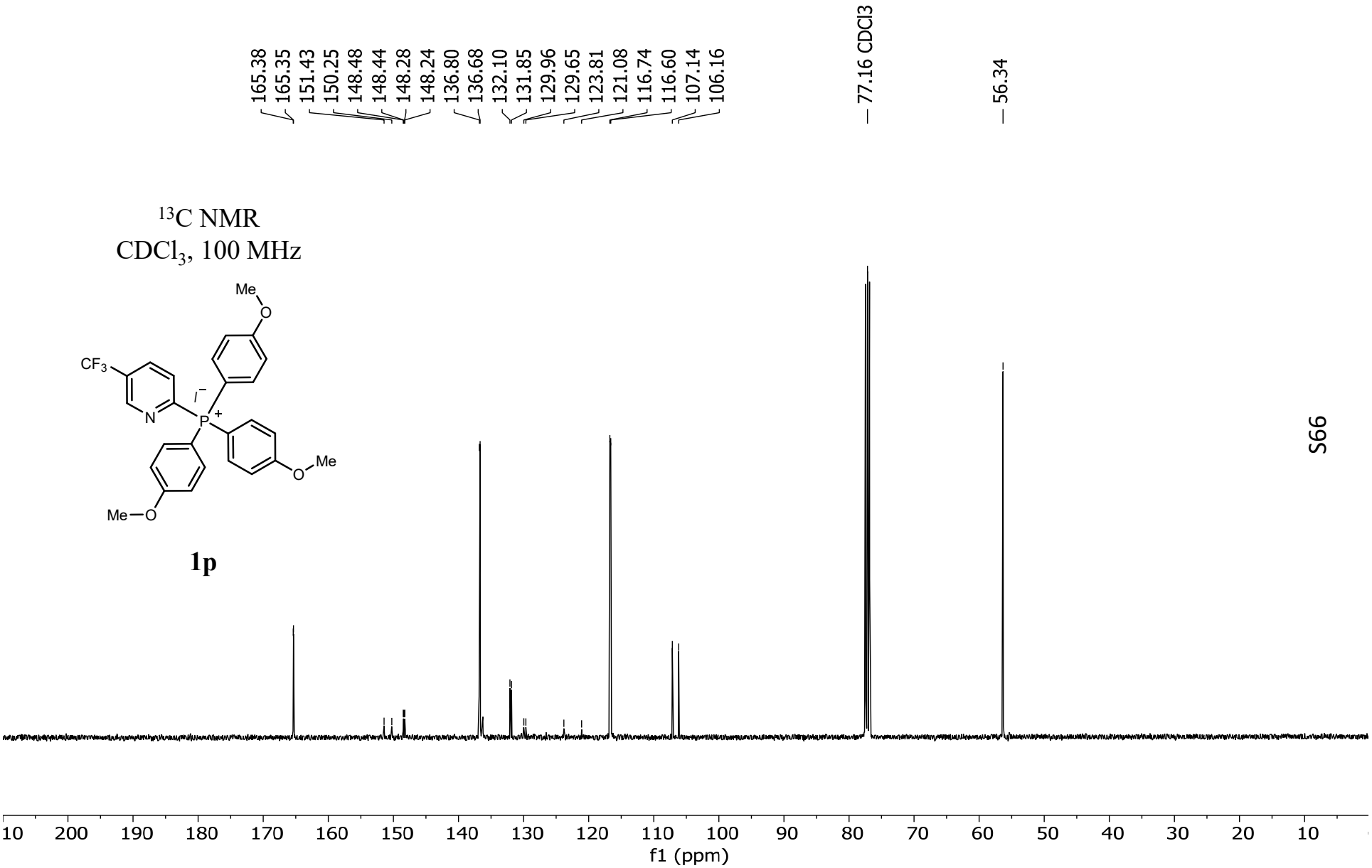
1o

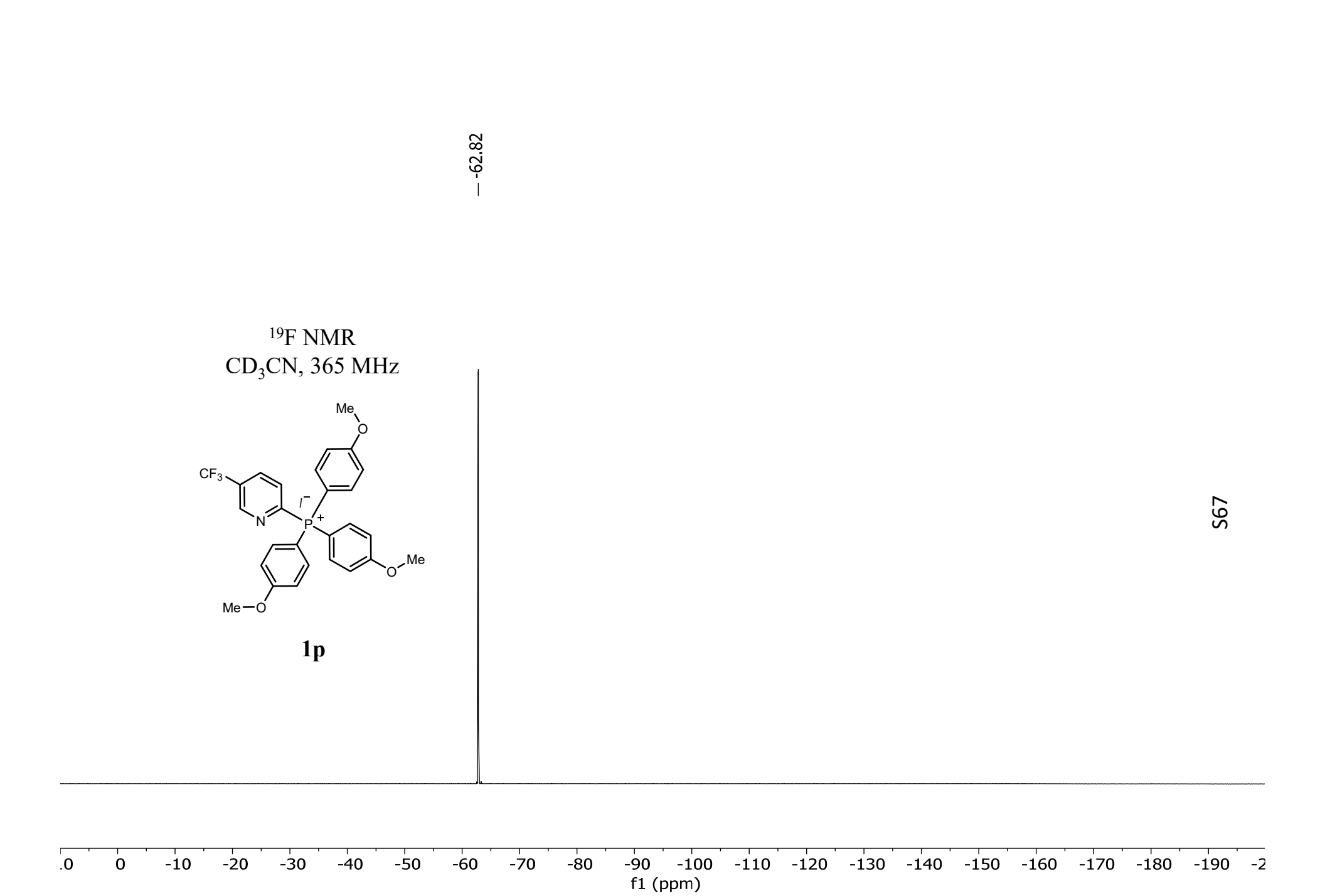


^{1}H NMR
$CDCl_3$, 400 MHz

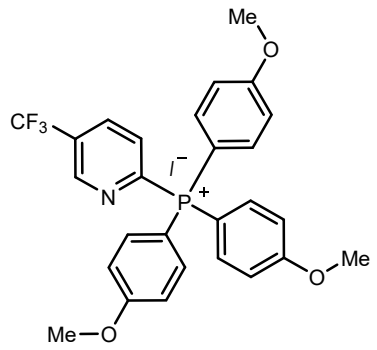


1p

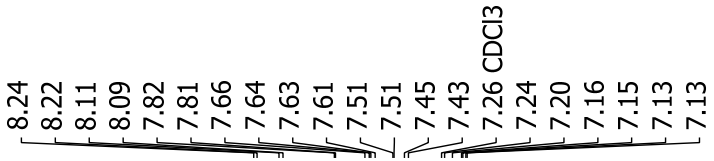

165.38
165.35
151.43
150.25
148.48
148.44
148.28
148.24
136.80
136.68
132.10
131.85
129.96
129.65
123.81
121.08
116.74
116.60
107.14
106.16
77.16 CDCl3
56.34
13C NMR
CDCl3, 100 MHz
Me
O
CF3
I−
N
P+
Me
O
Me—O
1p
S66
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


-62.82
19F NMR
CD3CN, 365 MHz
Me
O
CF3
I−
N
P+
O
Me
Me—O
1p
S67
.0
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-2
f1 (ppm)

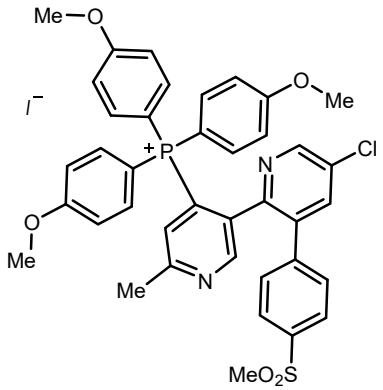
^{31}P NMR
$CDCl_3$, 162 MHz



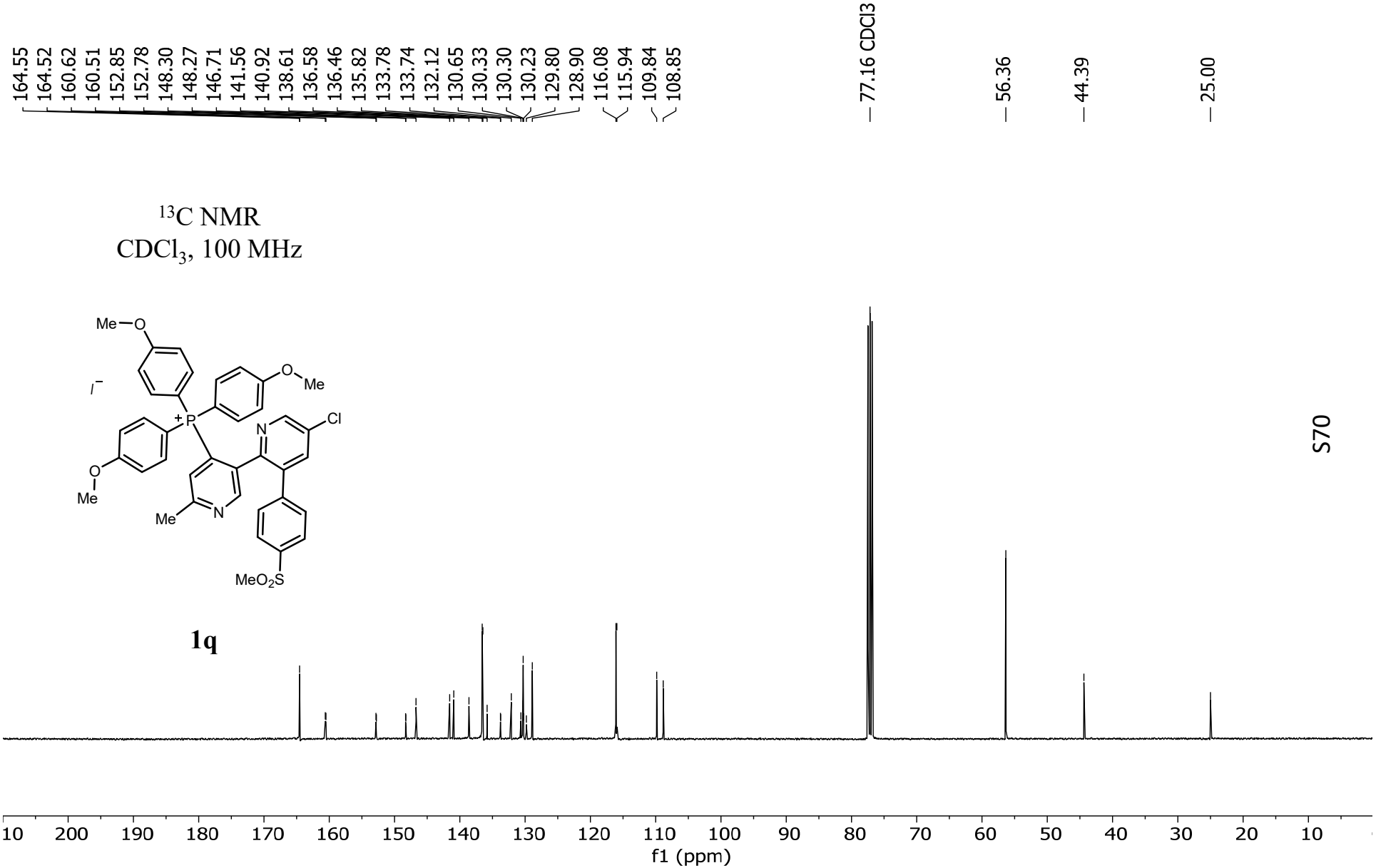
1p



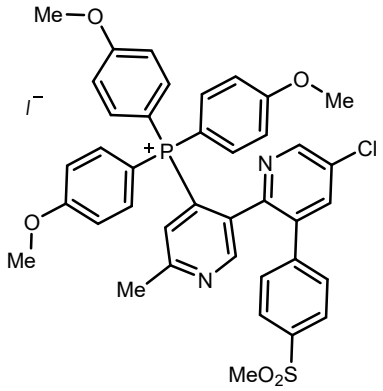
^{1}H NMR
$CDCl_3$, 400 MHz



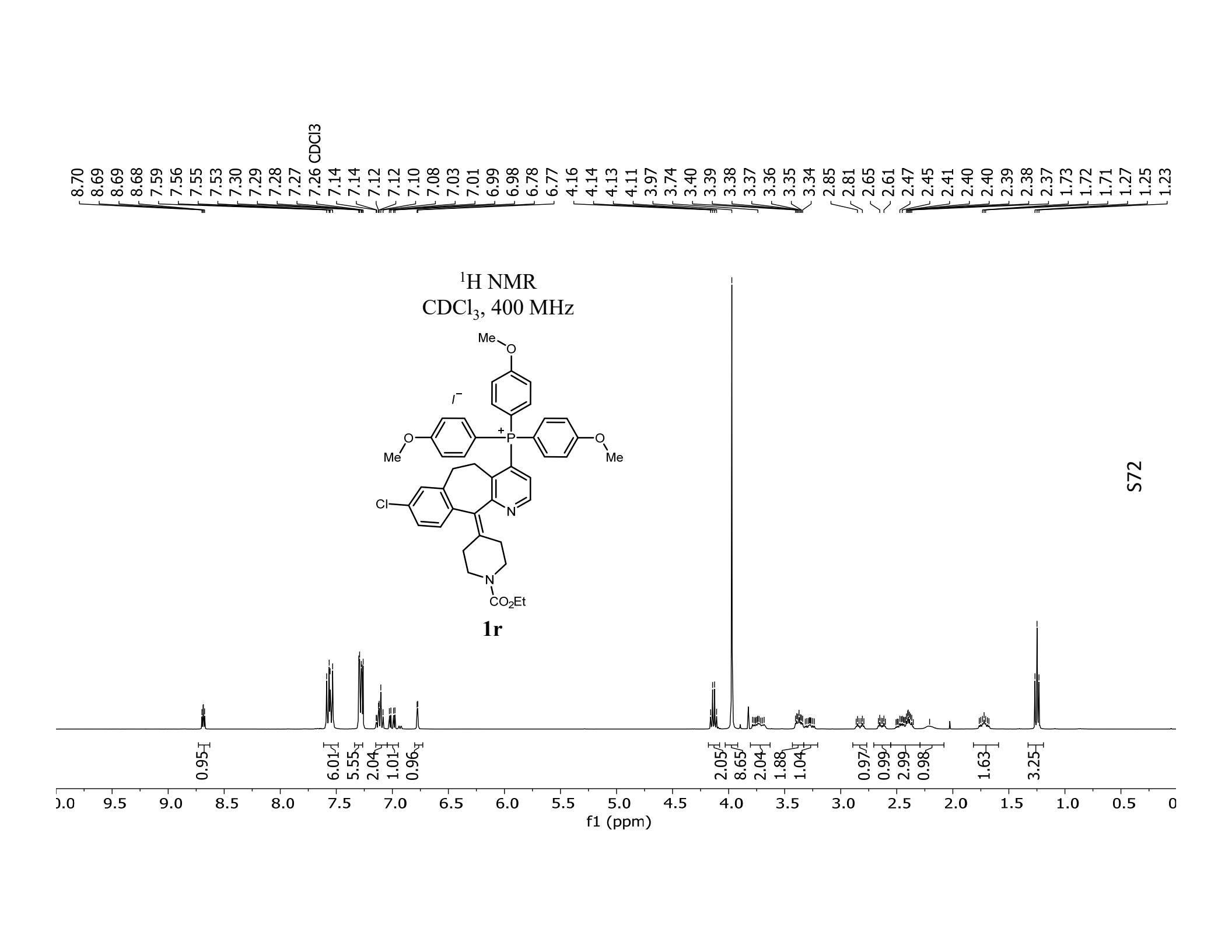
1q

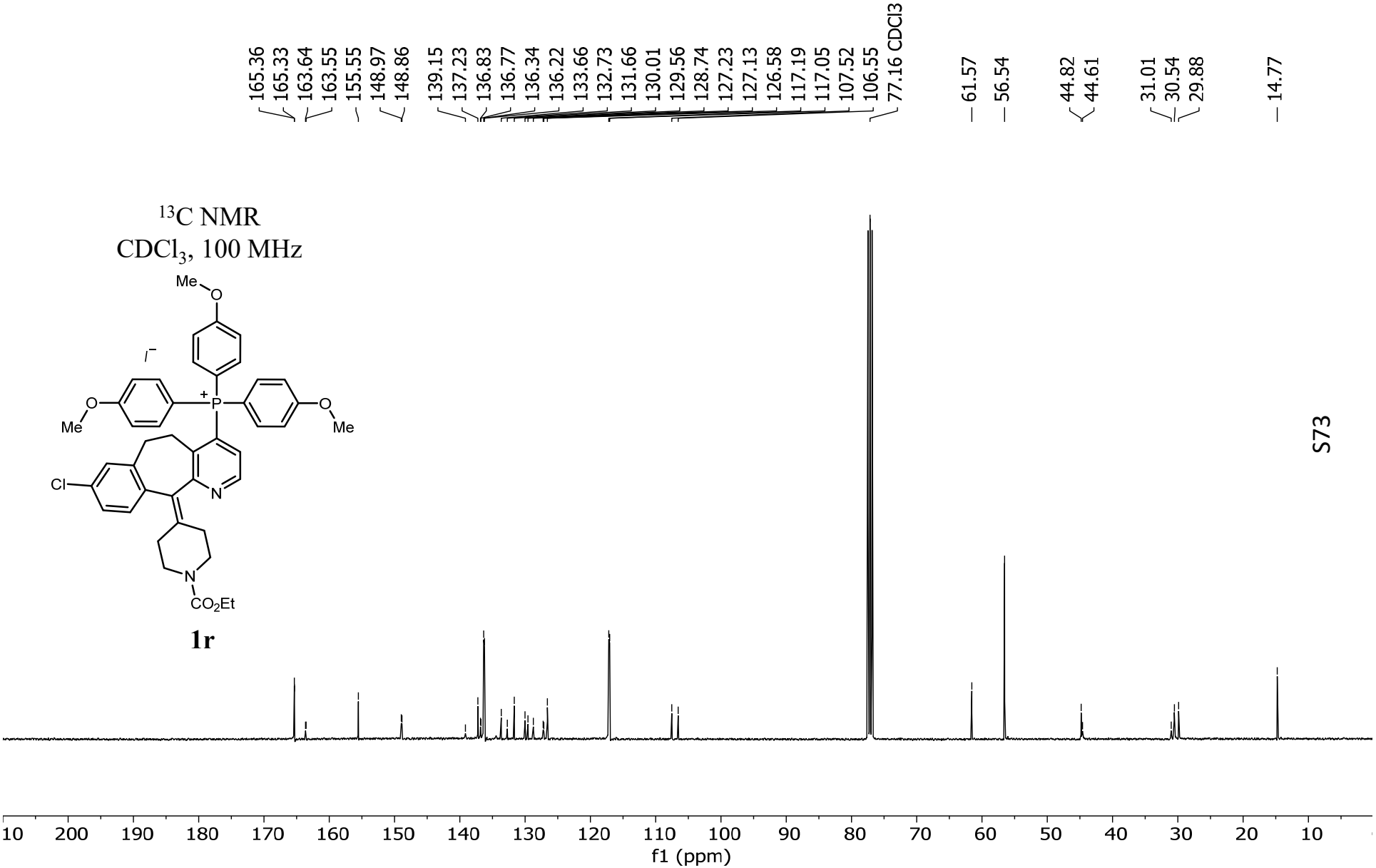

164.55
164.52
160.62
160.51
152.85
152.78
148.30
148.27
146.71
141.56
140.92
138.61
136.58
136.46
135.82
133.78
133.74
132.12
130.65
130.33
130.30
130.23
129.80
128.90
116.08
115.94
109.84
108.85
77.16 CDCl3
56.36
44.39
25.00
13C NMR
CDCl3, 100 MHz
Me—O
O
Me
I−
P+
N
Cl
O
Me
Me
N
MeO2S
1q
S70
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

^{31}P NMR
$CDCl_3$, 162 MHz



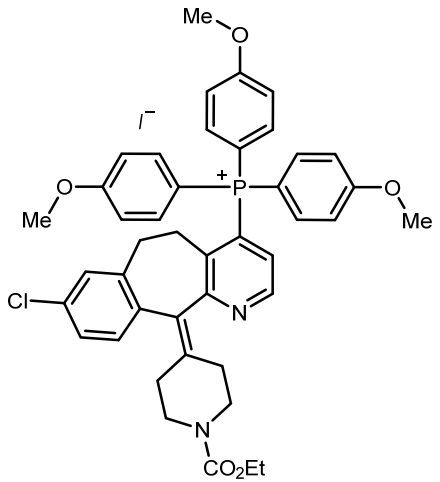
1q


8.70 8.69 8.69 8.68 7.59 7.56 7.55 7.53 7.30 7.29 7.28 7.27 7.26 CDCl3 7.14 7.14 7.12 7.12 7.10 7.08 7.03 7.01 6.99 6.98 6.78 6.77 4.16 4.14 4.13 4.11 3.97 3.74 3.40 3.39 3.38 3.37 3.36 3.35 3.34 2.85 2.81 2.65 2.61 2.47 2.45 2.41 2.40 2.40 2.39 2.38 2.37 1.73 1.72 1.71 1.27 1.25 1.23
^{1}H NMR
$CDCl_3$, 400 MHz
Me
O
I^-
O
Me
+
P
O
Me
Cl
N
N
CO_2Et
1r
S72
0.95
6.01
5.55
2.04
1.01
0.96
2.05
8.65
2.04
1.88
1.04
0.97
0.99
2.99
0.98
1.63
3.25
f1 (ppm)


165.36
165.33
163.64
163.55
155.55
148.97
148.86
139.15
137.23
136.83
136.77
136.34
136.22
133.66
132.73
131.66
130.01
129.56
128.74
127.23
127.13
126.58
117.19
117.05
107.52
106.55
77.16 CDCl3
61.57
56.54
44.82
44.61
31.01
30.54
29.88
14.77
13C NMR
CDCl3, 100 MHz
Me
O
I−
O
Me
+
P
O
Me
Cl
N
N
CO2Et
1r
S73
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

^{31}P NMR

$CDCl_3$, 162 MHz



1r