Supporting Information

Deoxyfluorination of Phenols

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Materials and Methods

Except as indicated otherwise, reactions were performed in oven-dried, screw-cap vials with teflon seals under inert atmosphere with vigorous stirring. Solvents were dried by passage through alumina.[1] CsF was purchased from Aldrich Co. and was dried at 200 ºC for 24 h under high vacuum (<1 torr) prior to use and was stored and weighed inside an inert atmosphere box. Toluene was dried with sodium /benzophenone and distilled prior to use. All commercially available phenols were purchased and dried in a vacuum desiccator for 24 h prior to use (Phenol, 4-nitrophenol, 4-fluorophenol, 2-hydroxycarbazol, methyl 4-hydroxybenzoate, 4-hydroxybenzaldehyde, 4-phenylphenol, 4-(thiophen-3-yl)phenol, 3,5-dichlorophenol, 4-bromophenol, 4-methoxyphenol, *p*-cresol, *o*-cresol, 4-aminophenol, 3-dimethylaminophenol, 8-quinolinol, 6-hydroxyquinoline, 3-hydroxypyridine, 2-hydroxypyridine, estrone, qunine were purchased from Aldrich Co., trifluoro-*p*-cresol, 4-hydroxybenzophenone, 4-hydroxyindole, 4-hydroxypyridine were purchase from Acros Co., ethyl 4-hydroxy-3-methoxycinnamate was purchase from TCI Co., zearalenone was purchase from Chemfinder Co.). Flash chromatography was performed on Silicycle silica gel 60 (40–60 μm) using a forced flow of eluant at 0.3–0.5 bar pressure.[2] NMR spectra were recorded on either a Varian Unity/Inova 500 spectrometer operating at 500 MHz and 125 MHz for ^{1}H and ^{13}C acquisitions, respectively, or a Varian Mercury 400 spectrometer operating at 400 HMz and 375 MHz for ^{1}H and ^{19}F acquisitions, respectively. Chemical shifts are reported in ppm with the solvent resonance as the internal standard. For ^{1}H NMR: $CDCl_3$ = δ 7.26 ppm, CD_3CN = δ 1.94 ppm, toluene-d_8 = δ 2.08, 6.97, 7.01, 7.09 ppm. For ^{13}C NMR: $CDCl_3$ = δ 77.16 ppm, CD_3CN = δ 1.32, 118.26 ppm, toluene-d_8 = δ 137.48, 128.87, 127.96, 125.13, 20.43 ppm.[3] Data is reported as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad; coupling constants in Hz; integration. High-resolution mass spectra were obtained on an Agilent 6210 Time-of-Flight LC/MS. NMR spectroscopic data of known compounds correspond to the data given in the appropriate references. NMR spectra of new compounds are attached.

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[1] Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518–1520.

[2] Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2925–2927.

[3] Fulmer, G. R.; Miller, A. J. M.; Sherden, N. H.; Gottlieb, H. E.; Nudelman, A.; Stoltz, B. M.; Bercaw, J. E.; Goldberg, K. I. *Organometallics.* **2010**, *29*, 2176–2179.

Experimental Data

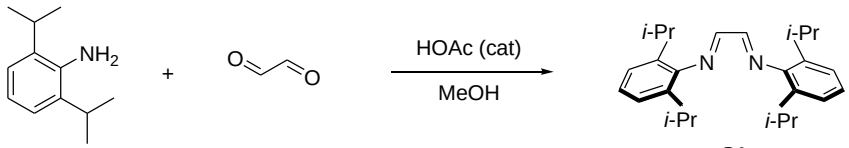
Experimental Procedures and Compound Characterization

General Procedure

Reagent **1** can be treated as a solid in air for short periods (< 1h). Upon prolonged storage in air it will hydrolyze to the urea derivative. Reaction solvents and reagents must be dry for optimal results. The following is a standard procedure:

In air, CsF (1.50 mmol, 3.00 equiv) was added to a vial and dried at 200 ºC for 1 h under high vacuum (<1 torr). After cooling to 23 ºC, a phenol (0.500 mmol, 1.00 equiv), *N*,*N*'-1,3-bis(2,6-diisopropylphenyl)-2,2-difluoroimidazolidene (**1**) (0.600 mmol, 1.20 equiv) and toluene (5 mL) were added to the vial or flask under a flow of nitrogen. The vial or flask was sealed, and the reaction mixture was stirred at 23 ºC for 30 min and subsequently heated at 80 ºC or 110 ºC for the appropriate time. Once cooled to 23 ºC, the reaction mixture was filtered through a pad of celite, eluting with CH_2Cl_2 (3 x 2 mL), and the filtrate was concentrated in vacuo. The residue was purified by chromatography on silica gel to afford a fluorinated compound.

***N,N'*-1,4-Bis(2,6-diisopropylphenyl)-1,4-diaza-butadiene (S1)**



S1

In air, to a solution of 2,6-diisopropylaniline (197 g, 1.00 mol, 2.00 equiv) and HOAc (1.0 mL, 0.018 mol, 0.035 equiv) in 250 mL of MeOH at 50 ºC in a flask was added a solution of glyoxal (73 g, 40% in water, 0.50 mol, 1.0 equiv) in 250 mL of MeOH. The reaction mixture was stirred at 50 ºC for 15 min and then stirred at 23 ºC for 10 h. The reaction mixture was filtered. The filter cake was washed with MeOH (3 x 100 mL) and dried in vacuo to afford 169 g of compound **S1** as a yellow solid (90% yield).

NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$, 23 ºC, δ): 8.11 (s, 2H), 7.20–7.16 (m, 6H), 2.98–2.92 (m, 4H), 1.20 (d, J = 9.5 Hz, 24H). ^{13}C NMR (125 MHz, $CDCl_3$, 23 ºC, δ): 163.2, 148.2, 136.9, 125.3, 123.3, 28.2, 23.5. These spectroscopic data correspond to previously

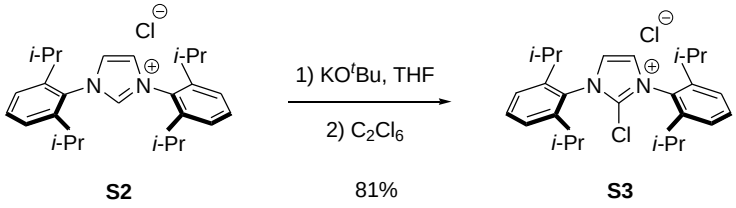
reported data.[4]

***N,N'*-1,3-Bis(2,6-diisopropylphenyl)imidazolium chloride (S2)**

In air, to *N,N'*-1,4-bis(2,6-diisopropylphenyl)-1,4-diaza-butadiene (**S1**) (226 g, 0.600 mol, 1.00 equiv) and paraformaldehyde (18.1 g, 0.603 mol, 1.03 equiv) in 5.4 L of EtOAc in a flask at 70 ºC was added a solution of TMSCl (76.5 mL, 0.603 mol, 1.03 equiv) in 80 mL of EtOAc dropwise over 45 min with vigorous stirring. The reaction mixture was stirred at 70 ºC for 2 h. After cooling to 10 ºC with stirring, the reaction mixture was filtered. The filter cake was washed with EtOAc (3 x 500 mL) and dried in vacuo to afford 220 g of compound **S2** as a colorless solid (86% yield).

NMR Spectroscopy: ^{1}H NMR (500 MHz, CD_3CN, 23 ºC, δ): 10.36 (s, 1H), 7.94 (s, 2H), 7.68 (t, *J* = 7.5 Hz, 2H), 7.50 (d, *J* = 7.5 Hz, 4H), 2.49–2.41 (m, 4H), 1.31 (d, *J* = 7.0 Hz, 12H), 1.25 (d, *J* = 7.0 Hz, 12H). ^{13}C NMR (125 MHz, CD_3CN, 23 ºC, δ): 145.6, 139.8, 132.2, 126.0, 124.9, 29.2, 23.9, 23.0. These spectroscopic data correspond to previously reported data.[4]

***N,N'*-1,3-Bis(2,6-diisopropylphenyl)-2-dichloroimidazolium chloride (S3)**



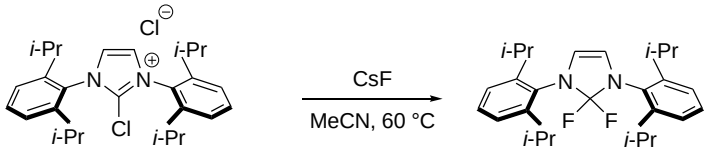
To *N,N'*-1,3-bis(2,6-diisopropylphenyl)imidazolium chloride (**S2**) (150 g, 353 mmol, 1.00 equiv) in 700 mL of THF in a flask at 23 ºC was added KO^{t}Bu (47.4 g, 423 mmol, 1.20 equiv). The reaction mixture was stirred at 23 ºC for 4 h. The reaction mixture was cooled to −40 ºC and 1,1,1,2,2,2-hexachloroethane (100 g, 423 mmol, 1.20 equiv) was added. The reaction mixture was warmed to 23 ºC and stirred at this temperature for 24 h. The reaction mixture was cooled to

[4] Hintermann, L. *Beil. J. Org. Chem.*. **2007**, No 22..

–40 ºC and filtered. The filter cake was washed with cold THF (–20 ºC, 3 x 100 mL) and toluene (6 x 100 mL). It was then dissolved in CH_2Cl_2 (500 mL) and filtered through a pad of Celite (10 g) eluting with CH_2Cl_2 (3 x 50 mL). The filtrate was concentrated under reduced pressure to afford 131 g of compound **S3** as a colorless solid (81% yield).

NMR Spectroscopy: ^{1}H NMR (500 MHz, CD_3CN, 23 ºC, δ): 8.51 (s, 2H), 7.75 (t, *J* = 7.8 Hz, 2H), 7.56 (d, *J* = 7.8 Hz, 4H), 2.37 (m, 4H), 1.31 (d, *J* = 6.8 Hz, 12H), 1.25 (d, *J* = 6.8 Hz, 12H). ^{13}C NMR (125 MHz, CD_3CN, 23 ºC, δ): 146.4, 133.8, 129.5, 127.8, 126.3, 118.3, 30.2, 24.3, 23.5. These spectroscopic data correspond to previously reported data. [5]

***N,N'*-1,3-Bis(2,6-diisopropylphenyl)-2,2-difluoroimidazolidene (1)**



S3 87% **1**

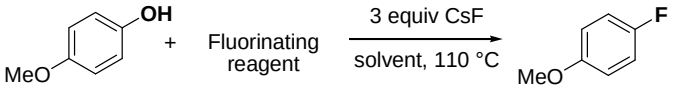
To *N,N'*-1,3-bis(2,6-diisopropylphenyl)-2-dichloroimidazolium chloride (**S3**) (1.20 g, 2.60 mmol, 1.00 equiv) in 20 mL of MeCN at 23 ºC was added CsF (1.58 g, 10.4 mmol, 4.00 equiv). The reaction mixture was stirred for 24 h at 60 ºC. The reaction mixture was cooled to 23 ºC and concentrated under reduced pressure. To the residue was added toluene (20 mL) and the mixture was filtered through a pad of Celite eluting with toluene (3 x 5 mL). The filtrate was concentrated under reduced pressure and the residue was washed with cold MeCN (–20 ºC, 3 x 2 mL) to afford 960 mg of compound **1** as a colorless solid (87% yield).

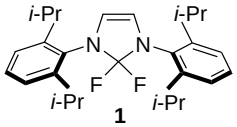
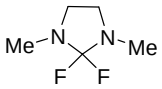
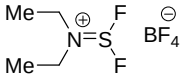
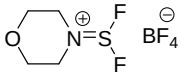
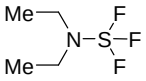
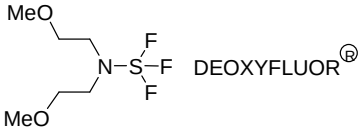
NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$, 23 ºC, δ): 7.46 (t, *J* = 7.0 Hz, 2H), 7.31 (d, *J* = 7.0 Hz, 4H), 5.98 (br s, 2H), 3.48–3.44 (m, 4H), 1.36 (d, *J* = 6.0 Hz, 12H), 1.31 (d, *J* = 6.0 Hz, 12H). ^{13}C NMR (125 MHz, $CDCl_3$, 23 ºC, δ): 150.8, 131.1, 129.5, 125.8 (t, *J* = 233 Hz), 124.1, 112.5, 28.6, 25.6, 23.9. ^{19}F NMR (375 MHz, $CDCl_3$, 23 ºC, δ): –36.5. Mass Spectrometry: HRMS-FIA (m/z): Calcd for $[C_{27}H_{36}F_2N_2 - F + H]^+$, 408.2935. Found, 408.2908.

Evaluation of commercially available fluorinating reagents

Table S1:

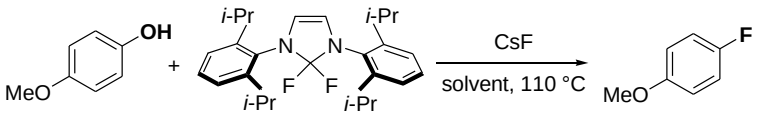
[5] Mendoza-Espinosa, D.; Donnadieu, B.; Bertrand, G. *J. Am. Chem. Soc.* **2010**, *132*, 7264-7265.



Fluorinating reagent:	MeCN	dioxane	toluene
 **1**	**<1%**	**88%**	**82%**
	<1%	<1%	<1%
 Xtalfluor-E®	<1%	<1%	<1%
 Xtalfluor-M®	<1%	<1%	<1%
 DAST®	<1%	<1%	<1%
 DEOXYFLUOR®	<1%	<1%	<1%

To 4-methoxyphenol (2.48 mg, 0.0200 mmol, 1.00 equiv) in solvent (0.2 mL) at 23 ºC, CsF (9.12 mg, 0.0600 mmol, 3.00 equiv) and fluorinating reagent (0.0240 mmol, 1.20 equiv) were added. The reaction mixture was stirred at 110 ºC for 20 h in a sealed vial, then cooled to 23 ºC. To the reaction mixture was added 3-nitrofluorobenzene (2.00 μL, 0.0188 mmol, 0.940 equiv). The yields were determined by comparing integration of the ^{19}F NMR (375 MHz, 23 ºC, toluene) resonance of 4-methoxyfluorobenzene (–126.8 ppm) with that of 3-nitrofluorobenzene (–112.0 ppm). Yields are reported in Table S1.

Evaluation of fluorination reaction in different solvents



1

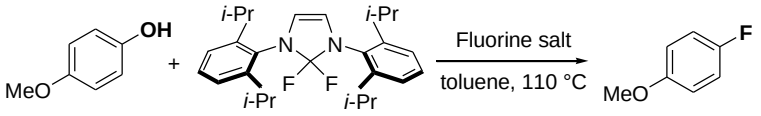
To 4-methoxyphenol (2.48 mg, 0.0200 mmol, 1.00 equiv) in solvent (0.2 mL) at 23 ºC, CsF (9.12 mg, 0.0600 mmol, 3.00 equiv) and *N*,*N*′-1,3-bis(2,6-diisopropylphenyl)-2,2-

difluoroimidazolidene (**1**) (10.2 mg, 0.0240 mmol, 1.20 equiv) were added. The reaction mixture was stirred at 110 ºC for 20 h in a sealed vial, then cooled to 23 ºC. To the reaction mixture was added 3-nitrofluorobenzene (2.00 μL, 0.0188 mmol, 0.940 equiv). The yields were determined by comparing integration of the ^{19}F NMR (375 MHz, 23 ºC, toluene) resonance of 4-methoxyfluorobenzene (–126.8 ppm) with that of 3-nitrofluorobenzene (–112.0 ppm). Yields are reported in Table S2.

Table S2: Evaluation of fluorination reaction in different solvents

Solvent	**Yield[%]** (^{19}F NMR)
Toluene	82
1,4-dioxane	88
DMF	10
THF	6
MeCN	<1
DCE	<1
MeOH	<1
AcOH	<1
1,2-dichlorobenzene	57

Evaluation of fluorination reaction with different fluorine salts



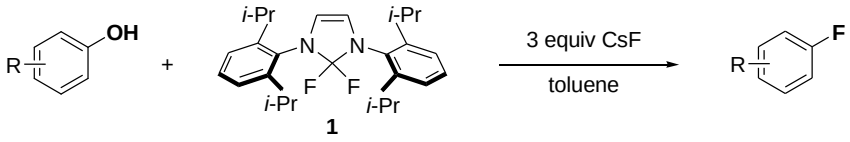
1

To 4-methoxyphenol (2.48 mg, 0.0200 mmol, 1.00 equiv) in toluene (0.2 mL) at 23 ºC, fluorine salt (0.0600 mmol, 3.00 equiv) and *N*,*N*′-1,3-bis(2,6-diisopropylphenyl)-2,2-difluoroimidazolidene (**1**) (10.2 mg, 0.0240 mmol, 1.20 equiv) were added. The reaction mixture was stirred at 110 ºC for 20 h in a sealed vial, then cooled to 23 ºC. To the reaction mixture was added 3-nitrofluorobenzene (2.00 μL, 0.0188 mmol, 0.940 equiv). The yields were determined by comparing integration of the ^{19}F NMR (375 MHz, 23 ºC, toluene) resonance of 4-methoxyfluorobenzene (–126.8 ppm) with that of 3-nitrofluorobenzene (–112.0 ppm). Yields are reported in Table S3.

Table S3: Evaluation of fluorination with different fluorine salts

Fluorine salt	Yield[%] (^{19}F NMR)
CsF	82
KF	4
LiF	9
AgF	<1
ZnF_2	3
NMe_4F	<1
$Bu_4NPh_3SiF_2$	9

General procedure (for volatile compounds)



To arylphenol (0.300 mmol, 1.00 equiv) in toluene (3.0 mL) at 23 ºC was added CsF (137 mg, 0.900 mmol, 3.00 equiv), and *N,N'*-1,3-bis(2,6-diisopropylphenyl)-2,2-difluoroimidazolidene (**1**) (153 mg, 0.360 mmol, 1.20 equiv). The reaction mixture was stirred in a sealed vial at 23 ºC for 30 min and then at 80 ºC or 110 ºC. Once cooled to 23 ºC, to the reaction mixture was added 3-nitrofluorobenzene (10.0 μL, 0.0939 mmol, 0.313 equiv). The yields were determined by comparing the integration of the ^{19}F NMR (375 MHz, 23 ºC, toluene) resonance of an arylfluoride with that of 3-nitrofluorobenzene (–112.0 ppm). Yields are reported in Table S4. [6]

Table S4: Synthesis of volatile arylfluorides

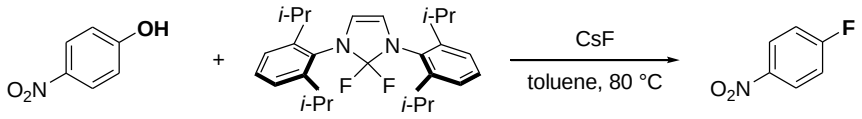
R	Time, temp	^{19}F chemical shift	Yield[%] (^{19}F NMR)
4-CO_2Me (**3**)	3 h, 80 ºC	–108.6 ppm	98
4-CHO (**5**)	3 h, 80 ºC	–106.1 ppm	95
4-CF_3 (**6**)	3 h, 80 ºC	–109.7 ppm	92
H (**7**)	18 h, 80 ºC	–115.2 ppm	82
3, 5-Cl (**10**)	18 h, 80 ºC	–111.2 ppm	88

[6] ^{19}F NMR chemical shifts given in Table S4 correspond to those of authentic samples purchased from Aldrich, Alfa, or TCI. All of the ^{19}F NMR spectra of these compounds are shown in the Spectra data with the ^{19}F NMR spectra of commercial compounds.

4-Br (**11**)	18 h, 80 ºC	–117.6 ppm	88
4-OMe (**12**)	20 h, 110 ºC	–126.8 ppm	82
4-Me (**13**)	20 h, 110 ºC	–120.5 ppm	81
2-Me (**14**)[a]	20 h, 110 ºC	–119.7 ppm	55 (87[b])
4-NH_2 (**15**)[a]	20 h, 110 ºC	–131.1 ppm	75
4-F (**16**)	20 h, 110 ºC	–121.7 ppm	74
4-pyridine (**23**)	18 h, 80 ºC	–106.2 ppm	90
3-pyridine (**24**)	20 h, 110 ºC	–128.9 ppm	84
2-pyridine (**25**)[a]	20 h, 110 ºC	–69.3 ppm	25 (50[b])
4-CH_2OH	20 h, 110 ºC	–117.2 ppm	5

a) 1,4-dioxane was used as solvent. b) 20 mol% $ZnPh_2$ was added.

4-Fluoronitrobenzene (2)

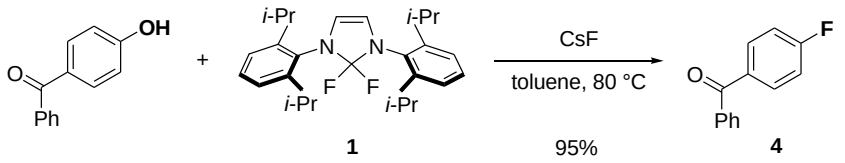


1 93% **2**

To 4-hydroxynitrobenzene (97.4 mg, 0.700 mmol, 1.00 equiv) in toluene (7.0 mL) at 23 ºC was added CsF (319 mg, 2.10 mmol, 3.00 equiv) and *N*,*N*′-1,3-bis(2,6-diisopropylphenyl)-2,2-difluoroimidazolidene (**1**) (357 mg, 0.840 mmol, 1.20 equiv). The reaction mixture was stirred in a sealed vial at 23 ºC for 30 min and then at 80 ºC for 3 h. Once cooled to 23 ºC, the reaction mixture was filtered through a pad of celite, eluting with CH_2Cl_2 (3 x 2 mL), and the filtrate was concentrated in vacuo. The residue was purified by chromatography on silica gel, eluting with hexane/EtOAc 20:1 (v/v), to afford 91.8 mg of the title compound as a yellow oil (93% yield).

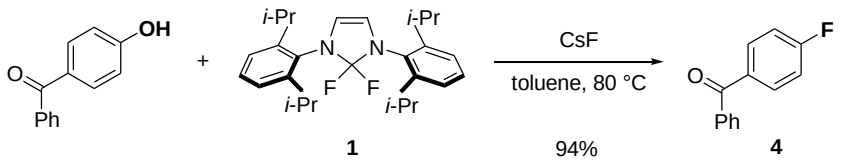
R_f = 0.60 (hexanes/EtOAc 10:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$, 23 ºC, δ): 8.28 (dd, *J* = 7.0, 4.5 Hz, 2H), 7.22 (t, *J* = 7.5 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$, 23 ºC, δ): 166.4 (d, *J* = 258 Hz), 144.5, 126.4 (d, *J* = 10 Hz), 116.5 (d, *J* = 24 Hz). ^{19}F NMR (375 MHz, $CDCl_3$, 23 ºC, δ): –106.2. The spectroscopic data corresponds with that of an authentic sample purchased from Alfa Aesar.

4-Fluorobenzophenone (4)



To 4-hydroxybenzophenone (99.1 mg, 0.500 mmol, 1.00 equiv) in toluene (5.0 mL) at 23 ºC was added CsF (228 mg, 1.50 mmol, 3.00 equiv) and *N*,*N'*-1,3-bis(2,6-diisopropylphenyl)-2,2-difluoroimidazolidene (1) (256 mg, 0.600 mmol, 1.20 equiv). The reaction mixture was stirred in a sealed vial at 23 ºC for 30 min and then at 80 ºC for 3 h. Once cooled to 23 ºC, the reaction mixture was filtered through a pad of celite, eluting with CH_2Cl_2 (3 x 2 mL), and the filtrate was concentrated in vacuo. The residue was purified by chromatography on silica gel, eluting with hexane/EtOAc 20:1 (v/v), to afford 95.1 mg of the title compound as a colorless solid (95% yield). R_f = 0.50 (hexane/EtOAc 10:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$, 23 ºC, δ): 7.86–7.84 (m, 2H), 7.78–7.76 (m, 2H), 7.61–7.58 (m, 1H), 7.51–7.48 (m, 2H), 7.18–7.15 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$, 23 ºC, δ): 195.5, 165.6 (d, J = 252 Hz), 137.7, 133.9, 132.9 (d, J = 9.1 Hz), 132.7, 131.1, 128.6, 115.7 (d, J = 22 Hz). ^{19}F NMR (375 MHz, $CDCl_3$, 23 ºC, δ): –108.7. The spectroscopic data corresponds with that previously reported.[7]

Fluorination of 4-fluorobenzophenone (4) outside the glovebox

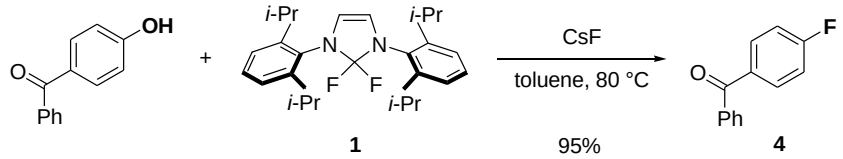


In air, CsF (228 mg, 1.50 mmol, 3.00 equiv) was added to a vial and dried at 200 ºC for 1 h under high vacuum (<1 torr). After cooling to 23 ºC, 4-hydroxybenzophenone (99.1 mg, 0.500 mmol, 1.00 equiv), *N*,*N'*-1,3-bis(2,6-diisopropylphenyl)-2,2-difluoroimidazolidene (**1**) (256 mg, 0.600 mmol, 1.20 equiv) and toluene (5 mL) was added to the vial under nitrogen atmosphere. The vial was sealed under nitrogen atmosphere and the reaction mixture was stirred at 23 ºC for 30 min and then at 80 ºC for 3 h. Once cooled to 23 ºC, the reaction mixture was filtered through a pad of celite, eluting with CH_2Cl_2 (3 x 2 mL), and the filtrate was concentrated in vacuo. The residue

[7] Xing, D.; Guan, B.; Cai, G.; Fang, Z.; Yang, L.; Shi, Z. *Org. Lett.* **2006**, *8*, 693–696.

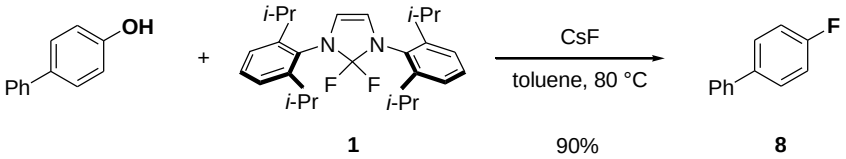
was purified by chromatography on silica gel, eluting with hexane/EtOAc 20:1 (v/v), to afford 94.1 mg of the title compound as a colorless solid (94% yield).

25-Mmol-scale fluorination of 4-fluorobenzophenone (4)



To 4-hydroxybenzophenone (5.00 g, 25.2 mmol, 1.00 equiv) in toluene (252 mL) at 23 ºC was added CsF (11.5 g, 75.6 mmol, 3.00 equiv) and *N*,*N*'-1,3-bis(2,6-diisopropylphenyl)-2,2-difluoroimidazolidene (**1**) (12.9 g, 30.2 mmol, 1.20 equiv). The reaction mixture was stirred in a 500 mL flask under nitrogen atmosphere at 23 ºC for 30 min and then at 80 ºC for 6 h. Once cooled to 23 ºC, the reaction mixture was filtered through a pad of celite, eluting with CH_2Cl_2 (3 x 20 mL), and the filtrate was concentrated in vacuo. The residue was purified by chromatography on silica gel, eluting with hexane/EtOAc 20:1 (v/v), to afford 4.79 g of the title compound as a colorless solid (95% yield).

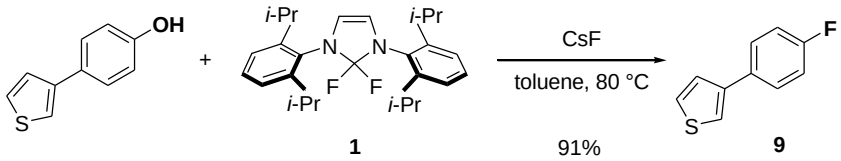
4-Fluorobiphenyl (8)



To 4-phenylphenol (102 mg, 0.600 mmol, 1.00 equiv) in toluene (6.0 mL) at 23 ºC was added CsF (274 mg, 1.80 mmol, 3.00 equiv) and *N*,*N*'-1,3-bis(2,6-diisopropylphenyl)-2,2-difluoroimidazolidene (**1**) (306 mg, 0.720 mmol, 1.20 equiv). The reaction mixture was stirred in a sealed vial at 23 ºC for 30 min and then at 80 ºC for 18 h. Once cooled to 23 ºC, the reaction mixture was filtered through a pad of celite, eluting with CH_2Cl_2 (3 x 2 mL), and the filtrate was concentrated in vacuo. The residue was purified by chromatography on silica gel, eluting with hexane/EtOAc 19:1 (v/v), to afford 92.9 mg of the title compound as a colorless solid (90% yield). R_f = 0.60 (hexanes/EtOAc 19:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$, 23 ºC, δ): 7.60–7.54 (m, 4H), 7.47 (dd, *J* = 7.5, 7.0 Hz, 2H), 7.36 (t, *J* = 7.5 Hz, 1H), 7.14 (dd, *J* = 8.0, 7.5 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$, 23 ºC, δ): 162.6 (d, *J* = 244 Hz), 140.4, 137.5, 128.9,

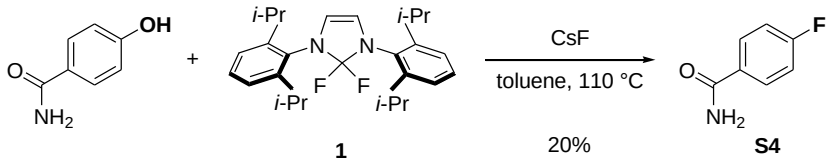
128.8 (d, J = 8.5 Hz), 127.4, 127.2, 115.8 (d, J = 21 Hz). ^{19}F NMR (375 MHz, $CDCl_3$, 23 ºC, δ): –117.2. The spectroscopic data corresponds with that previously reported.[8]

3-(4-Fluorophenyl)thiophene (9)



To 4-(thiophen-3-yl)phenol (106 mg, 0.600 mmol, 1.00 equiv) in toluene (6.0 mL) at 23 ºC was added CsF (274 mg, 1.80 mmol, 3.00 equiv) and *N*,*N*'-1,3-bis(2,6-diisopropylphenyl)-2,2-difluoroimidazolidene (**1**) (306 mg, 0.720 mmol, 1.20 equiv). The reaction mixture was stirred in a sealed vial at 23 ºC for 30 min and then at 80 ºC for 18 h. Once cooled to 23 ºC, the reaction mixture was filtered through a pad of celite, eluting with CH_2Cl_2 (3 x 2 mL), and the filtrate was concentrated in vacuo. The residue was purified by chromatography on silica gel, eluting with hexane/EtOAc 30:1 (v/v), to afford 97.2 mg of the title compound as a colorless solid (91% yield). R_f = 0.60 (hexanes/EtOAc 8:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$, 23 ºC, δ): 7.56 (dd, J = 8.8, 5.2 Hz, 2H), 7.39 (d, J = 3.5 Hz, 2H), 7.34 (t, J = 3.5 Hz, 1H), 7.09 (d, J = 8.8 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$, 23 ºC, δ): 162.2 (d, J = 245 Hz), 141.4, 132.2, 128.1 (d, J = 8.3 Hz), 126.5, 126.4, 120.2, 115.8 (d, J = 22 Hz). ^{19}F NMR (375 MHz, $CDCl_3$, 23 ºC, δ): –115.7. The spectroscopic data corresponds with that previously reported.[9]

4-Fluorobenzamide (S4)



To 4-hydroxybenzamide (96.0 mg, 0.700 mmol, 1.00 equiv) in toluene (7.0 mL) at 23 ºC was added CsF (319 mg, 2.10 mmol, 3.00 equiv) and *N*,*N*'-1,3-bis(2,6-diisopropylphenyl)-2,2-difluoroimidazolidene (**1**) (357 mg, 0.840 mmol, 1.20 equiv). The reaction mixture was stirred in a sealed vial at 23 ºC for 30 min and then at 110 ºC for 20 h. Once cooled to 23 ºC, the reaction

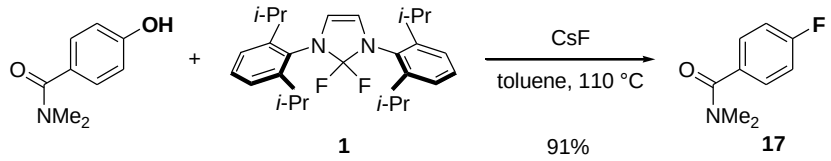
[8] Furuya, T.; Kaiser, H. M.; Ritter, T. *Angew. Chem. Int. Ed*. **2008**, *47*, 5993–5996.

[9] Sastry, C. V. R.; Marwah, A. K.; Marwah, P. ; Rao, G. S.; Shridhar, D. R. *Synthesis.* **1987**, *11*, 1024–1025.

mixture was filtered through a pad of celite, eluting with CH_2Cl_2 (3 x 2 mL), and the filtrate was concentrated in vacuo. The residue was purified by chromatography on silica gel, eluting with EtOAc to afford 19.5 mg of the title compound as a colorless solid (20% yield).

R_f = 0.40 (EtOAc). NMR Spectroscopy: ^{1}H NMR (500 MHz, CD_3CN, 23 ºC, δ): 7.91 (dd, *J* = 9.0, 5.5 Hz, 2H), 7.23 (t, *J* = 8.5 Hz, 2H), 6.80 (br s, 1H), 6.11 (br s, 1H). ^{13}C NMR (125 MHz, CD_3CN, 23 ºC, δ): 167.8, 164.9 (d, *J* = 249 Hz), 130.7, 130.3 (d, *J* = 9.1 Hz), 115.4 (d, *J* = 22 Hz). ^{19}F NMR (375 MHz, CD_3CN, 23 ºC, δ): –105.7. The spectroscopic data corresponds with that of an authentic sample purchased from Alfa Aesar.

***N,N*-Dimethyl-4-fluorobenzamide (17)**

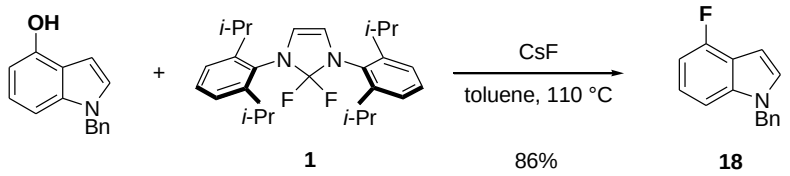


To *N,N*-dimethyl-4-hydroxybenzamide (100 mg, 0.610 mmol, 1.00 equiv) in toluene (6.1 mL) at 23 ºC was added CsF (278 mg, 1.83 mmol, 3.00 equiv) and *N,N'*-1,3-bis(2,6-diisopropylphenyl)-2,2-difluoroimidazolidene (**1**) (312 mg, 0.732 mmol, 1.20 equiv). The reaction mixture was stirred in a sealed vial at 23 ºC for 30 min and then at 110 ºC for 20 h. Once cooled to 23 ºC, the reaction mixture was filtered through a pad of celite, eluting with CH_2Cl_2 (3 x 2 mL), and the filtrate was concentrated in vacuo. The residue was purified by chromatography on silica gel, eluting with hexane/EtOAc 1:2 (v/v), to afford 92.7 mg of the title compound as a colorless solid (91% yield).

R_f = 0.25 (hexanes/EtOAc 1:2 (v/v)). NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$, 23 ºC, δ): 7.38 (dd, *J* = 8.8, 5.2 Hz, 2H), 7.04 (t, *J* = 8.8 Hz, 2H), 3.06 (br s, 3H), 2.95 (br s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$, 23 ºC, δ): 170.7, 163.3 (d, *J* = 248 Hz), 132.3 (d, *J* = 3.6 Hz), 129.4 (d, *J* = 9.1 Hz), 115.4 (d, *J* = 22 Hz), 39.7, 35.5. ^{19}F NMR (375 MHz, $CDCl_3$, 23 ºC, δ): –111.2. The spectroscopic data corresponds with that previously reported.[10]

[10] Ekoue-Kovi, K.; Wolf, C. *Org. Lett.* **2007**, *9*, 3429–3432.

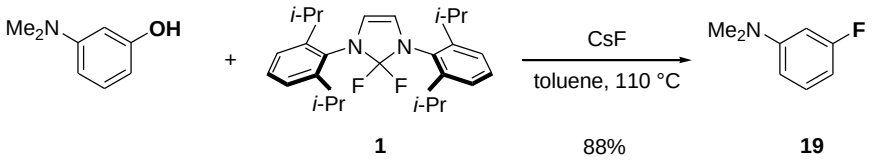
4-Fluoro-1-benzylindole (18)



1 86% **18**

To 4-hydroxy-1-benzylindole[11] (112 mg, 0.500 mmol, 1.00 equiv) in toluene (5.0 mL) at 23 ºC was added CsF (228 mg, 1.50 mmol, 3.00 equiv) and *N*,*N*′-1,3-bis(2,6-diisopropylphenyl)-2,2-difluoroimidazolidene (**1**) (256 mg, 0.600 mmol, 1.20 equiv). The reaction mixture was stirred in a sealed vial at 23 ºC for 30 min and then at 110 ºC for 20 h. Once cooled to 23 ºC, the reaction mixture was filtered through a pad of celite, eluting with CH_2Cl_2 (3 x 2 mL), and the filtrate was concentrated in vacuo. The residue was purified by chromatography on silica gel, eluting with hexane/EtOAc 10:1 (v/v), to afford 96.7 mg of the title compound as a colorless solid (86% yield). R_f = 0.50 (hexane/EtOAc 6:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$, 23 ºC, δ): 7.33–7.28 (m, 3H), 7.12–7.06 (m, 5H), 6.80–6.77 (m, 1H), 6.64 (d, *J* = 3.0 Hz, 1H), 5.32 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$, 23 ºC, δ): 156.6 (d, *J* = 307 Hz), 139.1 (d, *J* = 15 Hz), 137.2, 128.9, 128.3, 127.9, 126.9, 122.3 (d, *J* = 10 Hz), 117.8 (d, *J* = 28 Hz), 105.9 (d, *J* = 4.5 Hz), 104.4 (d, *J* = 24 Hz), 97.9, 50.5. ^{19}F NMR (375 MHz, $CDCl_3$, 23 ºC, δ): –123.2. Mass Spectrometry: HRMS-FIA (m/z): Calcd for $[C_{15}H_{12}FN + H]^+$, 226.1026. Found, 226.1056.

3-Fluoro-*N*,*N*-dimethylaniline (19)



1 88% **19**

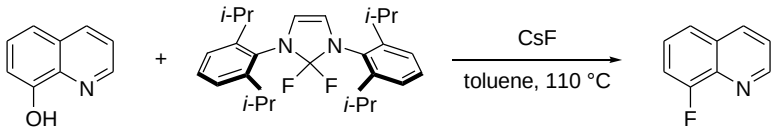
To 3-hydroxy-*N*,*N*-dimethylaniline (96.0 mg, 0.700 mmol, 1.00 equiv) in dioxane (7.0 mL) at 23 ºC was added CsF (319 mg, 2.10 mmol, 3.00 equiv) and *N*,*N*′-1,3-bis(2,6-diisopropylphenyl)-2,2-difluoroimidazolidene (**1**) (357 mg, 0.840 mmol, 1.20 equiv). The reaction mixture was stirred at 23 ºC for 30 min and then stirred at 110 ºC for 20 h in a sealed vial. Once cooled to 23 ºC, the reaction mixture was filtered through a pad of celite, eluting with CH_2Cl_2 (3 x 2 mL), and the filtrate was concentrated in vacuo. The residue was purified by chromatography on silica gel,

[11] Somei, M.; Tsuchiya, M. *Chem. Pharm. Bull.* **1981**, *29*, 3145–3157.

eluting with hexane/EtOAc 20:1 (v/v), to afford 85.7 mg of the title compound as a yellow oil (88% yield).

R_f = 0.50 (hexanes/EtOAc 10:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$, 23 ºC, δ): 7.18 (dd, *J* = 15.5, 8.0 Hz, 1H), 6.50–6.41 (m, 3H), 2.96 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$, 23 ºC, δ): 164.2 (d, *J* = 242 Hz), 152.3 (d, *J* = 10 Hz), 130.2 (d, *J* = 11 Hz), 108.0 (d, *J* = 1.8 Hz), 102.8 (d, *J* = 22 Hz), 99.4 (d, *J* = 26 Hz), 40.5. ^{19}F NMR (375 MHz, $CDCl_3$, 23 ºC, δ): –113.2. The spectroscopic data corresponds with that previously reported.[12]

8-Fluoroquinoline (20)



1 90% **20**

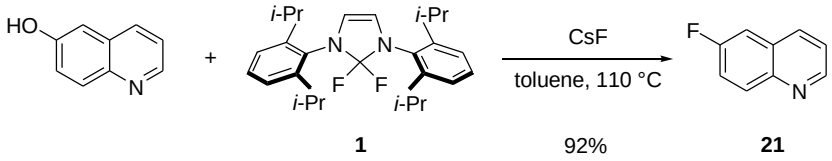
To 8-quinolinol (102 mg, 0.700 mmol, 1.00 equiv) in toluene (7.0 mL) at 23 ºC was added CsF (319 mg, 2.10 mmol, 3.00 equiv) and *N*,*N*'-1,3-bis(2,6-diisopropylphenyl)-2,2-difluoroimidazolidene (**1**) (357 mg, 0.840 mmol, 1.20 equiv). The reaction mixture was stirred in a sealed vial at 23 ºC for 30 min and then at 110 ºC for 20 h. Once cooled to 23 ºC, the reaction mixture was filtered through a pad of celite, eluting with CH_2Cl_2 (3 x 2 mL), and the filtrate was concentrated in vacuo. The residue was purified by chromatography on silica gel, eluting with hexane/EtOAc 3:1 (v/v), to afford 92.6 mg of the title compound as a colorless solid (90% yield).

R_f = 0.30 (hexane/EtOAc 3:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$, 23 ºC, δ): 8.91 (d, *J* = 3.5 Hz, 1H), 8.11 (d, *J* = 8.0 Hz, 1H), 7.54 (d, *J* = 8.0 Hz, 1H), 7.43–7.32 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$, 23 ºC, δ): 158.0 (d, *J* = 256 Hz), 150.5 (d, *J* = 1.8 Hz), 138.5 (d, *J* = 12 Hz), 135.7 (d, *J* = 2.8 Hz), 129.8, 126.3 (d, *J* = 8.3 Hz), 123.4 (d, *J* = 4.5 Hz), 122.0, 113.5 (d, *J* = 19 Hz). ^{19}F NMR (375 MHz, $CDCl_3$, 23 ºC, δ): –126.2 (dd, *J* = 10.3, *J* = 4.7 Hz). The spectroscopic data corresponds with that previously reported.[13]

[12] Watson, D. A.; Su, M.; Teverovskiy, G.; Zhang, Y.; García-Fortanet, J.; Kinzel, T.; Buchwald, S. L. *Science* **2009**, *325*, 1661.

[13] Chambers, R. D.; Holling, D.; Sandford, G.; Batsanov, A. S.; Howard, J. A. K. *J. Fluor. Chem.* **2004**, *125*, 661–671.

6-Fluoroquinoline (21)

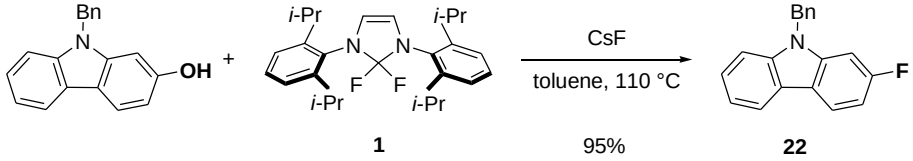


1 92% **21**

To 6-hydroxyquinoline (102 mg, 0.700 mmol, 1.00 equiv) in toluene (7.0 mL) at 23 ºC was added CsF (319 mg, 2.10 mmol, 3.00 equiv) and *N*,*N*'-1,3-bis(2,6-diisopropylphenyl)-2,2-difluoroimidazolidene (**1**) (357 mg, 0.840 mmol, 1.20 equiv). The reaction mixture was stirred in a sealed vial at 23 ºC for 30 min and then at 110 ºC for 20 h. Once cooled to 23 ºC, the reaction mixture was filtered through a pad of celite, eluting with CH_2Cl_2 (3 x 2 mL), and the filtrate was concentrated in vacuo. The residue was purified by chromatography on silica gel, eluting with hexane/EtOAc 1:1 (v/v), to afford 94.7 mg of the title compound as a colorless solid (92% yield).

R_f = 0.47 (EtOAc). NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$, 23 ºC, δ): 8.91 (dd, *J* = 4.5, 1.5 Hz, 1H), 8.18 (d, *J* = 8.0 Hz, 1H), 8.15 (dd, *J* = 9.0, *J* = 5.5 Hz, 1H), 7.53 (ddd, *J* = 9.0, 8.5, 2.0 Hz, 1H), 7.50–7.45 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$, 23 ºC, δ): 160.6 (d, *J* = 247 Hz), 149.9, 145.6, 135.6 (d, *J* = 4.5 Hz), 132.2 (d, *J* = 9.1 Hz), 129.1, 122.0, 120.1 (d, *J* = 26 Hz), 110.9 (d, *J* = 21 Hz). ^{19}F NMR (375 MHz, $CDCl_3$, 23 ºC, δ): –113.0. The spectroscopic data corresponds with that previously reported.[14]

2-Fluoro-9-benzylcarbazole (22)



1 95% **22**

To 2-hydroxy-9-benzylcarbazole[15] (109 mg, 0.400 mmol, 1.00 equiv) in toluene (4.0 mL) at 23 ºC was added CsF (182 mg, 1.20 mmol, 3.00 equiv) and *N*,*N*'-1,3-bis(2,6-diisopropylphenyl)-2,2-difluoroimidazolidene (**1**) (204 mg, 0.480 mmol, 1.20 equiv). The reaction mixture was stirred at 23 ºC for 30 min and then stirred at 110 ºC for 20 h in a sealed vial. Once cooled to 23 ºC, the reaction mixture was filtered through a pad of celite, eluting with CH_2Cl_2 (3 x 2 mL), and the filtrate was concentrated in vacuo. The residue was purified by chromatography on silica gel,

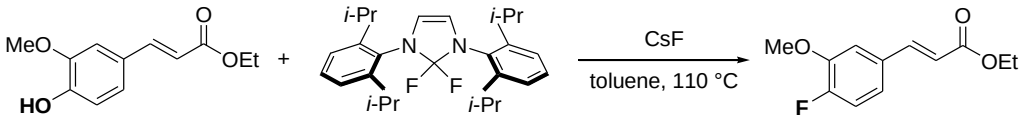
[14] Sveinbjornsson, A.; Bradlow, H. L.; Oae, S.; Vanderwerf, C. A. *J. Org. Chem.* **1951**, 16, 1450–1457.

[15] Elhalem, E.; Bailey, B. N.; Docampo, R.; Ujvary, I.; Szajnman, S. H.; Rodriguez, J. B. *J. Med. Chem.* **2002**, *45*, 3984–3999.

eluting with hexane/ CH_2Cl_2 10:1 (v/v), to afford 105 mg of the title compound as a colorless solid (95% yield).

R_f = 0.40 (hexane/EtOAc 20:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$, 23 ºC, δ): 8.09 (d, *J* = 8.0 Hz, 1H), 8.05 (dd, *J* = 8.5, 5.5 Hz, 1H), 7.43 (td, *J* = 8.5, 1.0 Hz, 1H), 7.37 (d, *J* = 8.0 Hz, 1H), 7.30–7.26 (m, 4H), 7.16–7.14 (m, 2H), 7.04 (dd, *J* = 9.5, 2.5 Hz, 1H), 7.00 (td, *J* = 9.0, 2.5 Hz, 1H), 5.46 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$, 23 ºC, δ): 162.3 (d, *J* = 241 Hz), 141.5 (d, *J* = 12 Hz), 141.3 (d, *J* = 1.9 Hz), 136.8, 129.0, 127.8, 126.5, 125.6, 122.9, 121.4 (d, *J* = 11 Hz), 120.1, 119.8, 119.5, 109.1, 107.4 (d, *J* = 25 Hz), 96.1 (d, *J* = 27 Hz), 46.9. ^{19}F NMR (375 MHz, $CDCl_3$, 23 ºC, δ): –115.1. Mass Spectrometry: HRMS-FIA (m/z): Calcd for $[C_{19}H_{14}FN + H]^+$, 276.1183. Found, 276.1173.

Ethyl 4-fluoro-3-methoxycinnamate[16] (26)



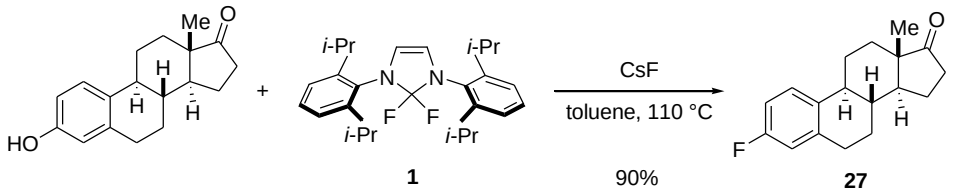
1 88% **26**

To ethyl 4-hydroxy-3-methoxycinnamate (111 mg, 0.500 mmol, 1.00 equiv) in toluene (4.0 mL) at 23 ºC was added CsF (228 mg, 1.50 mmol, 3.00 equiv) and *N*,*N*'-1,3-bis(2,6-diisopropylphenyl)-2,2-difluoroimidazolidene (**1**) (256 mg, 0.600 mmol, 1.20 equiv). The reaction mixture was stirred in a sealed vial at 23 ºC for 30 min and at 110 ºC for 20 h. Once cooled to 23 ºC, the reaction mixture was filtered through a pad of celite, eluting with CH_2Cl_2 (3 x 2 mL), and the filtrate was concentrated in vacuo. The residue was purified by chromatography on silica gel, eluting with hexane/EtOAc 10:1 (v/v), to afford 98.6 mg of the title compound as a colorless solid (88% yield).

R_f = 0.30 (hexane/EtOAc 10:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$, 23 ºC, δ): 7.61 (d, *J* = 16 Hz, 1H), 7.12–7.06 (m, 3H), 6.35 (d, *J* = 16 Hz, 1H), 4.26 (q, *J* = 7.0 Hz, 2H), 3.92 (s, 3H), 1.34 (q, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$, 23 ºC, δ): 166.9, 153.8 (d, *J* = 252 Hz), 148.1 (d, *J* = 11 Hz), 143.8, 131.2 (d, *J* = 3.6 Hz), 121.7 (d, *J* = 6.4 Hz), 118.3, 116.6 (d, *J* = 19 Hz), 112.4, 60.7, 56.4, 14.5. ^{19}F NMR (375 MHz, $CDCl_3$, 23 ºC, δ): –131.7. Mass Spectrometry: HRMS-FIA (m/z): Calcd for $[C_{12}H_{13}FO_3 + H]^+$, 225.0921. Found, 225.0932.

[16] Yoshida, I.; Suzuki, S. *Jpn. Kokai Tokkyo Koho* **2005**, 130 pp. JP 2005247833 A 20050915.

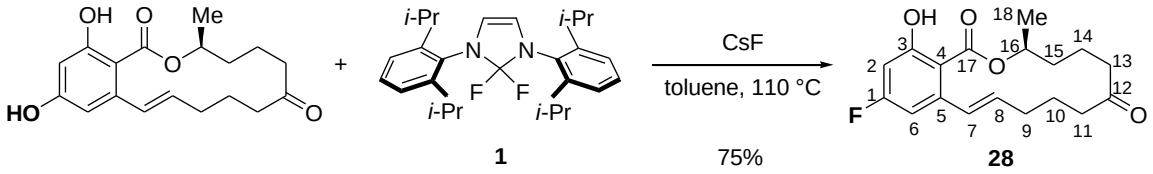
3-Deoxy-3-fluoroestrone (27)



To estrone (106 mg, 0.393 mmol, 1.00 equiv) in toluene (4.0 mL) at 23 ºC was added CsF (180 mg, 1.18 mmol, 3.00 equiv) and *N*,*N*'-1,3-bis(2,6-diisopropylphenyl)-2,2-difluoroimidazolidene (**1**) (201 mg, 0.472 mmol, 1.20 equiv). The reaction mixture was stirred in a sealed vial at 23 ºC for 30 min and at 110 ºC for 20 h. Once cooled to 23 ºC, the reaction mixture was filtered through a pad of celite, eluting with CH_2Cl_2 (3 x 2 mL), and the filtrate was concentrated in vacuo. The residue was purified by chromatography on silica gel, eluting with hexane/EtOAc 10:1 (v/v), to afford 96.3 mg of the title compound as a colorless solid (90% yield).

R_f = 0.33 (hexane/EtOAc 9:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$, 23 ºC, δ): 7.23 (dd, *J* = 8.0, 6.0 Hz, 1H), 6.85–6.77 (m, 2H), 2.92–2.88 (m, 2H), 2.51 (dd, *J* = 19.0, 9.0 Hz, 1H), 2.42–2.38 (m, 1H), 2.29–2.23 (m, 1H), 2.18–1.94 (m, 4H), 1.67–1.41 (m, 6H,), 0.91 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$, 23 ºC, δ): 220.9, 161.1 (d, *J* = 242 Hz), 138.9 (d, *J* = 7.3 Hz), 135.5, 127.0 (d, *J* = 7.3 Hz), 115.3 (d, *J* = 20 Hz), 112.7 (d, *J* = 20 Hz), 50.6, 48.1, 44.1, 38.3, 36.0, 31.7, 29.7, 26.5, 26.1, 21.8, 14.0. ^{19}F NMR (375 MHz, $CDCl_3$, 23 ºC, δ): –118.5. The spectroscopic data corresponds with that previously reported. [17]

1-Deoxy-1-fluorozearalenone (28)



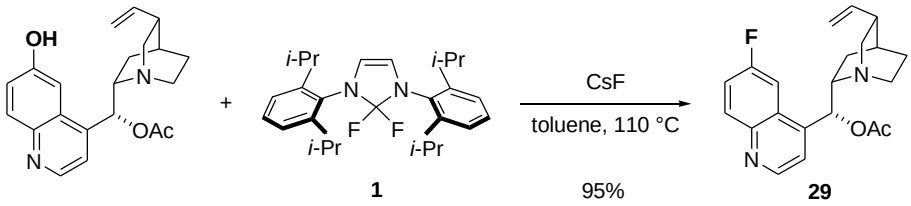
To zearalenone (31.8 mg, 0.100 mmol, 1.00 equiv) in toluene (1.0 mL) at 23 ºC was added CsF (45.6 mg, 0.300 mmol, 3.00 equiv) and *N*,*N*'-1,3-bis(2,6-diisopropylphenyl)-2,2-difluoroimidazolidene (**1**) (51.2 mg, 0.120 mmol, 1.20 equiv). The reaction mixture was stirred in a sealed vial at 23 ºC for 30 min and then at 110 ºC for 20 h. Once cooled to 23 ºC, the

[17] D. F. Morrow, R. M. Hofer, *J. Med. Chem.* **9**, 249 (1966).

reaction mixture was filtered through a pad of celite, eluting with CH_2Cl_2 (3 x 2 mL), and the filtrate was concentrated in vacuo. The residue was purified by chromatography on silica gel, eluting with hexane/EtOAc 6:1 (v/v), to afford 24.0 mg of the title compound as a colorless solid (75% yield).

R_f = 0.40 (hexane/EtOAc 3:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$, 23 ºC, δ): 12.01 (s, OH), 7.02 (d, *J* = 15 Hz, 1H, H-7), 6.62–6.56 (m, 2H, H-2, H-6), 5.75–5.69 (m, 1H, H-8), 5.04–5.01 (m, 1H, H-16), 2.84–2.78 (m, 1H, H-11), 2.61–2.57 (m, 1H, H-13), 2.39–2.36 (m, 1H, H-9), 2.25–2.12 (m, 4H, H-9, H-10, H-11, H-13), 1.78–1.71 (m, 2H, H-14), 1.69–1.63 (m, 2H, H-15), 1.54–1.50 (m, 1H, H-10), 1.40 (d, *J* = 6.5 Hz, 3H, H-18). ^{13}C NMR (125 MHz, $CDCl_3$, 23 ºC, δ): 210.9 (C-12), 171.1 (C-17), 166.0 (d, *J* = 254 Hz, C-1), 165.6 (d, *J* = 16 Hz, C-3), 144.6 (d, *J* = 11 Hz, C-5), 133.7 (C-8), 132.6 (C-7), 107.8 (d, *J* = 23 Hz, C-6), 107.1 (C-4), 103.4 (d, *J* = 24 Hz, C-2), 74.2 (C-16), 42.9 (C-13), 36.8 (C-11), 34.8 (C-15), 31.2 (C-9), 22.3 (C-14), 21.1 (C-10), 20.8 (C-18). ^{19}F NMR (375 MHz, $CDCl_3$, 23 ºC, δ): –104.3. Mass Spectrometry: HRMS-FIA (m/z): Calcd for $[C_{18}H_{21}FO_4 + H]^+$, 321.1497. Found, 321.1484.

6-Fluoro-*O*-acetyl-quinine (29)

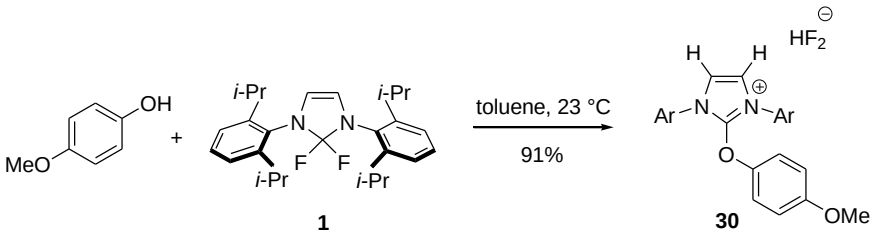


To 6-hydroxy-*O*-acetyl-quinine[10] (106 mg, 0.300 mmol, 1.00 equiv) in toluene (3.0 mL) at 23 ºC was added CsF (137 mg, 0.900 mmol, 3.00 equiv) and *N*,*N*'-1,3-bis(2,6-diisopropylphenyl)-2,2-difluoroimidazolidene (**1**) (153 mg, 0.360 mmol, 1.20 equiv). The reaction mixture was stirred in a sealed vial at 23 ºC for 30 min and then at 110 ºC for 20 h. Once cooled to 23 ºC, the reaction mixture was filtered through a pad of celite, eluting with CH_2Cl_2 (3 x 2 mL), and the filtrate was concentrated in vacuo. The residue was purified by chromatography on silica gel, eluting with CH_2Cl_2/MeOH 20:1 (v/v), to afford 101 mg of the title compound as a yellow foam (95% yield).

R_f = 0.50 (CH_2Cl_2/MeOH 10:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (500 MHz, CD_3CN, 23 ºC, δ): 8.86 (d, *J* = 4.5 Hz, 1H), 8.15 (dd, *J* = 9.3, 5.8 Hz, 1H), 8.02 (dd, *J* = 11.0, 2.5 Hz, 1H), 7.62–7.52 (m, 2H), 6.27 (d, *J* = 9.0 Hz, 1H), 5.99 (ddd, *J* = 17.5, 10.0, 8.0 Hz, 1H), 5.08–5.02 (m, 2H), 3.41 (dd, *J* = 17.5 Hz, 8.5 Hz, 1H), 3.13–3.09 (m, 1H), 2.87 (dd, *J* = 13.5, 10.0 Hz, 1H), 2.54–2.45 (m, 2H), 2.28 (m, 1H), 2.08–2.03 (m, 4H), 1.82 (m, 1H), 1.74–1.71 (m, 1H,), 1.55–1.45 (m,

2H). ^{13}C NMR (125 MHz, CD_3CN, 23 ºC, δ): 169.8, 159.9 (d, *J* = 245 Hz), 149.2, 145.7 (d, *J* = 6.2 Hz), 145.2, 142.0, 132.5 (d, *J* = 9.2 Hz), 126.6 (d, *J* = 10 Hz), 119.7, 118.7 (d, *J* = 26 Hz), 113.3, 107.1 (d, *J* = 23 Hz), 73.7, 59.5, 55.5, 41.3, 39.4, 27.2, 26.9, 24.9, 19.7. ^{19}F NMR (375 MHz, $CDCl_3$, 23 ºC, δ): –114.2. The spectroscopic data corresponds with that previously reported.[10]

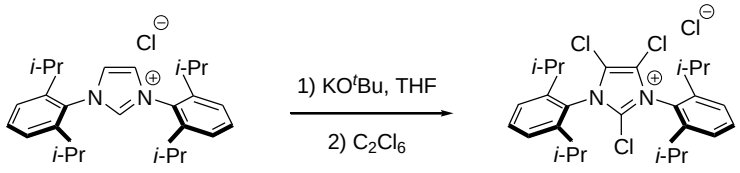
***N,N′*-1,3-Bis(2,6-diisopropylphenyl)-2-(4-methoxyphenyl)imidazolium bifluoride (30)**



To 4-methoxyphenol (68.0 mg, 0.547 mmol, 1.00 equiv) in toluene (6.5 mL) at 23 ºC, *N,N′*-1,3-bis(2,6-diisopropylphenyl)-2,2-difluoroimidazolidene (**1**) (279 mg, 0.657 mmol, 1.20 equiv) was added. The reaction mixture was stirred at 23 ºC for 1.5 h by which point compound **30** precipitated. The solid was collected over a pipette filter and washed with toluene (2 x 1 mL) and then diethyl ether (2 x 1 mL). The solid was eluted with CH_2Cl_2 (2 x 1 mL) and the filtrate was concentrated in vacuo to afford 274 mg of compound **30** as a pinkish white solid (91% yield).

NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$, 23 ºC, δ): 8.23 (s, 2H), 7.55 (t, *J* = 7.6 Hz, 2H), 7.30 (d, *J* = 7.6 Hz, 4H), 6.56 (d, *J* = 9.2 Hz, 2H), 6.30 (d, *J* = 9.2 Hz, 2H), 3.67 (s, 3H), 2.56–2.45 (m, 4H), 1.30 (d, *J* = 6.8 Hz, 12H), 1.19 (d, *J* = 6.8 Hz, 12H). ^{13}C NMR (100 MHz, $CDCl_3$, 23 ºC, δ): 158.1, 146.9, 145.5, 144.4, 132.2, 127.8, 125.0, 123.1, 119.3, 115.0, 55.8, 29.6, 25.5, 22.8. ^{19}FNMR (375 MHz, $CDCl_3$, 23 ºC, δ): –158.5 (broad). Mass Spectrometry: HRMS-FIA (m/z): Calcd for $[C_{34}H_{44}F_2N_2O_2 - HF_2 + H]^+$, 512.3397. Found, 512.3362.

***N,N′*-1,3-Bis(2,6-diisopropylphenyl)-4,5-dichloro-2-dicholoimidazolium chloride (S5)**

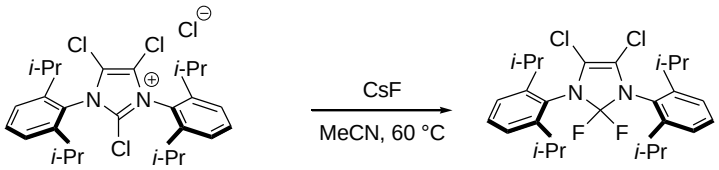


To *N,N′*-1,3-bis(2,6-diisopropylphenyl)imidazolium chloride (**S2**) (850 mg, 2.00 mmol, 1.00 equiv) in 20 mL of THF at 23 ºC was added KO^{t}Bu (806 mg, 7.20 mmol, 3.60 equiv). The

reaction mixture was stirred at 23 ºC for 4 h and then cooled to –40 ºC at which point 1,1,1,2,2,2-hexachloroethane (1.70 g, 7.20 mmol, 3.60 equiv) was added. The reaction mixture was then warmed to 23 ºC and stirred for 24 h. The reaction mixture was concentrated and toluene (50 mL) was added, then filtered through a pad of Celite eluting with toluene (6 x 5 mL). The filter cake was dissolved in CH_2Cl_2 (50 mL) and filtered through a pad of Celite eluting with CH_2Cl_2 (3 x 10 mL). The filtrate was concentrated under reduced pressure to afford 793 mg of compound **S5** as a colorless solid (75%).

NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$, 23 ºC, δ): 7.75 (t, *J* = 8.0 Hz, 2H), 7.48 (d, *J* = 7.5 Hz, 4H), 2.34–2.28 (m, 4H), 1.36 (d, *J* = 6.0 Hz, 12H), 1.34 (d, *J* = 6.0 Hz, 12H). ^{13}C NMR (125 MHz, $CDCl_3$, 23 ºC, δ): 145.6, 134.4, 126.2, 125.4, 124.9, 122.9, 30.1, 24.0, 23.9. Mass Spectrometry: HRMS-FIA (m/z): Calcd for $[C_{27}H_{34}Cl_4N_2 - Cl + H]^+$, 492.1860. Found, 492.1822.

***N,N'*-1,3-Bis(2,6-diisopropylphenyl)-4,5-dichloro-2,2-difluoroimidazolidene (S6)**

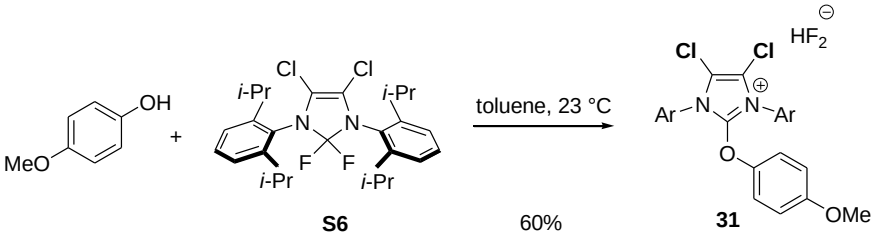


S5 80% **S6**

To *N,N'*-1,3-bis(2,6-diisopropylphenyl)-4,5-dichloro-2-dicholoimidazolium chloride (**S5**) (106 mg, 0.200 mmol, 1.00 equiv) in 10 mL of MeCN at 23 ºC was added CsF (122 mg, 0.800 mmol, 4.00 equiv). The reaction mixture was stirred for 24 h at 60 ºC. The reaction mixture was then cooled to 23 ºC and concentrated under reduced pressure. Toluene (5 mL) was added to the residue and the mixture was filtered through a pad of Celite eluting with toluene (3 x 1 mL). The filtrate was concentrated under reduced pressure and the residue was washed with cold MeCN (–20 ºC, 3 x 1 mL) to afford 79.2 mg of compound **S6** as a colorless solid (80%).

NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$, 23 ºC, δ): 7.47 (t, *J* = 7.5 Hz, 2H), 7.28 (d, *J* = 7.5 Hz, 4H), 3.27–3.22 (m, 4H), 1.29–1.28 (m, 24H). ^{13}C NMR (125 MHz, $CDCl_3$, 23 ºC, δ): 151.5, 130.4, 127.2, 124.4, 123.2 (t, *J* = 240 Hz), 108.1, 28.9, 25.1, 24.3. ^{19}F NMR (375 MHz, $CDCl_3$, 23 ºC, δ): –35.4. Mass Spectrometry: HRMS-FIA (m/z): Calcd for $[C_{27}H_{34}Cl_2F_2N_2 + H]^+$, 476.2156. Found, 476.2127.

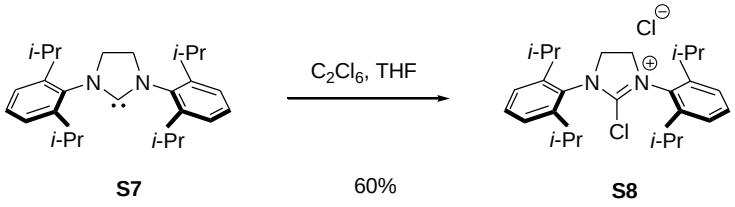
***N,N′*-1,3-Bis(2,6-diisopropylphenyl)-4,5-dichloro-2-(4-methoxyphenyl)imidazolium bifluoride (31)**



To 4-methoxyphenol (4.96 mg, 0.0400 mmol, 1.00 equiv) in toluene (0.4 mL) at 23 ºC, *N,N′*-1,3-bis(2,6-diisopropylphenyl)-4,5-dichloro-2,2-difluoroimidazolidene (**S6**) (23.8 mg, 0.0480 mmol, 1.20 equiv) was added. The reaction mixture was stirred at 23 ºC for 20 h in a sealed vial. The reaction mixture was concentrated under reduced pressure. Diethyl ether (2 mL) was added to the residue and the mixture was filtered through a pipette filter eluting with diethyl ether (3 x 1 mL). The filter cake was dried in vacuum to afford 14.8 mg of compound **31** as a colorless solid (60%).

NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$, 23 ºC, δ): 7.64 (t, *J* = 7.8 Hz, 2H), 7.38 (d, *J* = 8.0 Hz, 4H), 6.72 (d, *J* = 9.0 Hz, 2H), 6.59 (d, *J* = 9.0 Hz, 2H), 3.70 (s, 3H), 2.71–2.68 (m, 4H), 1.31 (d, *J* = 5.8 Hz, 12H), 1.22 (d, *J* = 5.8 Hz, 12H). ^{13}C NMR (125 MHz, $CDCl_3$, 23 ºC, δ): 158.7, 146.9, 146.7, 144.6, 133.6, 125.9, 124.9, 119.6, 118.9, 115.9, 56.1, 29.7, 24.9, 23.8. ^{19}F NMR (375 MHz, $CDCl_3$, 23 ºC, δ): –172.3. Mass Spectrometry: HRMS-FIA (m/z): Calcd for $[C_{34}H_{42}Cl_2F_2N_2O_2 – HF_2 + H]^+$, 580.2618. Found, 580.2575.

***N,N′*-1,3-Bis(2,6-diisopropylphenyl)-4,5-dihydro-2-dicholoimidazolium chloride (S8)**

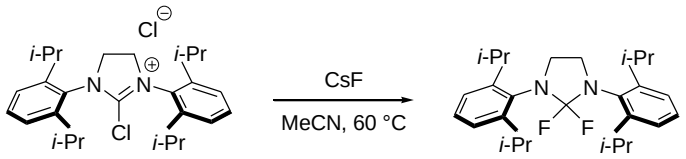


To *N,N′*-1,3-bis(2,6-diisopropylphenyl)-4,5-dihydro-imidazol-2-ylidene (**S7**) (180 mg, 0.500 mmol, 1.00 equiv) in 1.0 mL of THF at –40 ºC was added 1,1,1,2,2,2-hexachloroethane (142 mg, 0.600 mmol, 1.20 equiv). The reaction mixture was then warmed to 23 ºC and stirred for 24 h. The reaction mixture was cooled to –40 ºC and filtered. The filter cake was washed with cold THF (–20 ºC, 3 x 1 mL) and dried in vacuum to afford 138 mg of compound **S8** as a colorless solid (60%).

NMR Spectroscopy: ^{1}H NMR (500 MHz, CD_3CN, 23 ºC, δ): 7.63 (t, *J* = 8.0 Hz, 2H), 7.47 (d, *J* =

8.0 Hz, 4H), 4.72 (s, 4H), 3.08–3.03 (m, 4H), 1.39 (d, *J* = 6.5 Hz, 12H), 1.28 (d, *J* = 6.5 Hz, 12H). ^{13}C NMR (125 MHz, CD_3CN, 23 ºC, δ): 158.4, 146.9, 132.3, 129.1, 125.8, 53.6, 29.2, 24.2, 23.8. Mass Spectrometry: HRMS-FIA (m/z): Calcd for $[C_{27}H_{38}Cl_2N_2 - Cl + H]^+$, 426.2796. Found, 426.2808.

***N,N'*-1,3-Bis(2,6-diisopropylphenyl)-4,5-dihydro-2,2-difluoroimidazolidine (S9)**

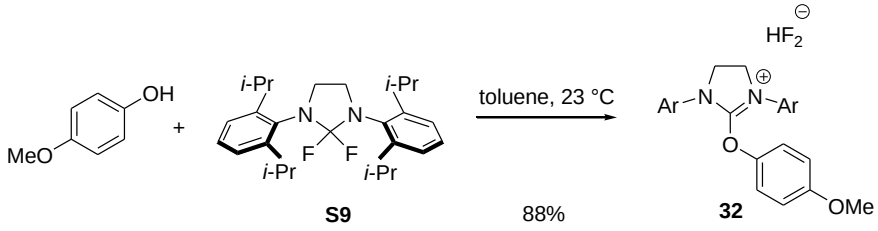


S8 75% **S9**

To *N,N'*-1,3-bis(2,6-diisopropylphenyl)-4,5-dihydro-2-dicholoimidazolium chloride (**S8**) (92.3 mg, 0.200 mmol, 1.00 equiv) in 2.0 mL of MeCN at 23 ºC was added CsF (122 mg, 0.800 mmol, 4.00 equiv). The reaction mixture was stirred for 24 h at 60 ºC. The reaction mixture was then cooled to 23 ºC and concentrated under reduced pressure. Toluene (5 mL) was added to the residue and the mixture was filtered through a pad of Celite eluting with toluene (3 x 1 mL). The filtrate was concentrated under reduced pressure and the residue was washed with cold MeCN (–20 ºC , 3 x 1 mL) to afford 64.1 mg of compound **S9** as a colorless solid (75%).

NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$, 23 ºC, δ): 7.37 (t, *J* = 7.5 Hz, 2H), 7.24 (d, *J* = 7.5 Hz, 4H), 3.79 (t, *J* = 4.0 Hz, 4H), 3.61–3.56 (m, 4H), 1.32 (d, *J* = 3.0 Hz, 12H), 1.31 (d, *J* = 3.0 Hz, 12H). ^{13}C NMR (125 MHz, $CDCl_3$, 23 ºC, δ): 151.1, 132.8, 128.8, 124.9 (t, *J* = 227 Hz), 124.3, 49.3, 28.8, 25.5, 24.2. ^{19}F NMR (375 MHz, $CDCl_3$, 23 ºC, δ): –56.2. Mass Spectrometry: HRMS-FIA (m/z): Calcd for $[C_{27}H_{38}F_2N_2 - F]^+$, 409.3019. Found, 409.3036.

***N,N'*-1,3-Bis(2,6-diisopropylphenyl)-4,5-dihydro-2-(4-methoxyphenyl)imidazolium bifluoride (32)**



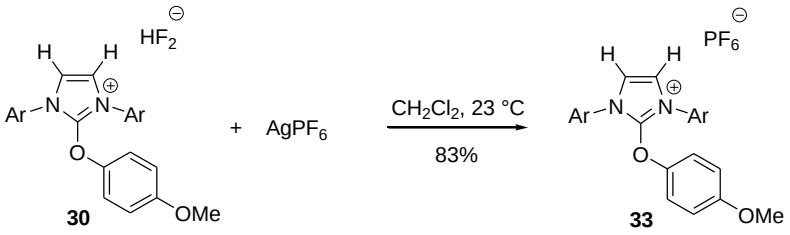
S9 88% **32**

To 4-methoxyphenol (4.96 mg, 0.0400 mmol, 1.00 equiv) in toluene (0.4 mL) at 23 ºC, *N,N'*-1,3-bis(2,6-diisopropylphenyl)-4,5-dihydro-2,2-difluoroimidazolidine (**S9**) (20.6 mg, 0.0480 mmol,

1.20 equiv) was added. The reaction mixture was stirred at 23 ºC for 20 h in a sealed vial. The reaction mixture was concentrated under reduced pressure. Diethyl ether (2 mL) was added to the residue and the mixture was filtered through a pipette filter eluting with diethyl ether (3 x 1 mL). The filter cake was dried in vacuum to afford 19.4 mg of compound **32** as a colorless solid (88%).

NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$, 23 ºC, δ): 7.36 (t, *J* = 7.5 Hz, 2H), 7.16 (d, *J* = 7.5 Hz, 4H), 6.63 (d, *J* = 9.0 Hz, 2H), 6.54 (d, *J* = 9.0 Hz, 2H), 4.72 (s, 4H), 3.64 (s, 3H), 3.25–3.20 (m, 4H), 1.37 (d, *J* = 6.5 Hz, 12H), 1.29 (d, *J* = 6.5 Hz, 12H). ^{13}C NMR (125 MHz, $CDCl_3$, 23 ºC, δ): 159.5, 157.9, 146.7, 145.1, 131.3, 128.8, 125.1, 119.4, 115.1, 55.8, 51.6, 29.2, 25.9, 23.8. ^{19}F NMR (375 MHz, $CDCl_3$, 23 ºC, δ): –162.5. Mass Spectrometry: HRMS-FIA (m/z): Calcd for $[C_{34}H_{46}Cl_2F_2N_2O_2 – HF_2 + H]^+$, 514.3553. Found, 514.3525.

***N,N'*-1,3-Bis(2,6-diisopropylphenyl)-2-(4-methoxyphenyl)imidazolium hexafluorophosphate (33)**

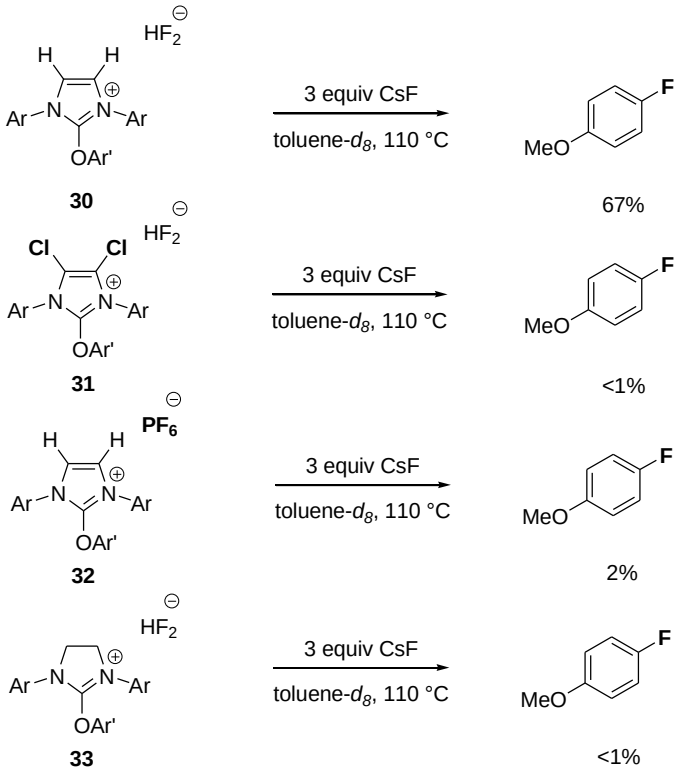


To *N,N'*-1,3-bis(2,6-diisopropylphenyl)-2-(4-methoxyphenyl)imidazolium bifluoride (**30**) (50.0 mg, 0.0907 mmol, 1.00 equiv) in CH_2Cl_2 (2.0 mL) at 23 °C was added $AgPF_6$ (23.0 mg, 0.907 mmol, 1.00 equiv). The reaction mixture was stirred at 23 °C for 1.5 h by which point a black precipitate formed. The mixture was filtered through a pipette filter and the filtrate was concentrated in vacuo. The residue was washed with diethyl ether (3 x 1 mL) to afford 60.0 mg of compound **32** as a colorless solid (83% yield).

NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$, 23 ºC, δ): 7.57 (t, *J* = 7.6 Hz, 2H), 7.56 (s, 2H), 7.32 (d, *J* = 8.0 Hz, 4H), 6.58 (d, *J* = 9.2 Hz, 2H), 6.32 (d, *J* = 9.2 Hz, 2H), 3.67 (s, 3H), 2.50–2.43 (m, 4H), 1.26 (d, *J* = 6.8 Hz, 12H), 1.21 (d, *J* = 6.8 Hz, 12H). ^{13}C NMR (100 MHz, $CDCl_3$, 23 ºC, δ): 158.1, 146.9, 145.5, 144.4, 132.2, 127.8, 125.0, 123.1, 119.3, 115.0, 55.8, 29.6, 25.5, 22.8. ^{19}FNMR (375 MHz, $CDCl_3$, 23 ºC, δ): 73.6 (d, *J* = 711 Hz). Mass Spectrometry: HRMS-FIA (m/z): Calcd for $[C_{34}H_{43}F_6N_2O_2P – PF_6 + H]^+$, 512.3397. Found, 512.3369.

Evaluation of fluorination reaction from 30, 31, 32, 33.

Scheme 1:

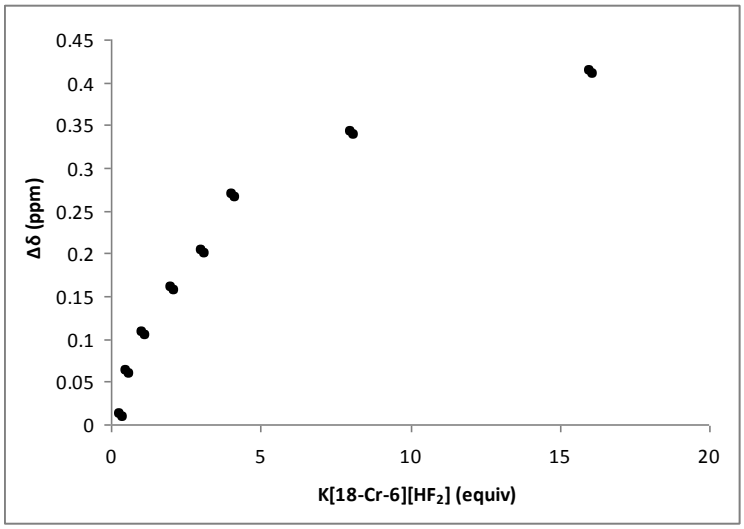


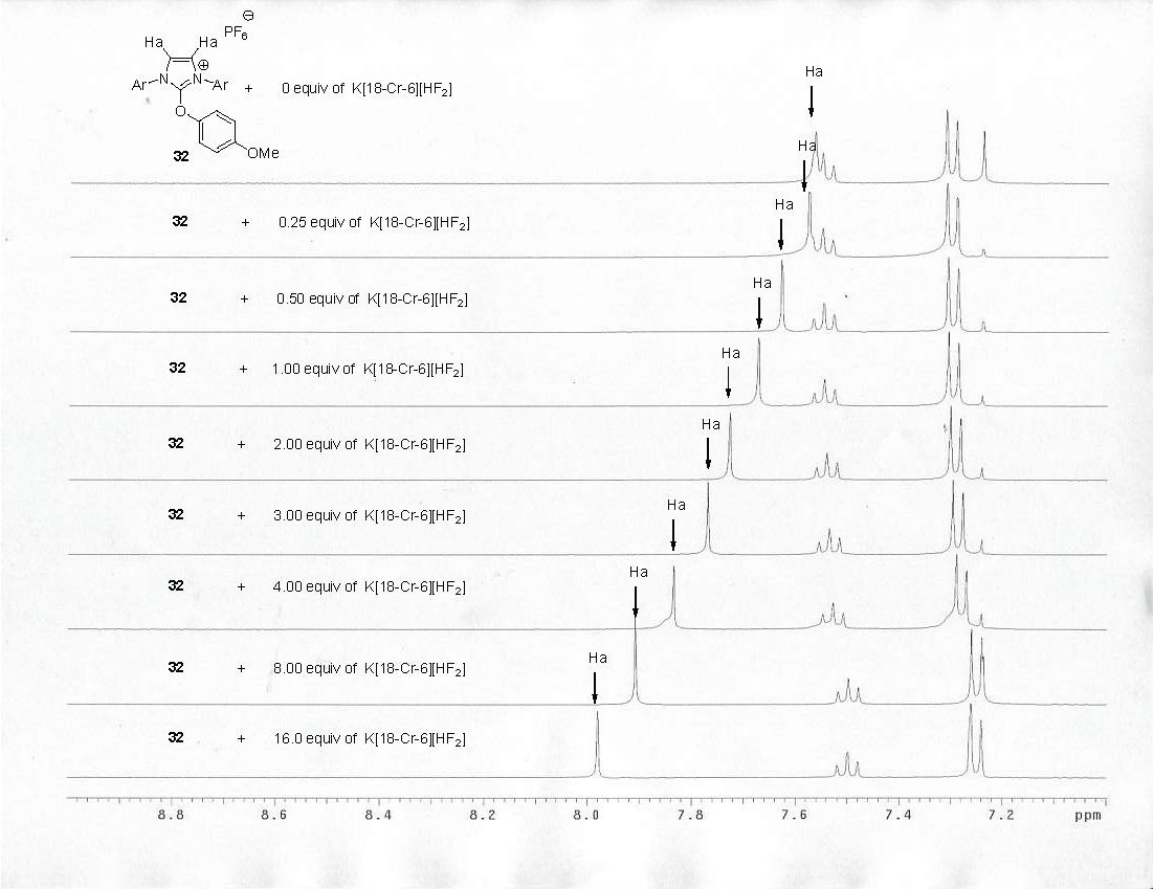
Ar = 2,6-diisopropylphenyl, Ar'= 4-methoxylphenyl

To intermediate (**30**, **31**, **32** or **33**) (0.0400 mmol, 1.00 equiv) in toluene-d_8 (0.4 mL) at 23°C was added CsF (18.6 mg, 3.00 equiv). 1,2-Dichloroethane (2.00 μL) was added into the reaction as the internal standard. The reaction mixture was stirred at 110 °C for 60 h. Once cooled to 23 ºC, the yields were determined by comparing the integration of the ^{1}H NMR (500 MHz, toluene-d_8, 23 ºC) resonance of 4-methoxyfluorobenzene (4.35 ppm, 3H) with that of 1,2-dichloroethane (4.95 ppm, 2H). Yields are reported in Scheme 1.

Titration Experiment

A titration experiment was performed on **32** to probe the hypothesis that hydrogen bonding is relevant for fluorination. A shift in the ^{1}H NMR resonance of the hydrogen atoms of the imidazolium heterocycle from 7.56 ppm to 7.98 ppm was observed when the hexafluorophosphate salt **32** was treated with up to 16 equivalents of bifluoride. Due to the insolubility of KHF_2 in toluene with 18-crown-6, $CDCl_3$ was chosen as the solvent ($\Delta\delta = \delta_{complex} - \delta_{32}$, $\delta_{complex}$ is the shift of hydrogen atoms of the imidazolium heterocycle which was treated with different amount of KHF_2). The experiment showed that under similar ionic strength (same concentration of K[18-cr-6]), increasing amounts of bifluoride shift the ^{1}H NMR resonance of the hydrogen atoms of the imidazolium heterocycle downfield.





A stock solution of *N*,*N*′-1,3-bis(2,6-diisopropylphenyl)-2-(4-methoxyphenyl)imidazolium hexafluorophosphate (**32**) (80.0 mg) in $CDCl_3$ (5.6 mL) was prepared and distributed evenly amongst 8 vials in 0.7 mL aliquots (each aliquot containing 10.0 mg, 0.0150 mmol, 1.00 equiv of **32**). Each vial had previously been prepared with the appropriate solid amounts of 18-crown-6

and KHF_2 (0.250 equiv, 0.500 equiv, 1.00 equiv, 2.00 equiv, 4.00 equiv, 8.00 equiv 16.0 equiv). After aliquot addition, 18-crown-6 and KHF_2 dissolved and the vials were stirred at 23 °C for 1.5 h.

Table S5: Amounts of starting material in the titration experiment

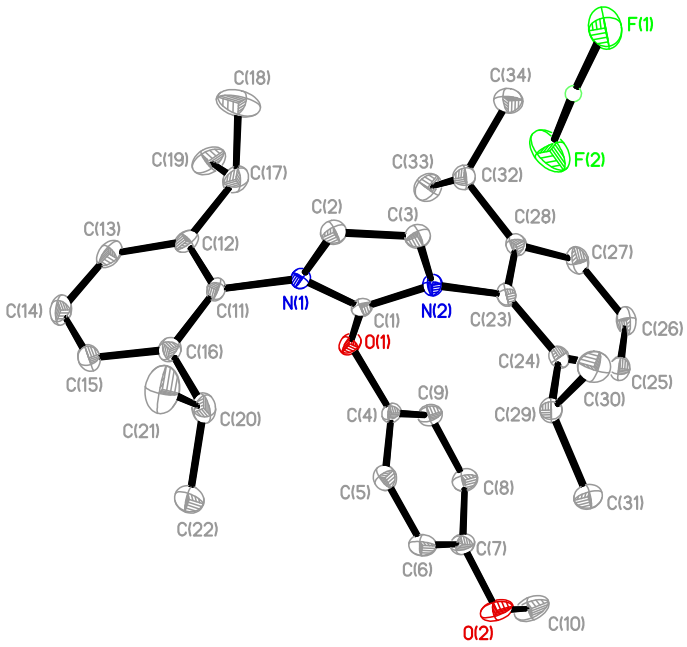
Entry	**KHF_2 (mg/equiv)**	**KPF_6 (mg/equiv)**	**18-Cr-6 (mg)**	**32 (mg)**	**$CDCl_3$ (mL)**
1	0.00/0.00	44.7/16.0	64.4	10.0	1.00
2	0.30/0.250	44.0/15.7	64.4	10.0	1.00
3	0.60/0.500	43.4/15.5	64.4	10.0	1.00
4	1.20/1.00	42.1/15.0	64.4	10.0	1.00
5	2.38/2.00	39.3/14.0	64.4	10.0	1.00
6	3.57/3.00	36.5/13.0	64.4	10.0	1.00
7	4.76/4.00	33.7/12.0	64.4	10.0	1.00
8	9.52/8.00	22.4/8.00	64.4	10.0	1.00
9	19.0/16.0	0.00/0.00	64.4	10.0	1.00

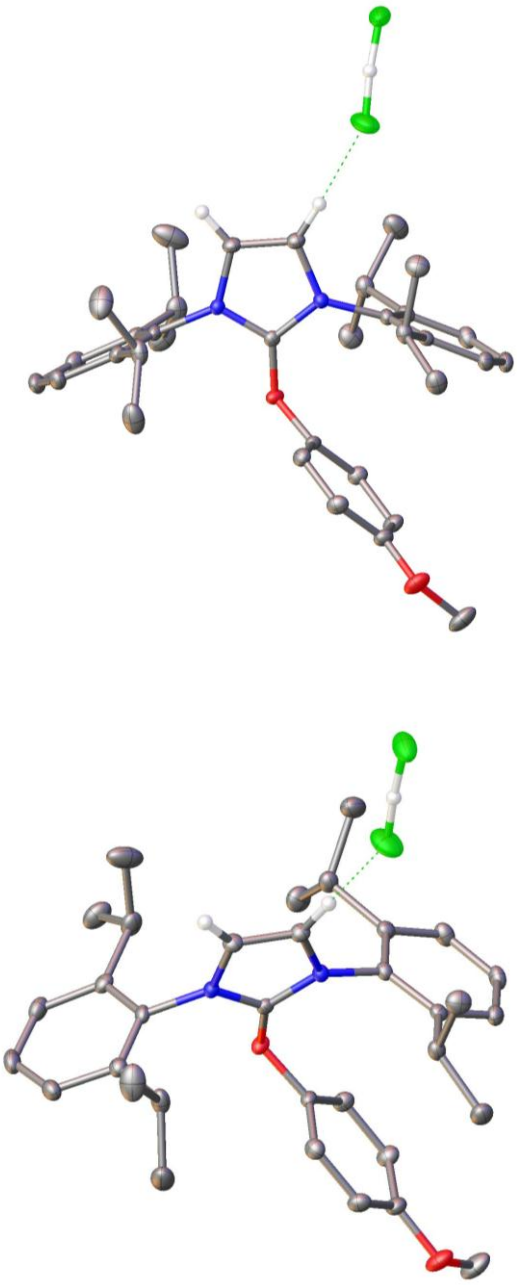
X-ray Crystallographic Analysis

N,N'-1,3-Bis(2,6-diisopropylphenyl)-2-(4-methoxyphenyl)imidazolium bifluoride (30)

Experimental

A crystal mounted on a diffractometer was collected data at 100 K. The intensities of the reflections were collected by means of a Bruker APEX II CCD diffractometer ($Mo_{K\alpha}$ radiation, λ=0.71073 Å), and equipped with an Oxford Cryosystems nitrogen flow apparatus. The collection method involved 0.5° scans in ω at 28° in 2θ. Data integration down to 0.74 Å resolution was carried out using SAINT V7.46 A (Bruker diffractometer, 2009) with reflection spot size optimisation. Absorption corrections were made with the program SADABS (Bruker diffractometer, 2009). The structure was solved by the direct methods procedure and refined by least-squares methods again F^2 using SHELXS-97 and SHELXL-97 (Sheldrick, 2008). Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were allowed to ride on the respective atoms. Crystal data as well as details of data collection and refinement are summarized in Table S6, geometric parameters are shown in Table S7 and hydrogen-bond parameters are listed in Table S8. The Ortep plots produced with SHELXL-97 program, and the other drawings were produced with Accelrys DS Visualizer 2.0 (Accelrys, 2007).





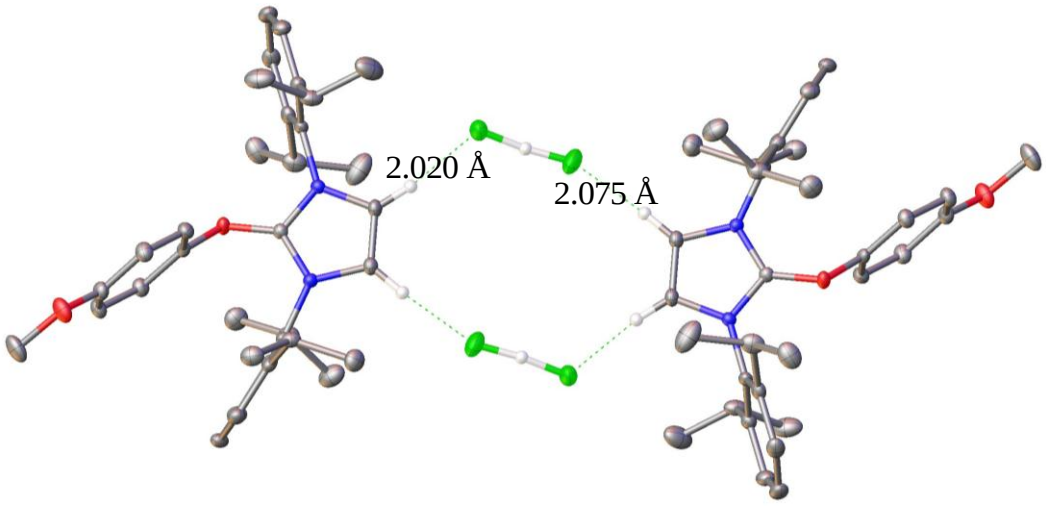


Table S6. Crystal data and structure refinement for the intermediate **30**

Chemical formula	$C_{36}H_{48}Cl_4F_2N_2O_2$
M_r	720.56
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	100
a, b, c (Å)	12.3348 (9), 13.9342 (11), 22.0311 (17)
β (°)	101.403 (1)
V (Å^3)	3711.9 (5)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.36
Crystal size (mm)	0.28 × 0.24 × 0.10
Data collection	
Diffractometer	CCD area detector diffractometer
Absorption correction	Multi-scan *SADABS*
T_{min}, T_{max}	0.905, 0.965

No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	62600, 8209, 6615
R_{int}	0.043
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.058, 0.155, 1.02
No. of reflections	8209
No. of parameters	447
No. of restraints	12
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.06, -1.04

Computer programs: *APEX2* v2009.3.0 (Bruker-AXS, 2009), *SAINT* 7.46A (Bruker-AXS, 2009), *SHELXS97* (Sheldrick, 2008), *SHELXL97* (Sheldrick, 2008), Bruker *SHELXTL*.

Table S7. Bond lengths [Å] and angles [°] for the intermediate **30**

O1—C1	1.322 (2)	C21—H21C	0.9800
O1—C4	1.427 (2)	C22—H22A	0.9800
O2—C7	1.370 (3)	C22—H22B	0.9800
O2—C10	1.432 (3)	C22—H22C	0.9800
N1—C1	1.333 (3)	C23—C28	1.396 (3)
N1—C2	1.395 (3)	C23—C24	1.399 (3)
N1—C11	1.454 (3)	C24—C25	1.392 (3)
N2—C1	1.339 (3)	C24—C29	1.521 (3)
N2—C3	1.400 (3)	C25—C26	1.386 (3)
N2—C23	1.451 (3)	C25—H25	0.9500
C2—C3	1.347 (3)	C26—C27	1.380 (3)
C2—H2	0.9500	C26—H26	0.9500
C3—H3	0.9500	C27—C28	1.398 (3)

C4—C9	1.371 (3)	C27—H27	0.9500
C4—C5	1.382 (3)	C28—C32	1.519 (3)
C5—C6	1.385 (3)	C29—C31	1.529 (3)
C5—H5	0.9500	C29—C30	1.536 (3)
C6—C7	1.394 (3)	C29—H29	1.0000
C6—H6	0.9500	C30—H30A	0.9800
C7—C8	1.388 (3)	C30—H30B	0.9800
C8—C9	1.390 (3)	C30—H30C	0.9800
C8—H8	0.9500	C31—H31A	0.9800
C9—H9	0.9500	C31—H31B	0.9800
C10—H10A	0.9800	C31—H31C	0.9800
C10—H10B	0.9800	C32—C33	1.529 (3)
C10—H10C	0.9800	C32—C34	1.532 (3)
C11—C16	1.391 (3)	C32—H32	1.0000
C11—C12	1.403 (3)	C33—H33A	0.9800
C12—C13	1.392 (3)	C33—H33B	0.9800
C12—C17	1.516 (3)	C33—H33C	0.9800
C13—C14	1.381 (4)	C34—H34A	0.9800
C13—H13	0.9500	C34—H34B	0.9800
C14—C15	1.377 (3)	C34—H34C	0.9800
C14—H14	0.9500	C35—Cl1	1.759 (3)
C15—C16	1.400 (3)	C35—Cl2	1.778 (4)
C15—H15	0.9500	C35—H35C	0.9900
C16—C20	1.516 (3)	C35—H35D	0.9900
C17—C18	1.525 (4)	C35D—Cl1D	1.751 (17)
C17—C19	1.526 (3)	C35D—Cl2D	1.777 (16)
C17—H17	1.0000	C35D—H35A	0.9900
C18—H18A	0.9800	C35D—H35B	0.9900
C18—H18B	0.9800	C36—Cl4	1.764 (4)

C18—H18C	0.9800	C36—Cl3	1.787 (4)
C19—H19A	0.9800	C36—H36C	0.9900
C19—H19B	0.9800	C36—H36D	0.9900
C19—H19C	0.9800	C36D—Cl3D	1.749 (18)
C20—C22	1.532 (4)	C36D—Cl4D	1.857 (18)
C20—C21	1.535 (4)	C36D—H36A	0.9900
C20—H20	1.0000	C36D—H36B	0.9900
C21—H21A	0.9800	F1—H1	1.16 (4)
C21—H21B	0.9800	F2—H1	1.11 (4)
C1—O1—C4	117.99 (16)	H21A—C21—H21C	109.5
C7—O2—C10	116.03 (18)	H21B—C21—H21C	109.5
C1—N1—C2	107.92 (17)	C20—C22—H22A	109.5
C1—N1—C11	124.72 (17)	C20—C22—H22B	109.5
C2—N1—C11	127.31 (17)	H22A—C22—H22B	109.5
C1—N2—C3	107.69 (17)	C20—C22—H22C	109.5
C1—N2—C23	122.55 (17)	H22A—C22—H22C	109.5
C3—N2—C23	128.51 (18)	H22B—C22—H22C	109.5
O1—C1—N1	122.45 (19)	C28—C23—C24	124.03 (19)
O1—C1—N2	127.68 (19)	C28—C23—N2	116.74 (18)
N1—C1—N2	109.56 (18)	C24—C23—N2	119.12 (18)
C3—C2—N1	107.58 (18)	C25—C24—C23	116.49 (19)
C3—C2—H2	126.2	C25—C24—C29	122.07 (19)
N1—C2—H2	126.2	C23—C24—C29	121.40 (19)
C2—C3—N2	107.25 (19)	C26—C25—C24	121.1 (2)
C2—C3—H3	126.4	C26—C25—H25	119.4
N2—C3—H3	126.4	C24—C25—H25	119.4
C9—C4—C5	122.3 (2)	C27—C26—C25	120.6 (2)
C9—C4—O1	117.44 (19)	C27—C26—H26	119.7

C5—C4—O1	120.05 (18)	C25—C26—H26	119.7
C4—C5—C6	118.4 (2)	C26—C27—C28	120.9 (2)
C4—C5—H5	120.8	C26—C27—H27	119.6
C6—C5—H5	120.8	C28—C27—H27	119.6
C5—C6—C7	120.2 (2)	C23—C28—C27	116.7 (2)
C5—C6—H6	119.9	C23—C28—C32	123.24 (19)
C7—C6—H6	119.9	C27—C28—C32	120.10 (19)
O2—C7—C8	123.9 (2)	C24—C29—C31	113.49 (19)
O2—C7—C6	115.7 (2)	C24—C29—C30	110.30 (18)
C8—C7—C6	120.4 (2)	C31—C29—C30	108.93 (19)
C7—C8—C9	119.3 (2)	C24—C29—H29	108.0
C7—C8—H8	120.4	C31—C29—H29	108.0
C9—C8—H8	120.4	C30—C29—H29	108.0
C4—C9—C8	119.4 (2)	C29—C30—H30A	109.5
C4—C9—H9	120.3	C29—C30—H30B	109.5
C8—C9—H9	120.3	H30A—C30—H30B	109.5
O2—C10—H10A	109.5	C29—C30—H30C	109.5
O2—C10—H10B	109.5	H30A—C30—H30C	109.5
H10A—C10—H10B	109.5	H30B—C30—H30C	109.5
O2—C10—H10C	109.5	C29—C31—H31A	109.5
H10A—C10—H10C	109.5	C29—C31—H31B	109.5
H10B—C10—H10C	109.5	H31A—C31—H31B	109.5
C16—C11—C12	123.6 (2)	C29—C31—H31C	109.5
C16—C11—N1	118.40 (19)	H31A—C31—H31C	109.5
C12—C11—N1	117.98 (19)	H31B—C31—H31C	109.5
C13—C12—C11	116.6 (2)	C28—C32—C33	111.94 (19)
C13—C12—C17	121.8 (2)	C28—C32—C34	110.46 (19)
C11—C12—C17	121.6 (2)	C33—C32—C34	111.1 (2)
C14—C13—C12	121.7 (2)	C28—C32—H32	107.7

C14—C13—H13	119.2	C33—C32—H32	107.7
C12—C13—H13	119.2	C34—C32—H32	107.7
C15—C14—C13	120.0 (2)	C32—C33—H33A	109.5
C15—C14—H14	120.0	C32—C33—H33B	109.5
C13—C14—H14	120.0	H33A—C33—H33B	109.5
C14—C15—C16	121.4 (2)	C32—C33—H33C	109.5
C14—C15—H15	119.3	H33A—C33—H33C	109.5
C16—C15—H15	119.3	H33B—C33—H33C	109.5
C11—C16—C15	116.8 (2)	C32—C34—H34A	109.5
C11—C16—C20	123.3 (2)	C32—C34—H34B	109.5
C15—C16—C20	119.9 (2)	H34A—C34—H34B	109.5
C12—C17—C18	110.5 (2)	C32—C34—H34C	109.5
C12—C17—C19	113.7 (2)	H34A—C34—H34C	109.5
C18—C17—C19	109.3 (2)	H34B—C34—H34C	109.5
C12—C17—H17	107.7	Cl1—C35—Cl2	111.05 (17)
C18—C17—H17	107.7	Cl1—C35—H35C	109.4
C19—C17—H17	107.7	Cl2—C35—H35C	109.4
C17—C18—H18A	109.5	Cl1—C35—H35D	109.4
C17—C18—H18B	109.5	Cl2—C35—H35D	109.4
H18A—C18—H18B	109.5	H35C—C35—H35D	108.0
C17—C18—H18C	109.5	Cl1D—C35D—Cl2D	109.6 (10)
H18A—C18—H18C	109.5	Cl1D—C35D—H35A	109.7
H18B—C18—H18C	109.5	Cl2D—C35D—H35A	109.7
C17—C19—H19A	109.5	Cl1D—C35D—H35B	109.7
C17—C19—H19B	109.5	Cl2D—C35D—H35B	109.7
H19A—C19—H19B	109.5	H35A—C35D—H35B	108.2
C17—C19—H19C	109.5	Cl4—C36—Cl3	109.53 (18)
H19A—C19—H19C	109.5	Cl4—C36—H36C	109.8
H19B—C19—H19C	109.5	Cl3—C36—H36C	109.8

C16—C20—C22	110.6 (2)	Cl4—C36—H36D	109.8
C16—C20—C21	110.5 (2)	Cl3—C36—H36D	109.8
C22—C20—C21	111.1 (2)	H36C—C36—H36D	108.2
C16—C20—H20	108.2	Cl3D—C36D—Cl4D	99.9 (11)
C22—C20—H20	108.2	Cl3D—C36D—H36A	111.8
C21—C20—H20	108.2	Cl4D—C36D—H36A	111.8
C20—C21—H21A	109.5	Cl3D—C36D—H36B	111.8
C20—C21—H21B	109.5	Cl4D—C36D—H36B	111.8
H21A—C21—H21B	109.5	H36A—C36D—H36B	109.5
C20—C21—H21C	109.5		
C4—O1—C1—N1	-134.5 (2)	C12—C11—C16—C15	-0.2 (3)
C4—O1—C1—N2	52.5 (3)	N1—C11—C16—C15	-179.69 (18)
C2—N1—C1—O1	-173.83 (18)	C12—C11—C16—C20	179.0 (2)
C11—N1—C1—O1	4.0 (3)	N1—C11—C16—C20	-0.5 (3)
C2—N1—C1—N2	0.3 (2)	C14—C15—C16—C11	0.7 (3)
C11—N1—C1—N2	178.16 (18)	C14—C15—C16—C20	-178.6 (2)
C3—N2—C1—O1	173.32 (19)	C13—C12—C17—C18	98.7 (3)
C23—N2—C1—O1	5.1 (3)	C11—C12—C17—C18	-79.3 (3)
C3—N2—C1—N1	-0.4 (2)	C13—C12—C17—C19	-24.5 (3)
C23—N2—C1—N1	-168.62 (18)	C11—C12—C17—C19	157.4 (2)
C1—N1—C2—C3	-0.1 (2)	C11—C16—C20—C22	-126.3 (2)
C11—N1—C2—C3	-177.8 (2)	C15—C16—C20—C22	52.8 (3)
N1—C2—C3—N2	-0.2 (2)	C11—C16—C20—C21	110.2 (3)
C1—N2—C3—C2	0.4 (2)	C15—C16—C20—C21	-70.7 (3)
C23—N2—C3—C2	167.6 (2)	C1—N2—C23—C28	73.0 (3)
C1—O1—C4—C9	-127.6 (2)	C3—N2—C23—C28	-92.6 (3)
C1—O1—C4—C5	57.7 (3)	C1—N2—C23—C24	-103.4 (2)
C9—C4—C5—C6	1.8 (3)	C3—N2—C23—C24	91.0 (3)

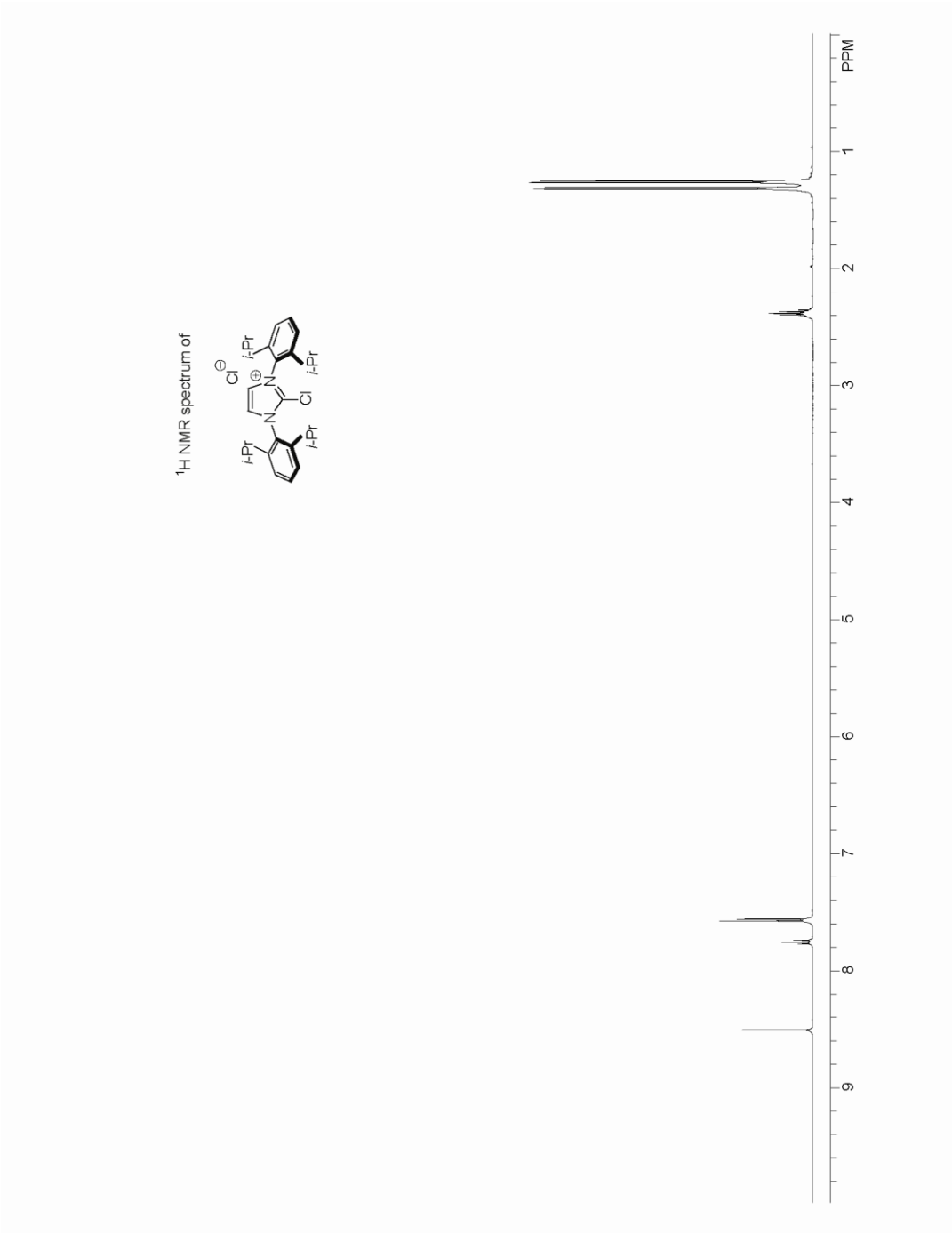
O1—C4—C5—C6	176.19 (19)	C28—C23—C24—C25	-4.3 (3)
C4—C5—C6—C7	-0.8 (3)	N2—C23—C24—C25	171.78 (19)
C10—O2—C7—C8	-2.4 (3)	C28—C23—C24—C29	173.4 (2)
C10—O2—C7—C6	177.6 (2)	N2—C23—C24—C29	-10.5 (3)
C5—C6—C7—O2	179.2 (2)	C23—C24—C25—C26	1.1 (3)
C5—C6—C7—C8	-0.7 (4)	C29—C24—C25—C26	-176.6 (2)
O2—C7—C8—C9	-178.7 (2)	C24—C25—C26—C27	2.6 (3)
C6—C7—C8—C9	1.3 (4)	C25—C26—C27—C28	-3.2 (3)
C5—C4—C9—C8	-1.2 (3)	C24—C23—C28—C27	3.8 (3)
O1—C4—C9—C8	-175.81 (19)	N2—C23—C28—C27	-172.43 (19)
C7—C8—C9—C4	-0.3 (3)	C24—C23—C28—C32	-175.7 (2)
C1—N1—C11—C16	100.4 (2)	N2—C23—C28—C32	8.1 (3)
C2—N1—C11—C16	-82.2 (3)	C26—C27—C28—C23	0.1 (3)
C1—N1—C11—C12	-79.1 (3)	C26—C27—C28—C32	179.6 (2)
C2—N1—C11—C12	98.3 (2)	C25—C24—C29—C31	-27.6 (3)
C16—C11—C12—C13	-0.5 (3)	C23—C24—C29—C31	154.8 (2)
N1—C11—C12—C13	178.95 (18)	C25—C24—C29—C30	94.9 (2)
C16—C11—C12—C17	177.7 (2)	C23—C24—C29—C30	-82.7 (2)
N1—C11—C12—C17	-2.9 (3)	C23—C28—C32—C33	-120.3 (2)
C11—C12—C13—C14	0.8 (3)	C27—C28—C32—C33	60.3 (3)
C17—C12—C13—C14	-177.3 (2)	C23—C28—C32—C34	115.3 (2)
C12—C13—C14—C15	-0.4 (4)	C27—C28—C32—C34	-64.1 (3)
C13—C14—C15—C16	-0.4 (4)		

Table S8. hydrogen-bond parameters for the intermediate **30**

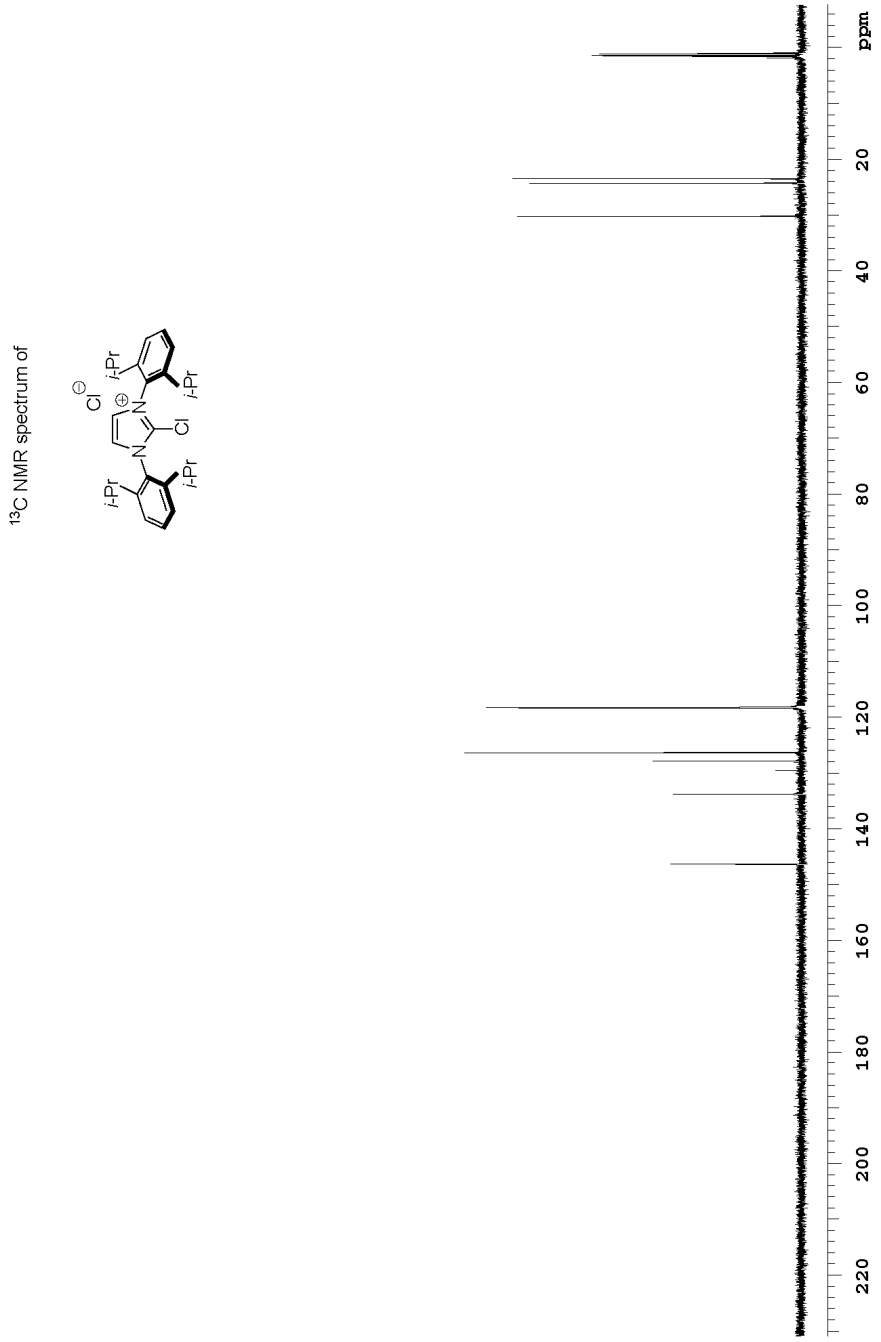
D—H···*A*	*D*—H (Å)	H···*A* (Å)	*D*···*A* (Å)	*D*—H···*A* (°)
F2—H1···F1	1.11 (4)	1.16 (4)	2.260 (2)	172 (3)

Spectroscopic Data

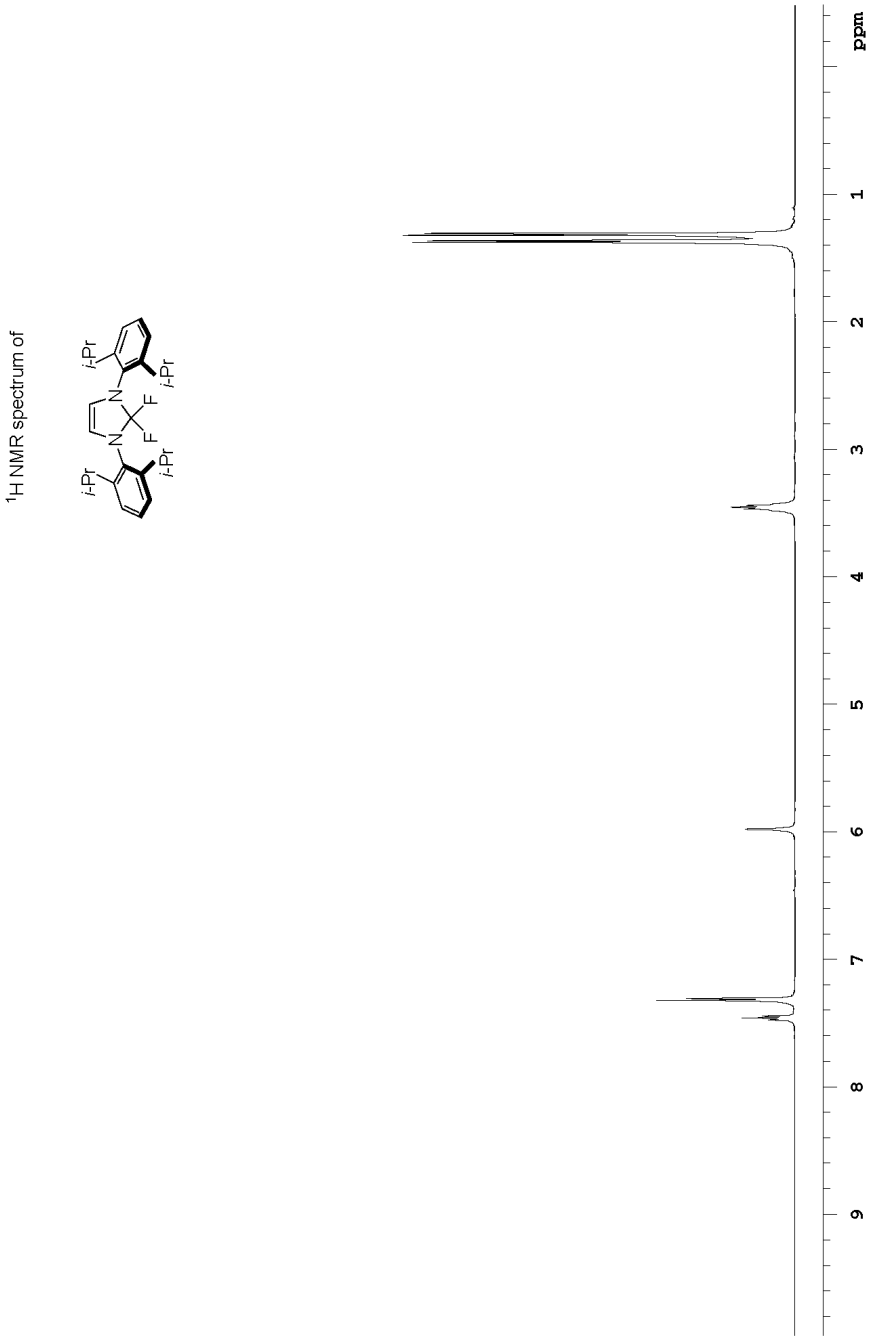
^{1}H NMR spectrum (500 MHz, CD_3CN, 23 ºC) of **S3**



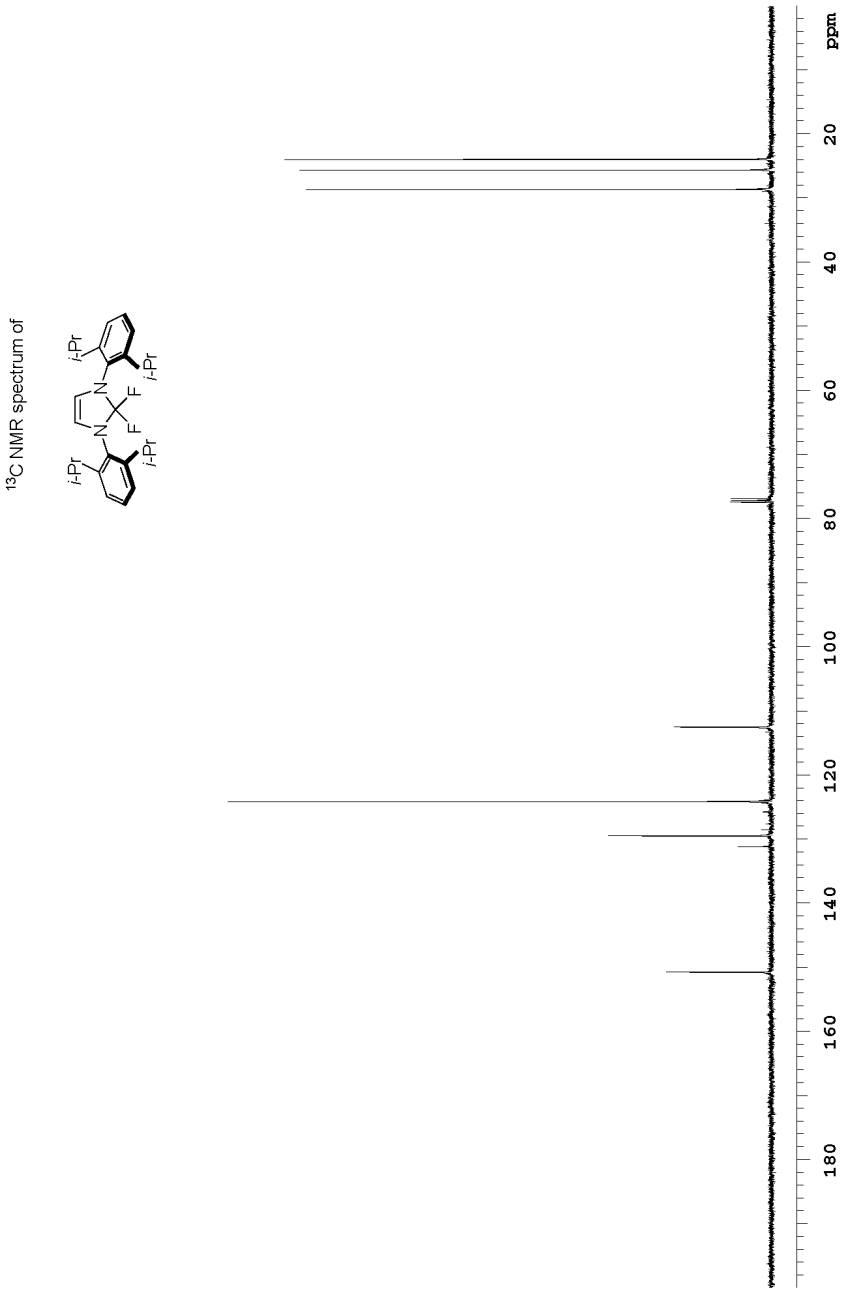
^{13}C NMR spectrum (125 MHz, CD_3CN, 23 ºC) of **S3**



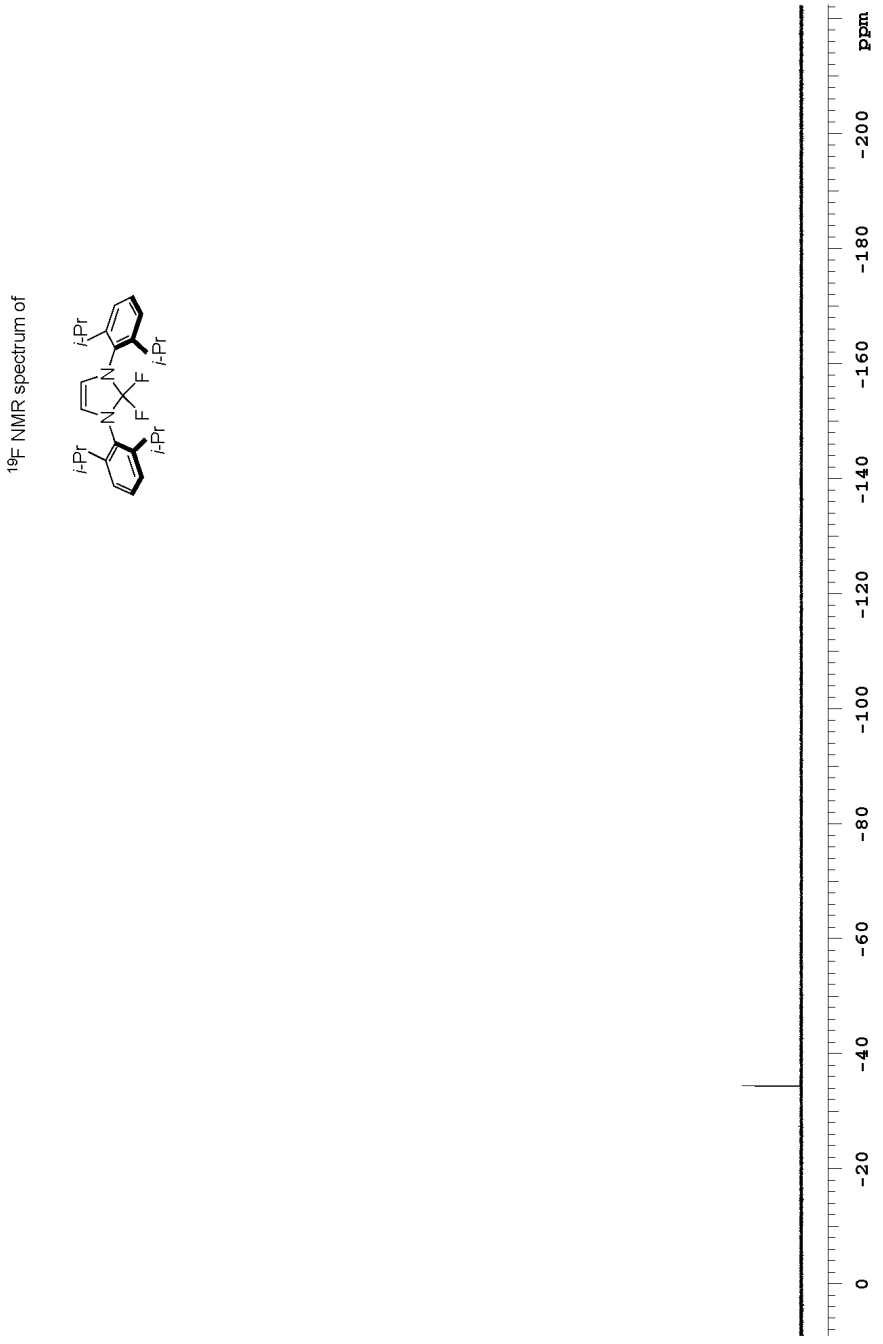
^{1}H NMR spectrum (500 MHz, $CDCl_3$, 23 ºC) of **1**



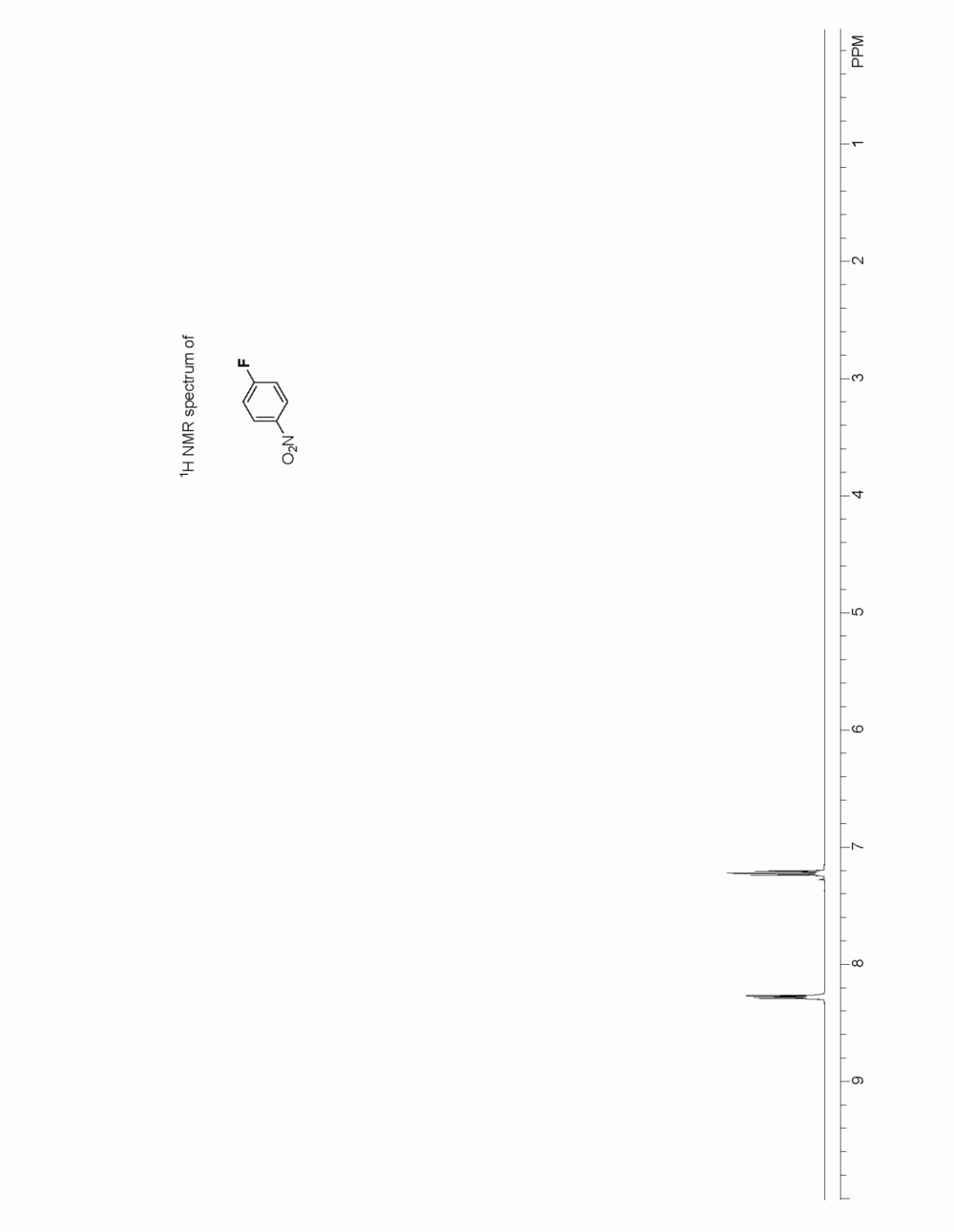
^{13}C NMR spectrum (125 MHz, $CDCl_3$, 23 ºC) of **1**



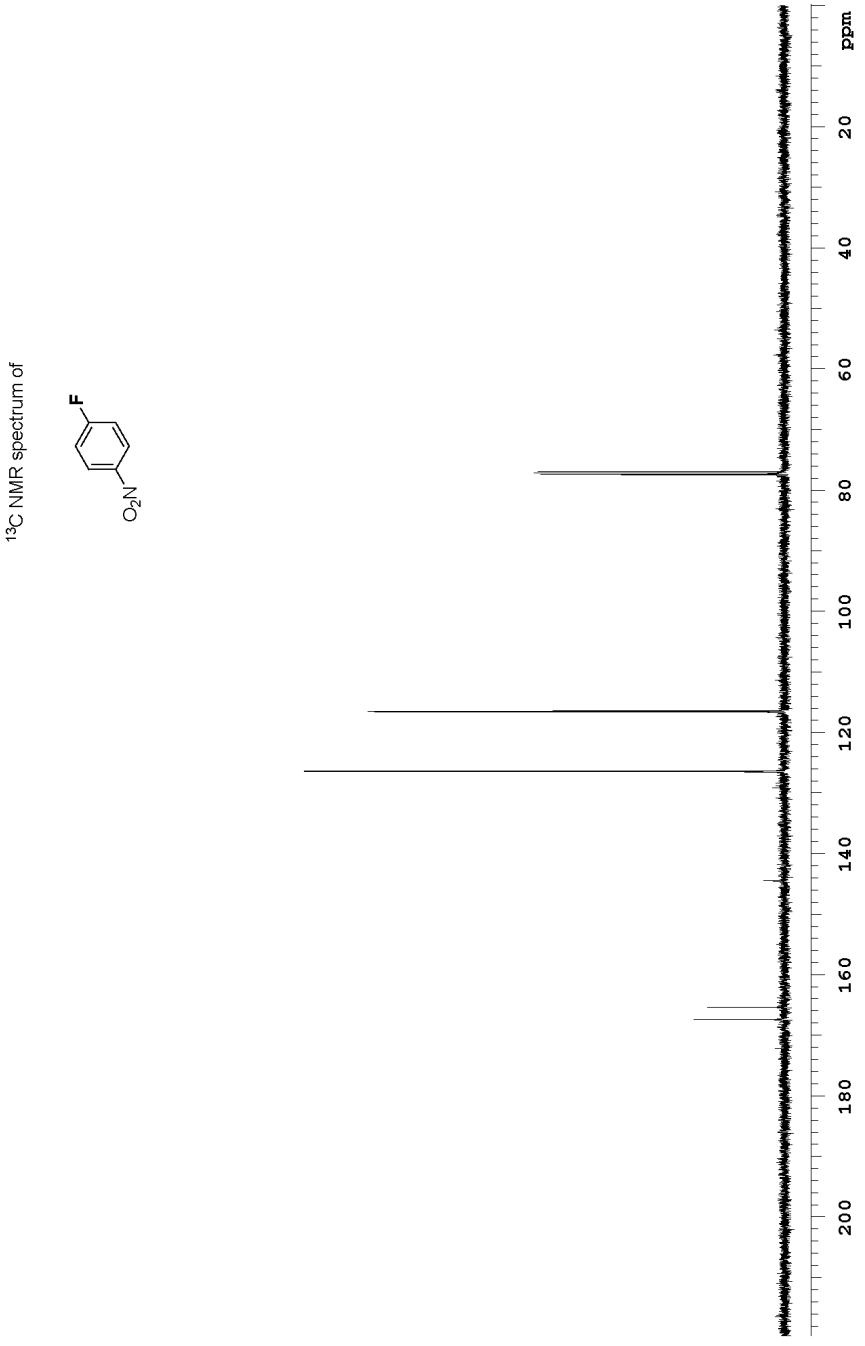
^{19}F NMR spectrum (375 MHz, $CDCl_3$, 23 ºC) of **1**



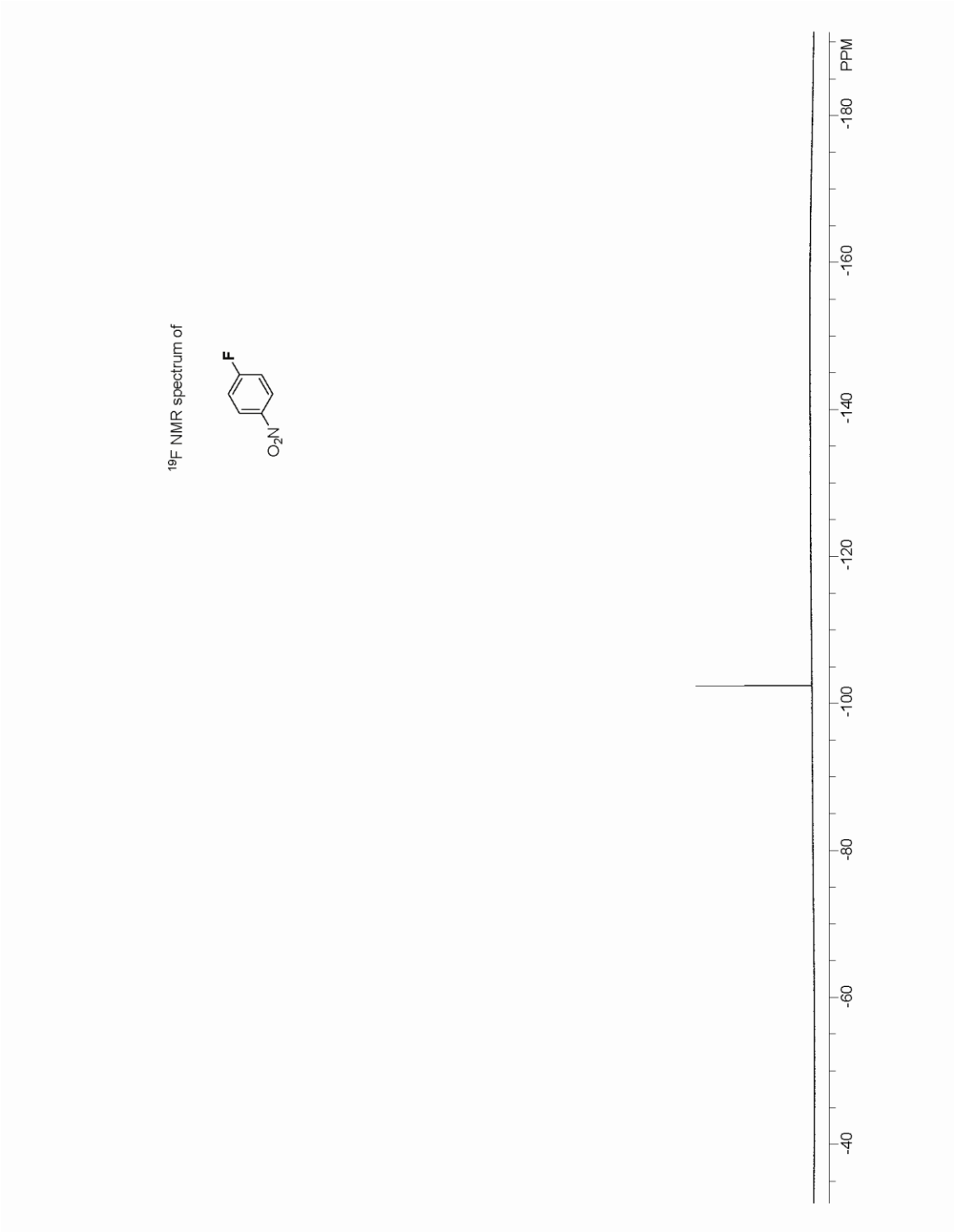
^{1}H NMR spectrum (500 MHz, $CDCl_3$, 23 ºC) of **2**



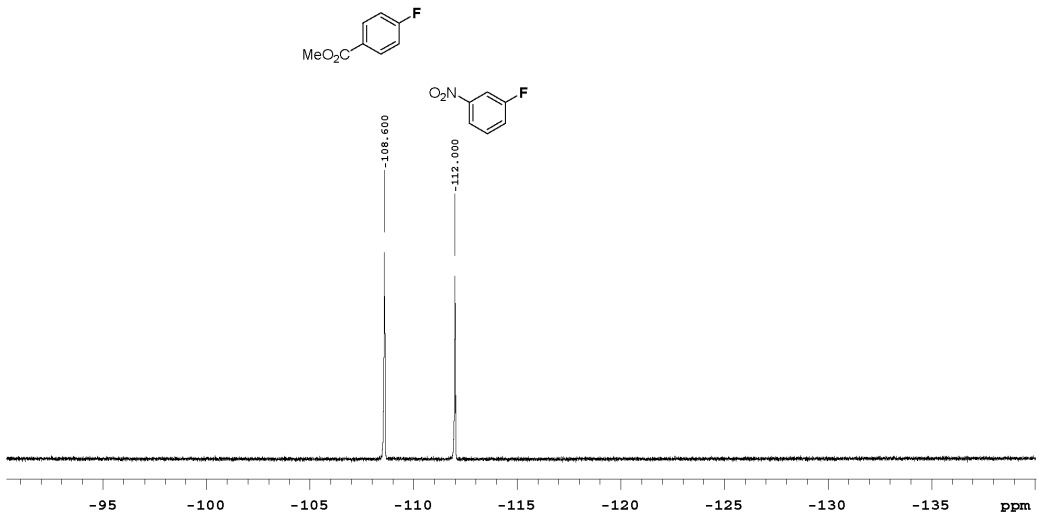
^{13}C NMR spectrum (125 MHz, $CDCl_3$, 23 ºC) of **2**



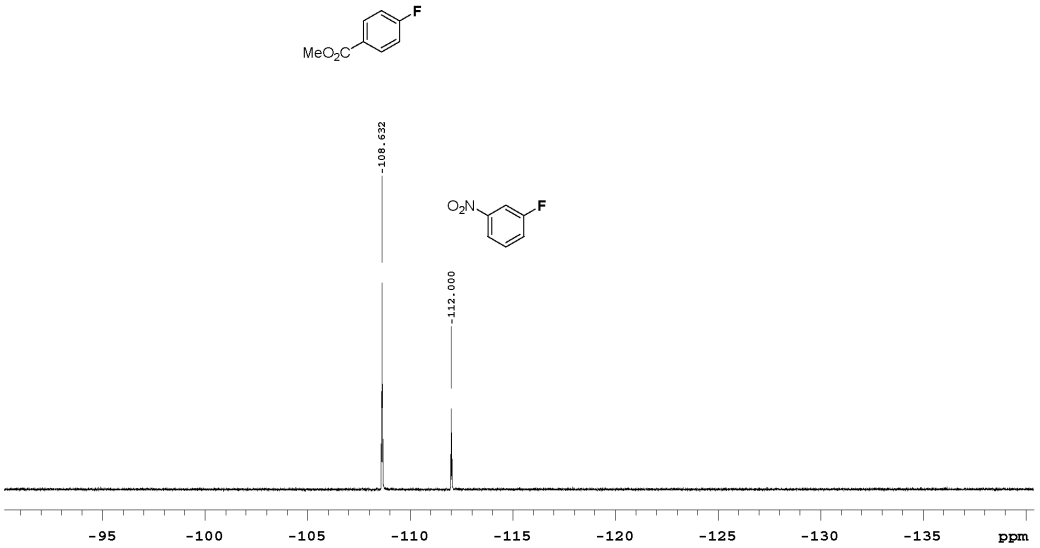
^{19}F NMR spectrum (375 MHz, $CDCl_3$, 23 ºC) of **2**



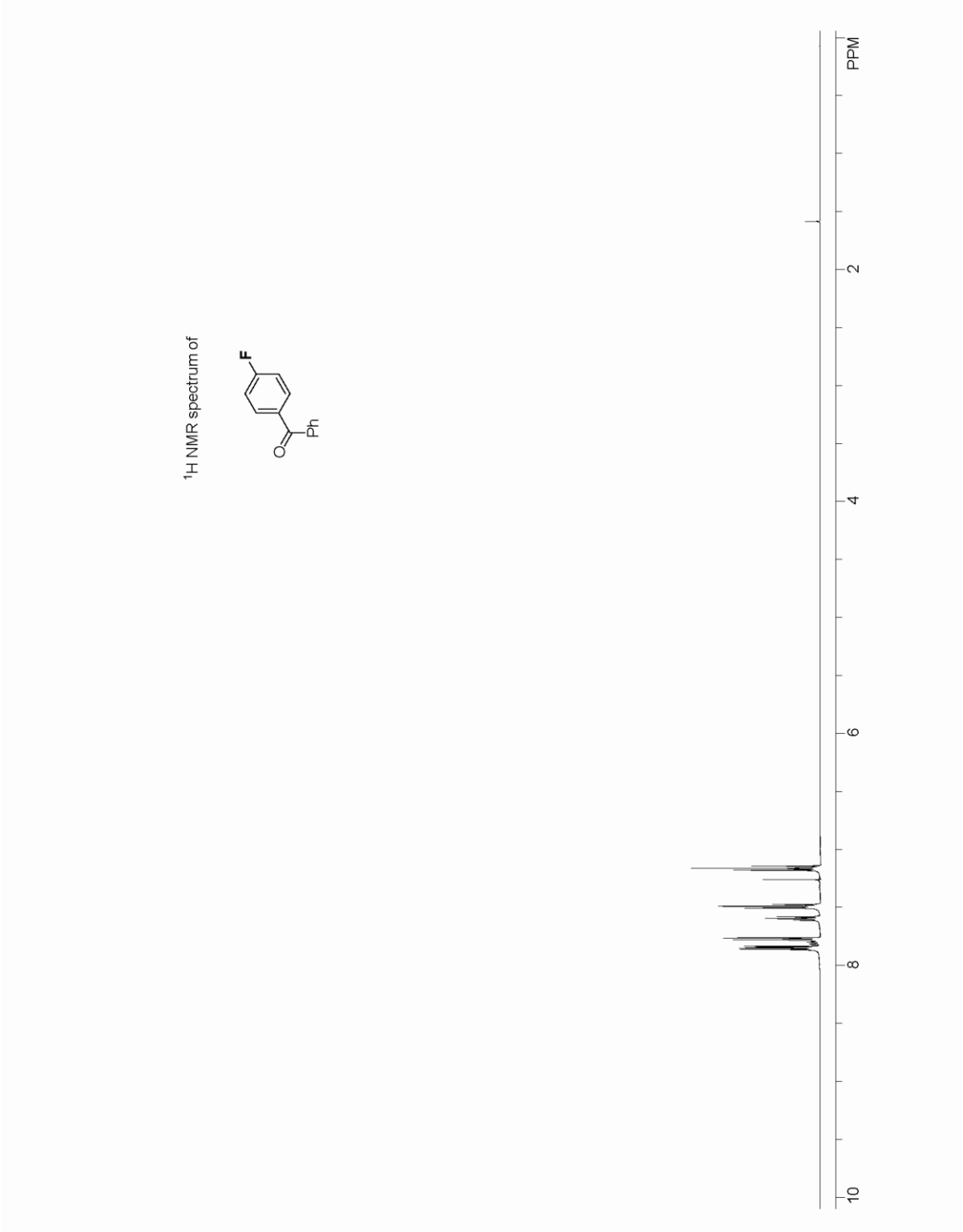
^{19}F NMR spectrum (375 MHz, toluene, 23 ºC) of **3**



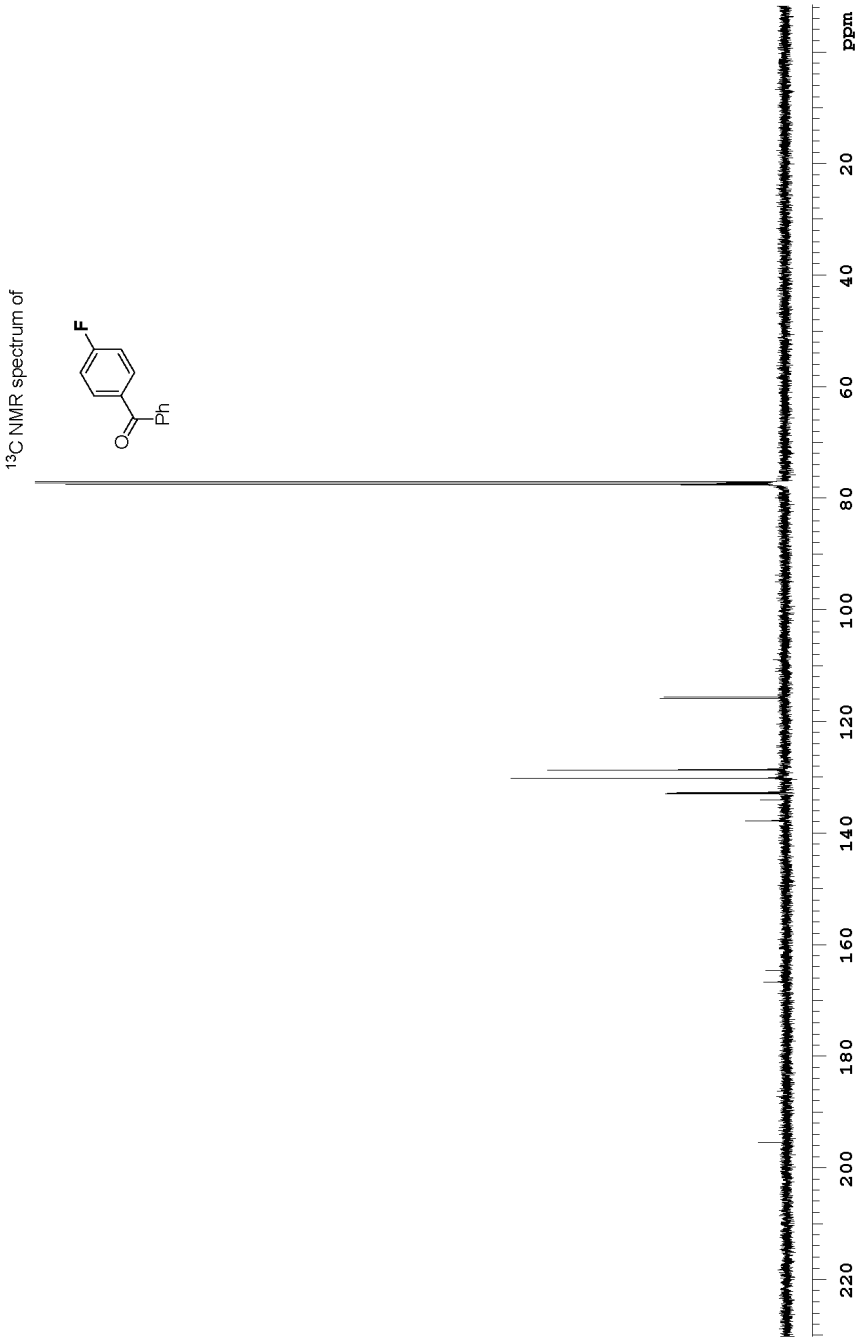
^{19}F NMR spectrum (375 MHz, toluene, 23 ºC) of commercial sample **3**



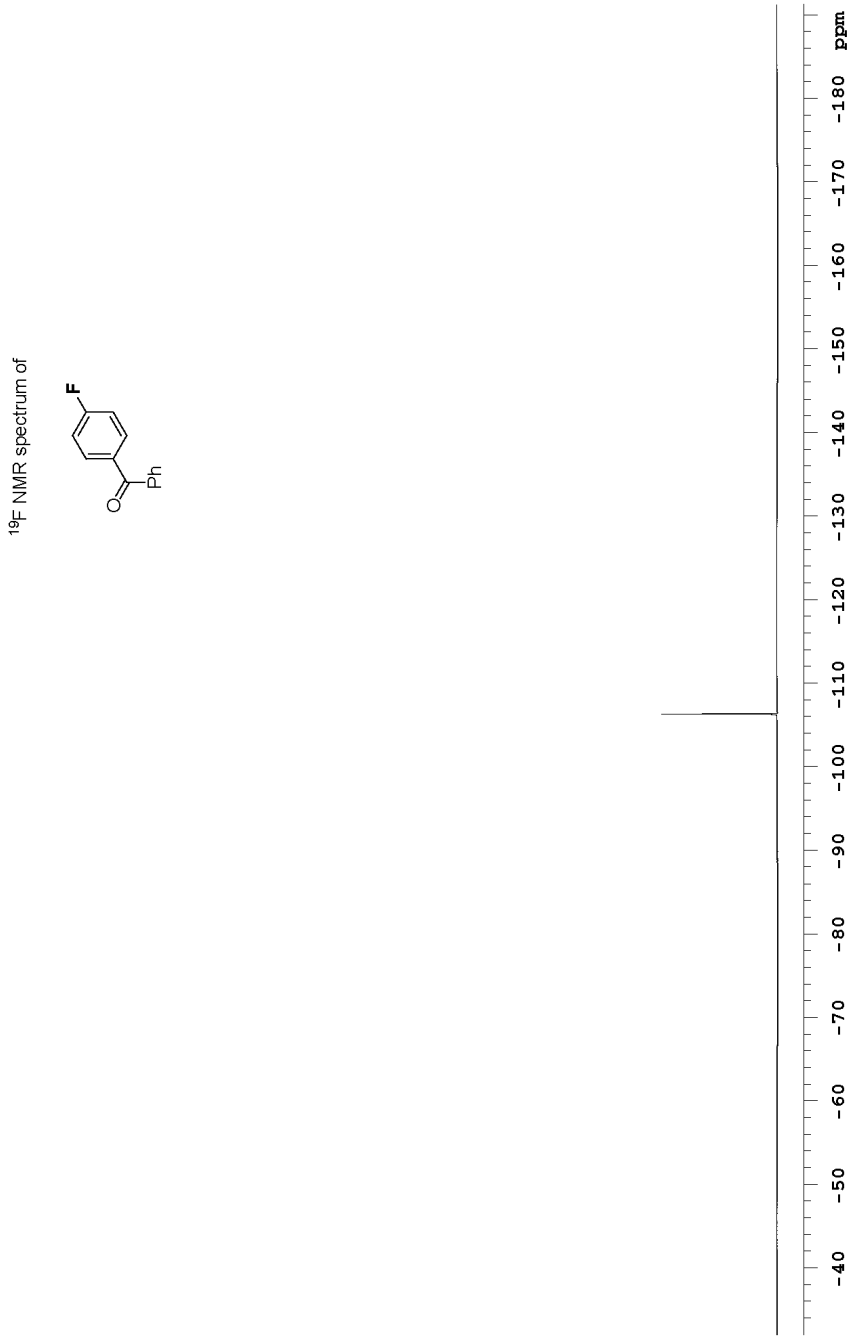
^{1}H NMR spectrum (500 MHz, $CDCl_3$, 23 ºC) of **4**



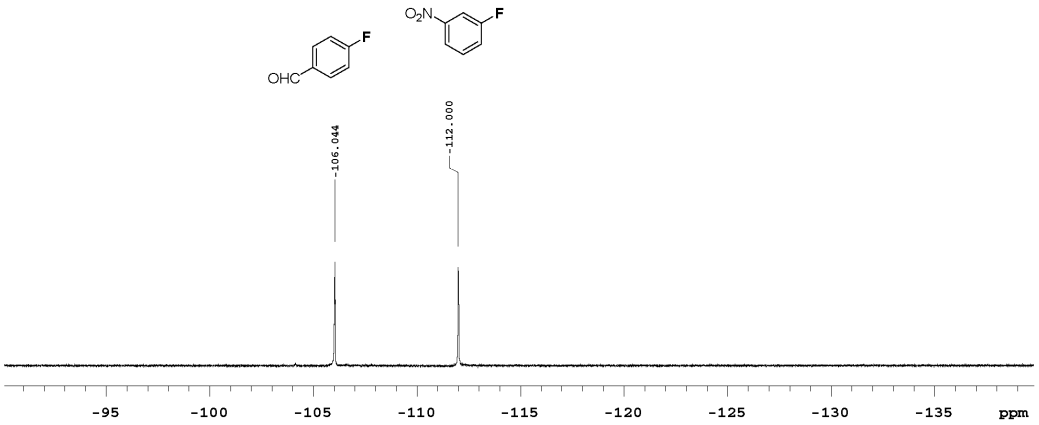
^{13}C NMR spectrum (125 MHz, $CDCl_3$, 23 ºC) of **4**



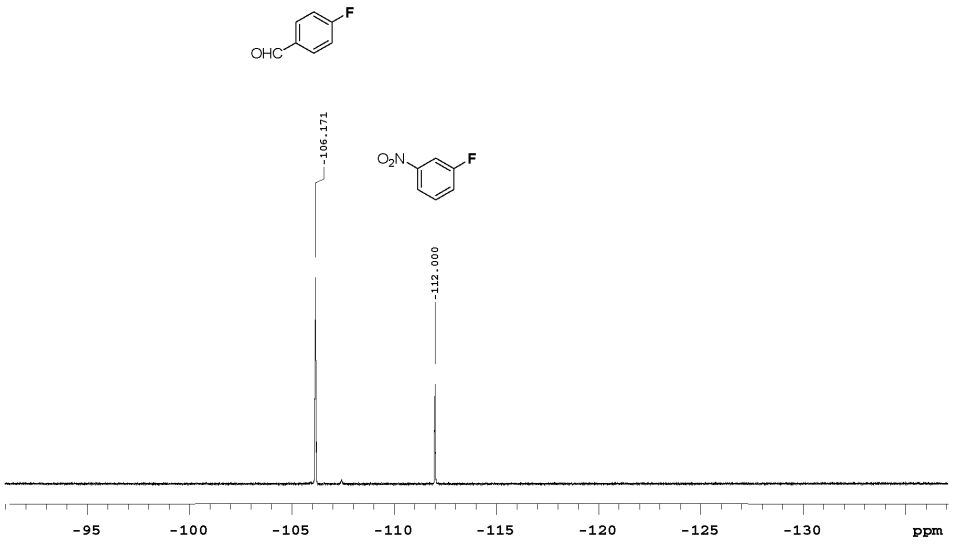
^{19}F NMR spectrum (375 MHz, $CDCl_3$, 23 ºC) of **4**



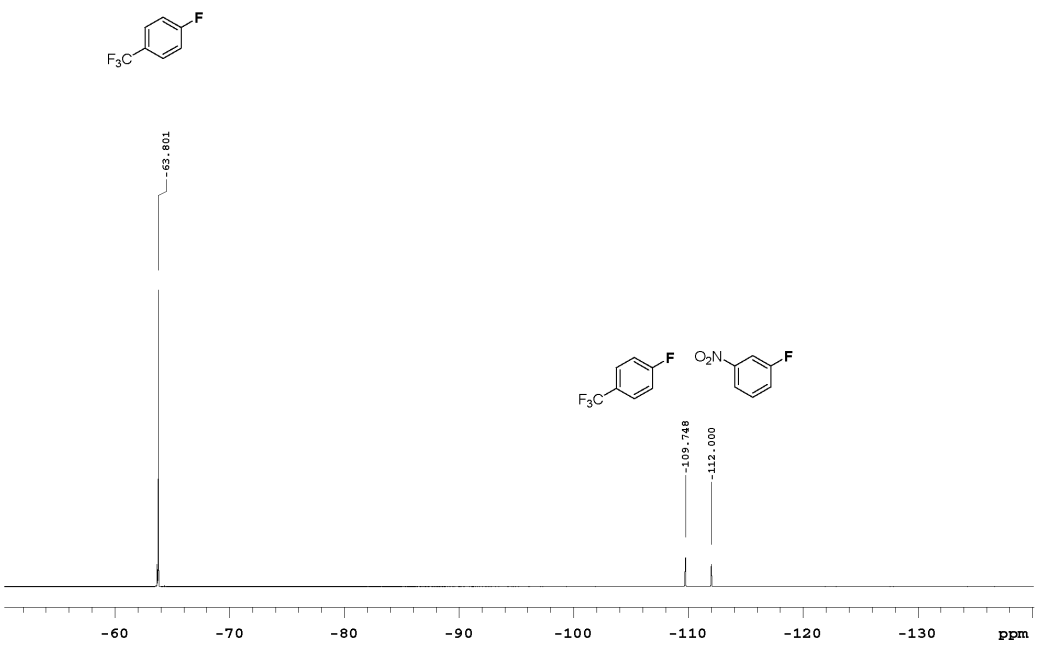
^{19}F NMR spectrum (375 MHz, toluene, 23 ºC) of **5**



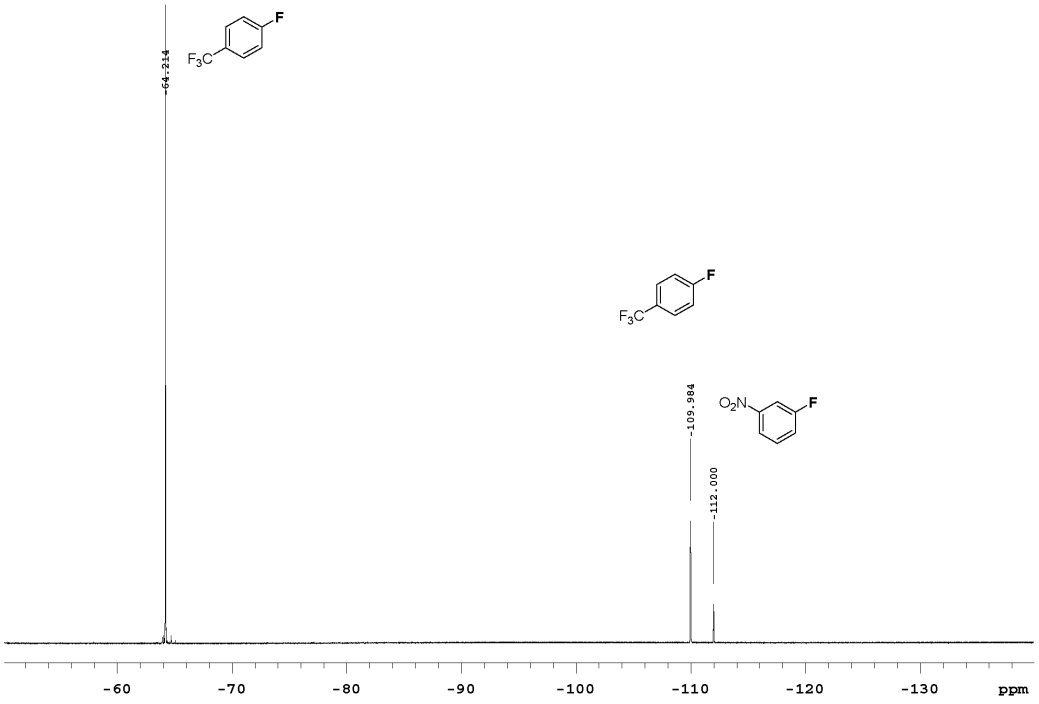
^{19}F NMR spectrum (375 MHz, toluene, 23 ºC) of commercial sample **5**



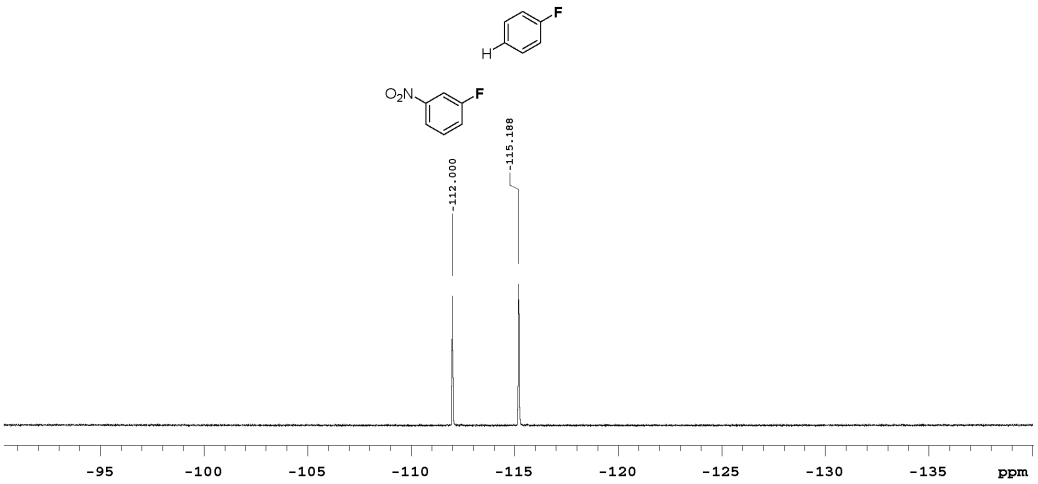
^{19}F NMR spectrum (375 MHz, toluene, 23 ºC) of **6**



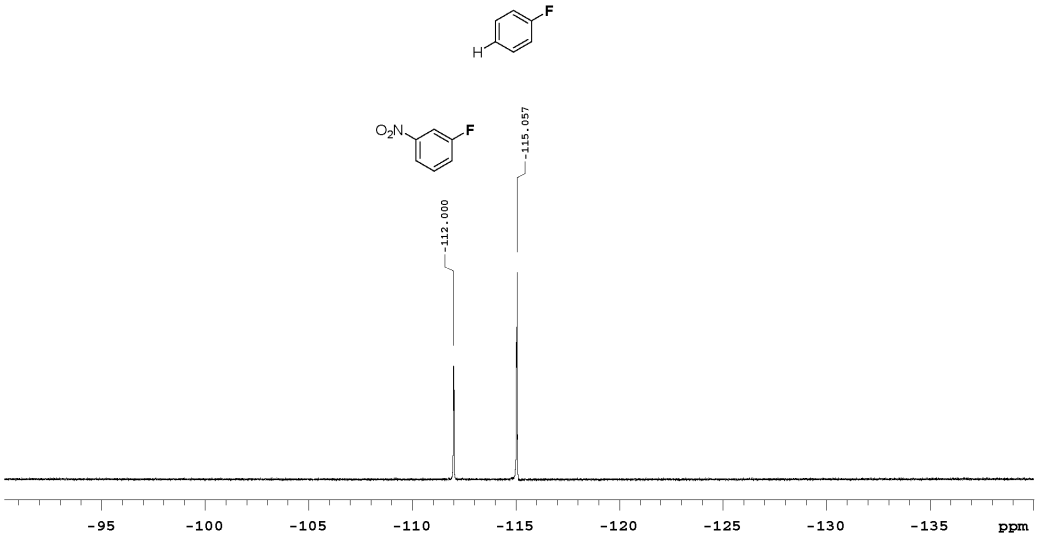
^{19}F NMR spectrum (375 MHz, toluene, 23 ºC) of commercial sample **6**



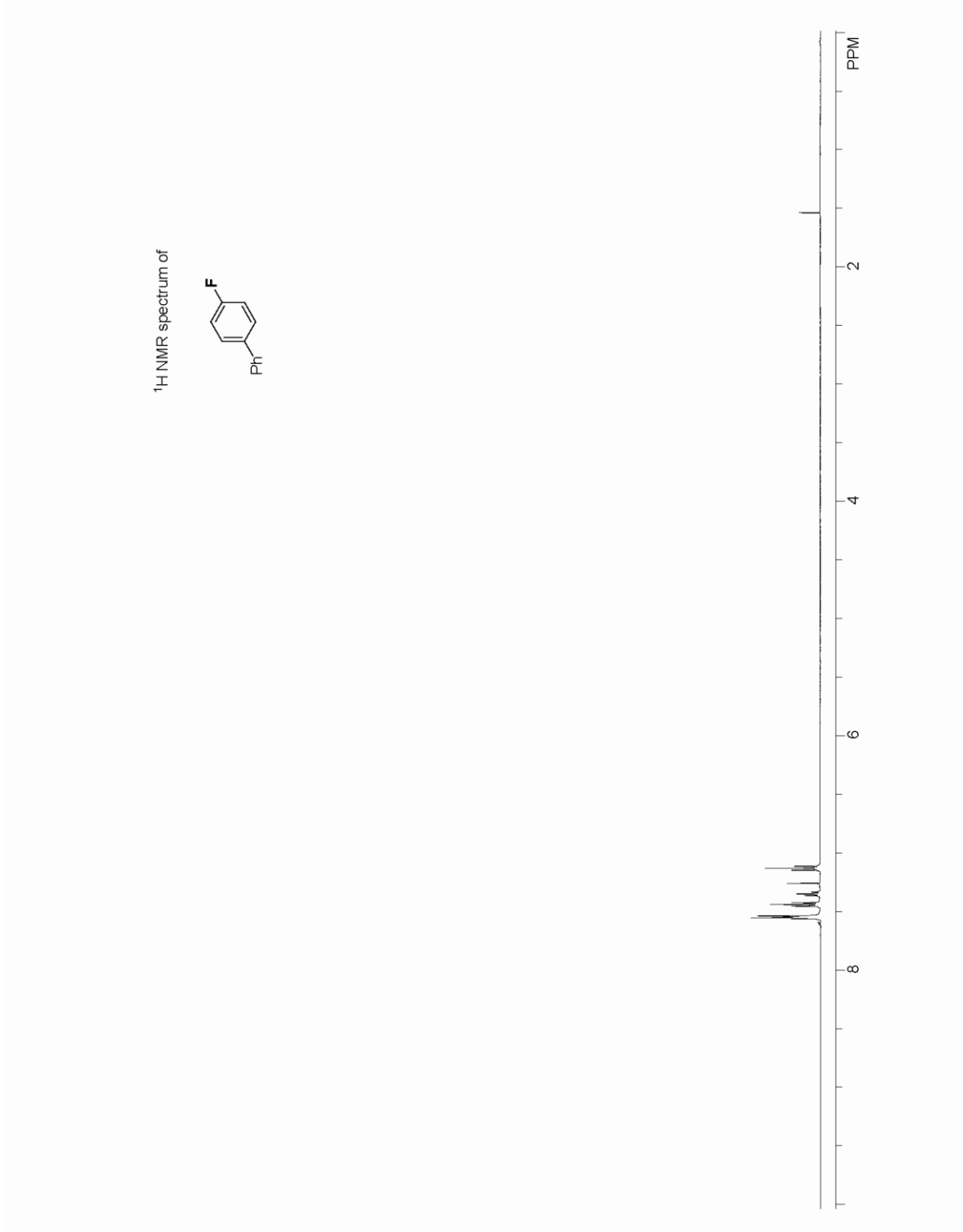
^{19}F NMR spectrum (375 MHz, toluene, 23 ºC) of **7**



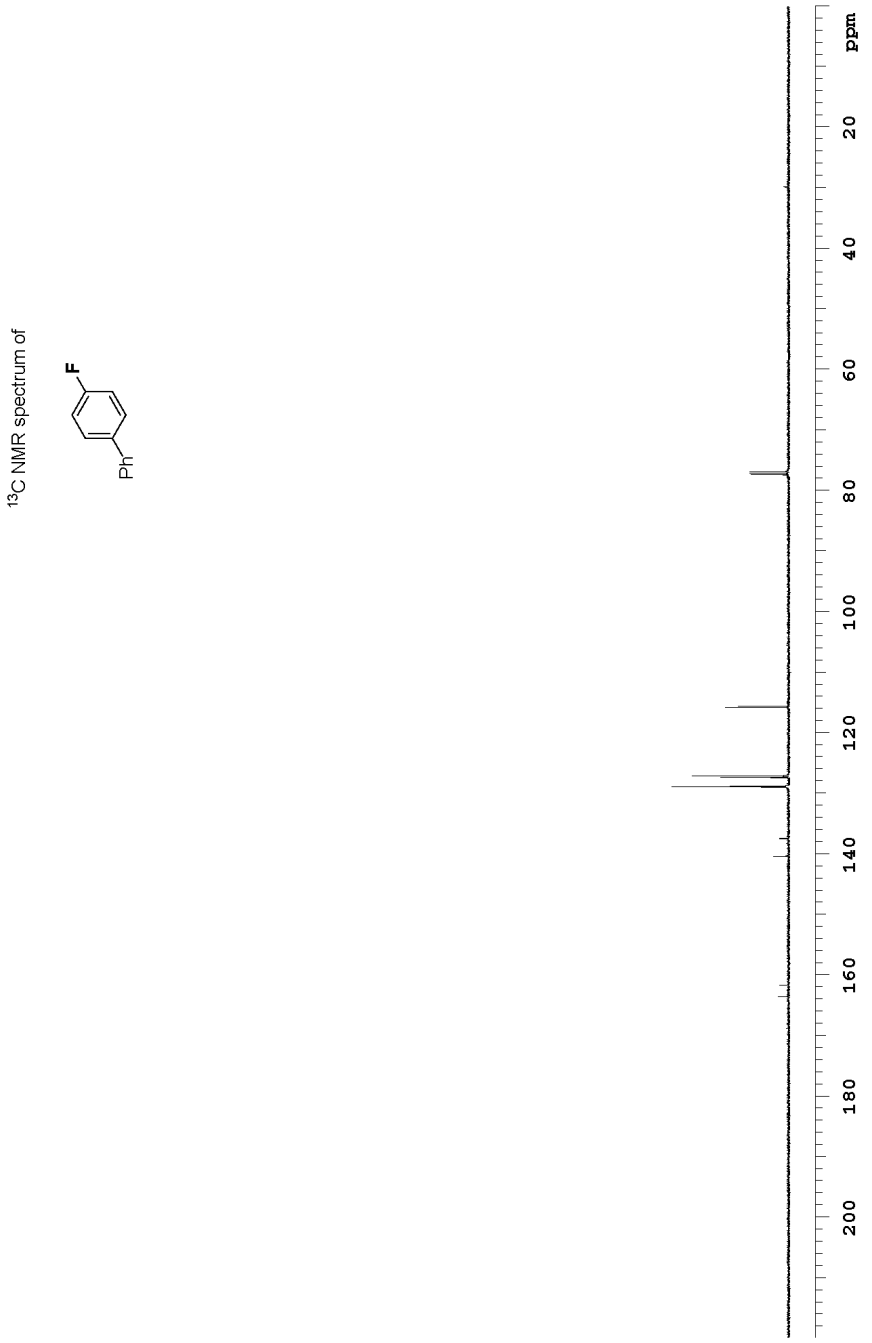
^{19}F NMR spectrum (375 MHz, toluene, 23 ºC) of commercial sample **7**



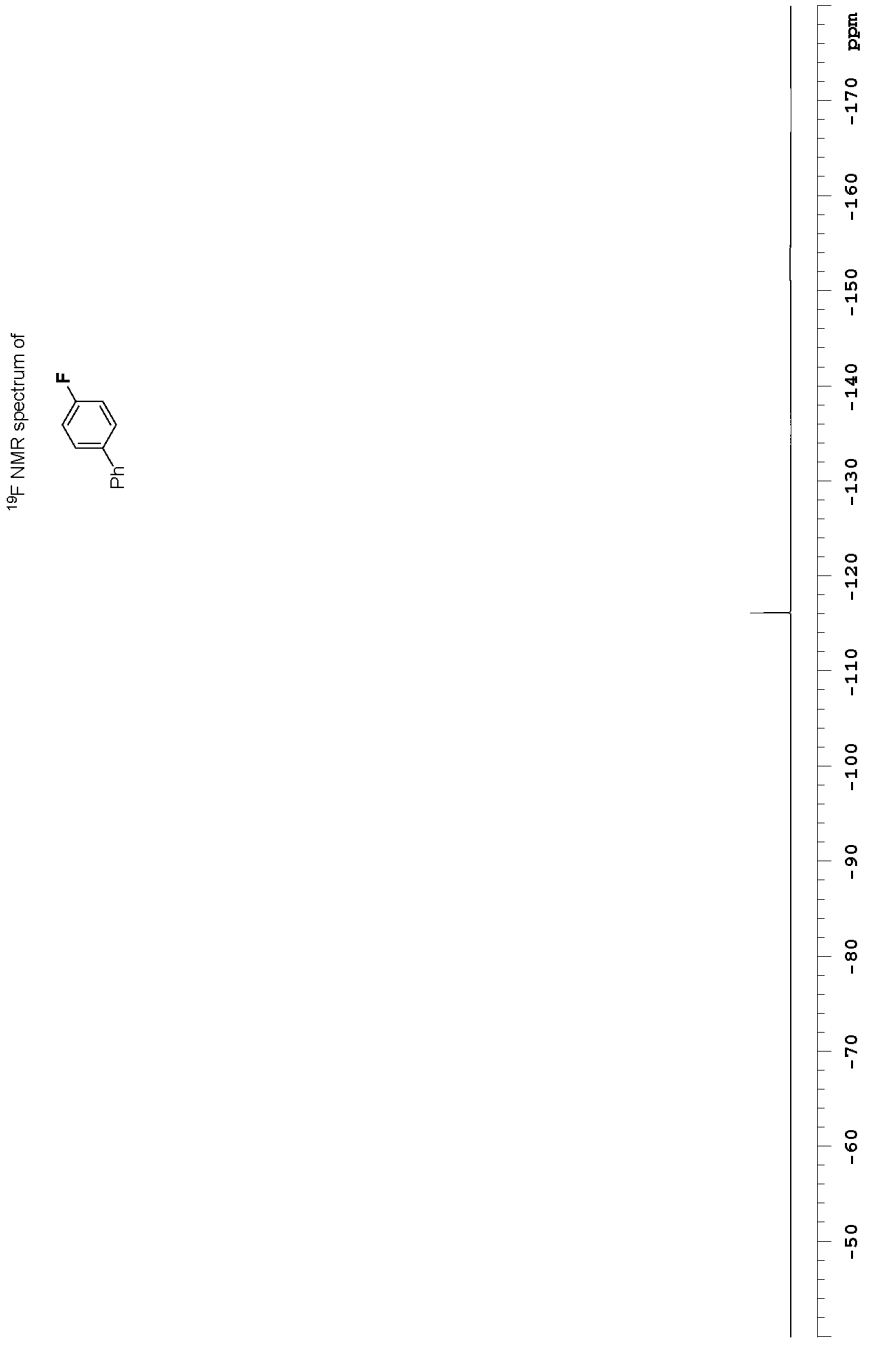
^{1}H NMR spectrum (500 MHz, $CDCl_3$, 23 ºC) of **8**



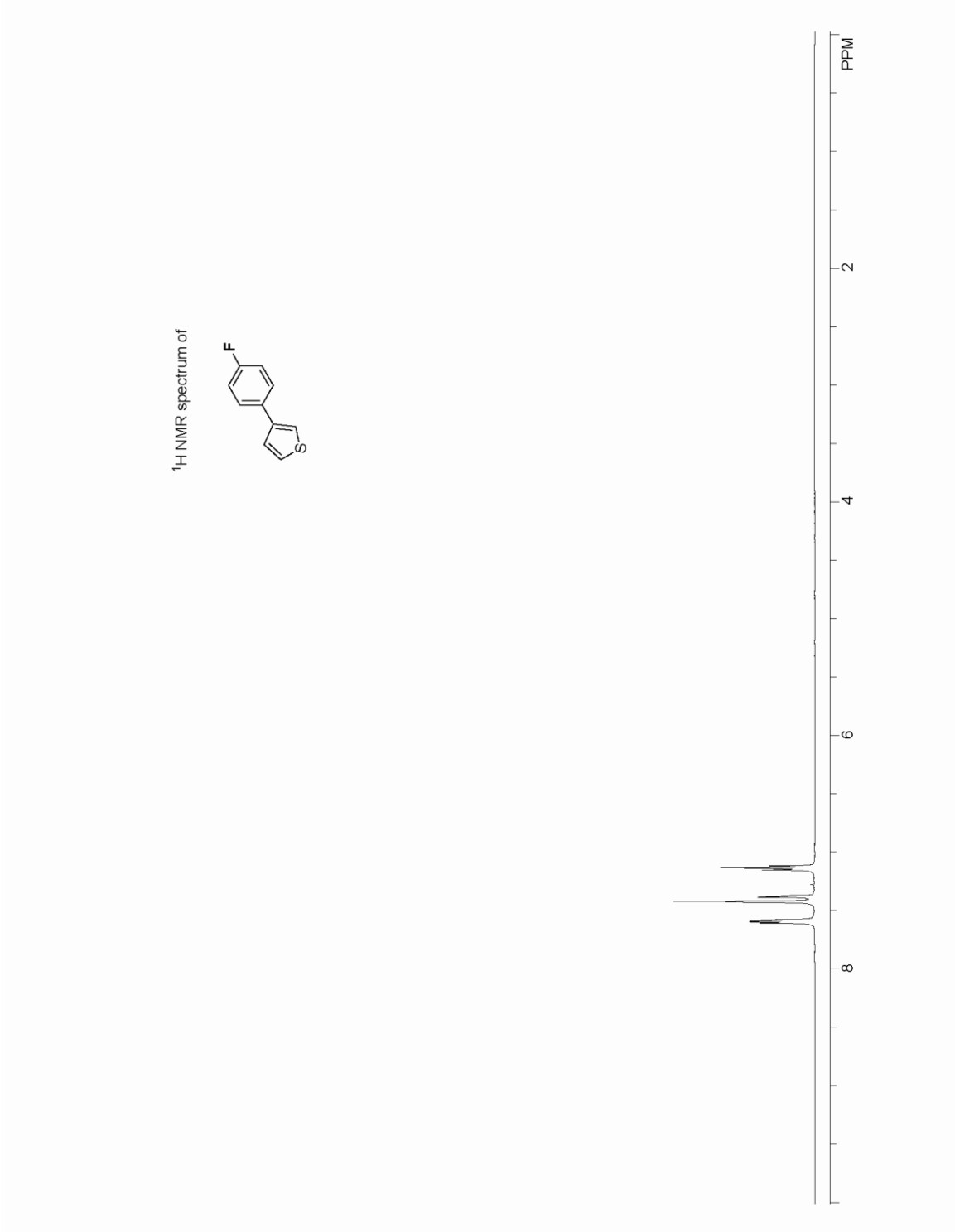
^{13}C NMR spectrum (125 MHz, $CDCl_3$, 23 ºC) of **8**



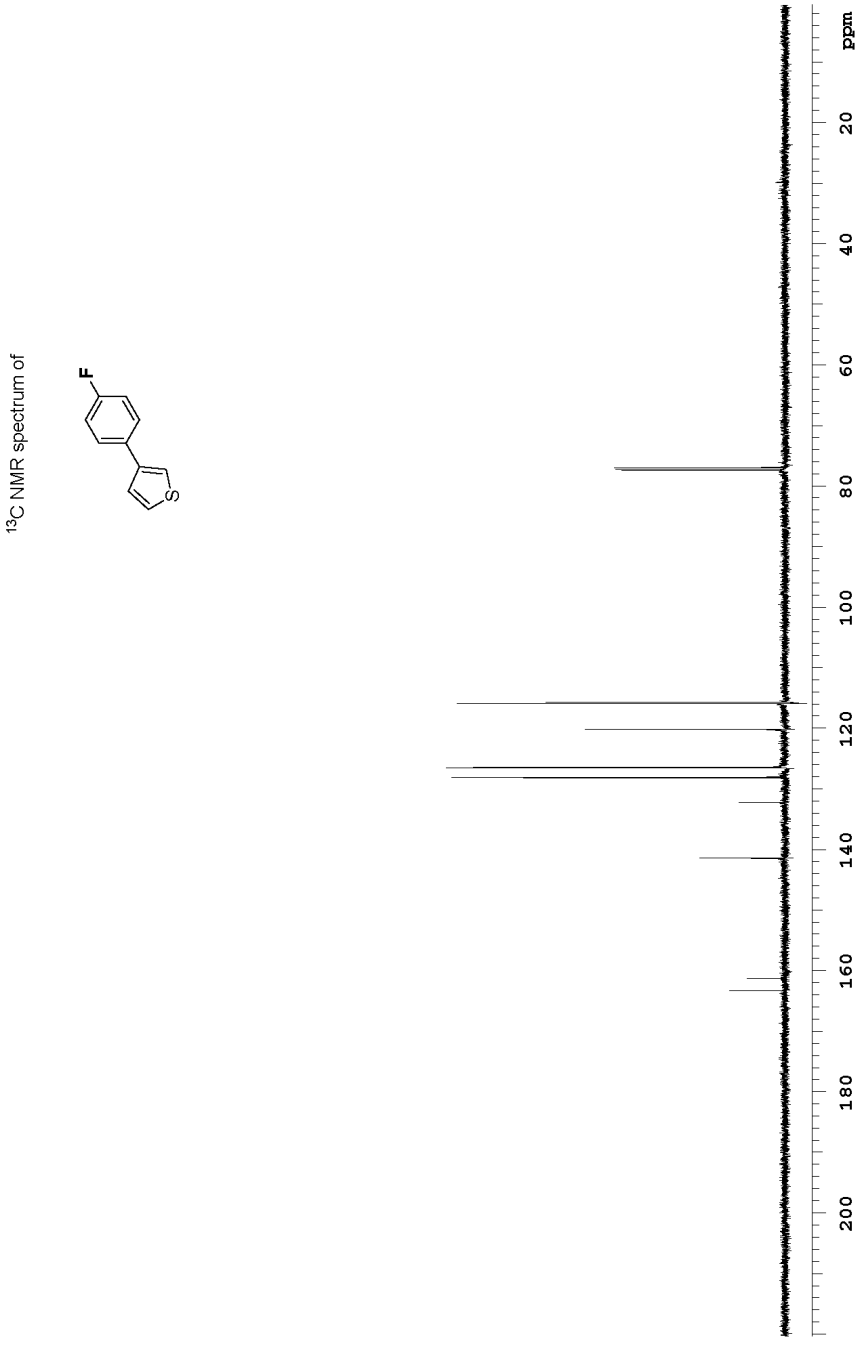
^{19}F NMR spectrum (375 MHz, $CDCl_3$, 23 ºC) of **8**



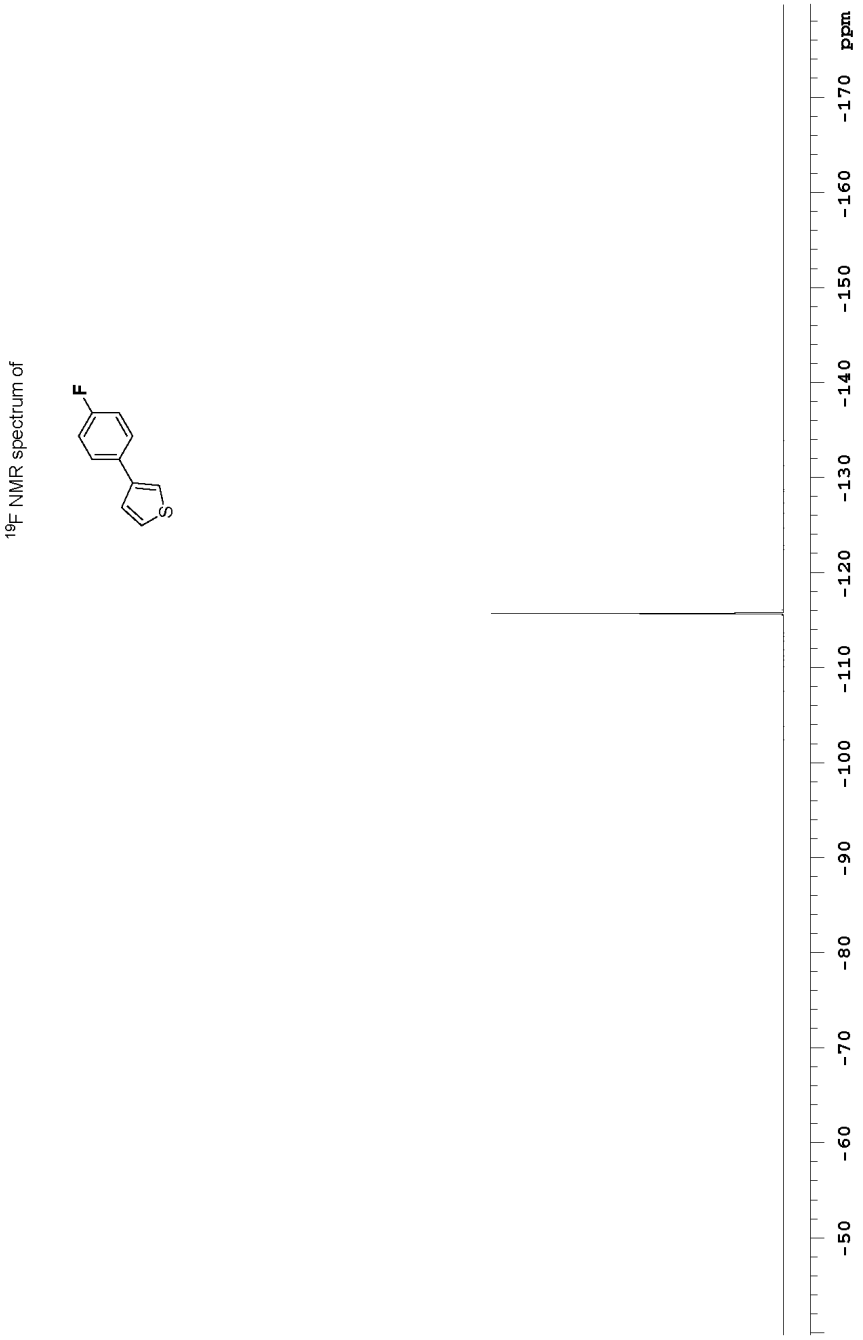
^{1}H NMR spectrum (500 MHz, $CDCl_3$, 23 ºC) of **9**



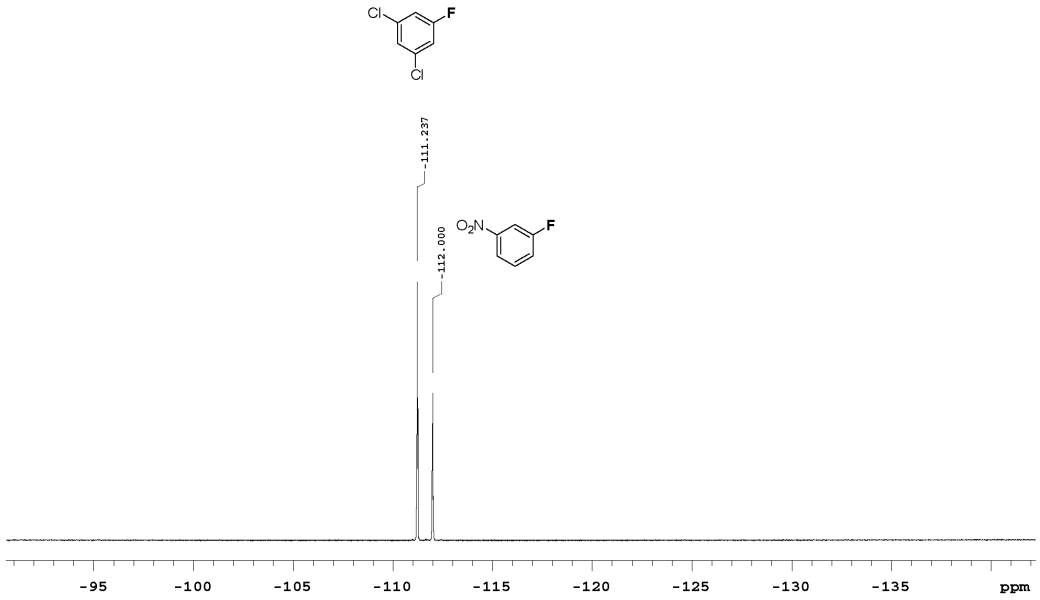
^{13}C NMR spectrum (125 MHz, $CDCl_3$, 23 ºC) of **9**



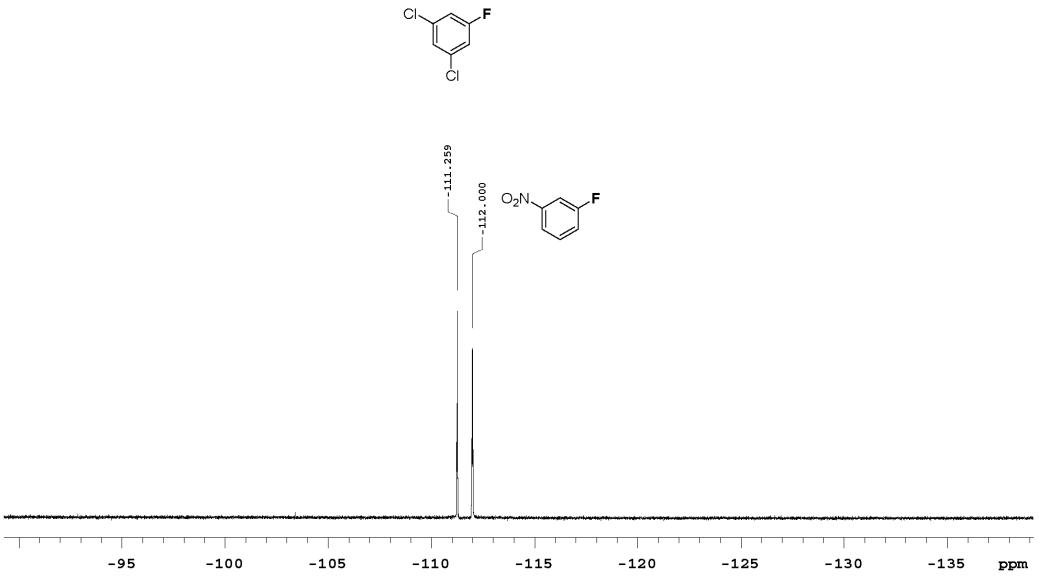
^{19}F NMR spectrum (375 MHz, $CDCl_3$, 23 ºC) of **9**



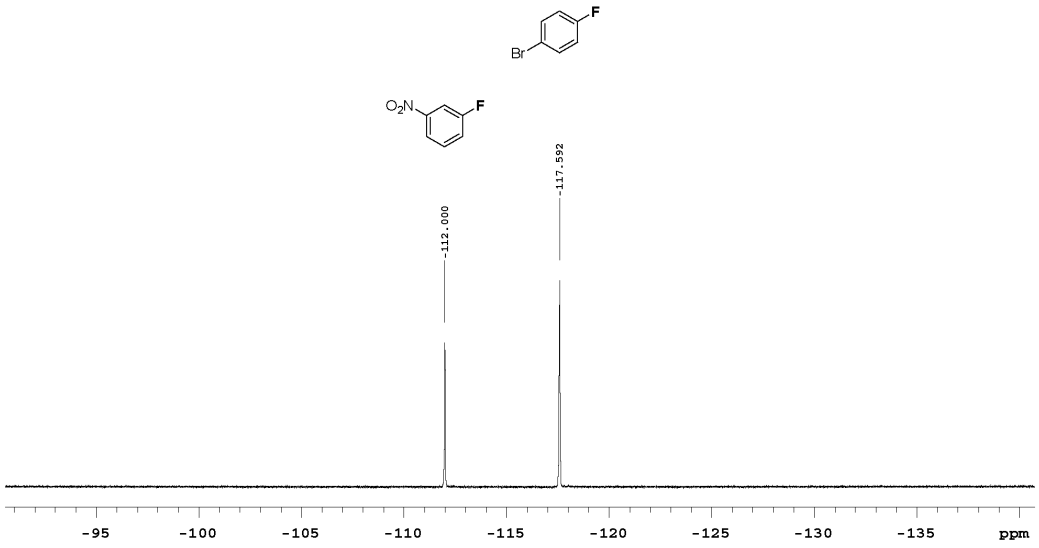
^{19}F NMR spectrum (375 MHz, toluene, 23 ºC) of **10**



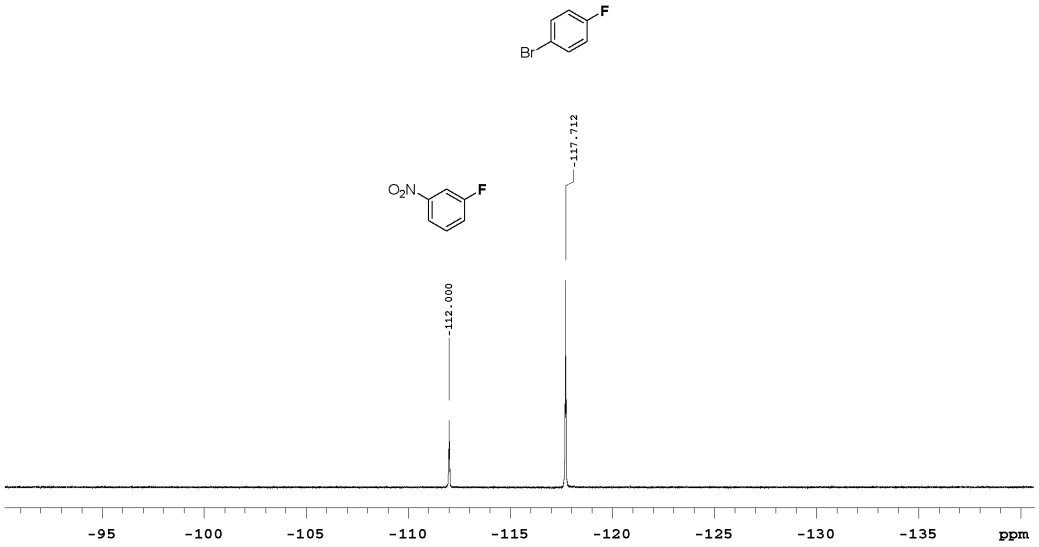
^{19}F NMR spectrum (375 MHz, toluene, 23 ºC) of commercial sample **10**



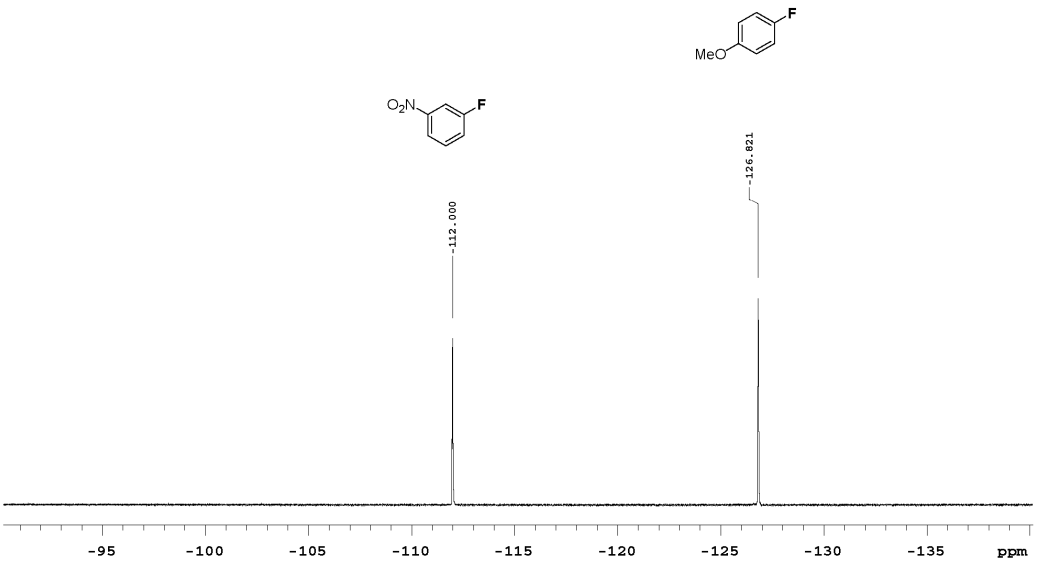
^{19}F NMR spectrum (375 MHz, toluene, 23 ºC) of **11**



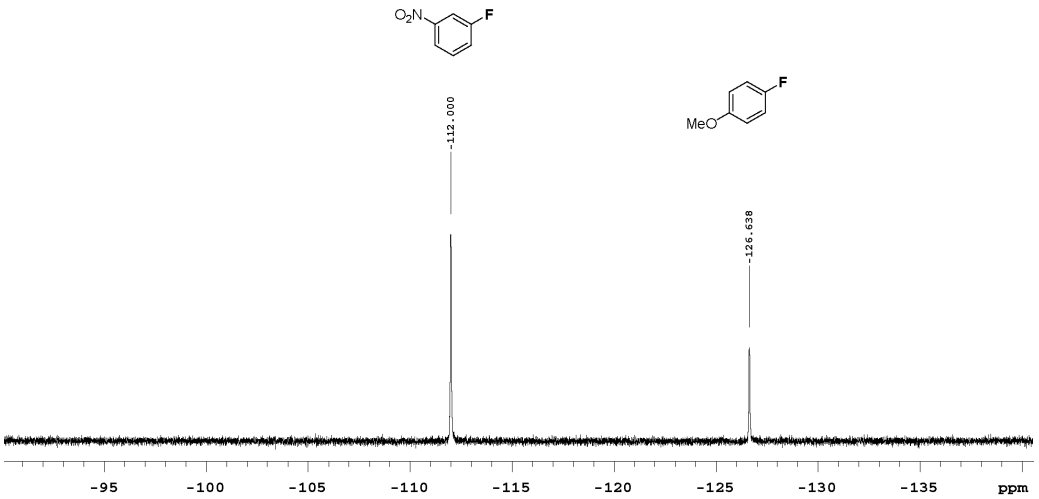
^{19}F NMR spectrum (375 MHz, toluene, 23 ºC) of commercial sample **11**



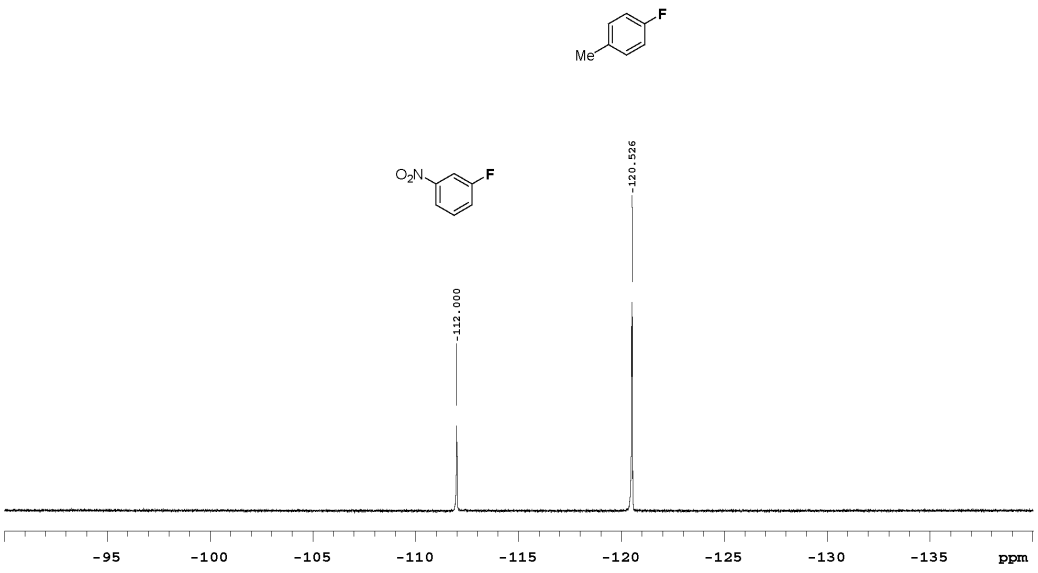
^{19}F NMR spectrum (375 MHz, toluene, 23 ºC) of **12**



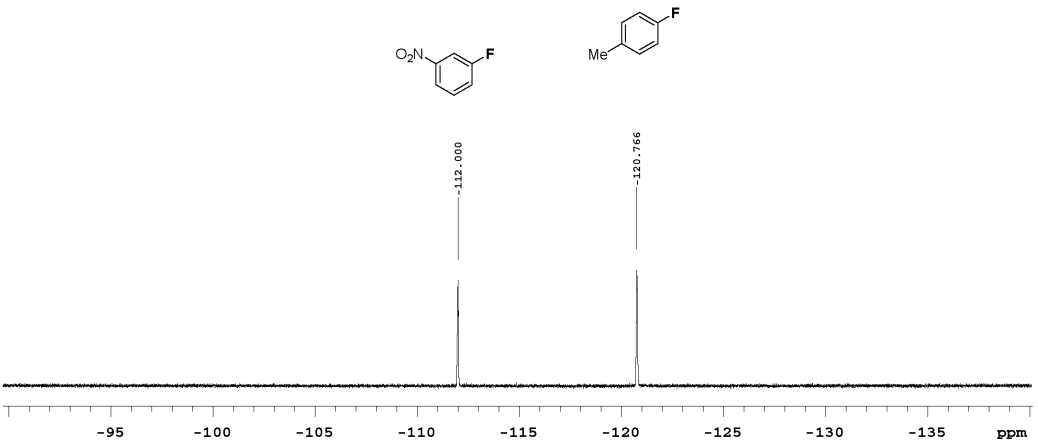
^{19}F NMR spectrum (375 MHz, toluene, 23 ºC) of commercial sample **12**



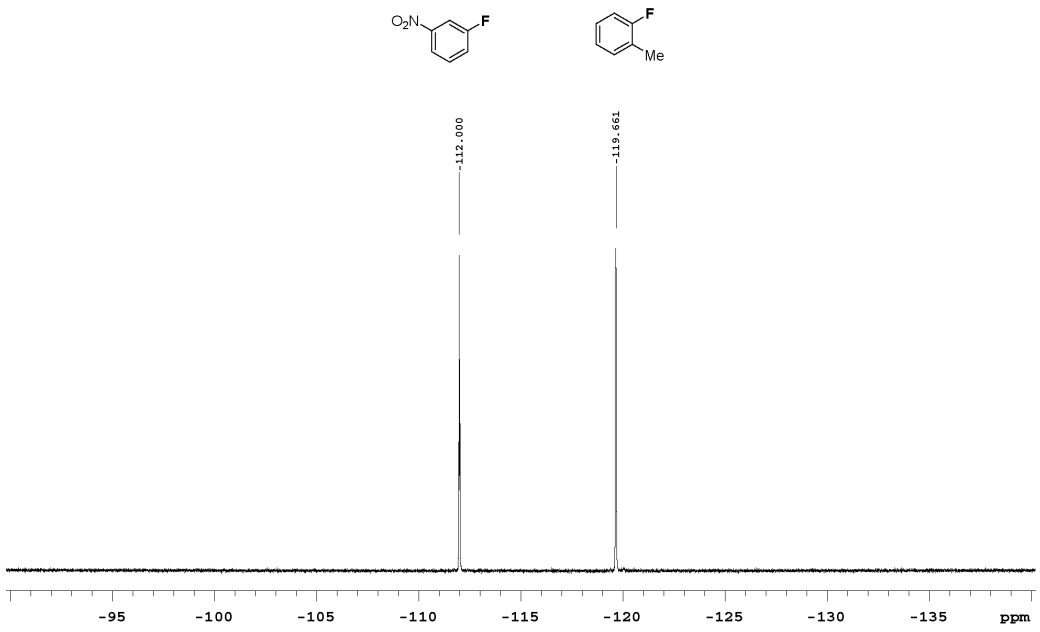
^{19}F NMR spectrum (375 MHz, toluene, 23 ºC) of **13**



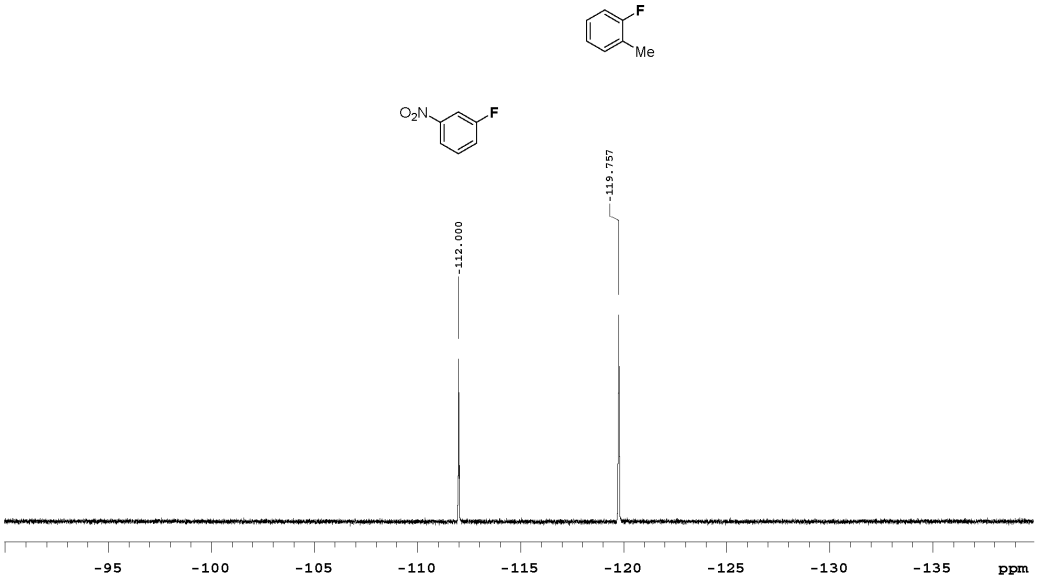
^{19}F NMR spectrum (375 MHz, toluene, 23 ºC) of commercial sample **13**



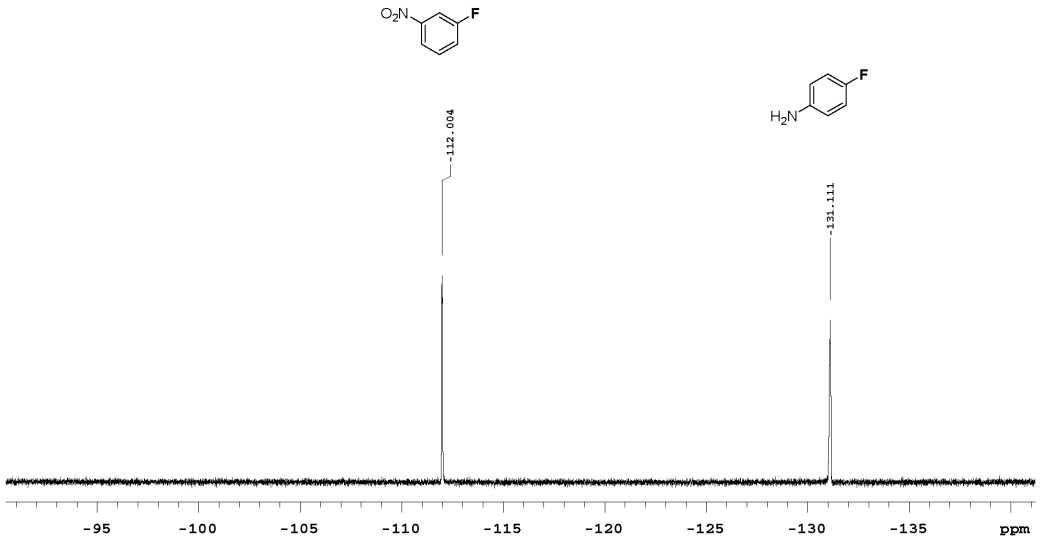
^{19}F NMR spectrum (375 MHz, toluene, 23 ºC) of **14**



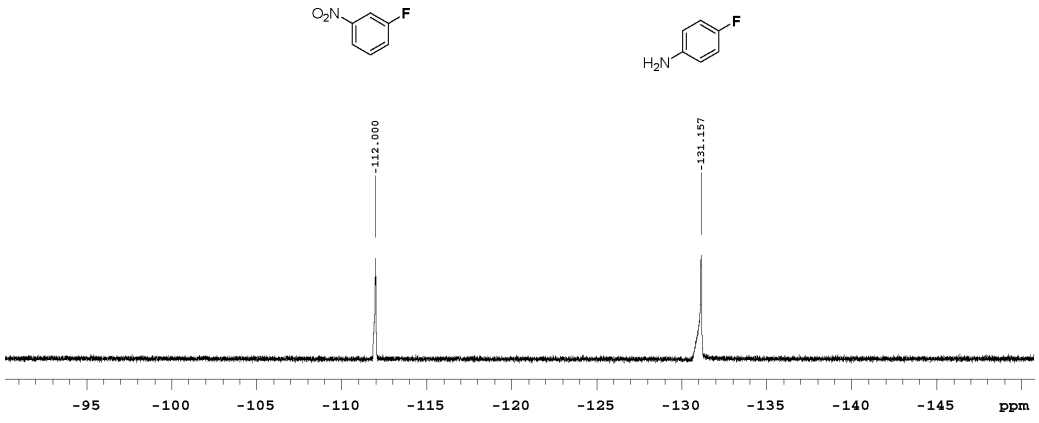
^{19}F NMR spectrum (375 MHz, toluene, 23 ºC) of commercial sample **14**



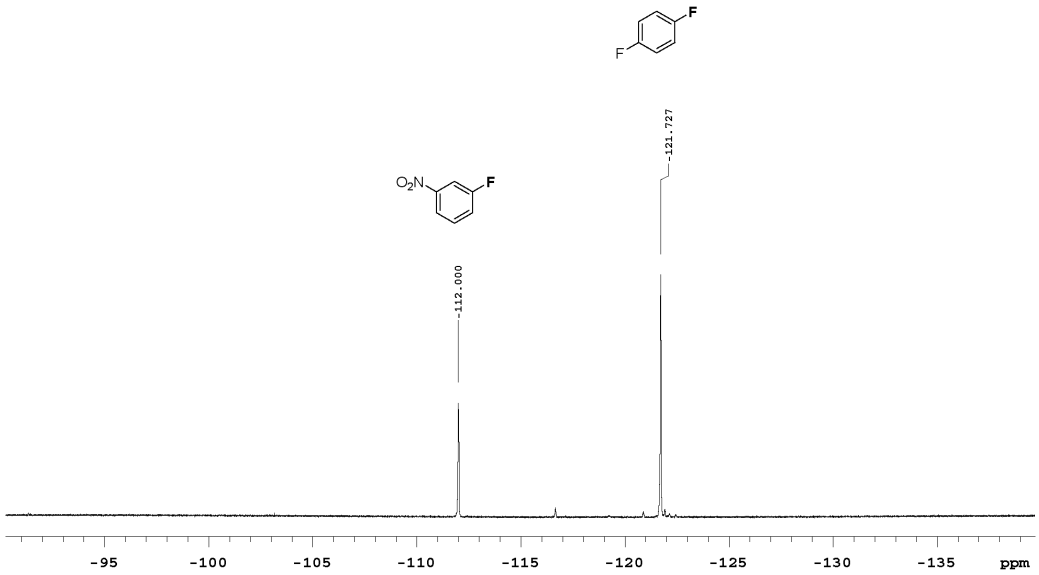
^{19}F NMR spectrum (375 MHz, toluene, 23 ºC) of **15**



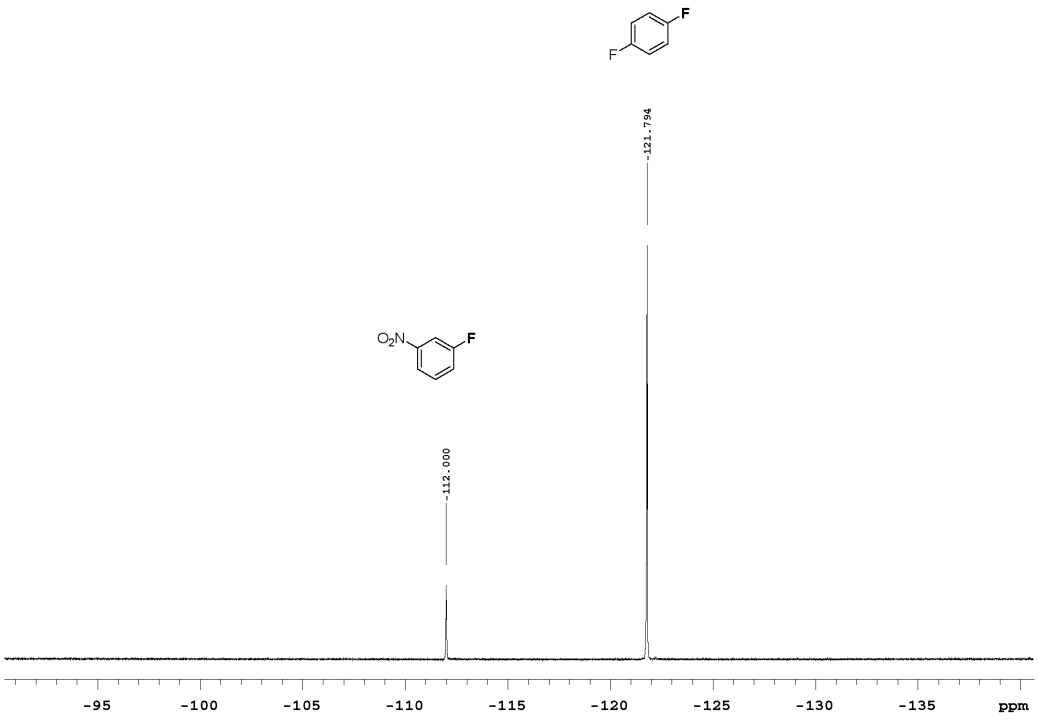
^{19}F NMR spectrum (375 MHz, toluene, 23 ºC) of commercial sample **15**



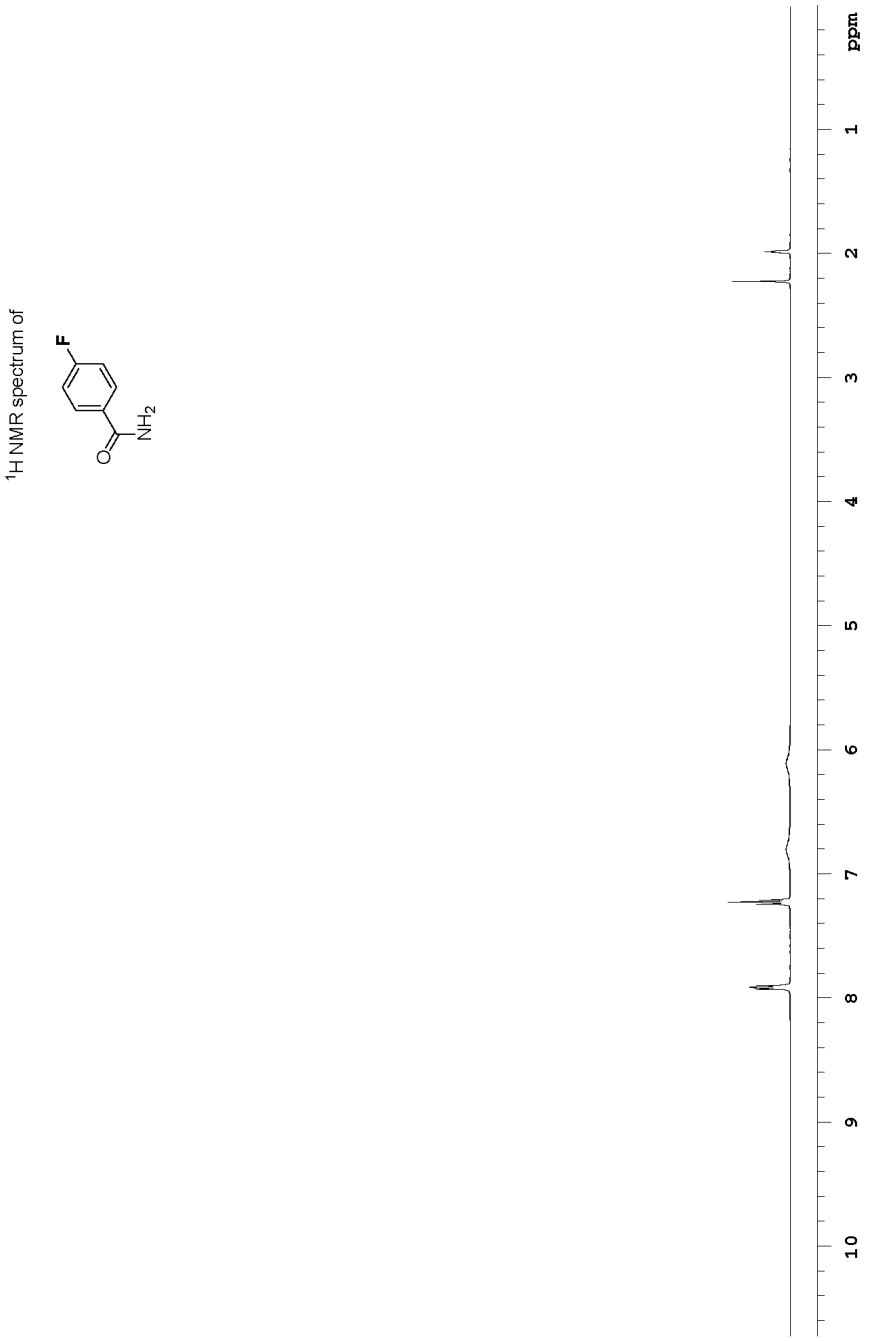
^{19}F NMR spectrum (375 MHz, toluene, 23 ºC) of **16**



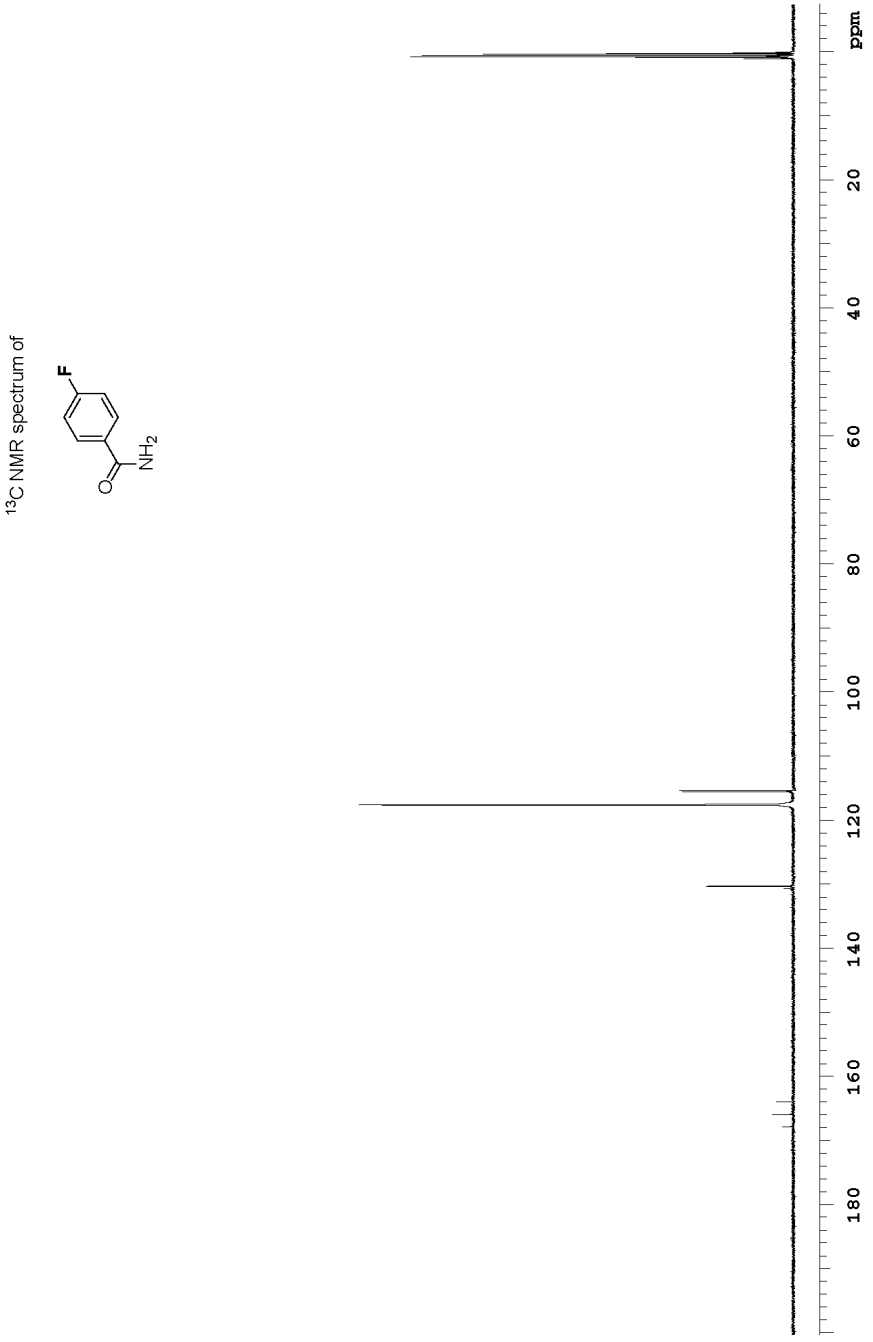
^{19}F NMR spectrum (375 MHz, toluene, 23 ºC) of commercial sample **16**



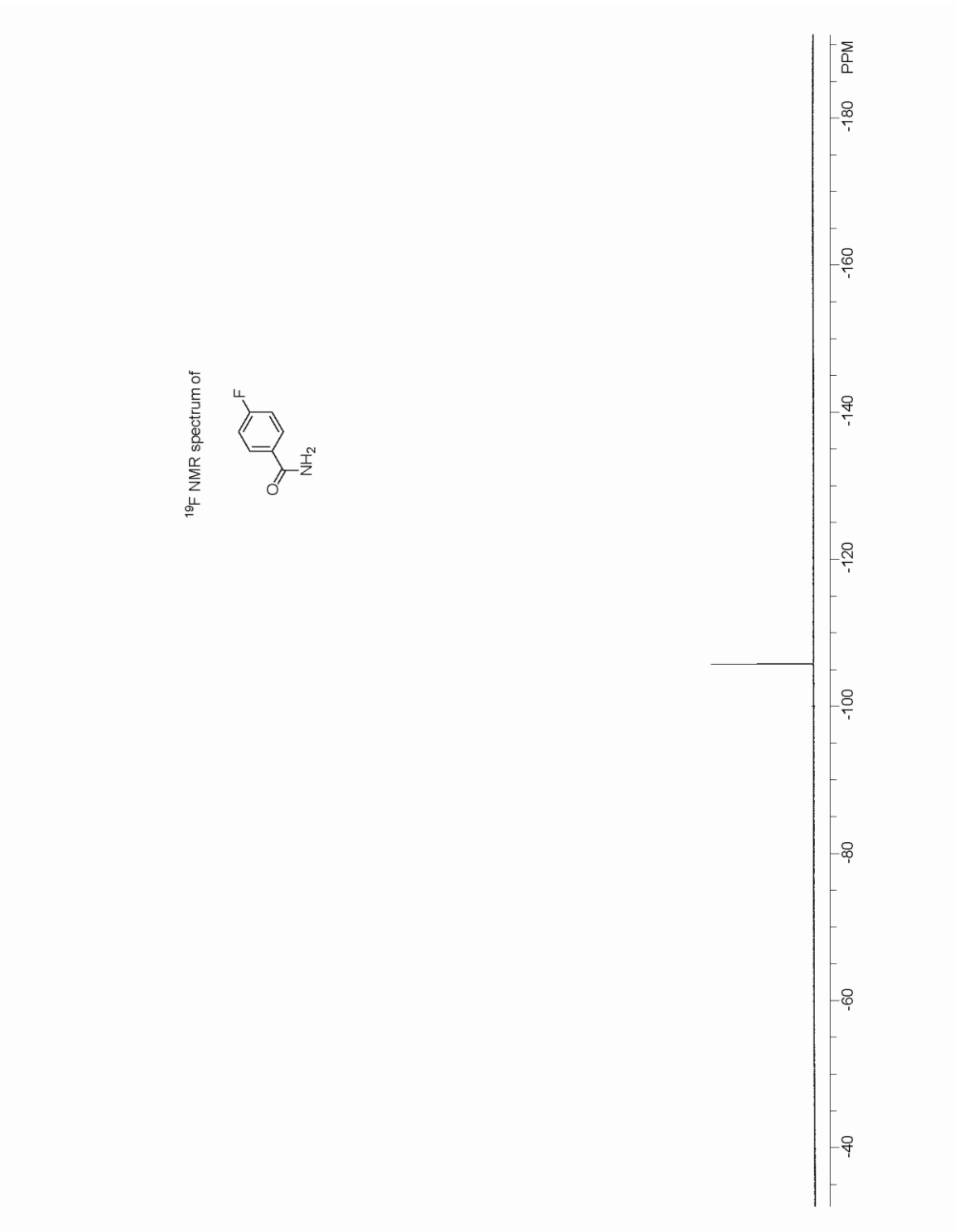
^{1}H NMR spectrum (500 MHz, CD_3CN, 23 ºC) of **S4**



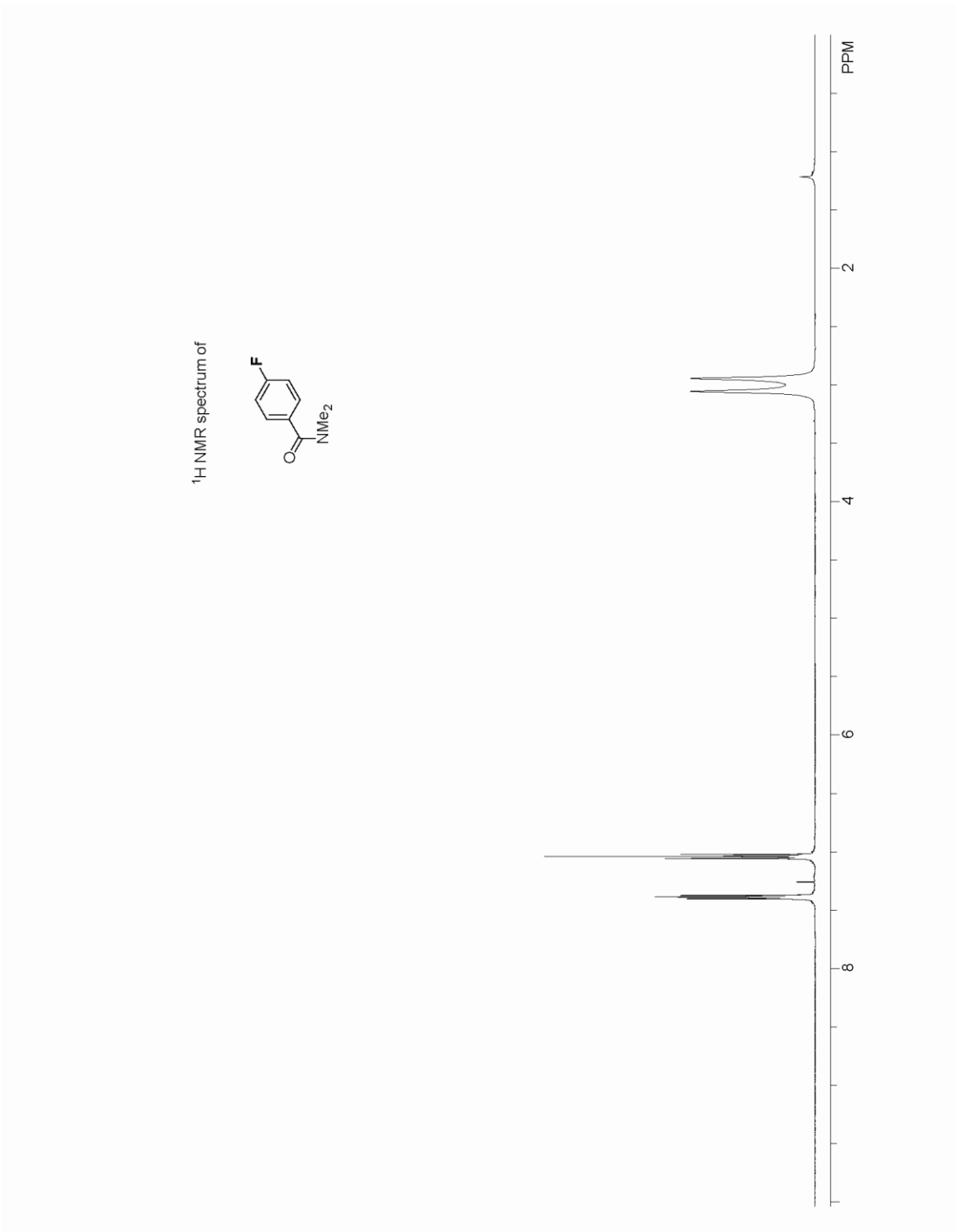
^{13}C NMR spectrum (125 MHz, CD_3CN, 23 ºC) of **S4**



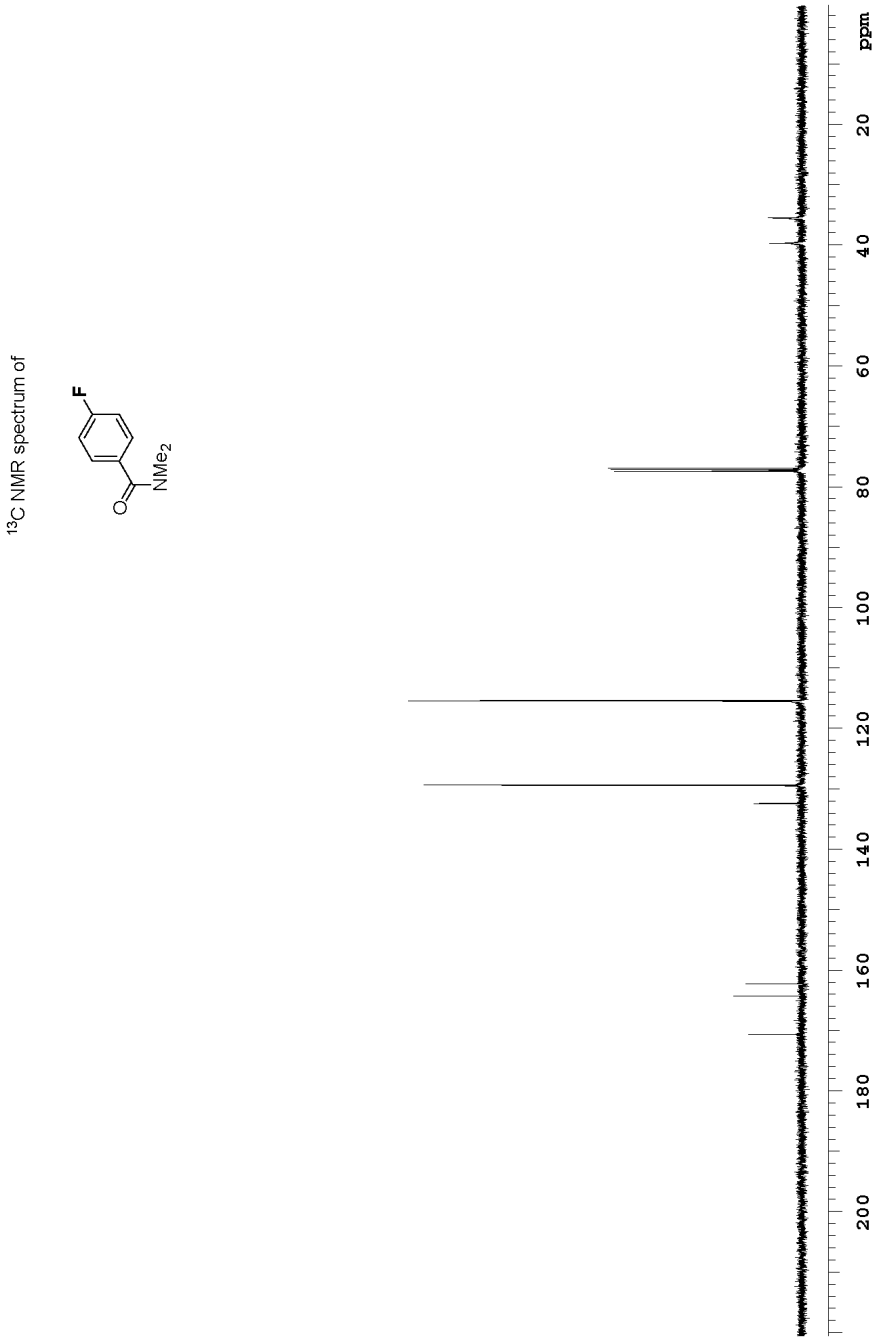
^{19}F NMR spectrum (375 MHz, CD_3CN, 23 ºC) of **S4**



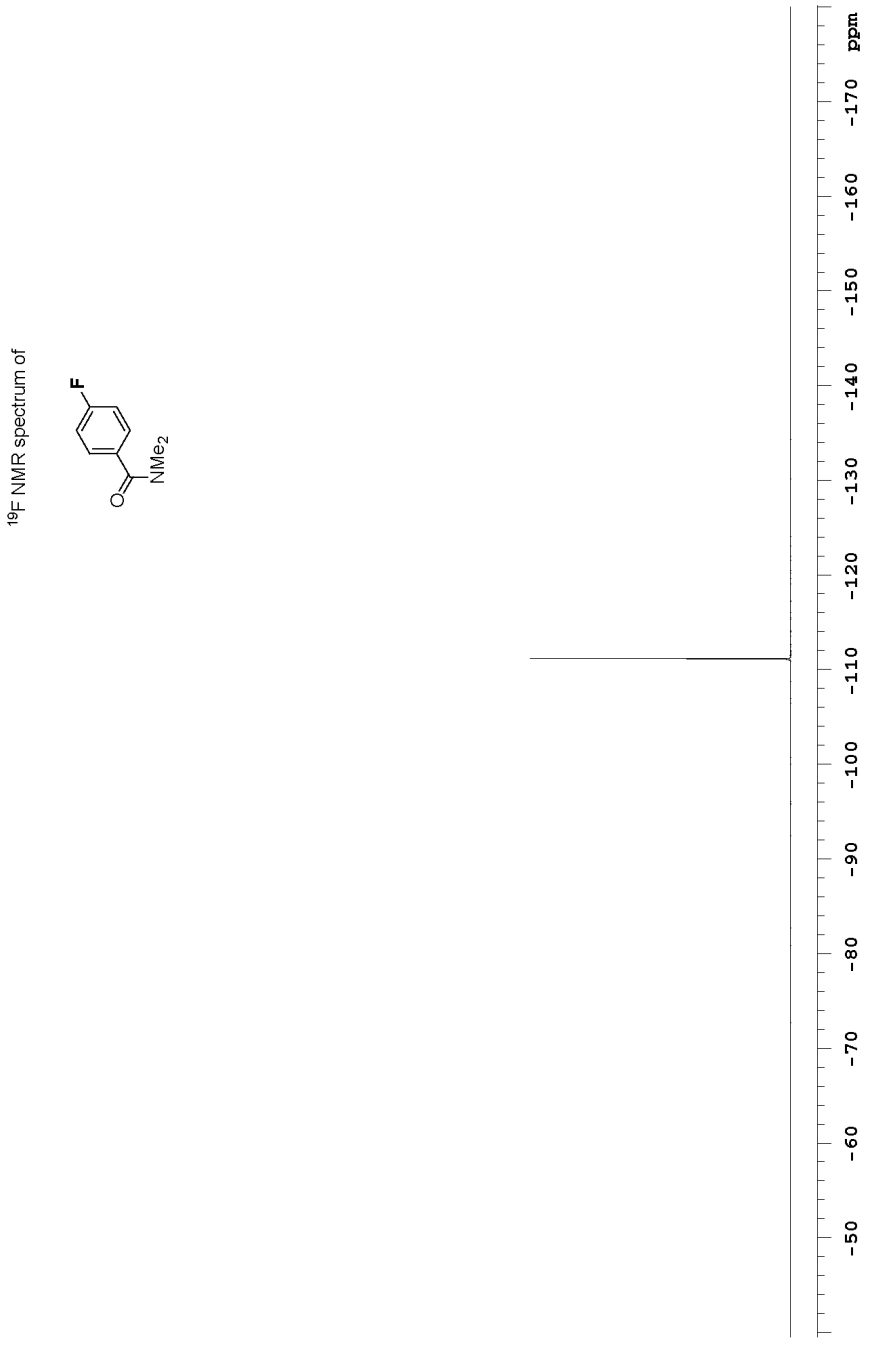
^{1}H NMR spectrum (500 MHz, $CDCl_3$, 23 ºC) of **17**



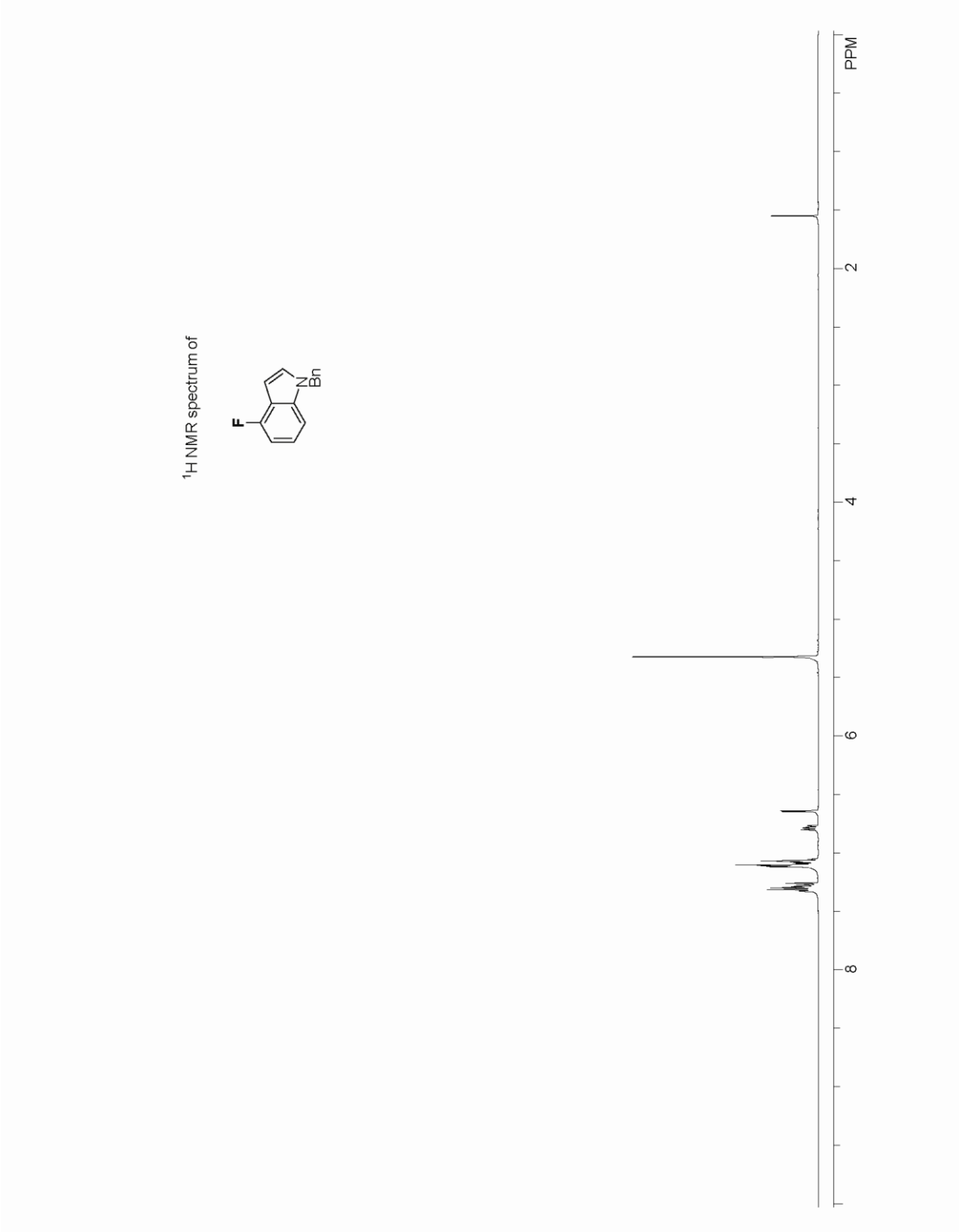
^{13}C NMR spectrum (125 MHz, $CDCl_3$, 23 ºC) of **17**



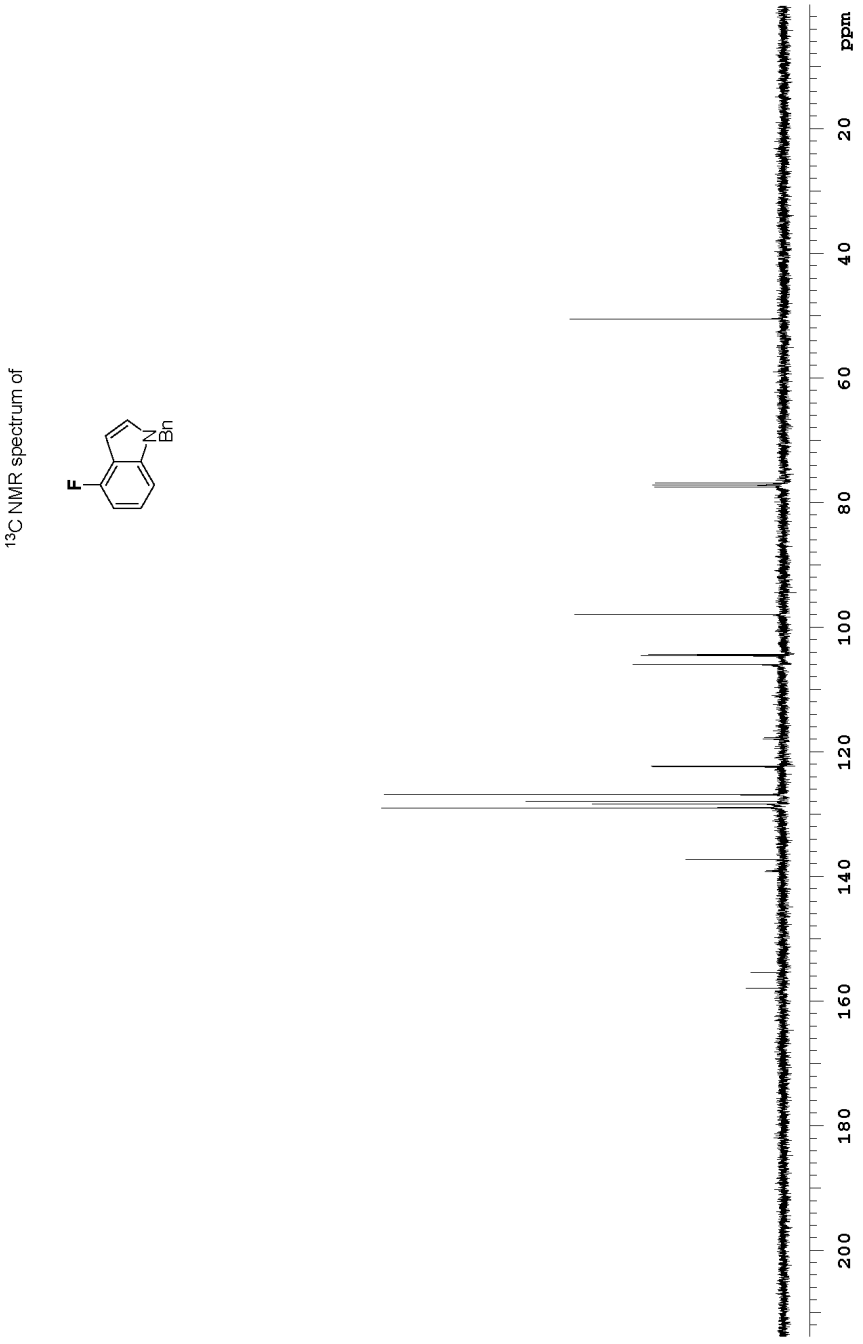
^{19}F NMR spectrum (375 MHz, $CDCl_3$, 23 ºC) of **17**



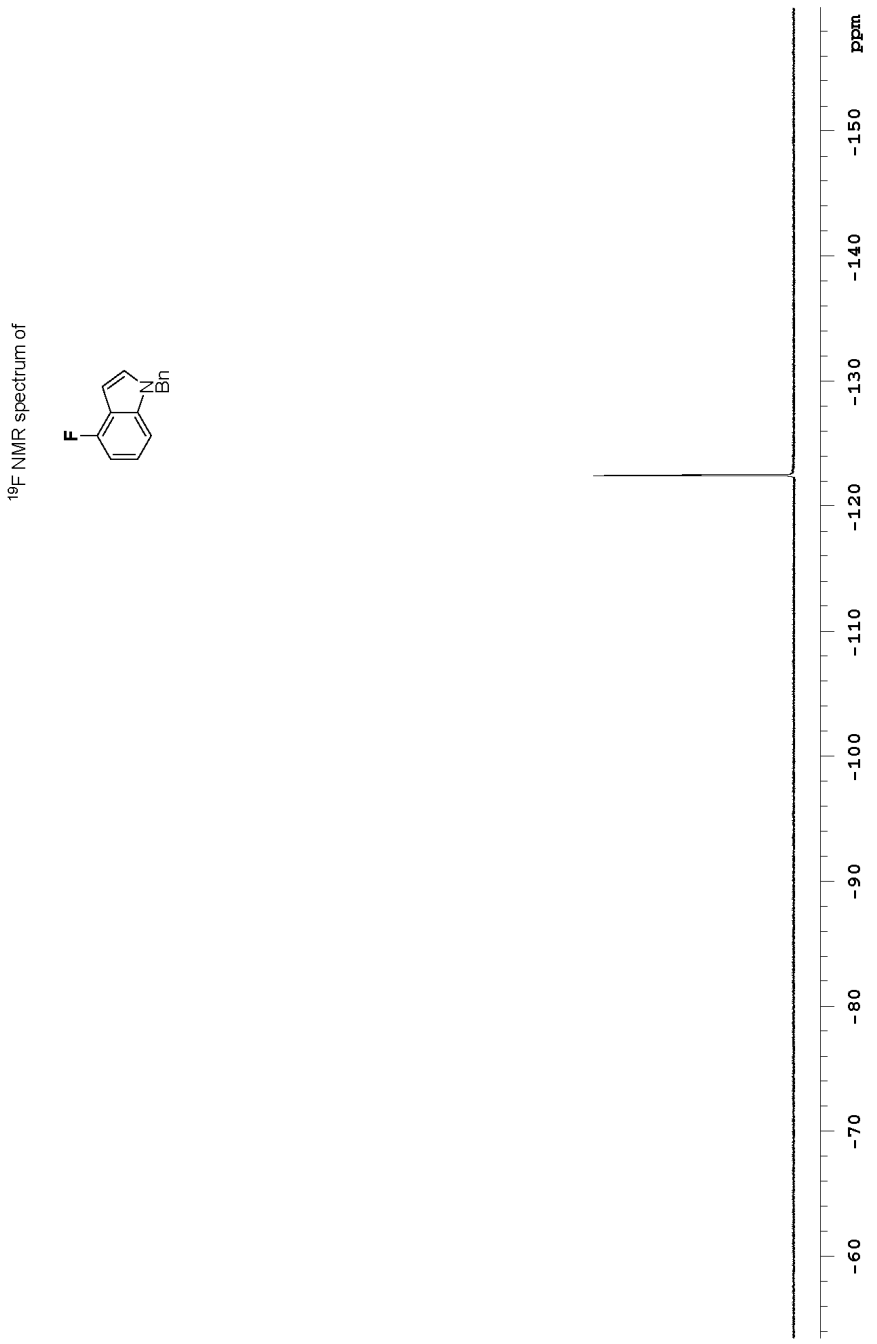
^{1}H NMR spectrum (500 MHz, $CDCl_3$, 23 ºC) of **18**



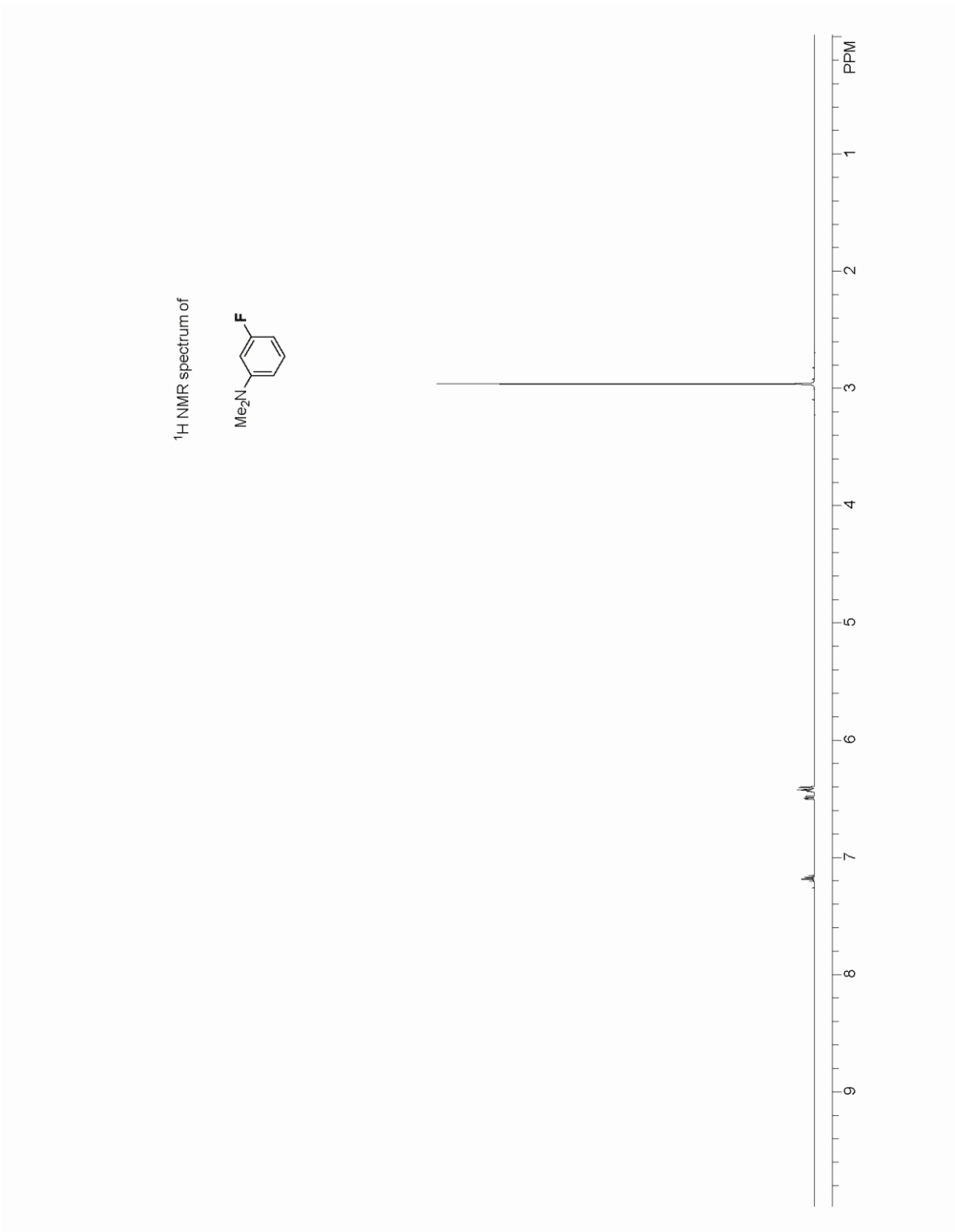
^{13}C NMR spectrum (125 MHz, $CDCl_3$, 23 ºC) of **18**



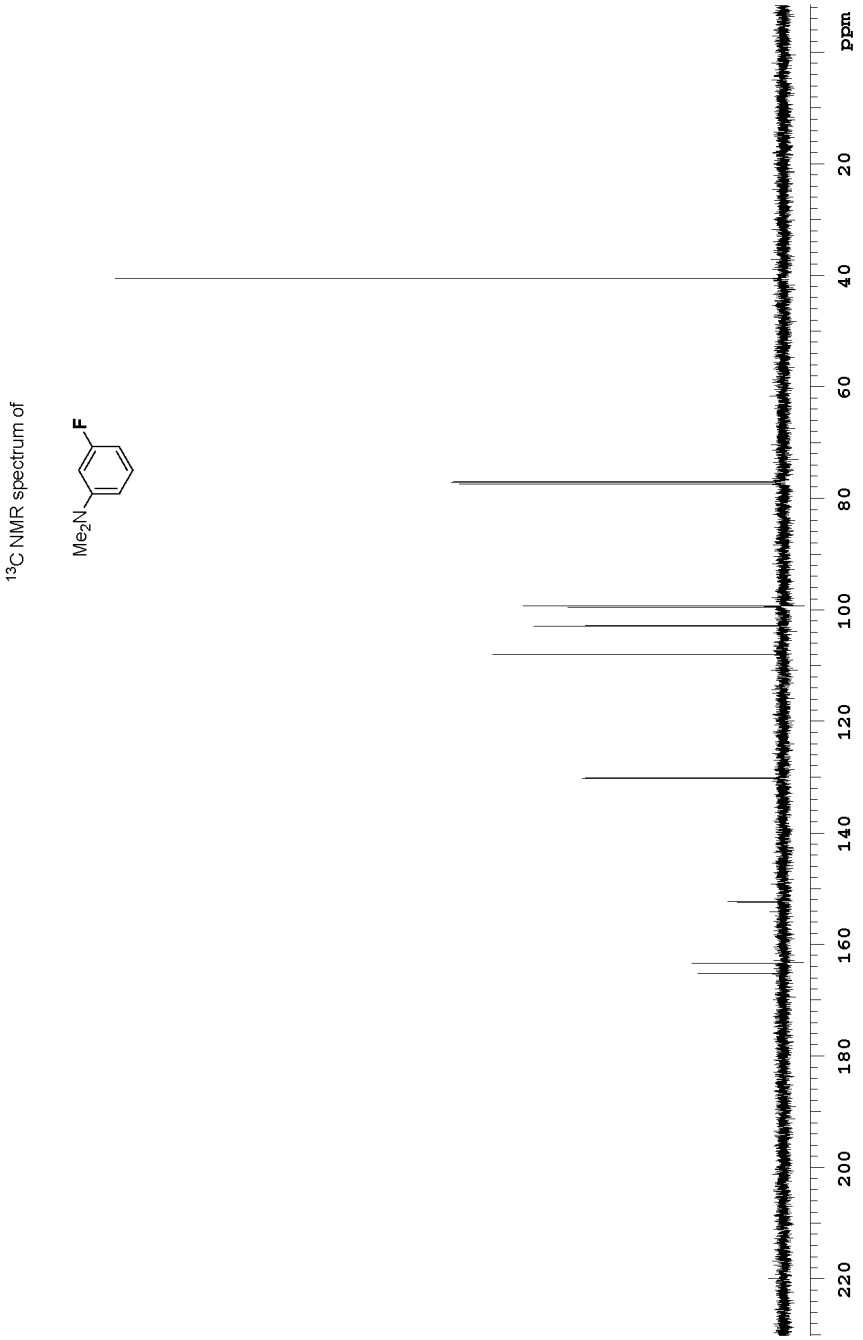
^{19}F NMR spectrum (375 MHz, $CDCl_3$, 23 ºC) of **18**



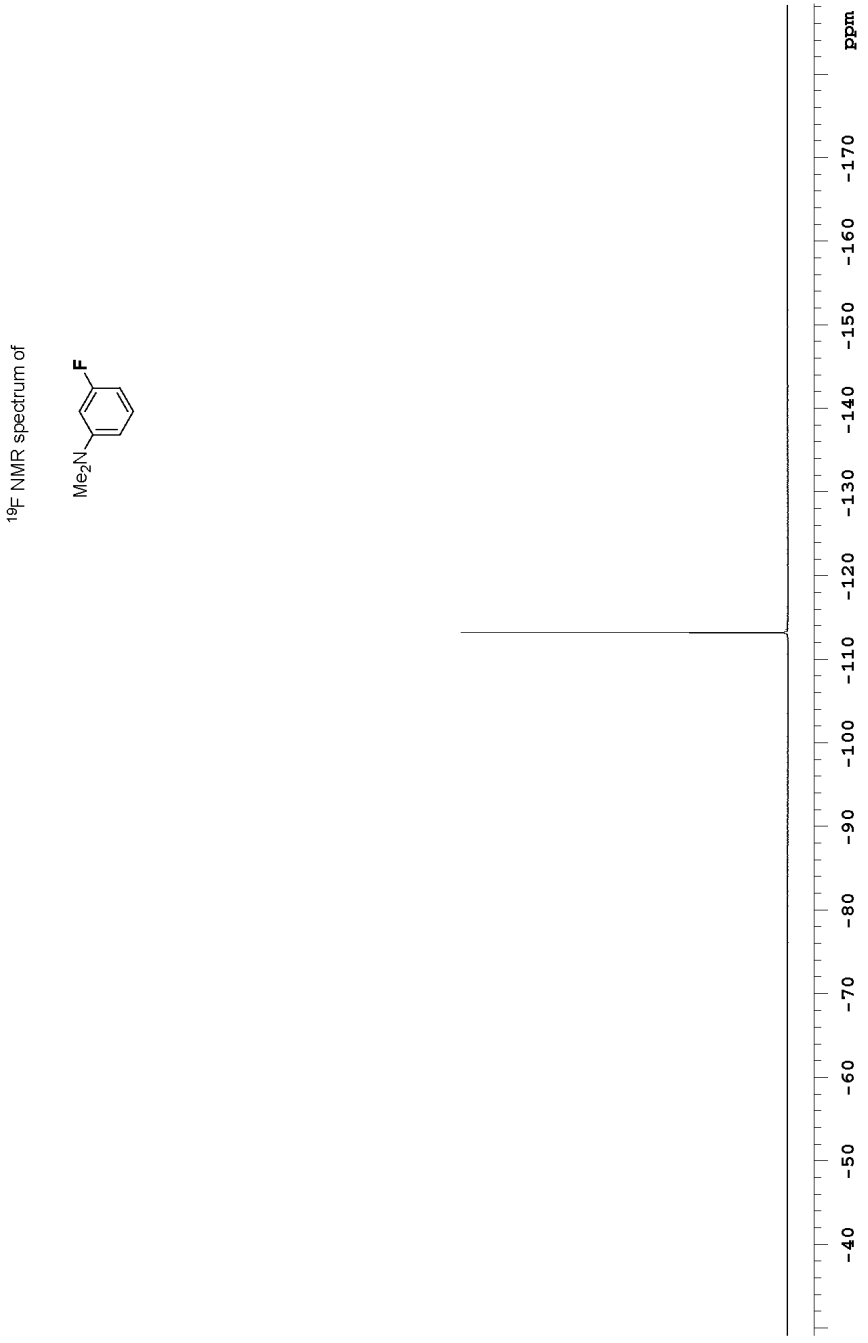
^{1}H NMR spectrum (500 MHz, $CDCl_3$, 23 ºC) of **19**



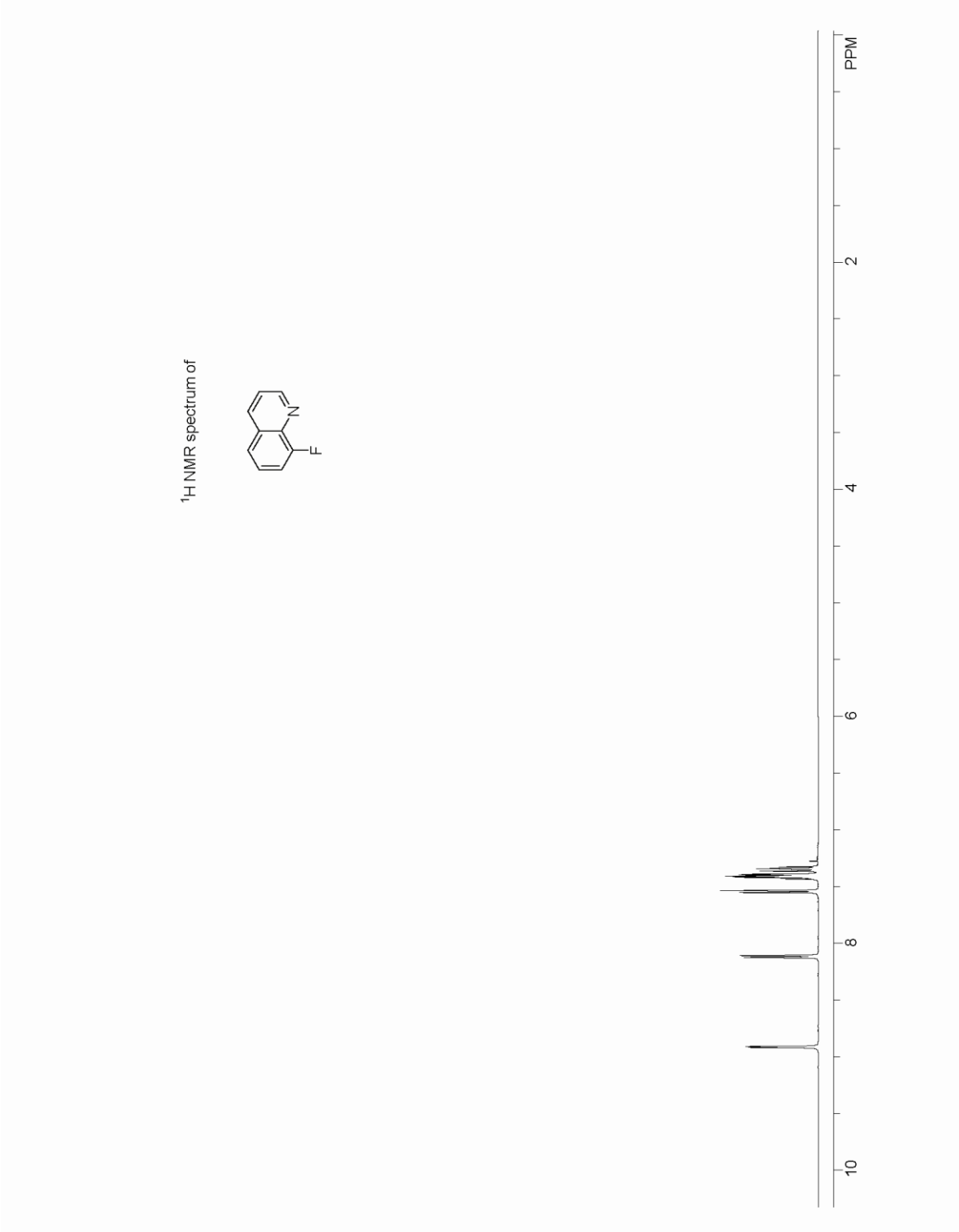
^{13}C NMR spectrum (125 MHz, $CDCl_3$, 23 ºC) of **19**



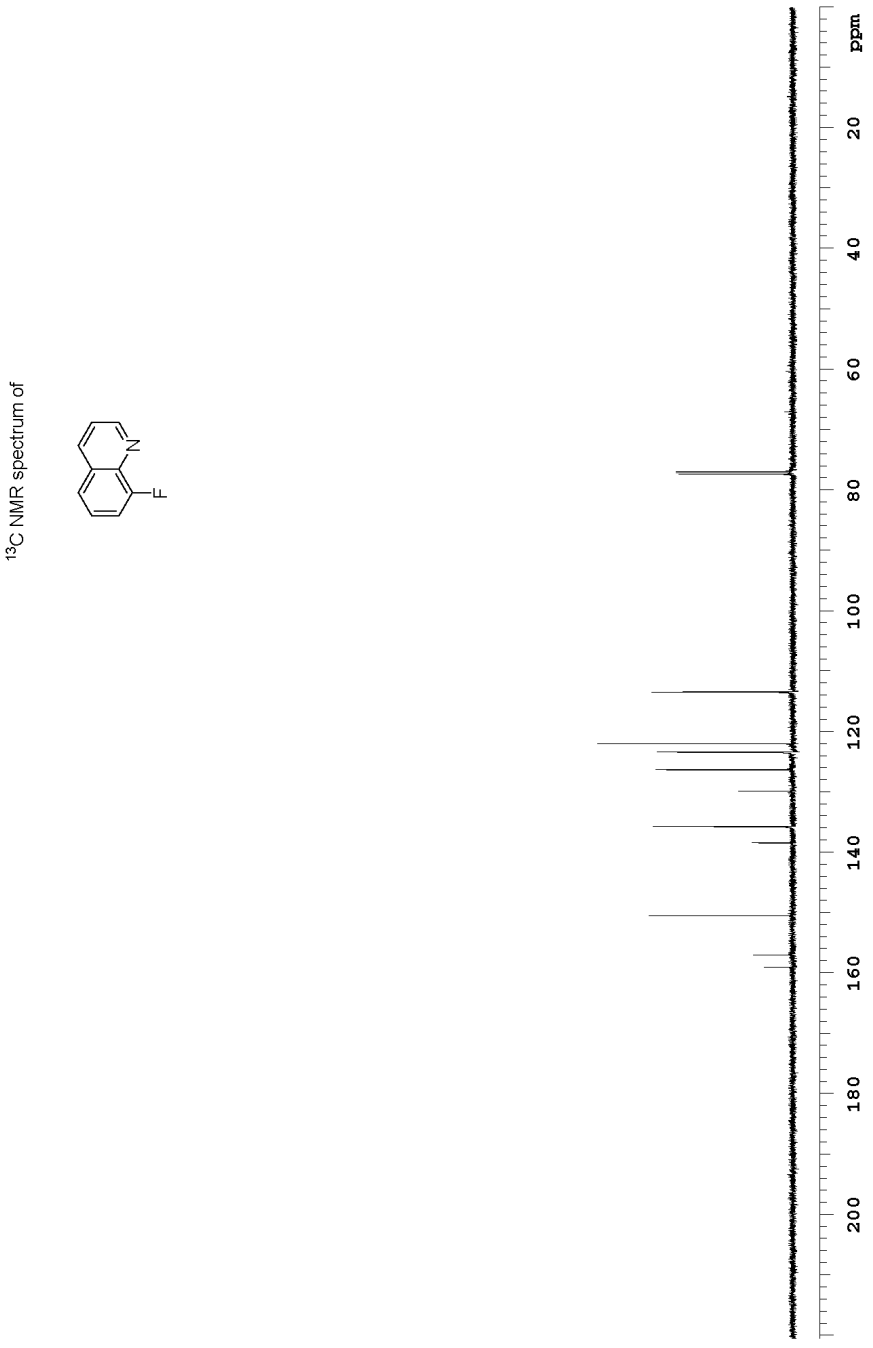
^{19}F NMR spectrum (375 MHz, $CDCl_3$, 23 ºC) of **19**



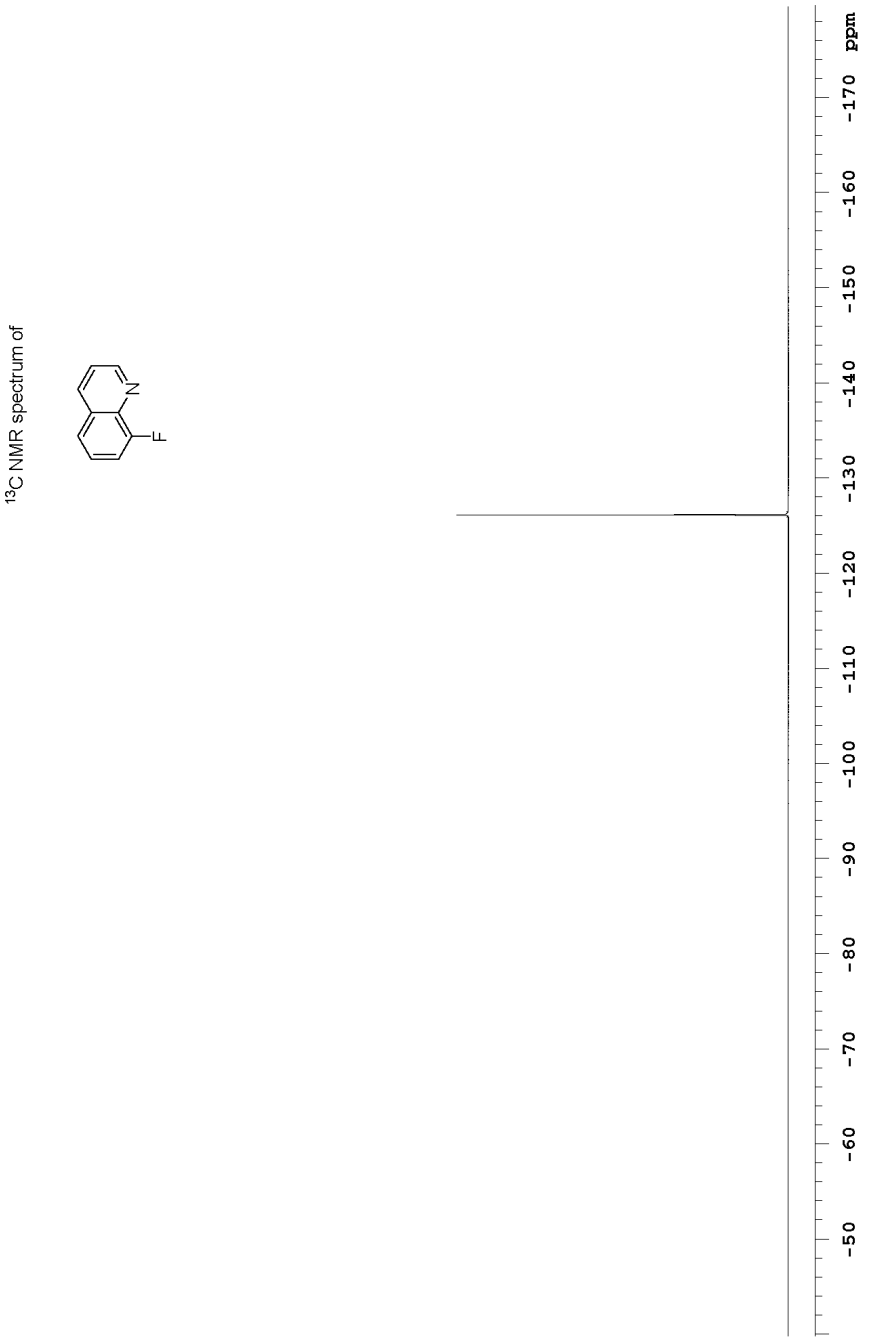
^{1}H NMR spectrum (500 MHz, $CDCl_3$, 23 ºC) of **20**



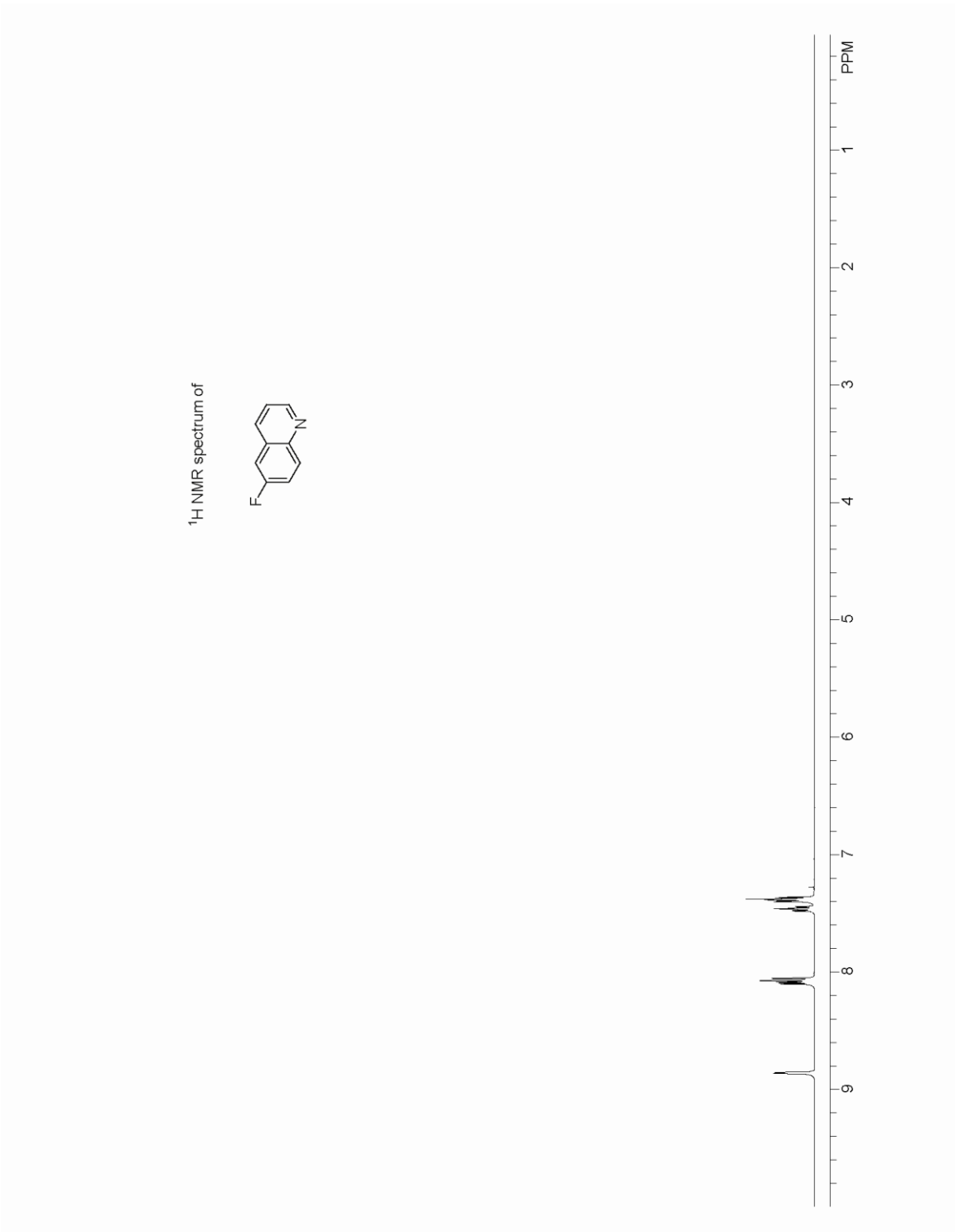
^{13}C NMR spectrum (125 MHz, $CDCl_3$, 23 ºC) of **20**



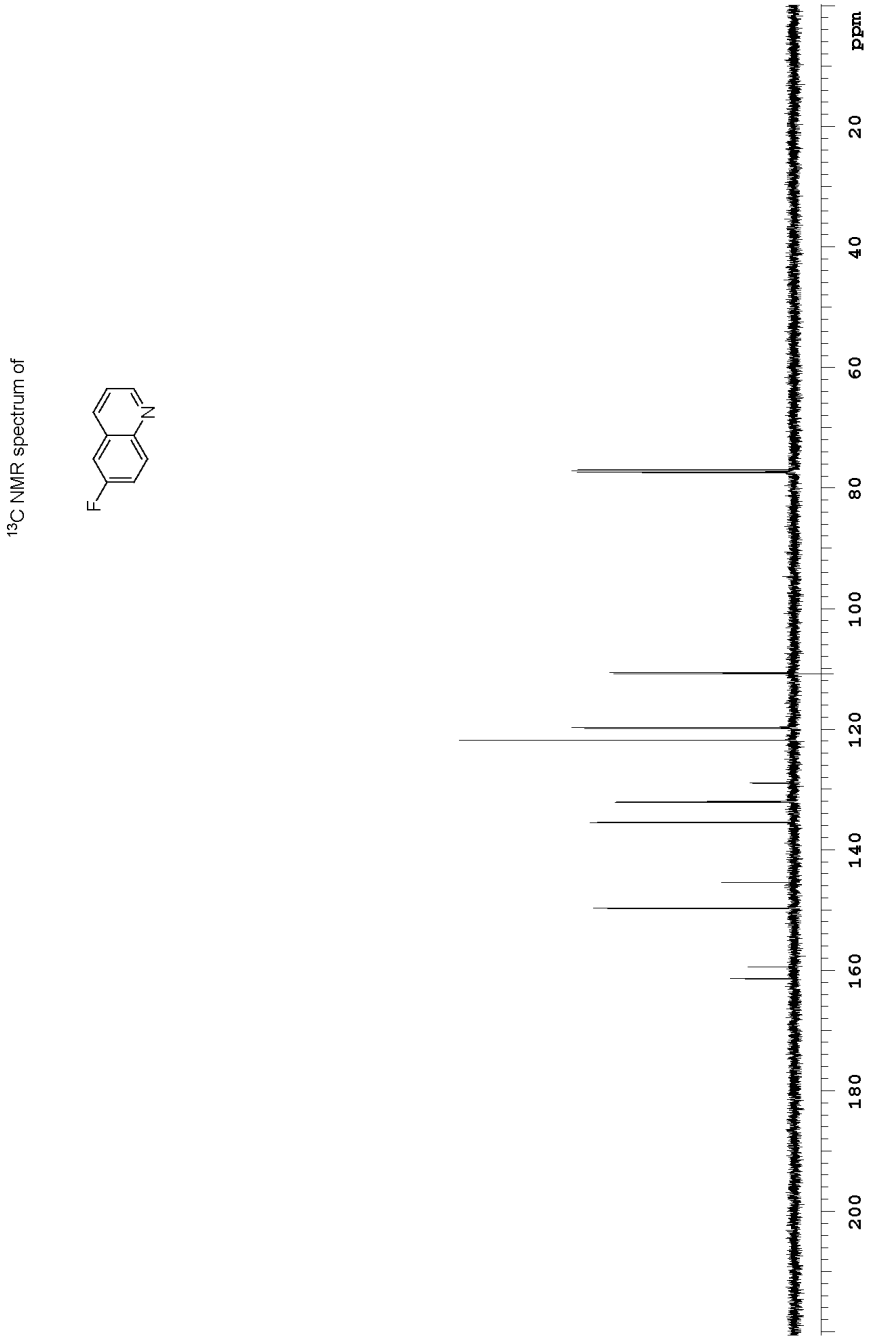
^{19}F NMR spectrum (375 MHz, $CDCl_3$, 23 ºC) of **20**



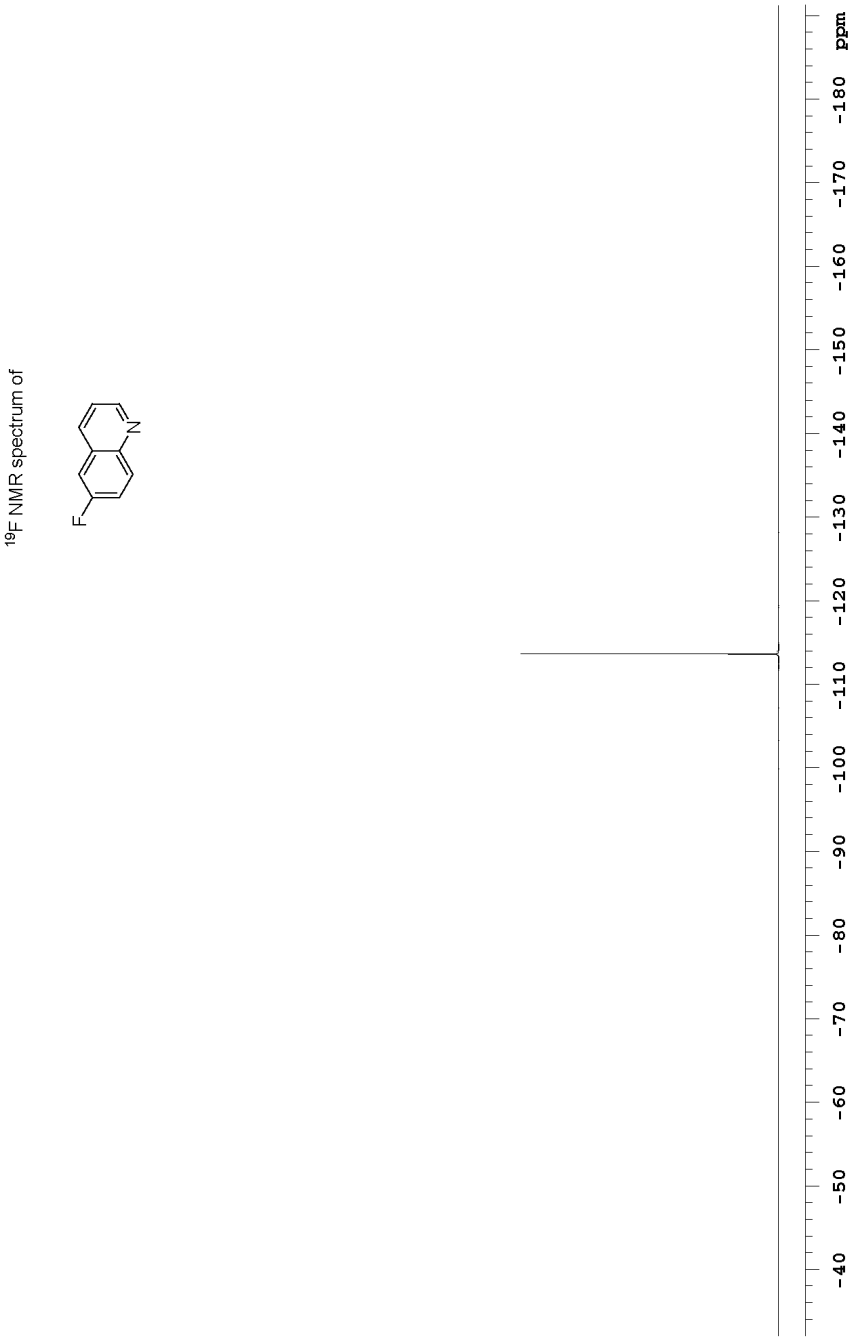
^{1}H NMR spectrum (500 MHz, $CDCl_3$, 23 ºC) of **21**



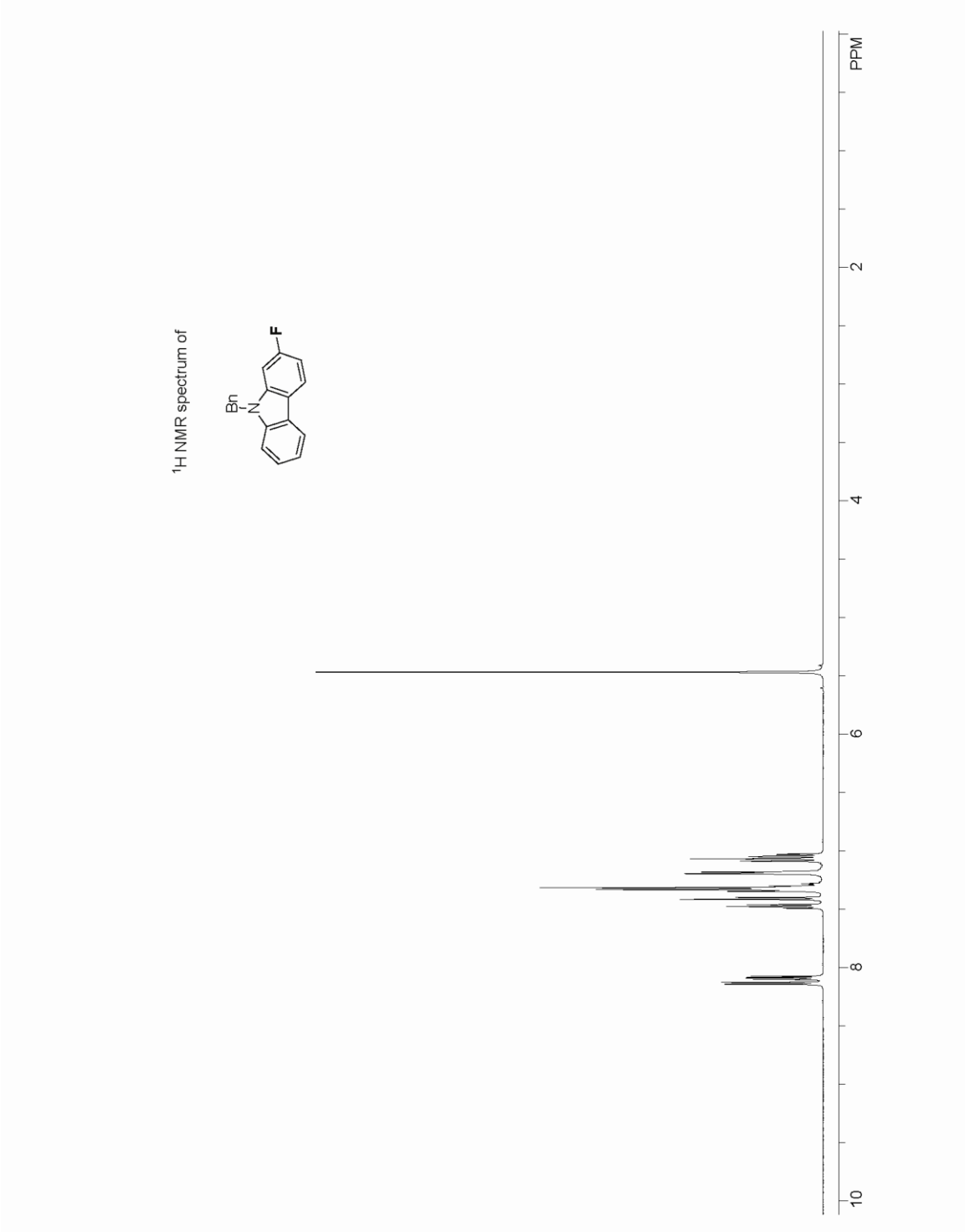
^{13}C NMR spectrum (125 MHz, $CDCl_3$, 23 ºC) of **21**



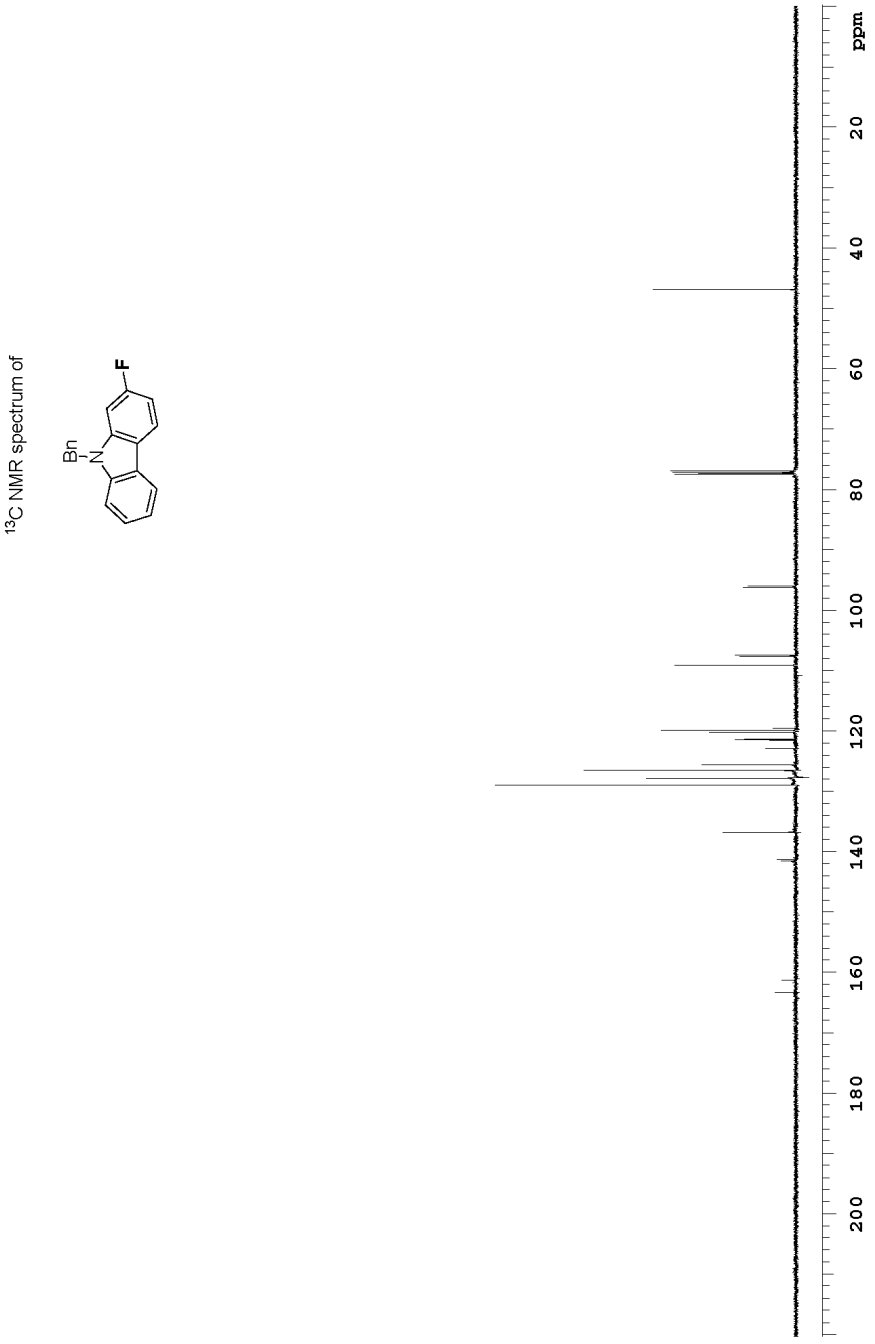
^{19}F NMR spectrum (375 MHz, $CDCl_3$, 23 ºC) of **21**



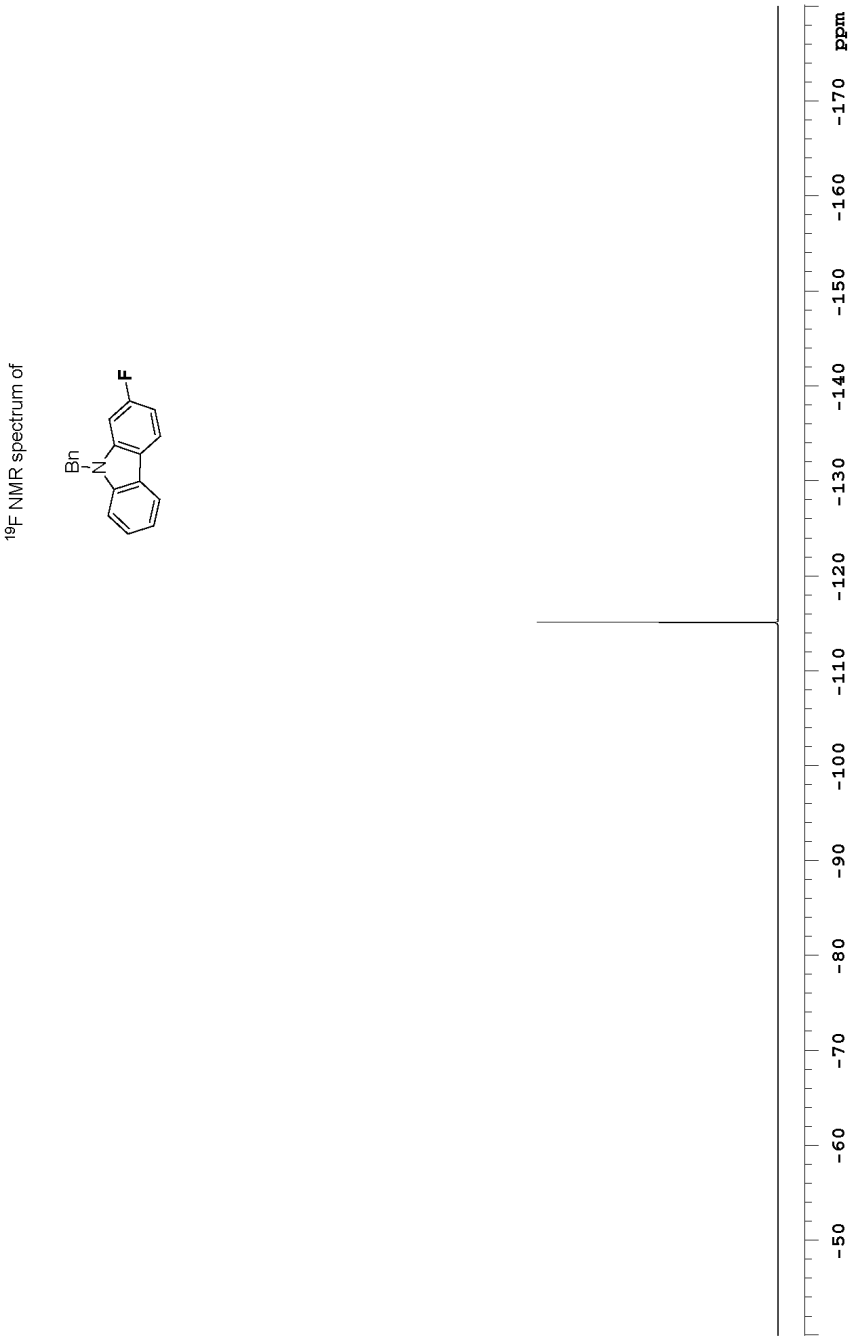
^{1}H NMR spectrum (500 MHz, $CDCl_3$, 23 ºC) of **22**



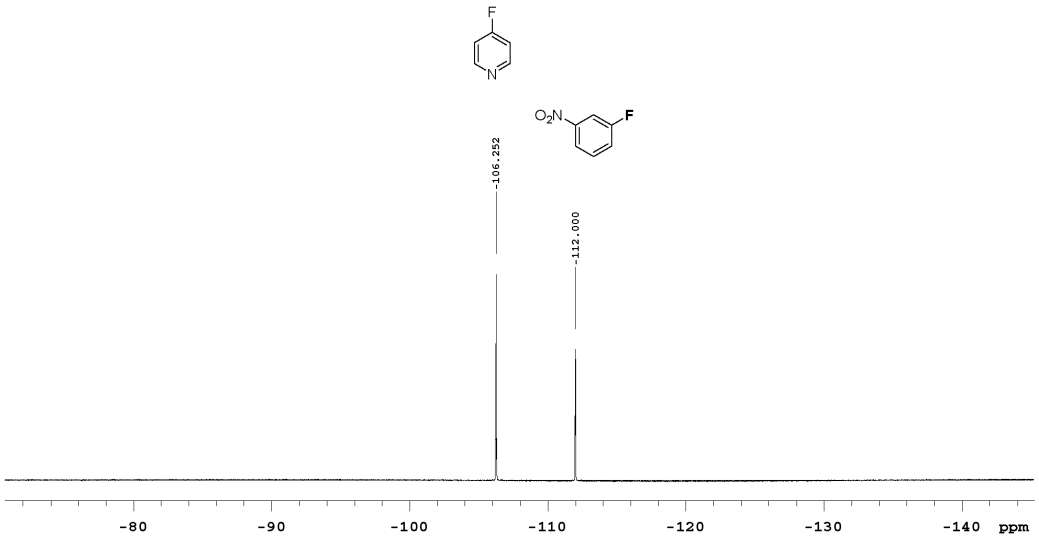
^{13}C NMR spectrum (125 MHz, $CDCl_3$, 23 ºC) of **22**



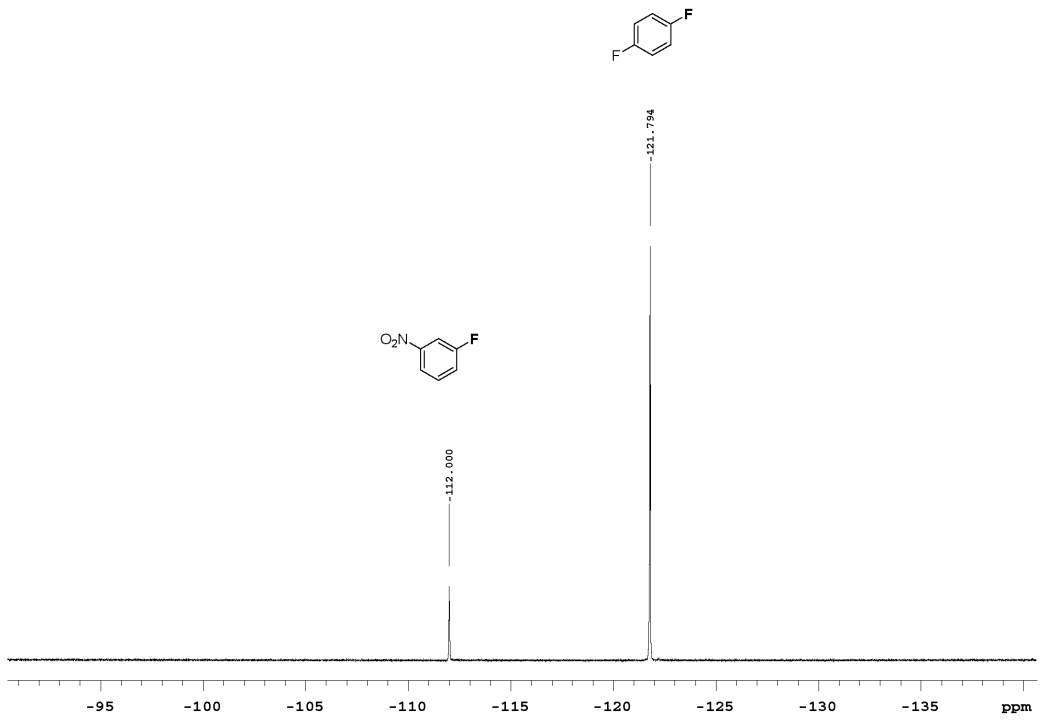
^{19}F NMR spectrum (375 MHz, $CDCl_3$, 23 ºC) of **22**



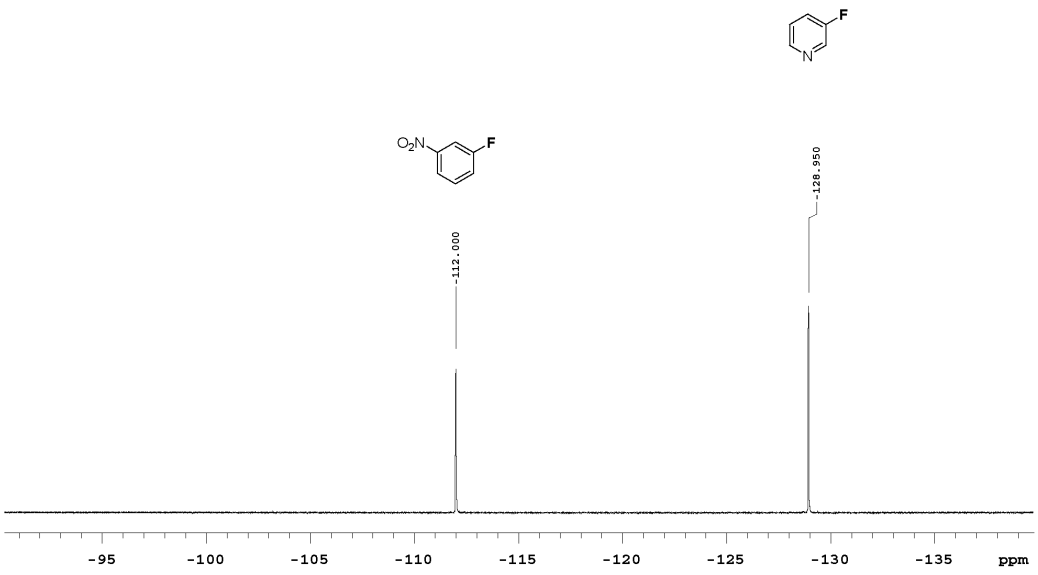
^{19}F NMR spectrum (375 MHz, toluene, 23 ºC) of **23**



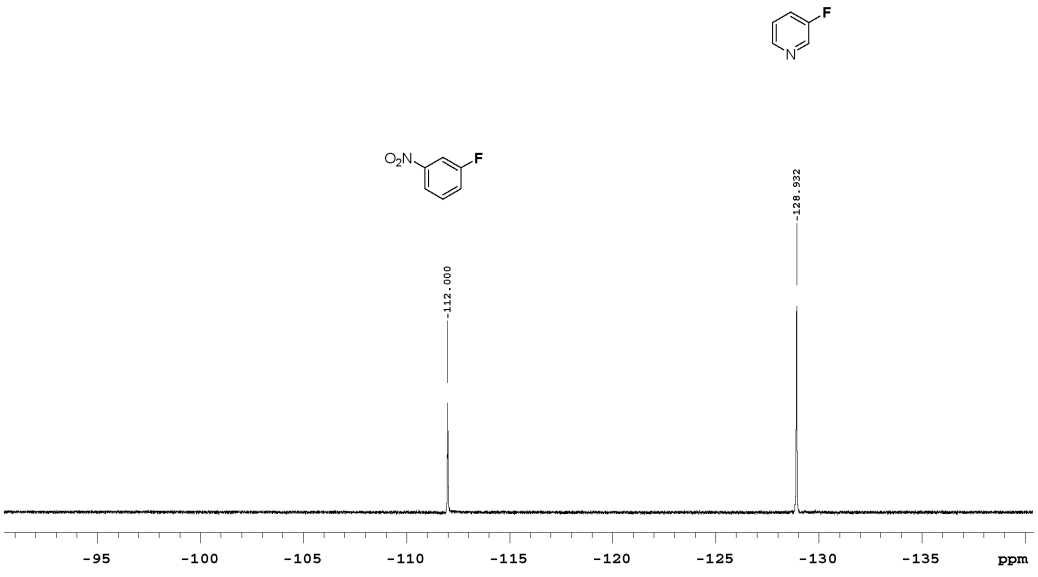
^{19}F NMR spectrum (375 MHz, toluene, 23 ºC) of commercial sample **23**



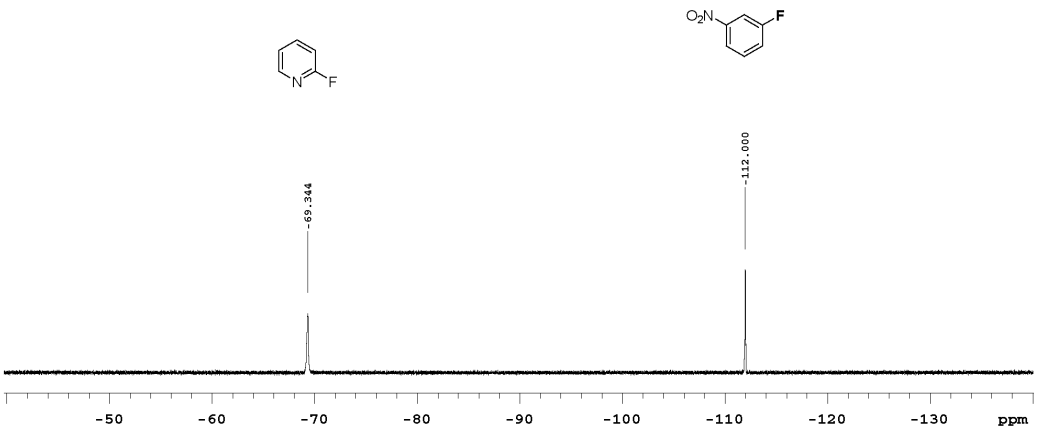
^{19}F NMR spectrum (375 MHz, toluene, 23 ºC) of **24**



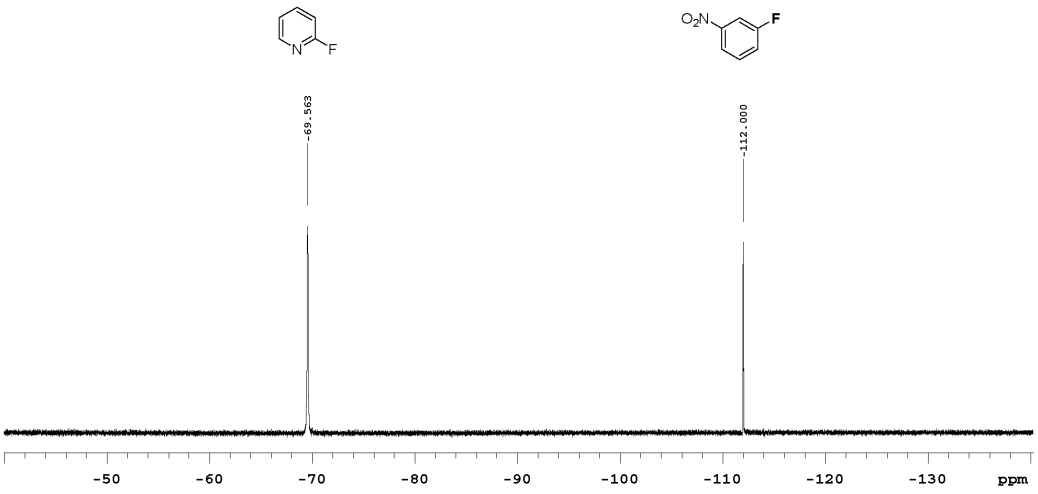
^{19}F NMR spectrum (375 MHz, toluene, 23 ºC) of commercial sample **24**



^{19}F NMR spectrum (375 MHz, toluene, 23 ºC) of **25**

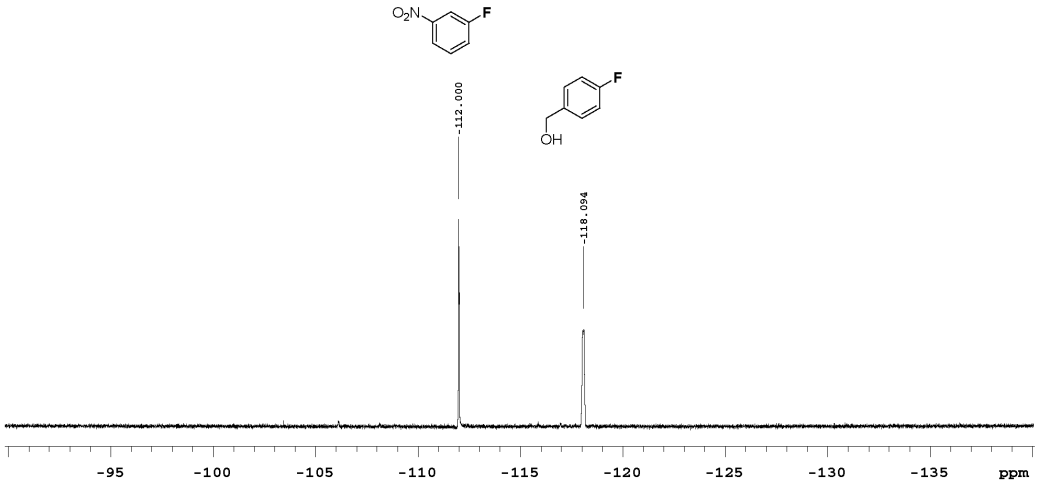


^{19}F NMR spectrum (375 MHz, toluene, 23 ºC) of commercial sample **25**

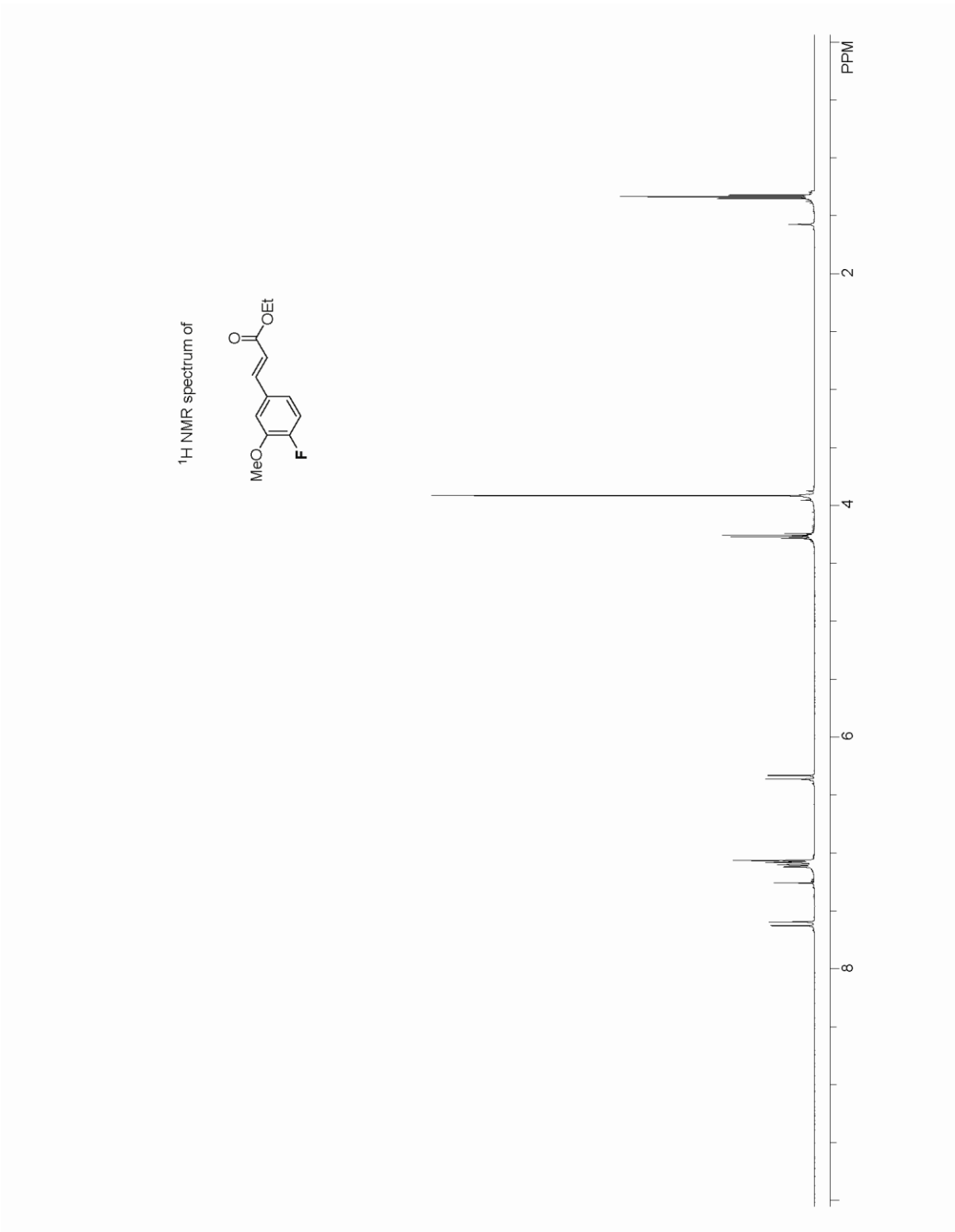


^{19}F NMR spectrum (375 MHz, toluene, 23 ºC) of 4-fluorobenzyl alcohol

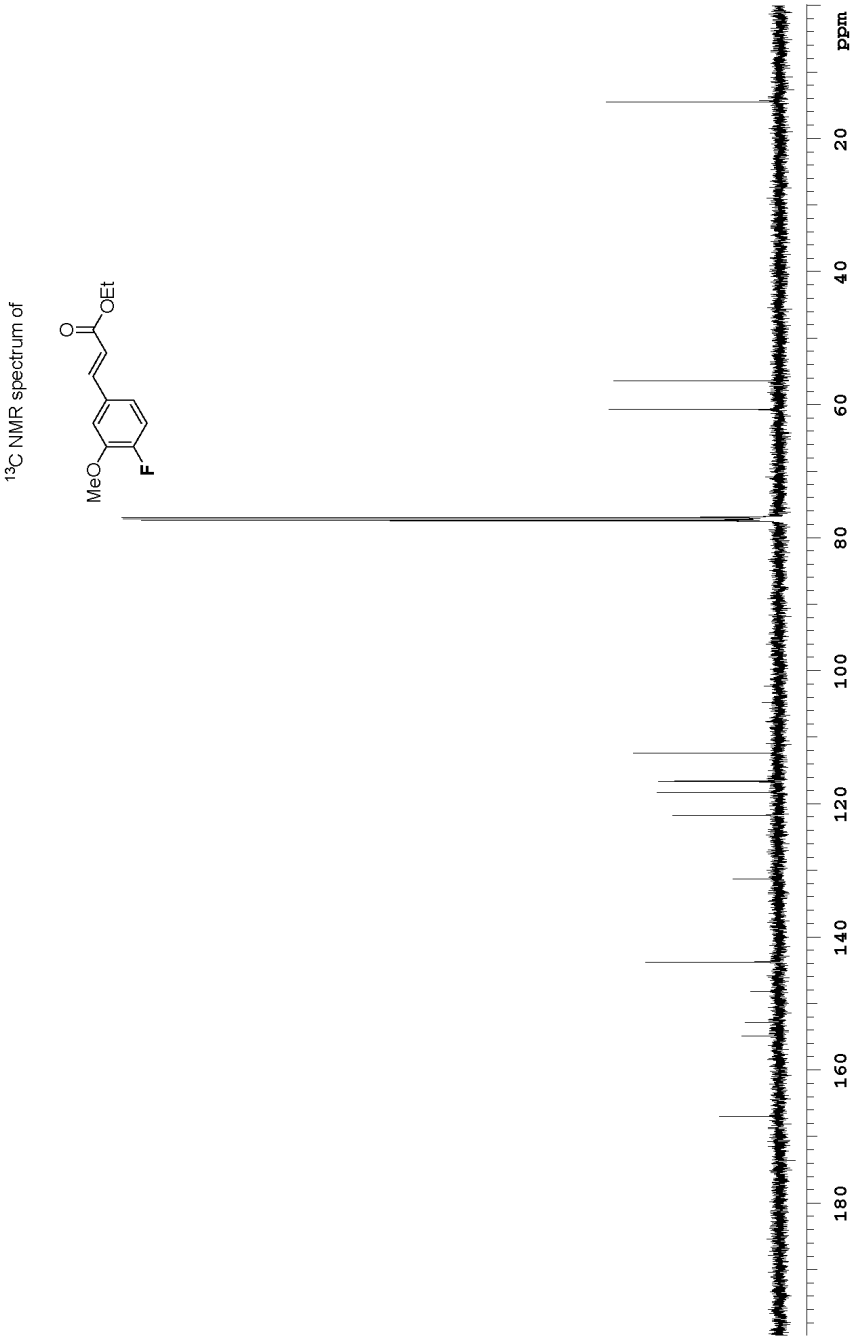
^{19}F NMR spectrum (375 MHz, toluene, 23 ºC) of commercial sample 4-fluorobenzyl alcohol



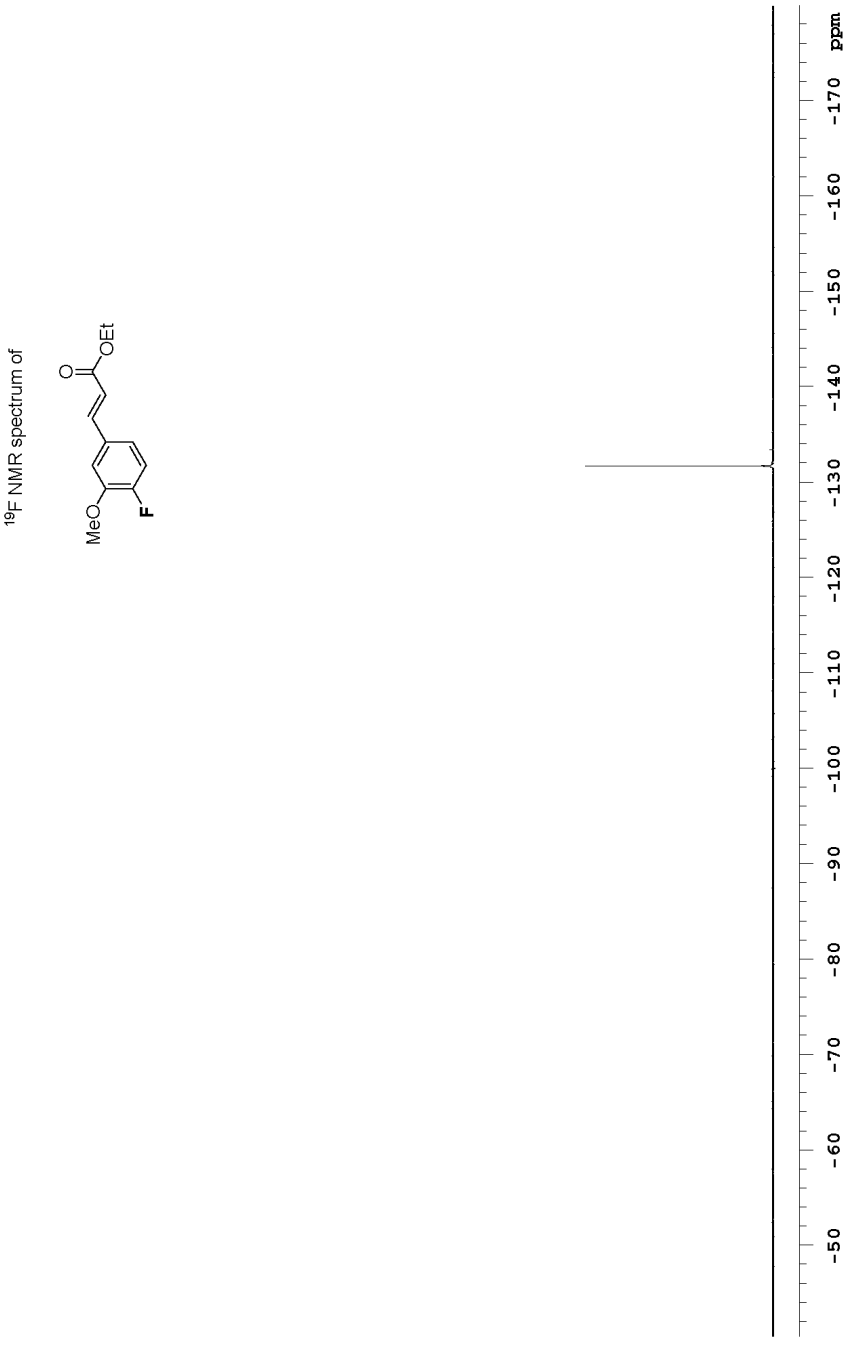
^{1}H NMR spectrum (500 MHz, $CDCl_3$, 23 ºC) of **26**



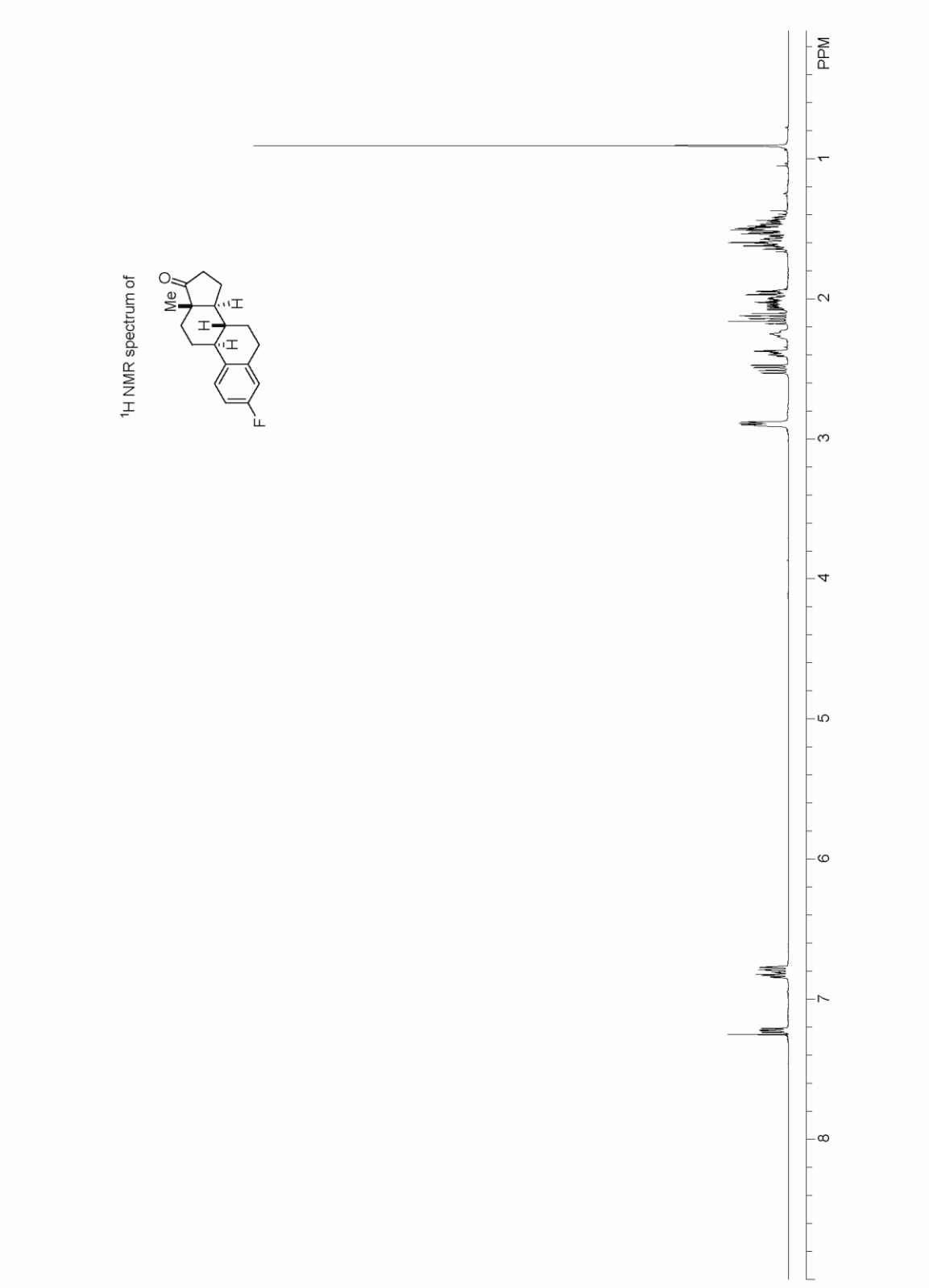
^{13}C NMR spectrum (125 MHz, $CDCl_3$, 23 ºC) of **26**



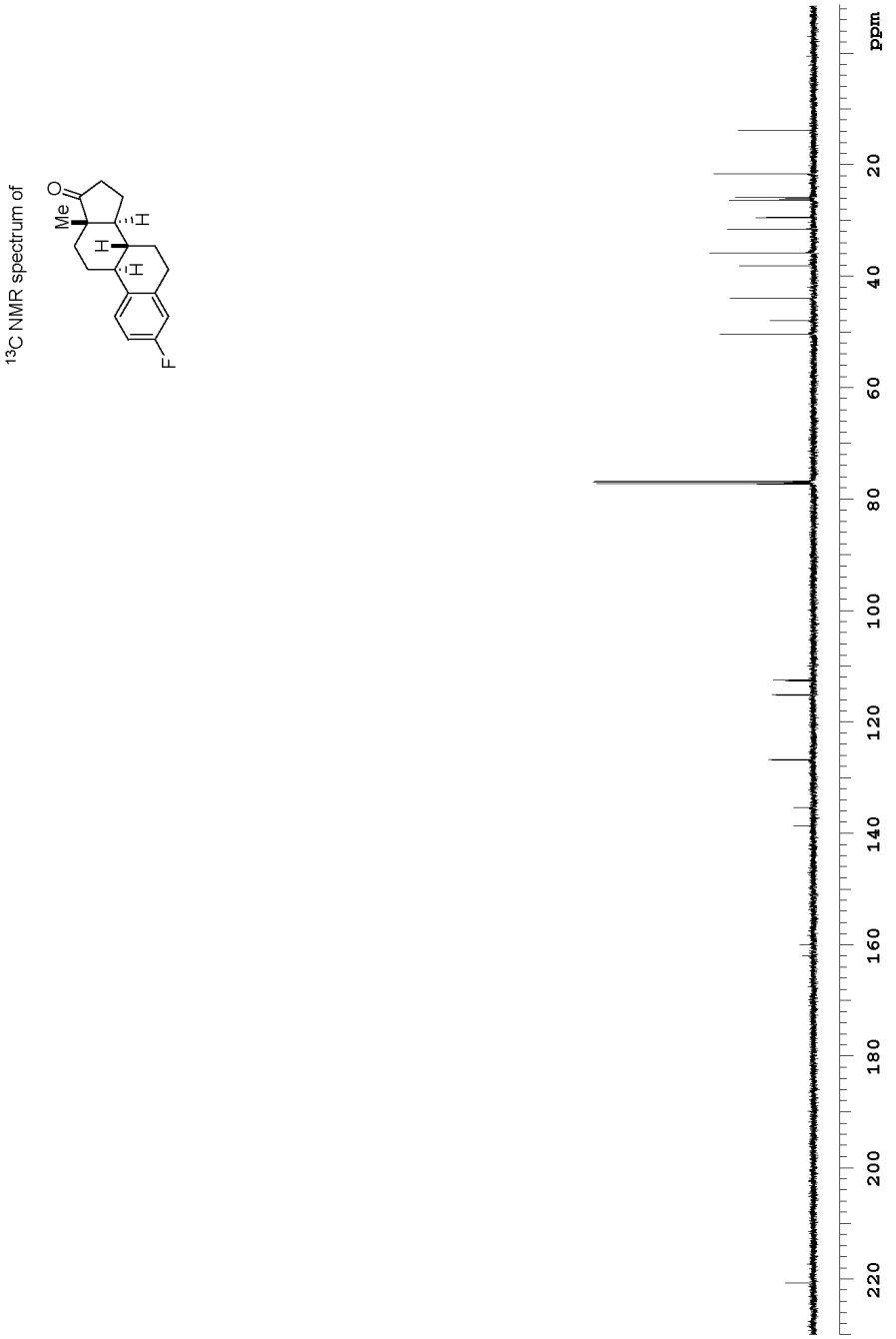
^{19}F NMR spectrum (375 MHz, $CDCl_3$, 23 ºC) of **26**



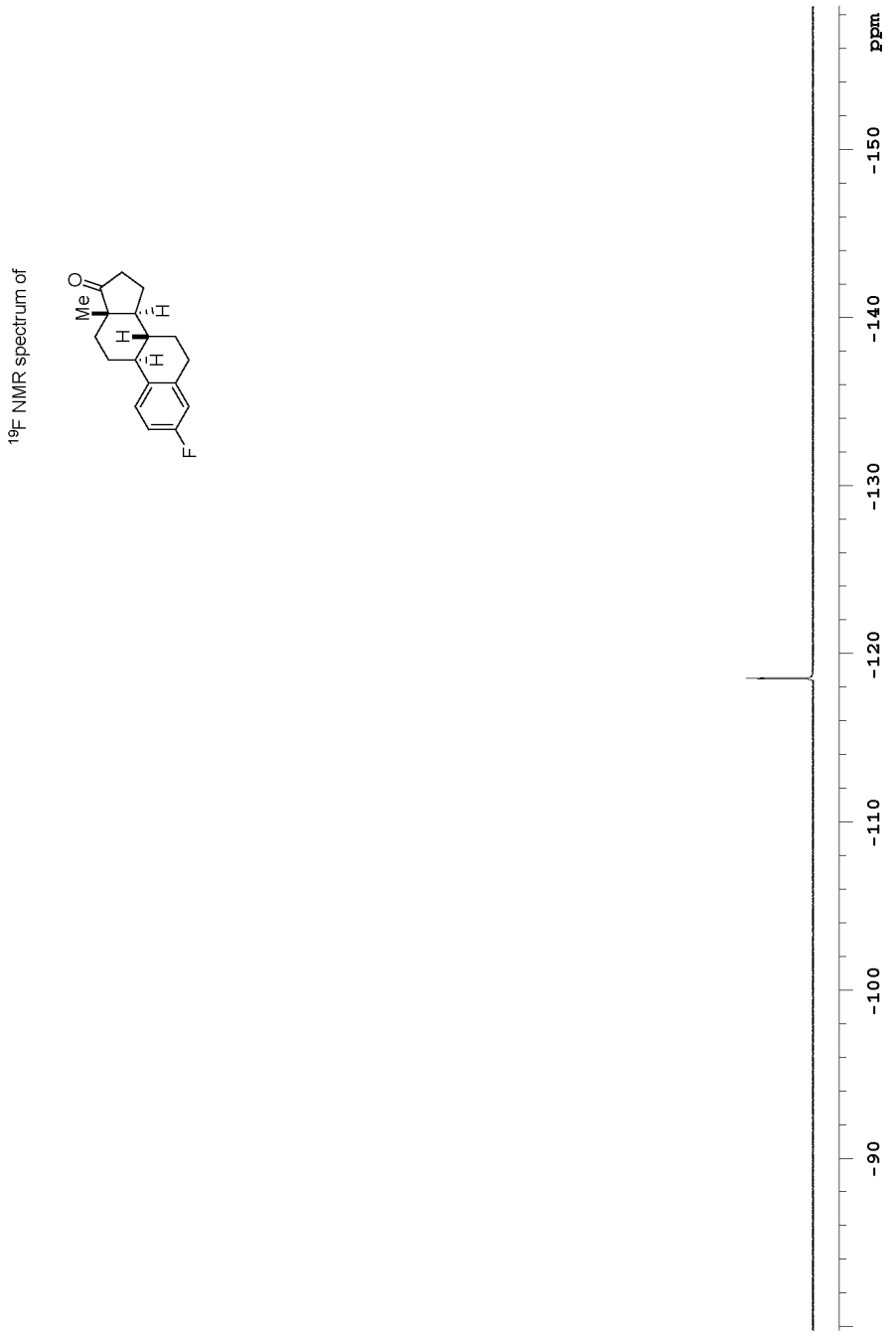
^{1}H NMR spectrum (500 MHz, $CDCl_3$, 23 ºC) of **27**



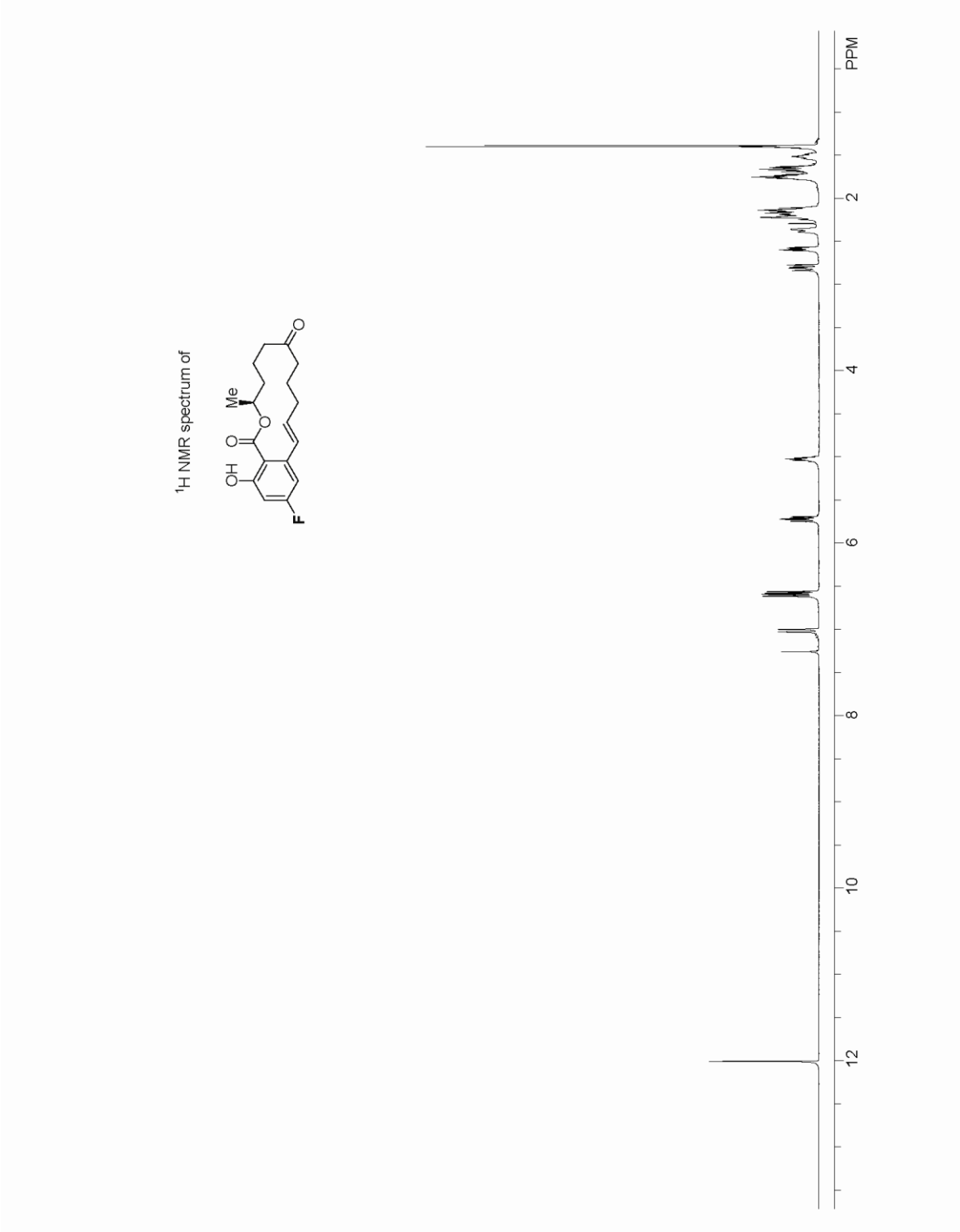
^{13}C NMR spectrum (125 MHz, $CDCl_3$, 23 ºC) of **27**



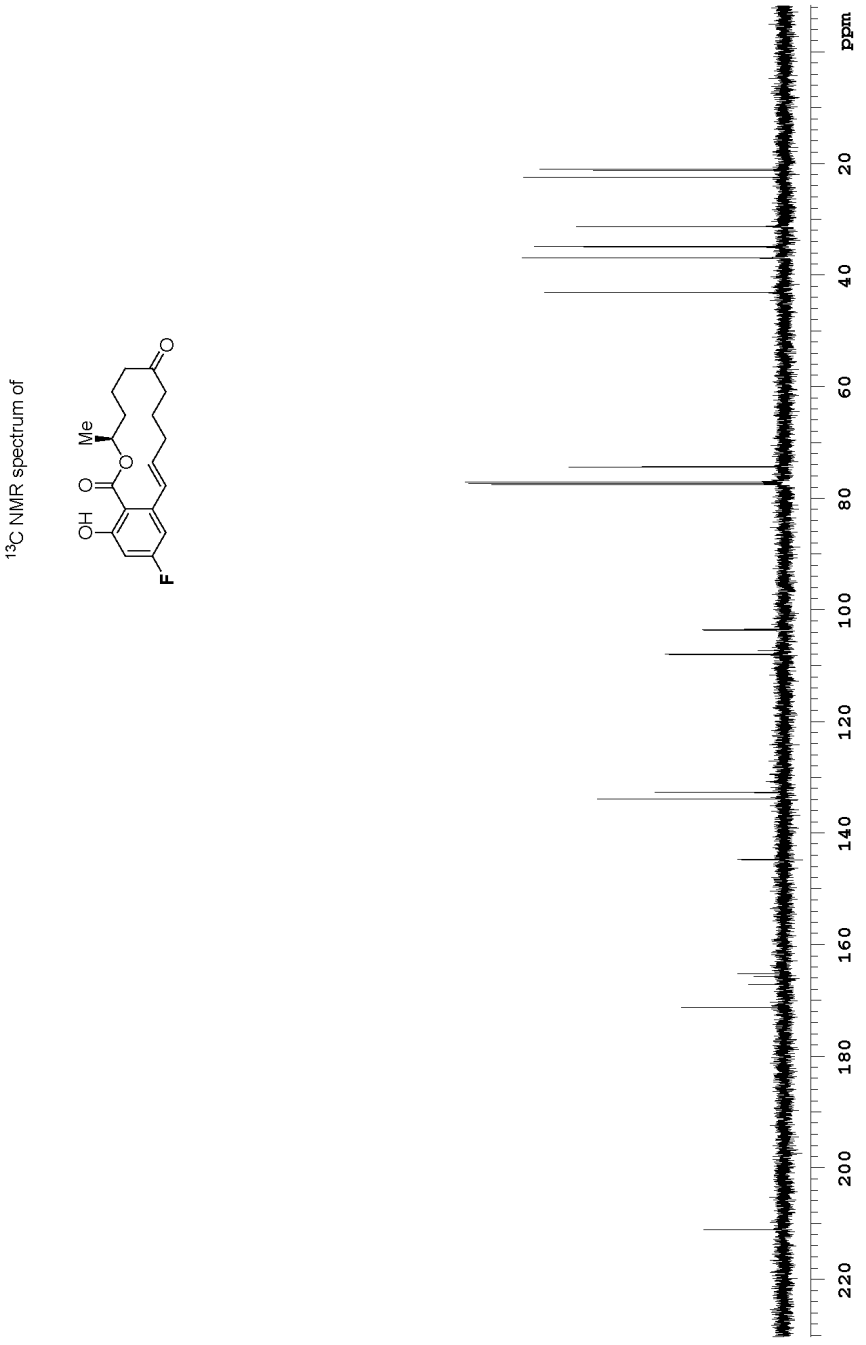
^{19}F NMR spectrum (375 MHz, $CDCl_3$, 23 ºC) of **27**



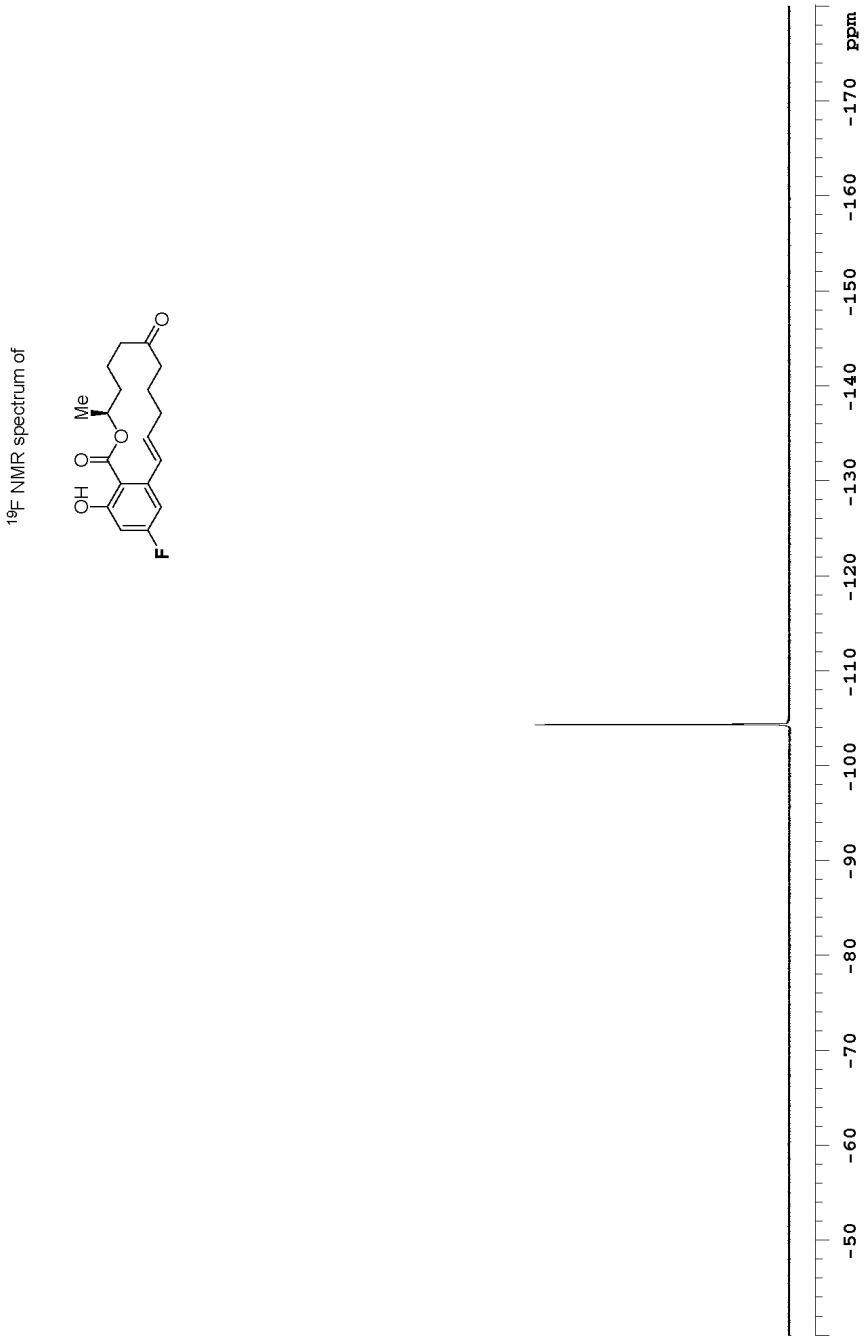
^{1}H NMR spectrum (500 MHz, $CDCl_3$, 23 ºC) of **28**



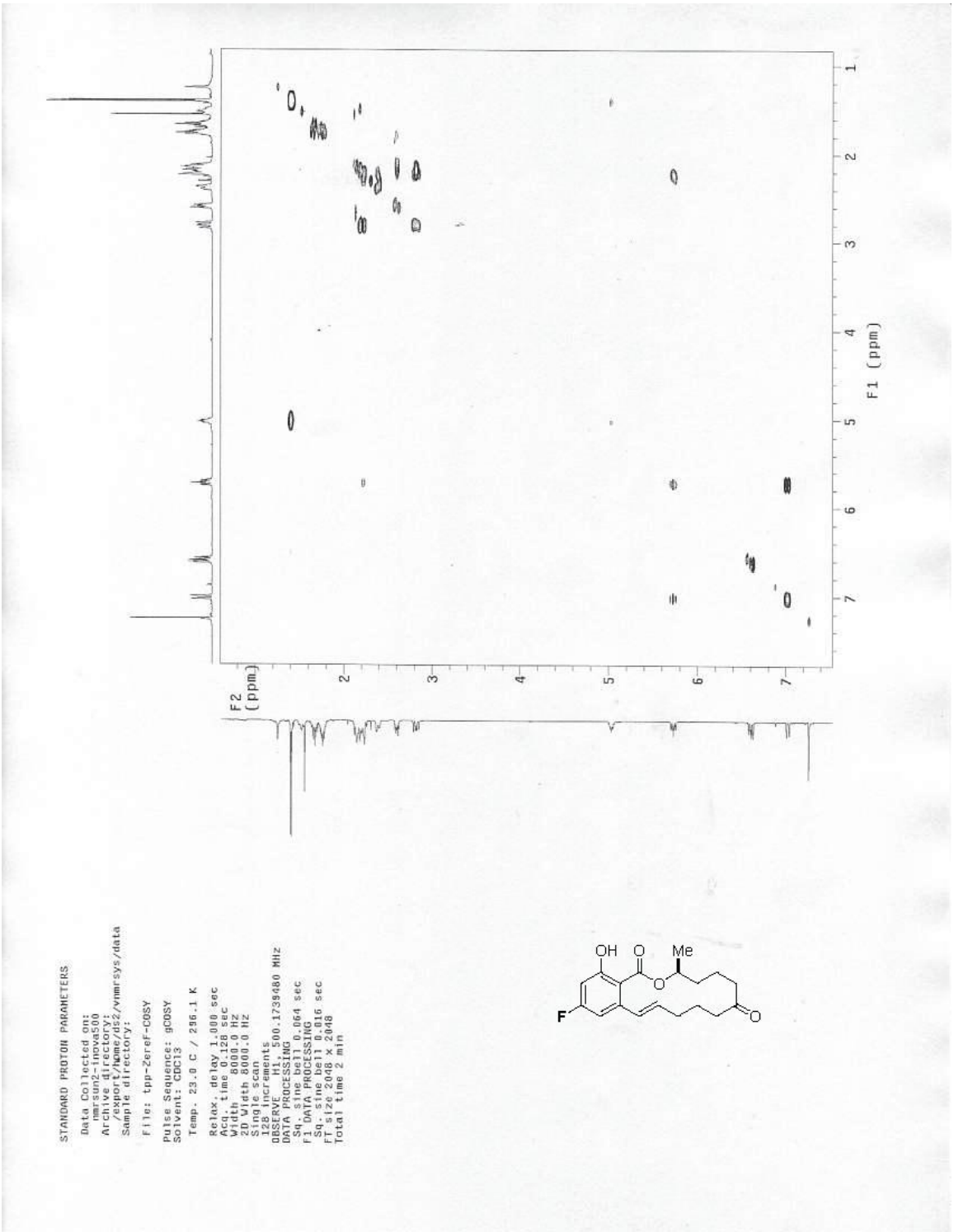
^{13}C NMR spectrum (125 MHz, $CDCl_3$, 23 ºC) of **28**



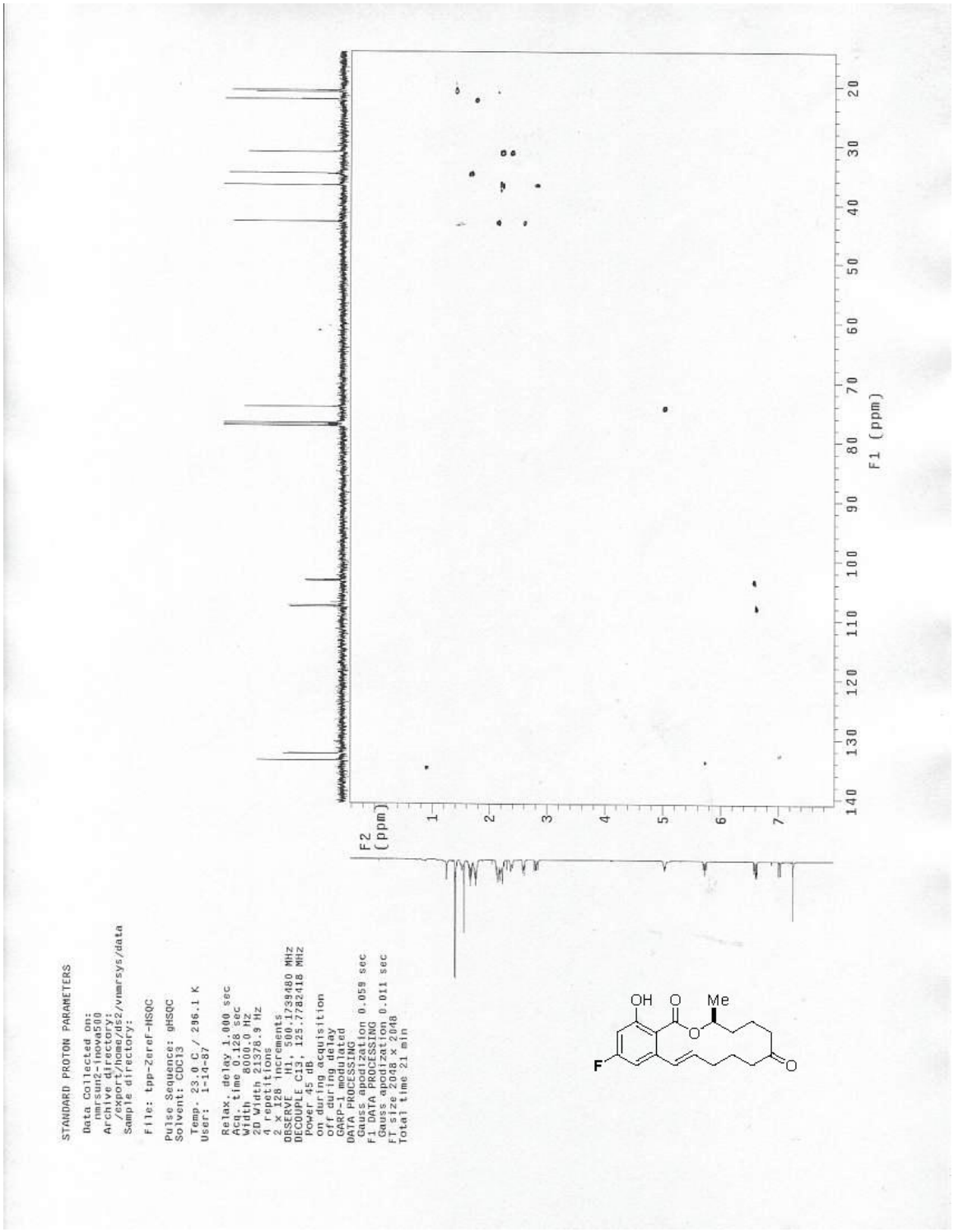
^{19}F NMR spectrum (375 MHz, $CDCl_3$, 23 ºC) of **28**



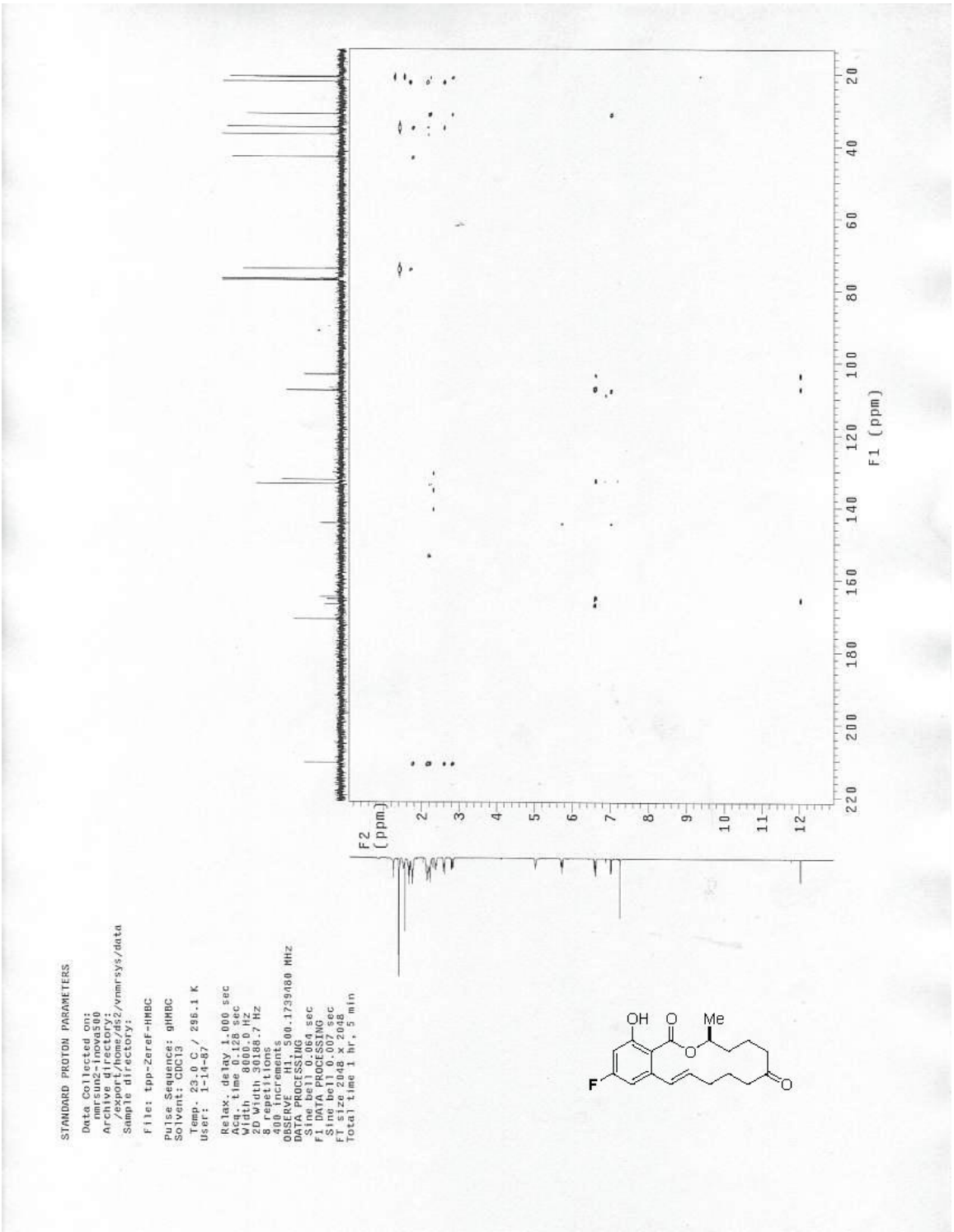
^{1}H-^{1}H COSY spectrum (500 MHz, $CDCl_3$, 23 ºC) of **28**



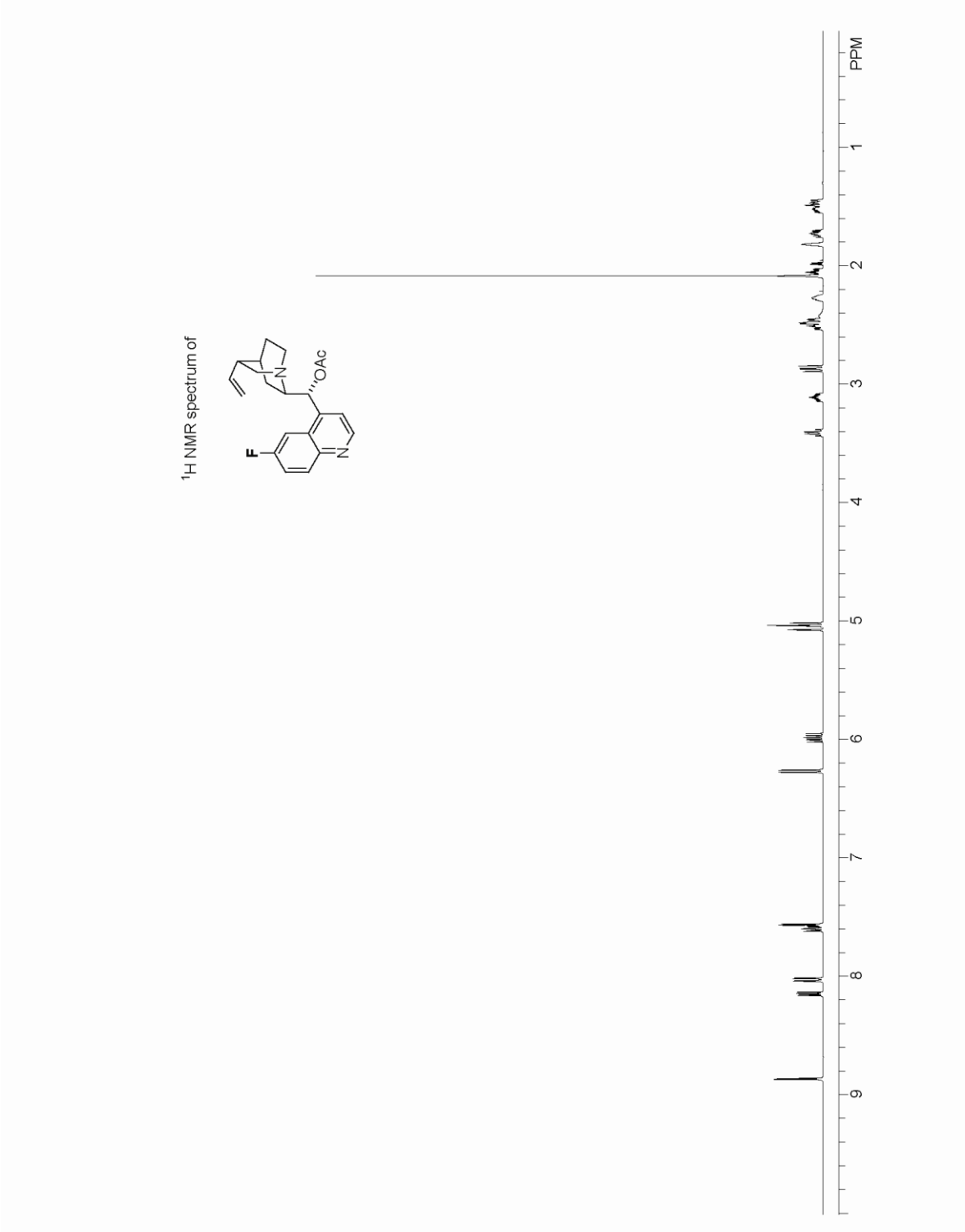
HSQC spectrum (500 MHz, $CDCl_3$, 23 ºC) of **28**



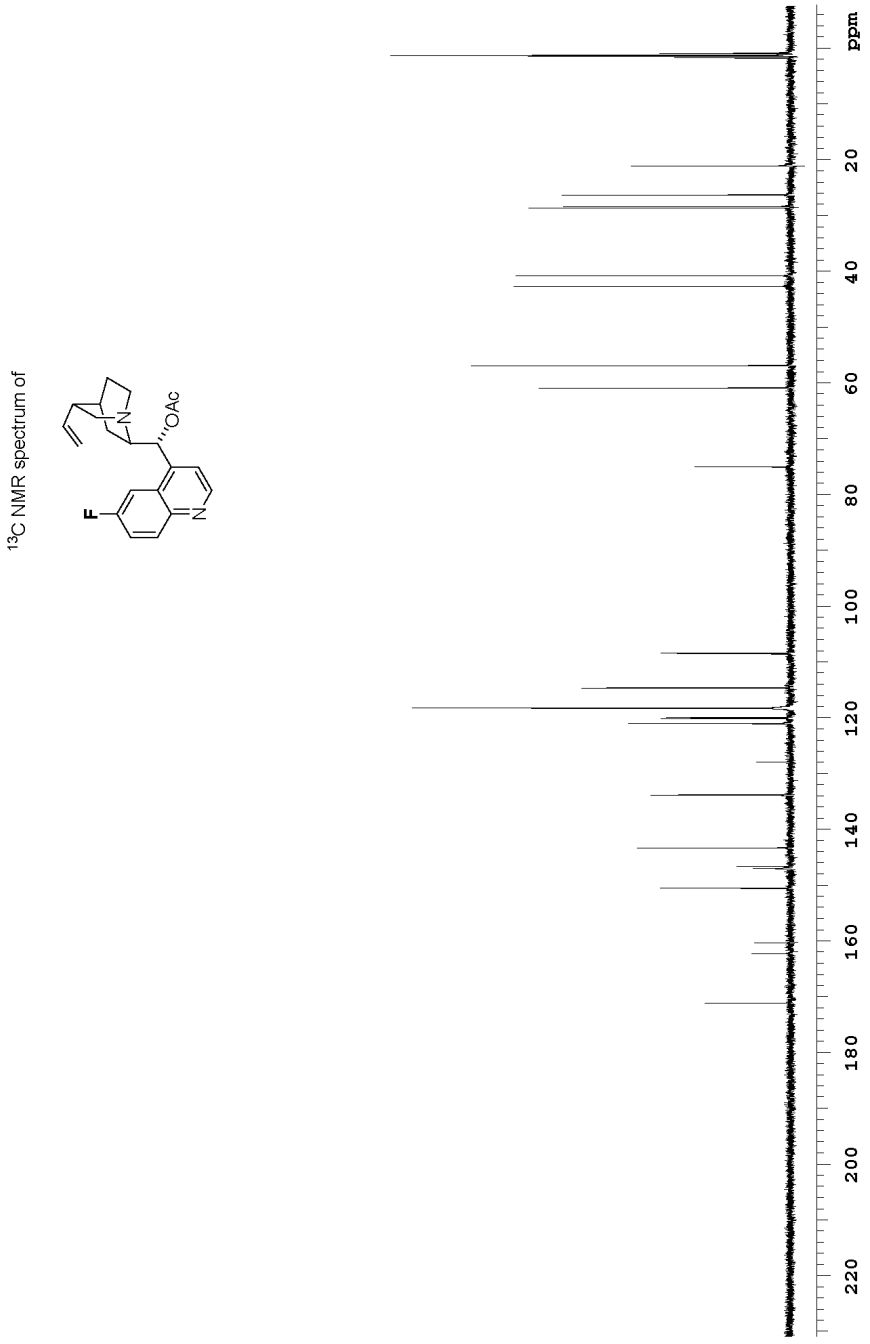
HMBC spectrum (500 MHz, $CDCl_3$, 23 ºC) of **28**



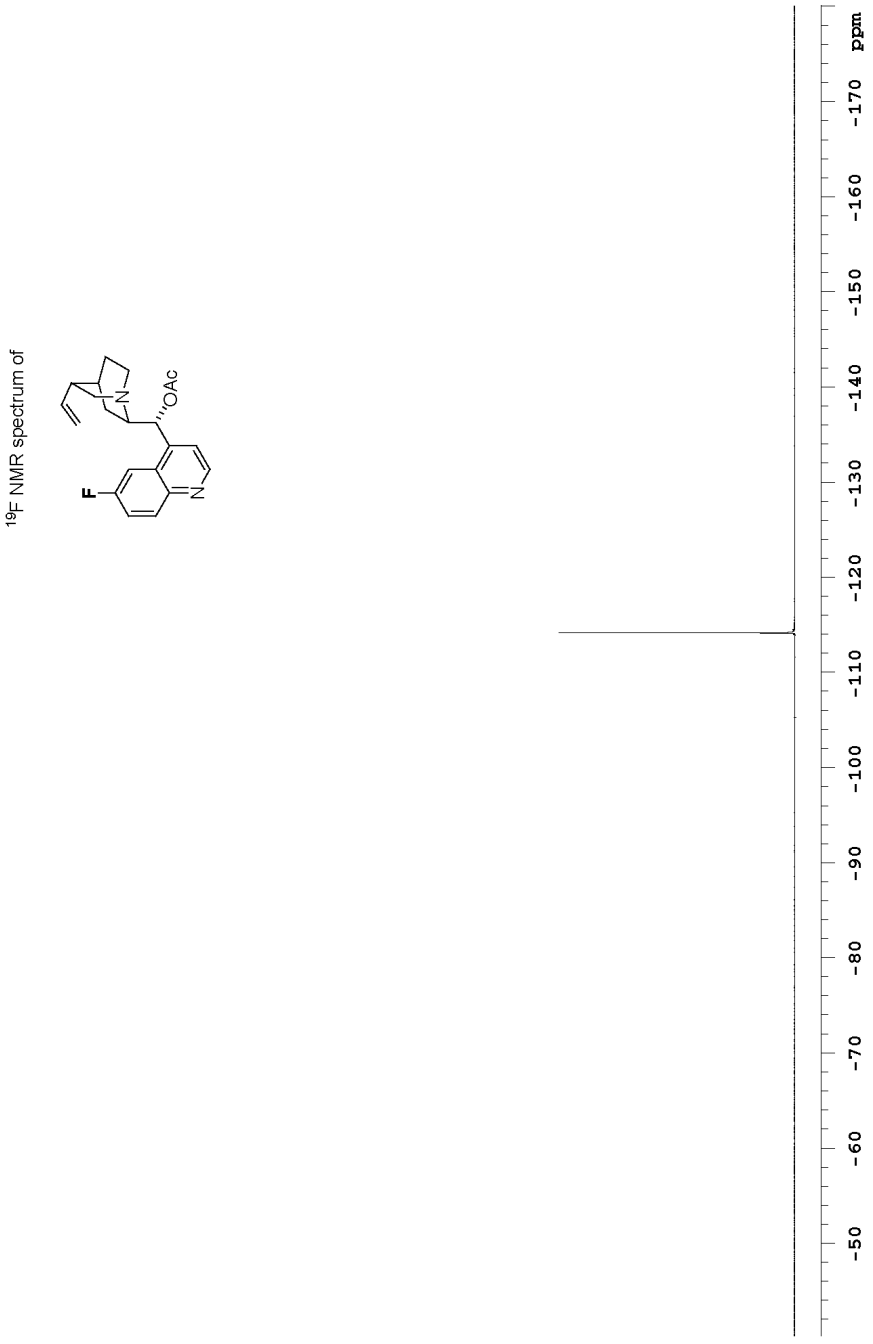
^{1}H NMR spectrum (500 MHz, CD_3CN, 23 ºC) of **29**



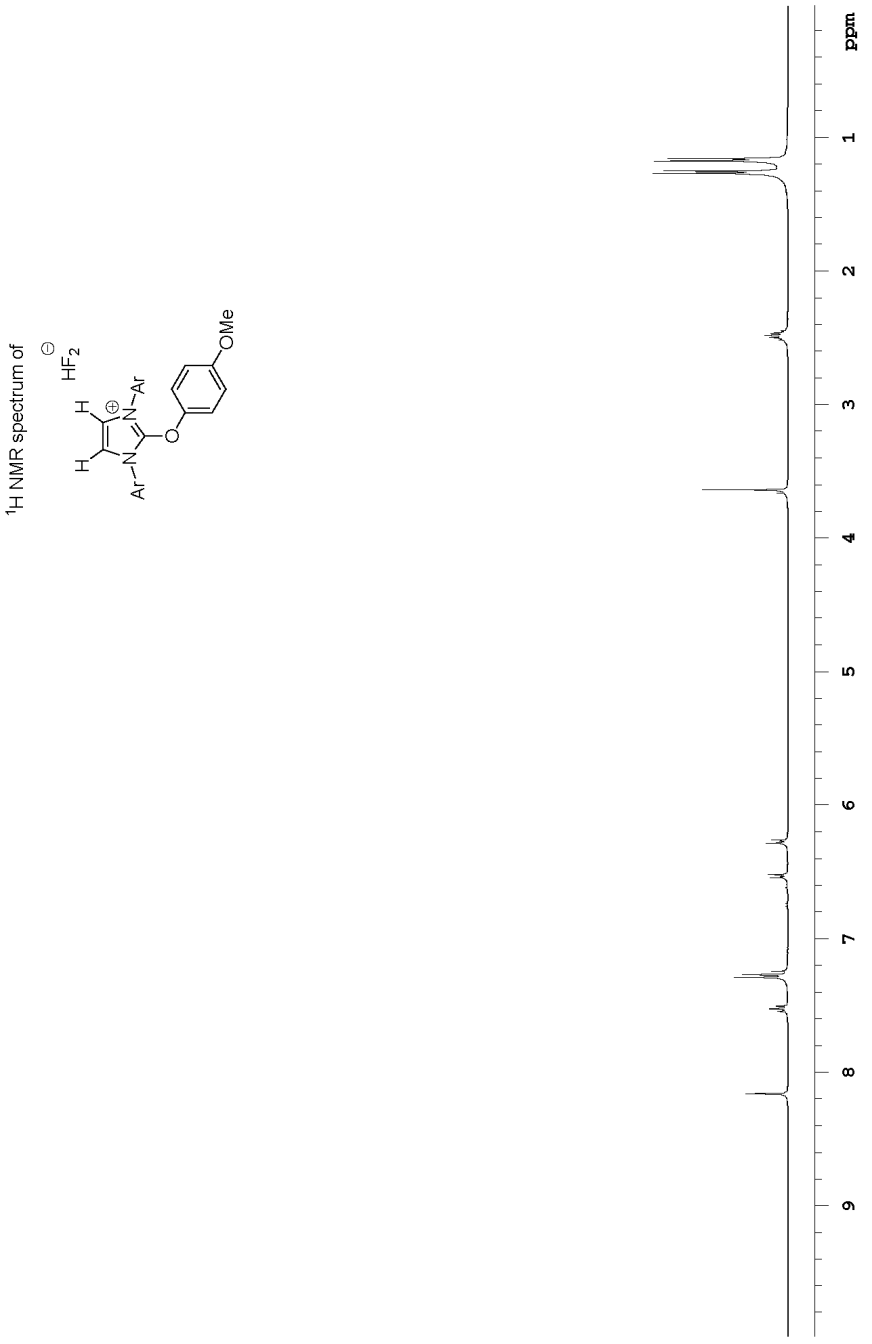
^{13}C NMR spectrum (125 MHz, CD_3CN, 23 ºC) of **29**



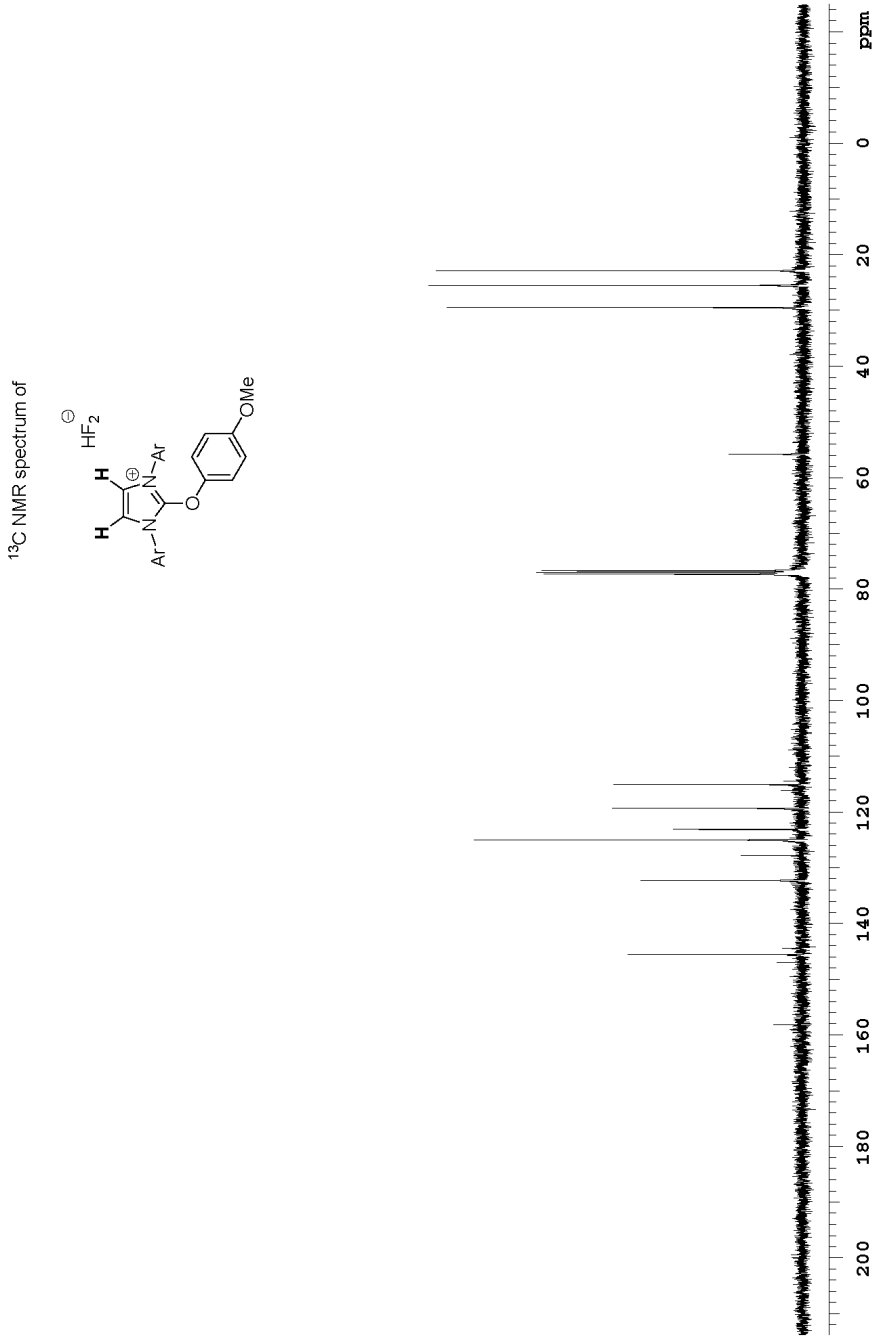
^{19}F NMR spectrum (375 MHz, $CDCl_3$, 23 ºC) of **29**



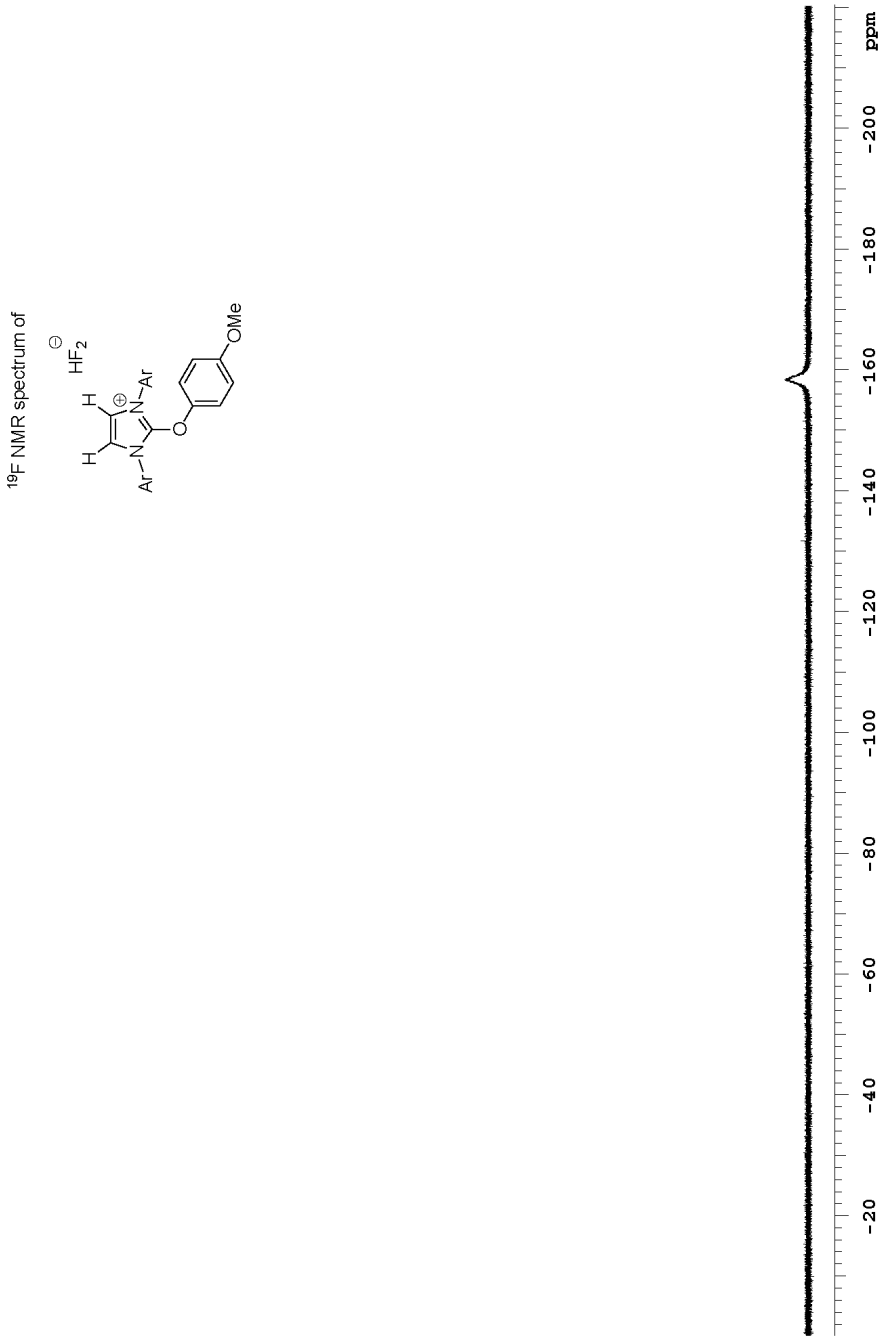
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of **30**



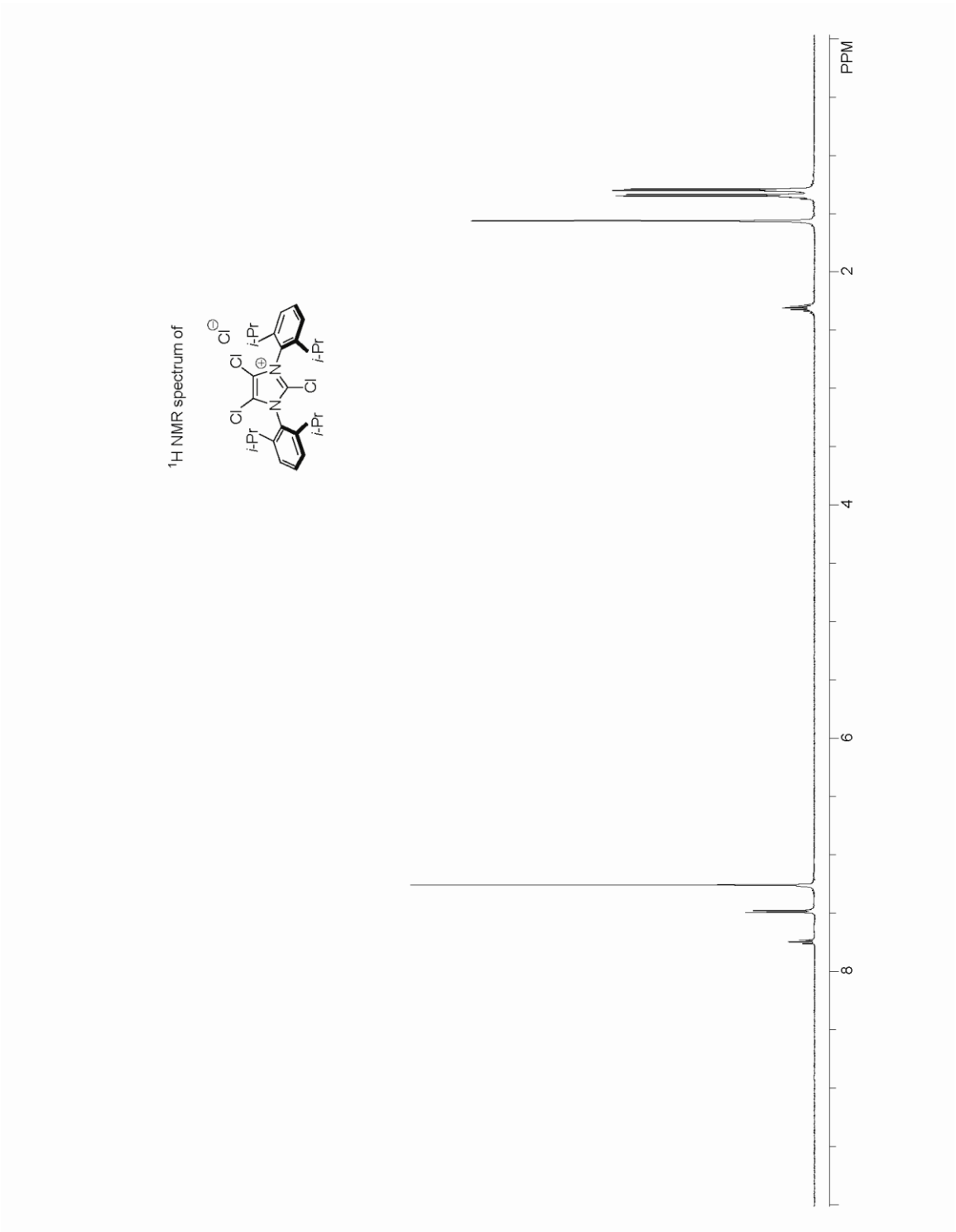
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ºC) of **30**



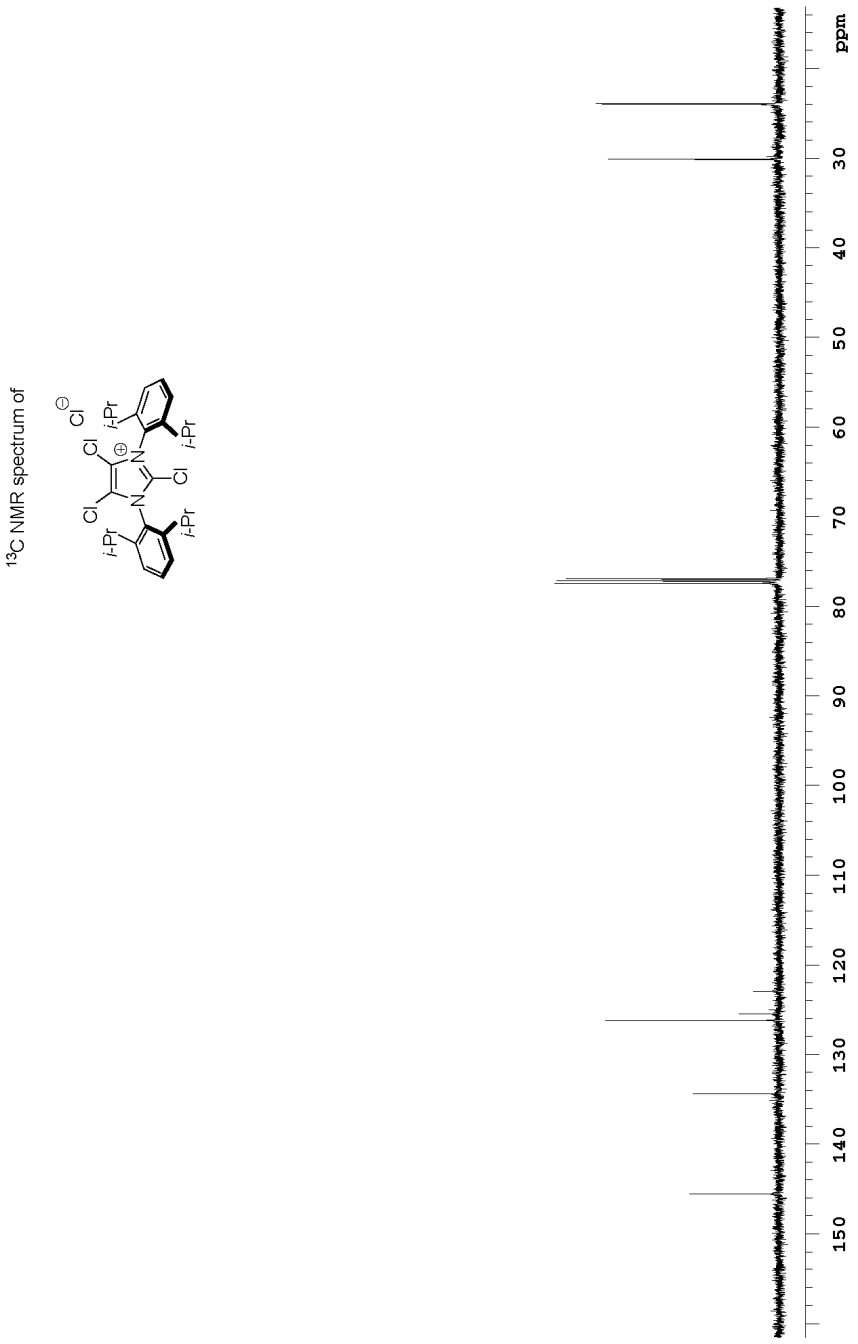
^{19}F NMR spectrum (375 MHz, $CDCl_3$, 23 ºC) of **30**



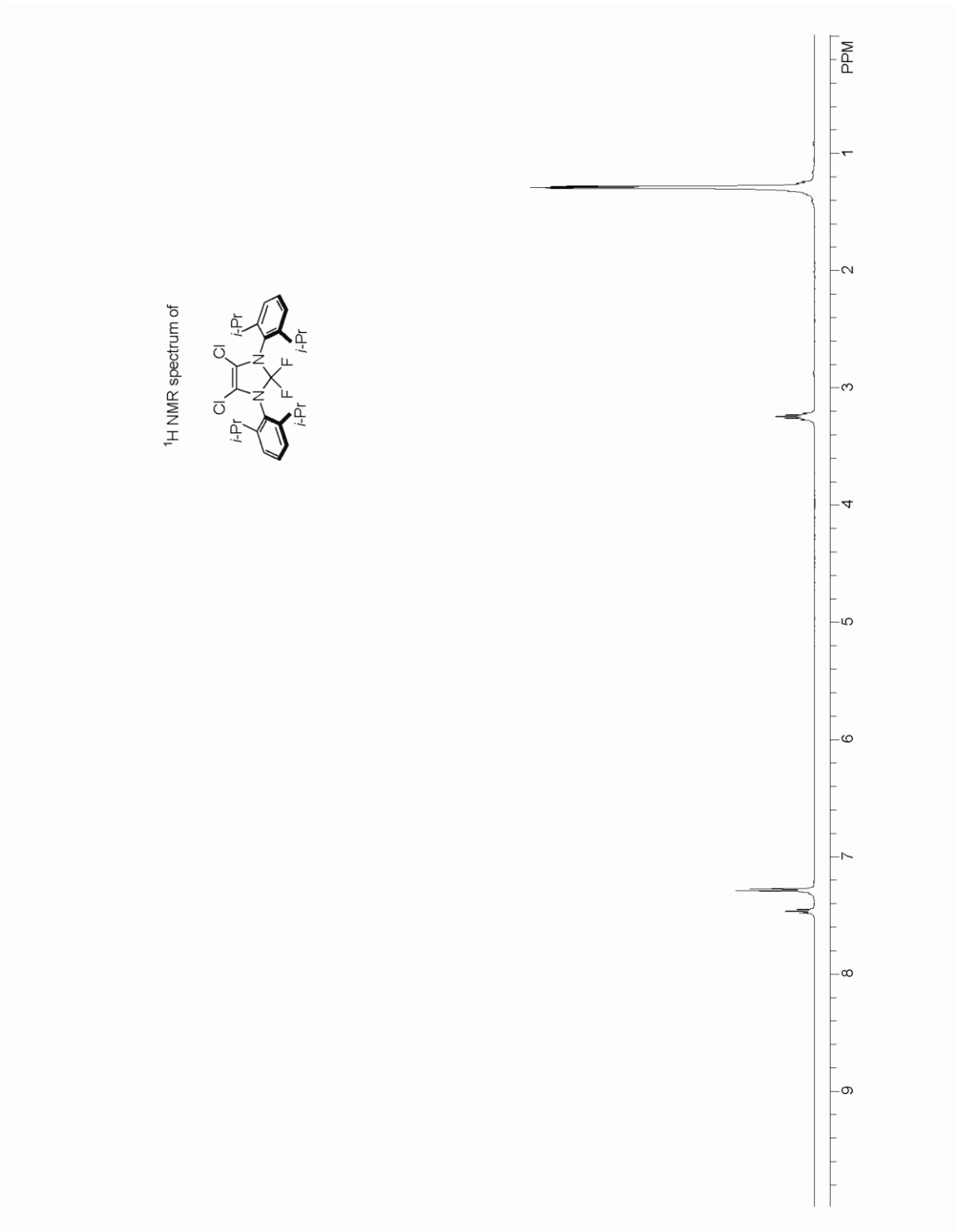
^{1}H NMR spectrum (500 MHz, $CDCl_3$, 23 ºC) of **S5**



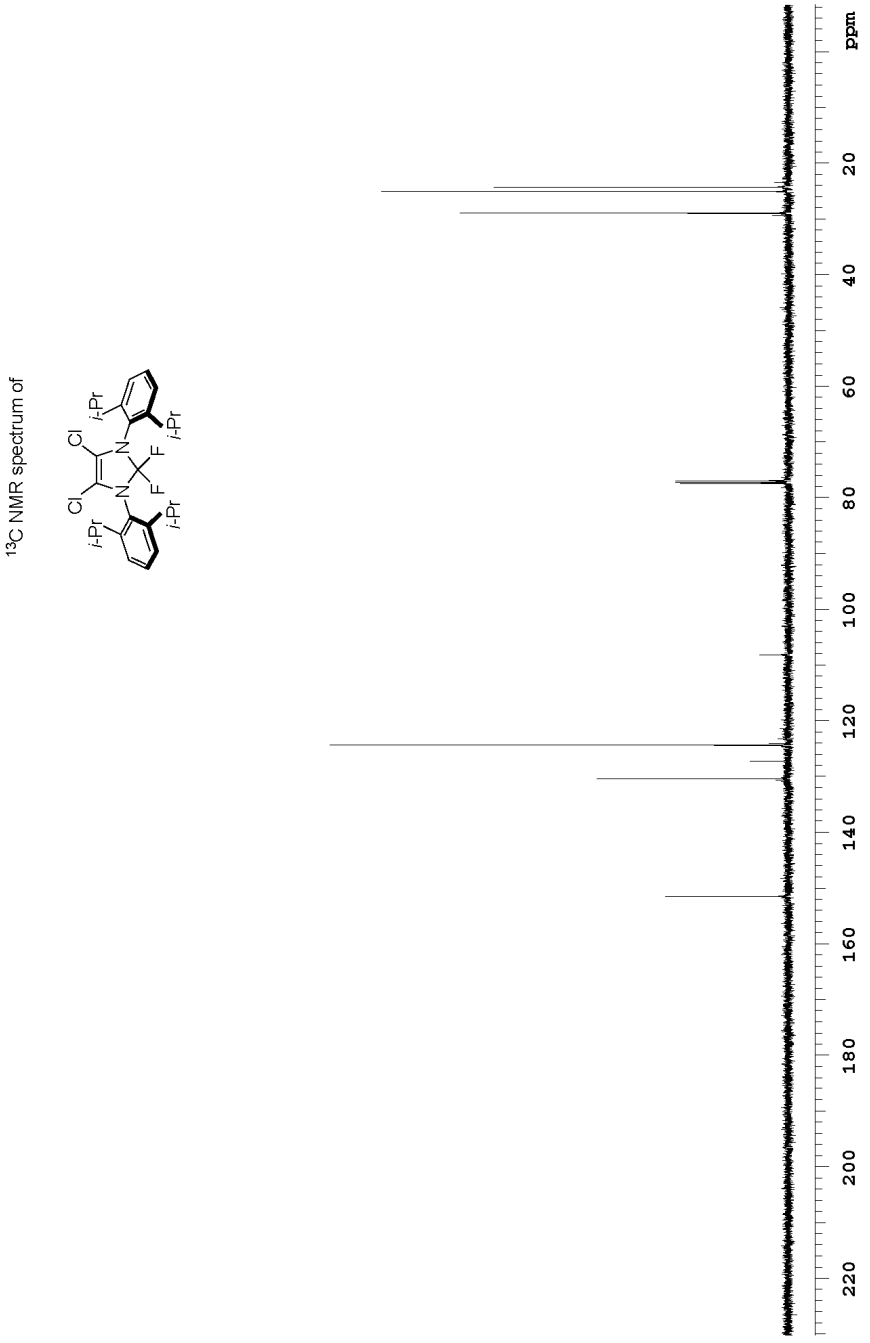
^{13}C NMR spectrum (125 MHz, $CDCl_3$, 23 ºC) of **S5**



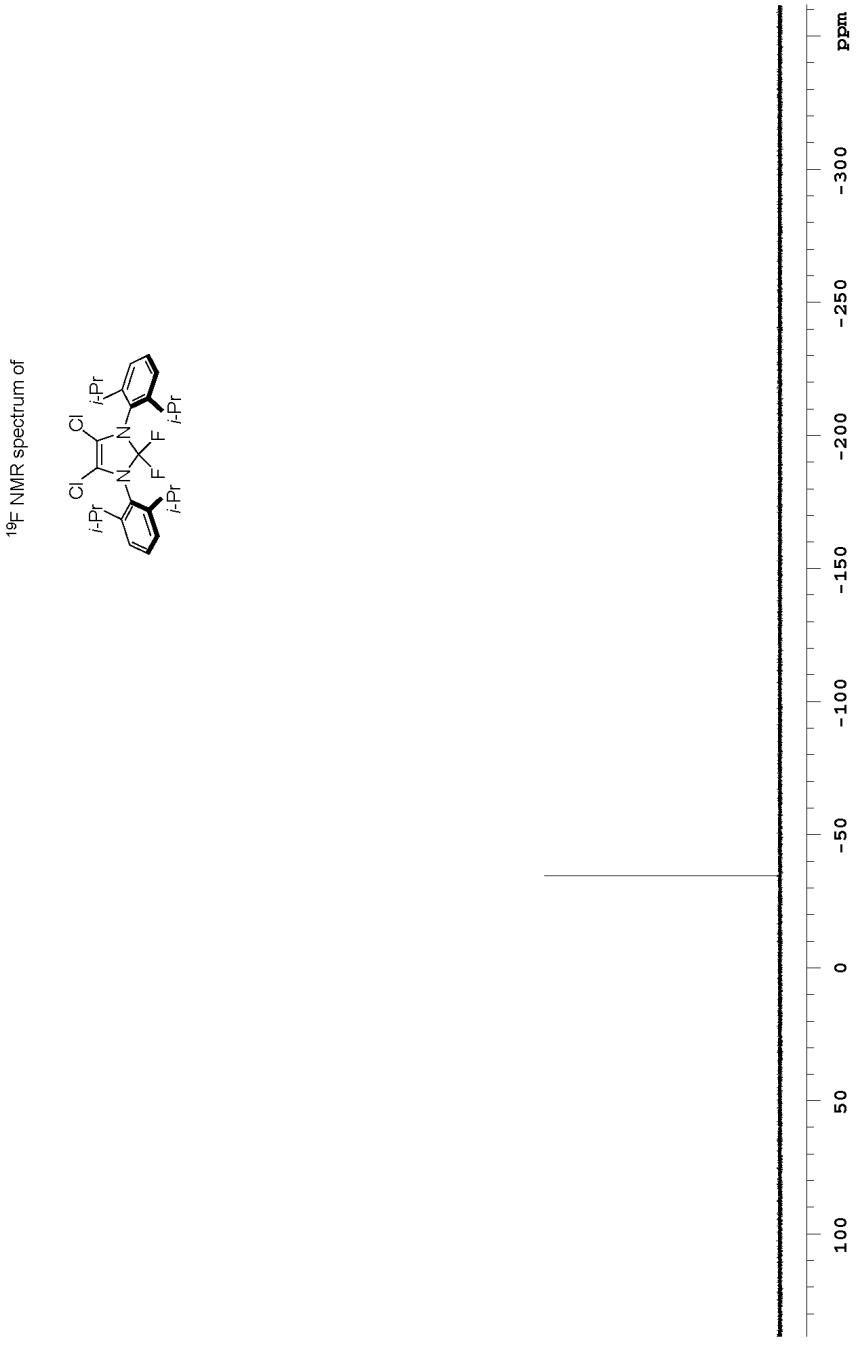
^{1}H NMR spectrum (500 MHz, $CDCl_3$, 23 ºC) of **S6**



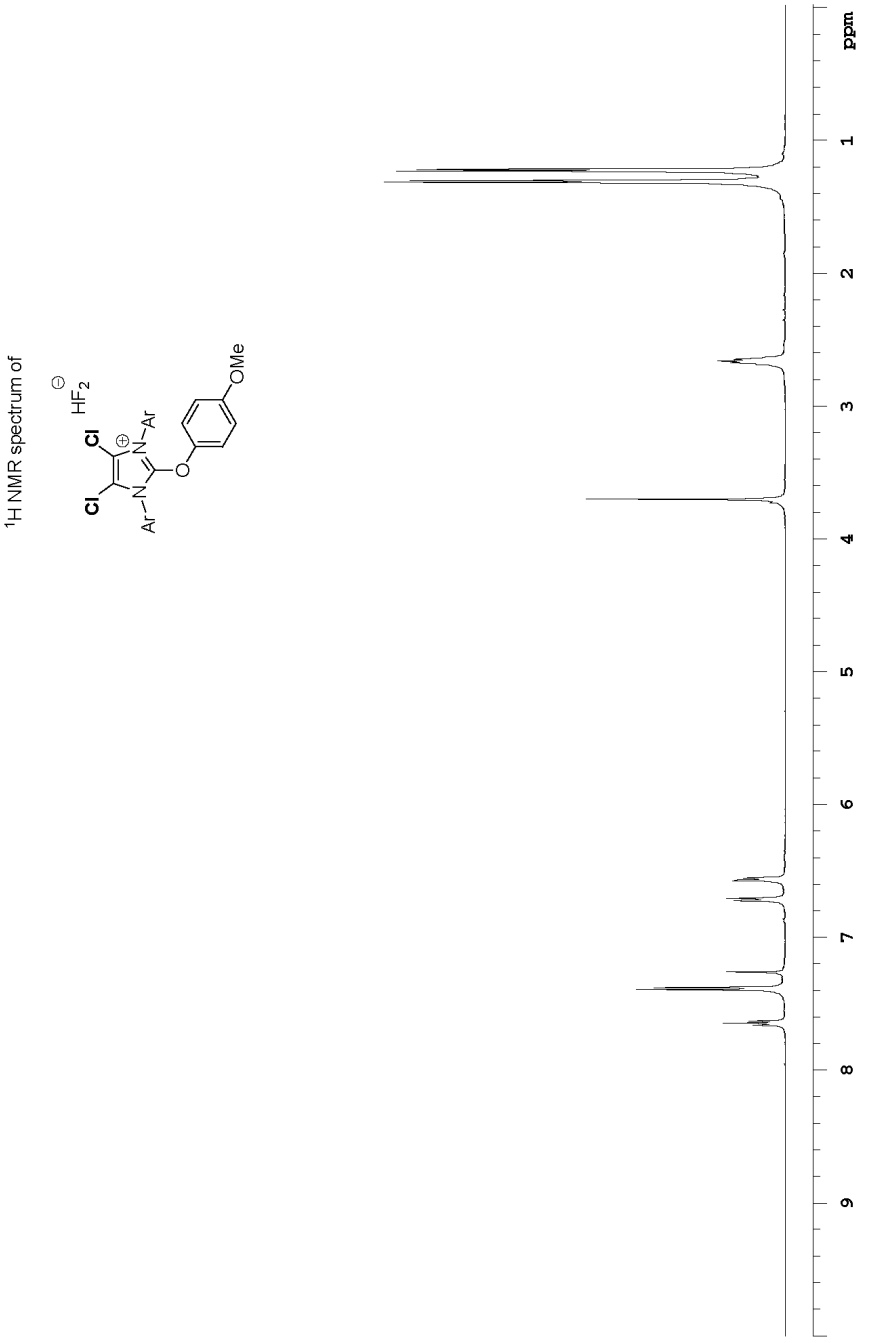
^{13}C NMR spectrum (125 MHz, $CDCl_3$, 23 ºC) of **S6**



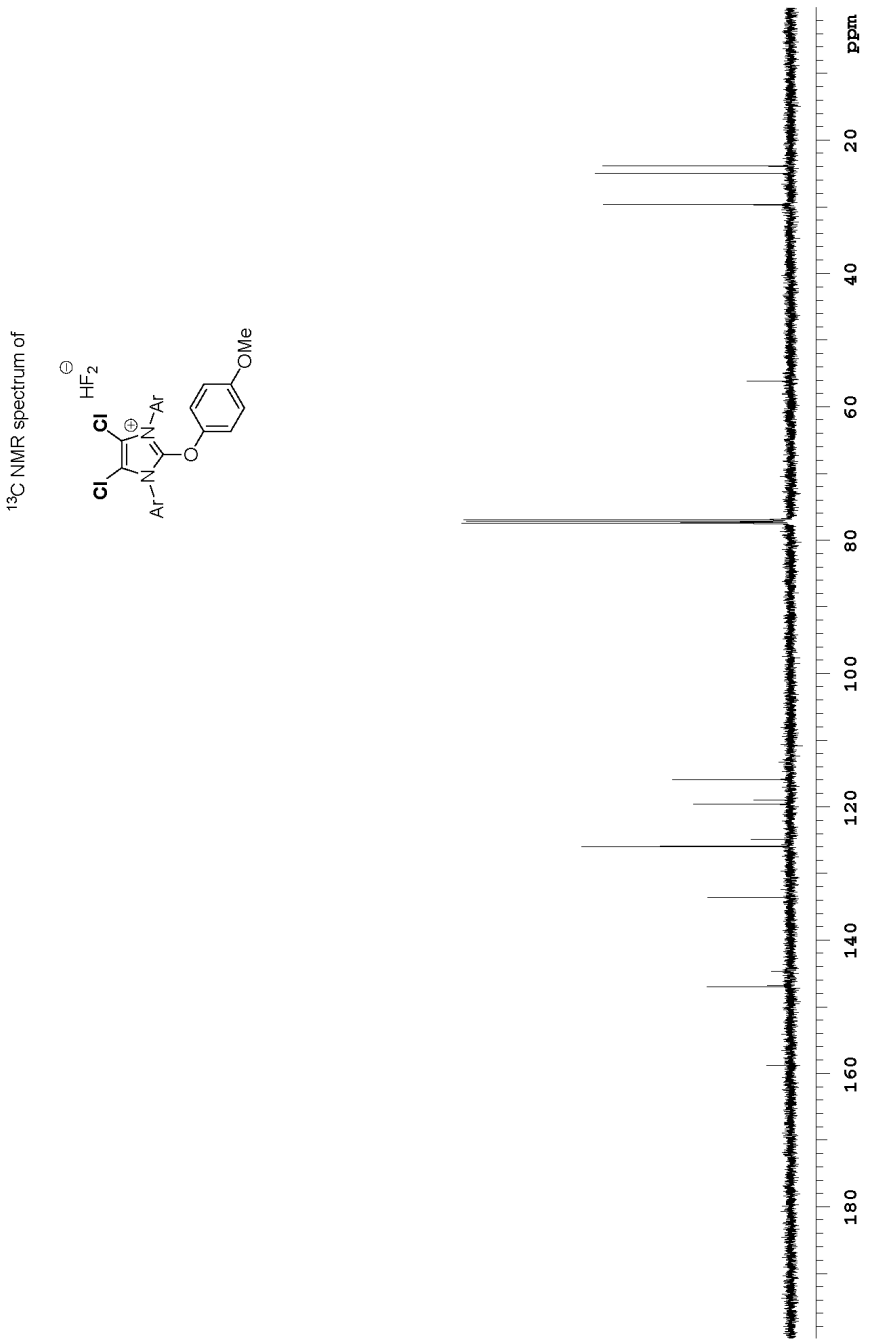
^{19}F NMR spectrum (375 MHz, $CDCl_3$, 23 ºC) of **S6**



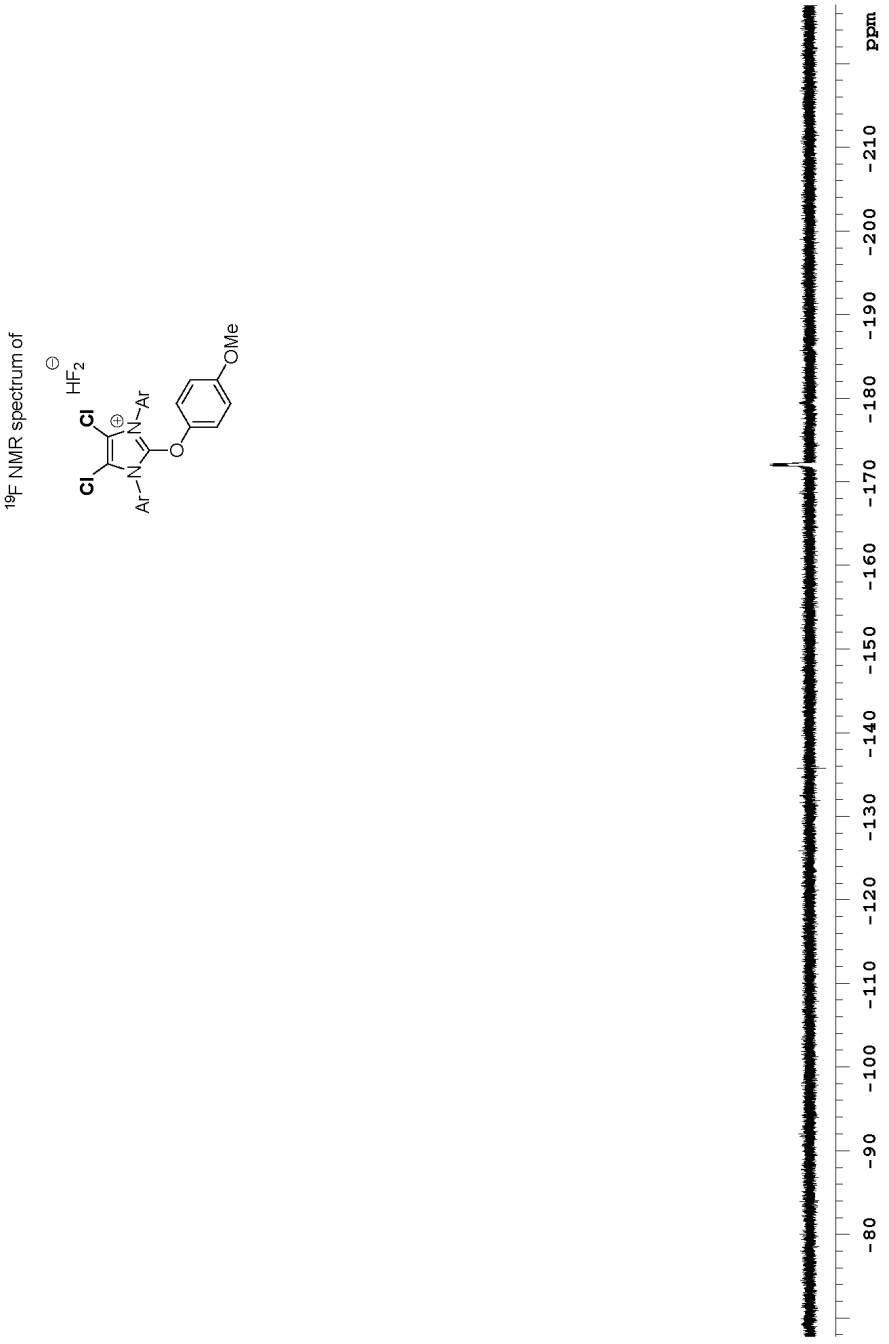
^{1}H NMR spectrum (500 MHz, $CDCl_3$, 23 ºC) of **31**



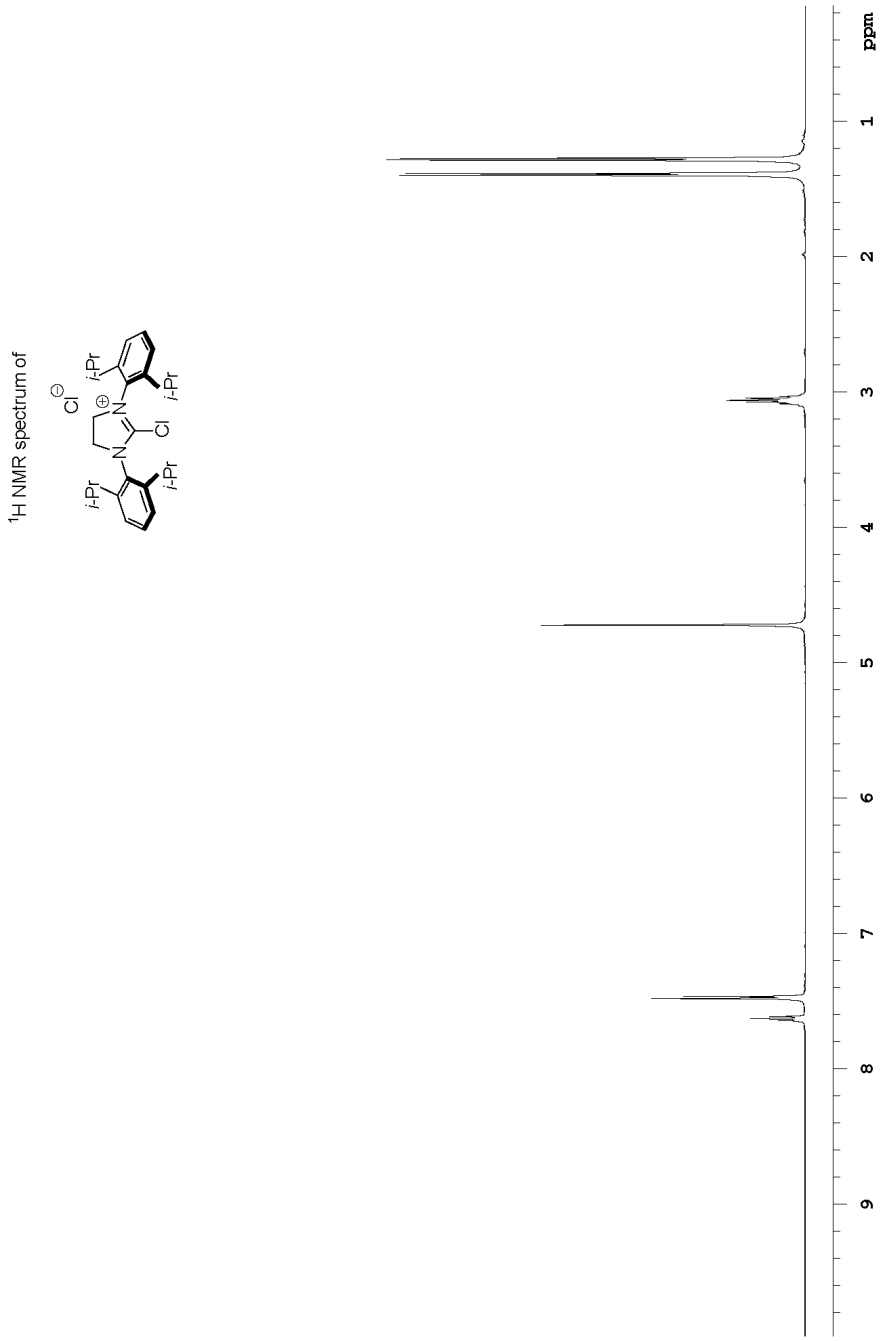
^{13}C NMR spectrum (125 MHz, $CDCl_3$, 23 ºC) of **31**



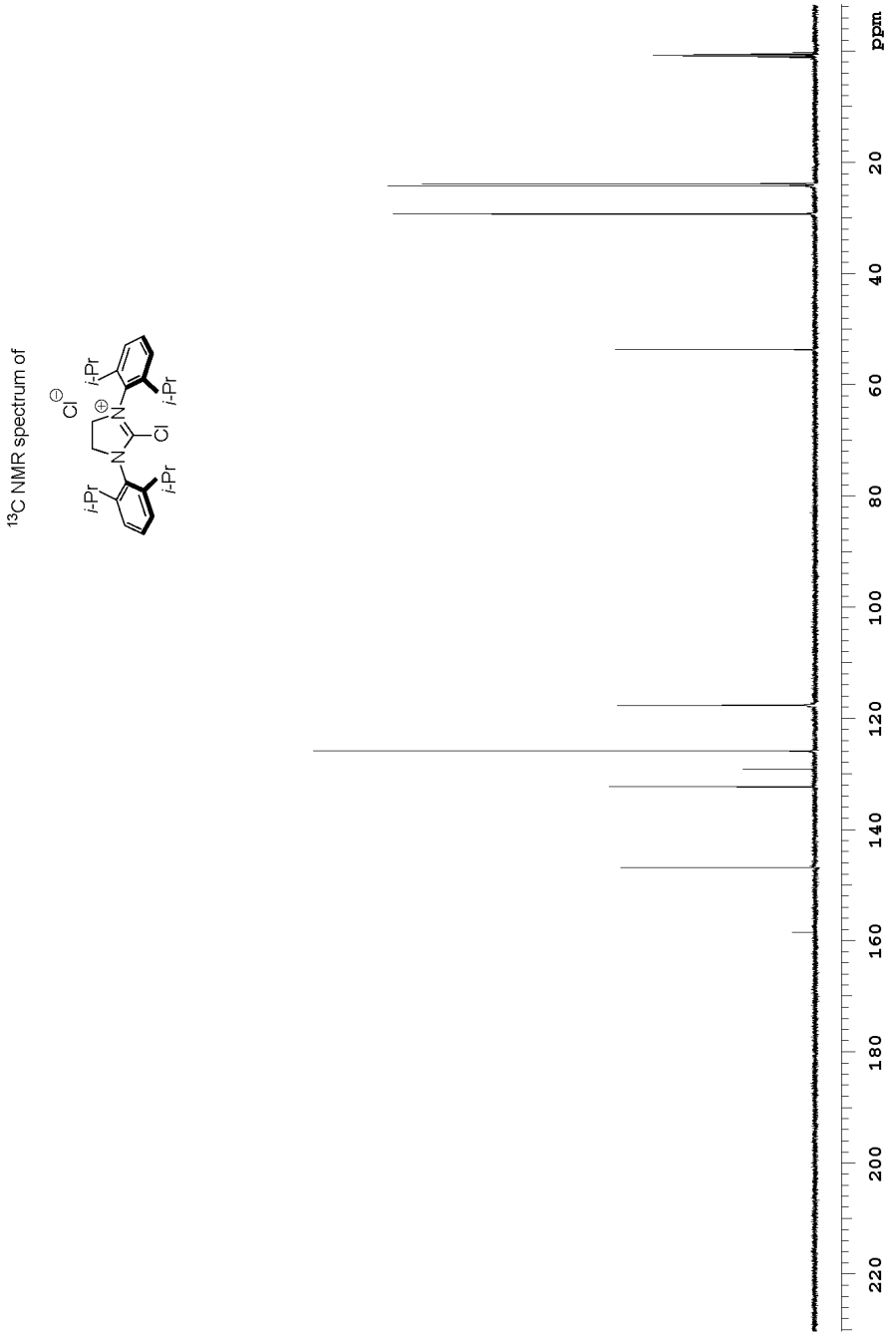
^{19}F NMR spectrum (375 MHz, $CDCl_3$, 23 ºC) of **31**



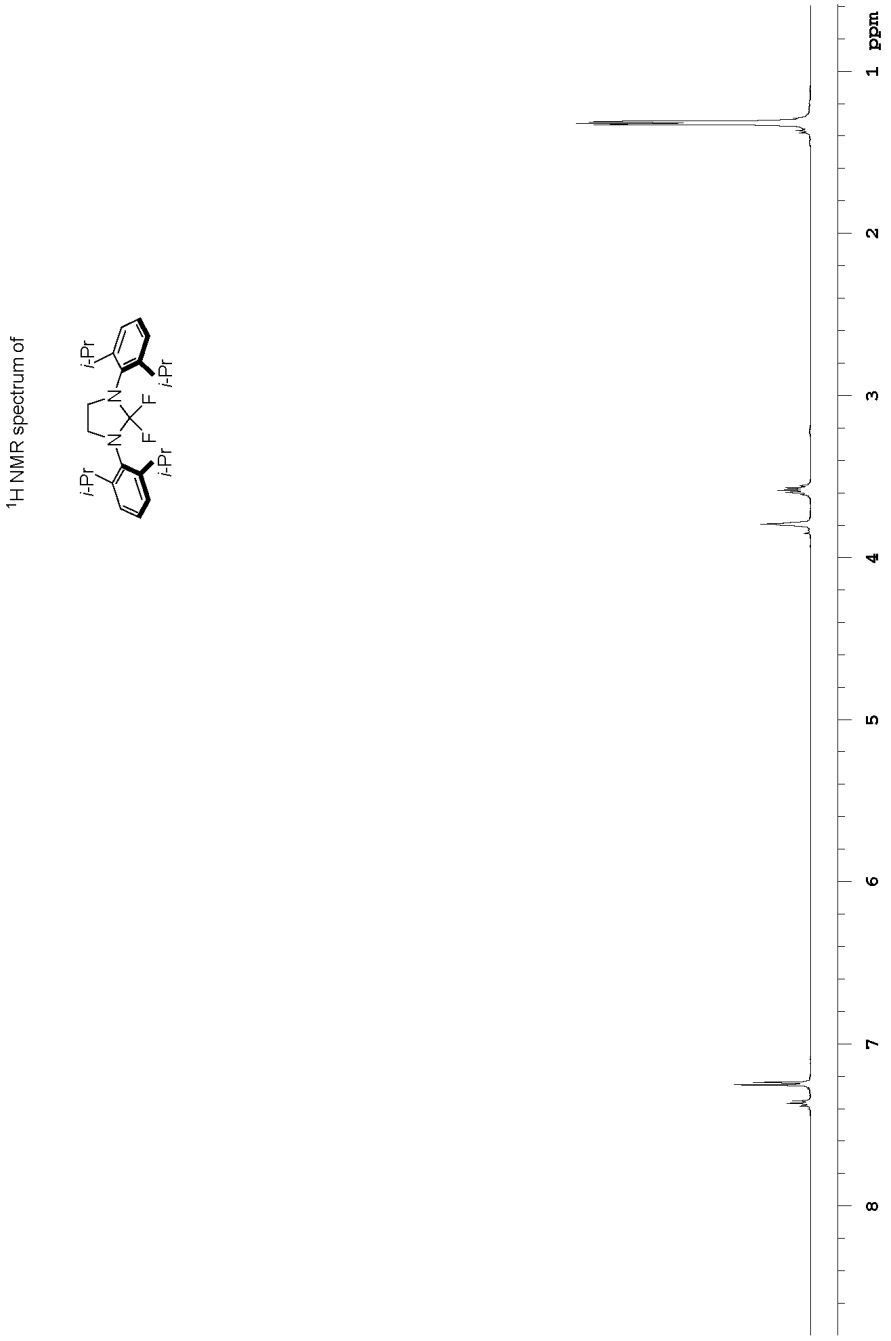
^{1}H NMR spectrum (500 MHz, CD_3CN, 23 ºC) of **S8**



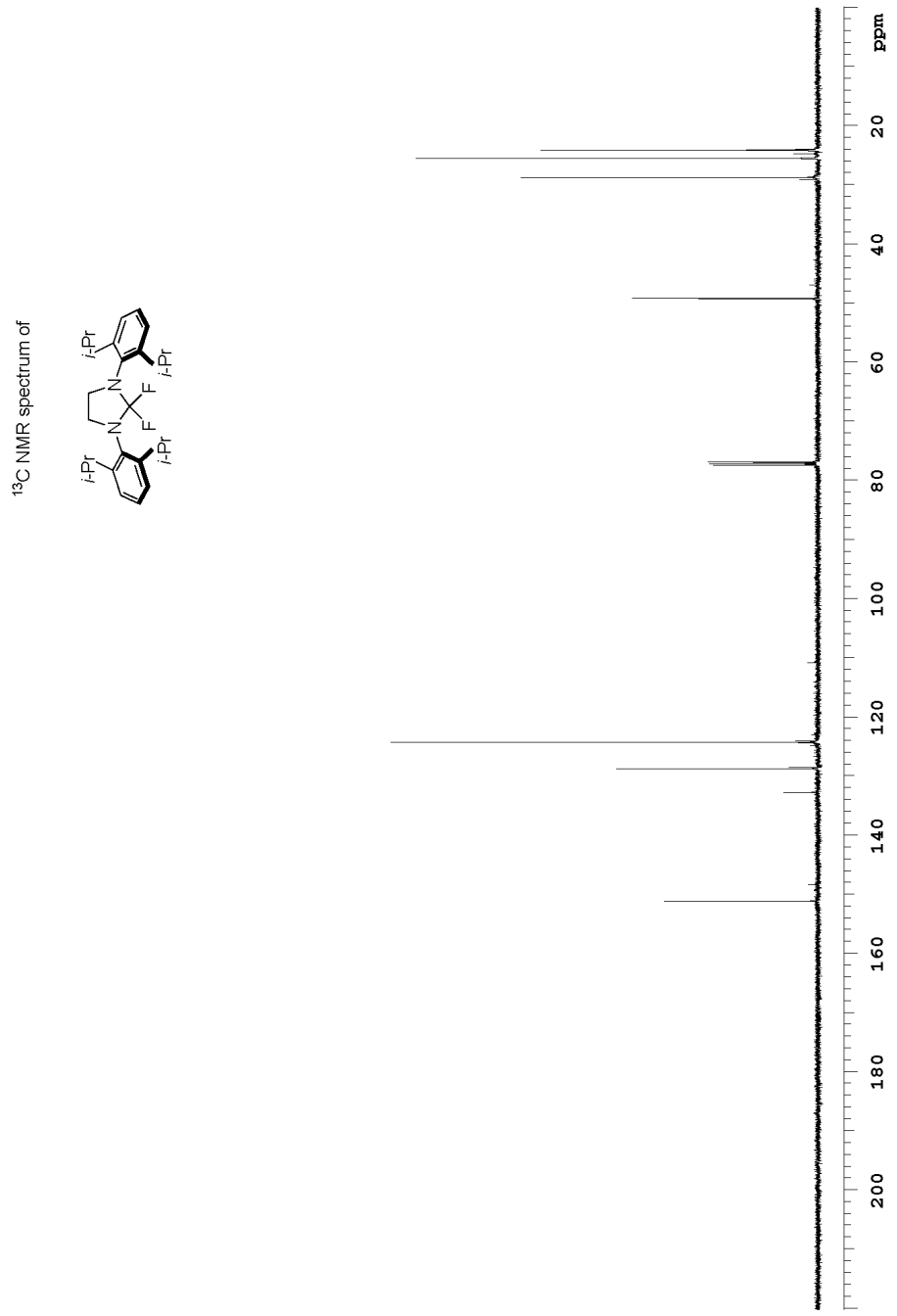
^{13}C NMR spectrum (125 MHz, CD_3CN, 23 ºC) of **S8**



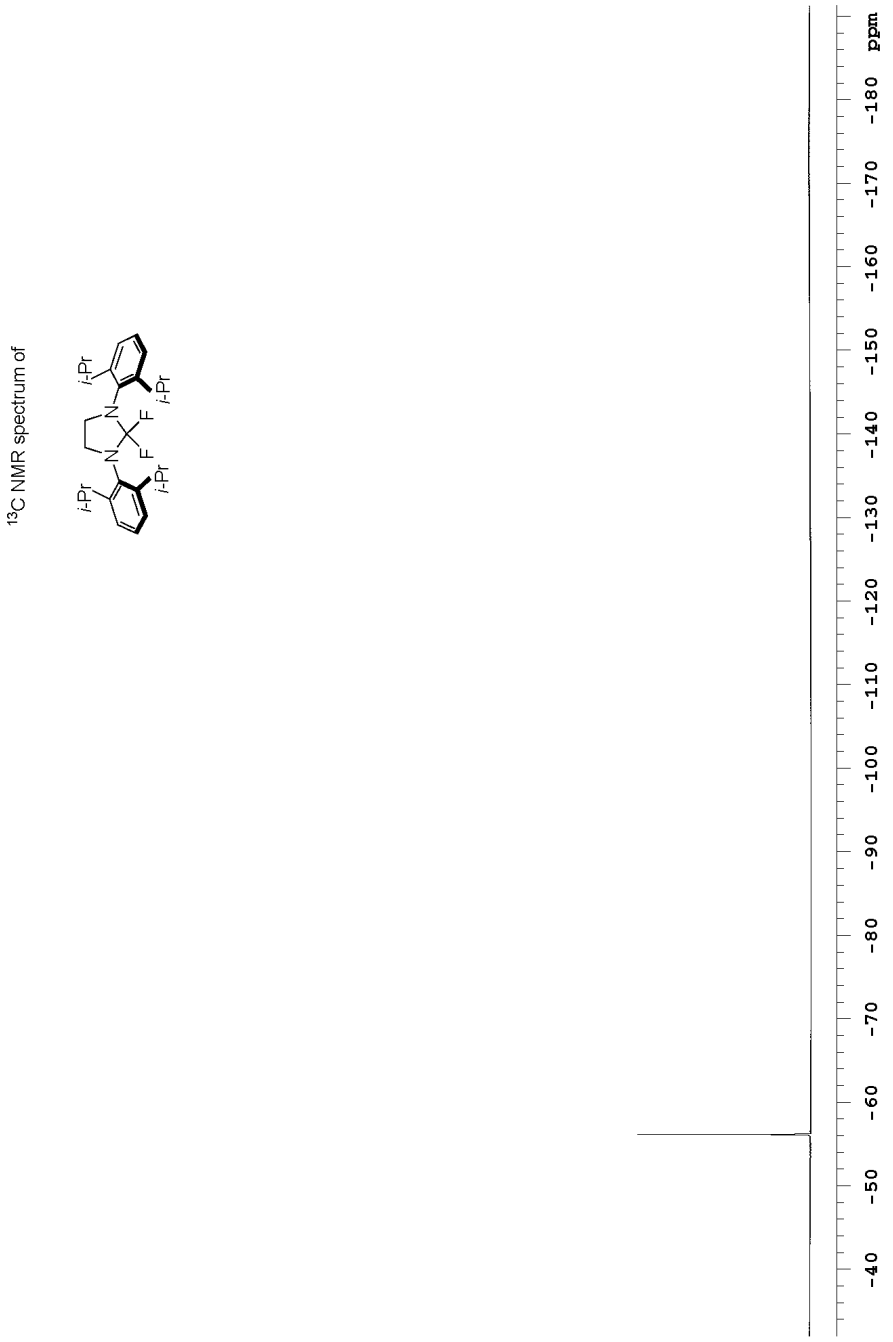
^{1}H NMR spectrum (500 MHz, $CDCl_3$, 23 °C) of **S9**



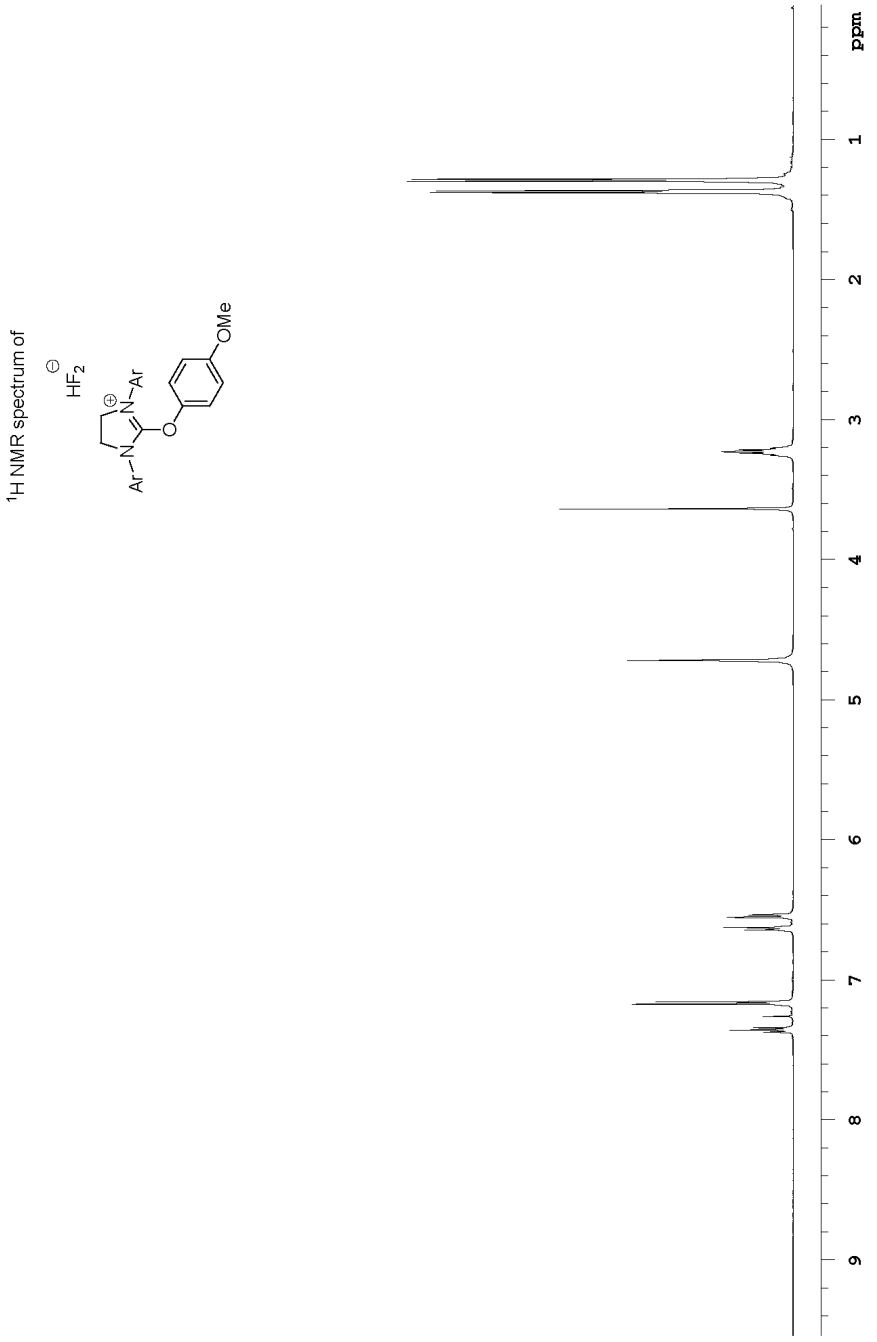
^{13}C NMR spectrum (125 MHz, $CDCl_3$, 23 ºC) of **S9**



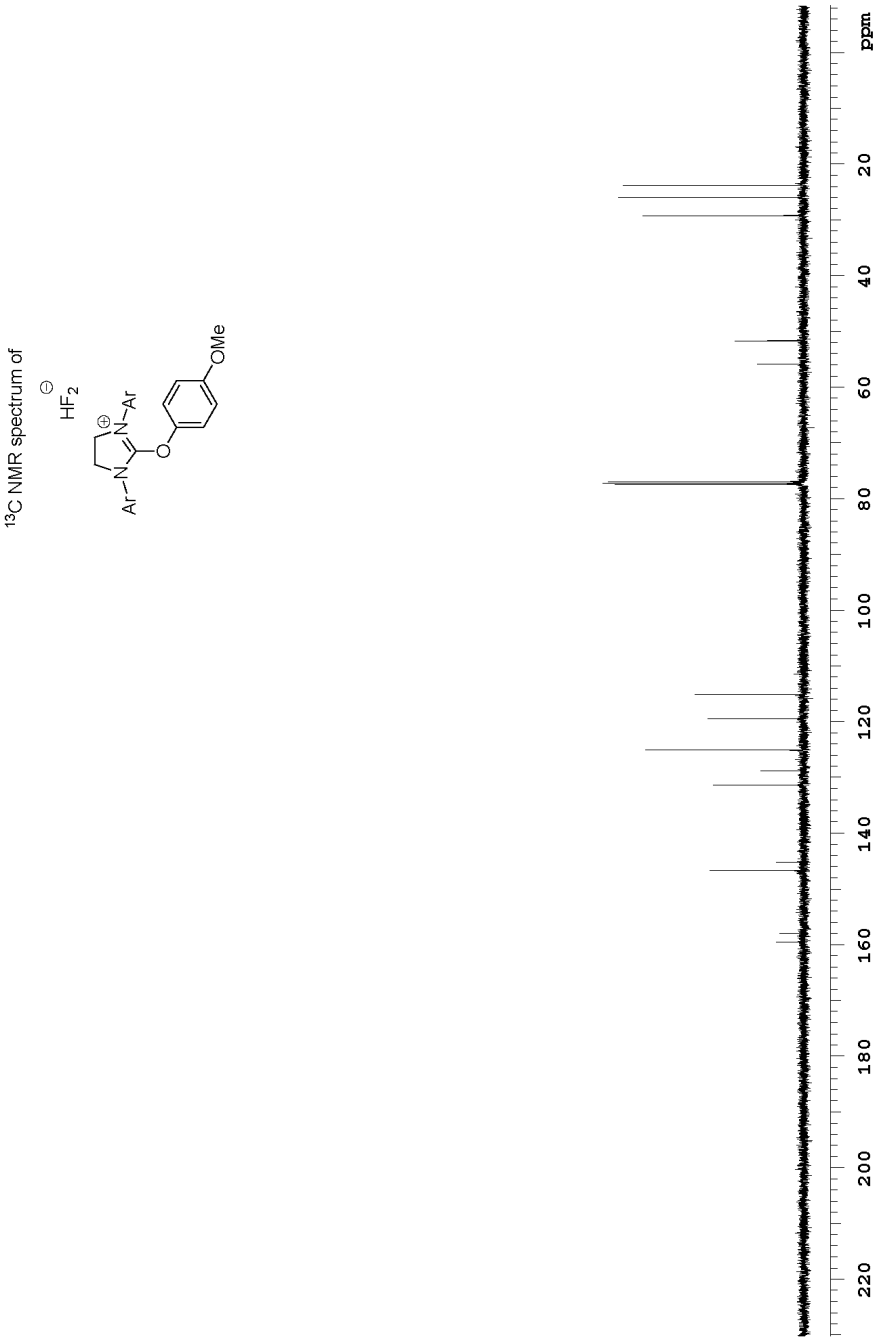
^{19}F NMR spectrum (375 MHz, $CDCl_3$, 23 ºC) of **S9**



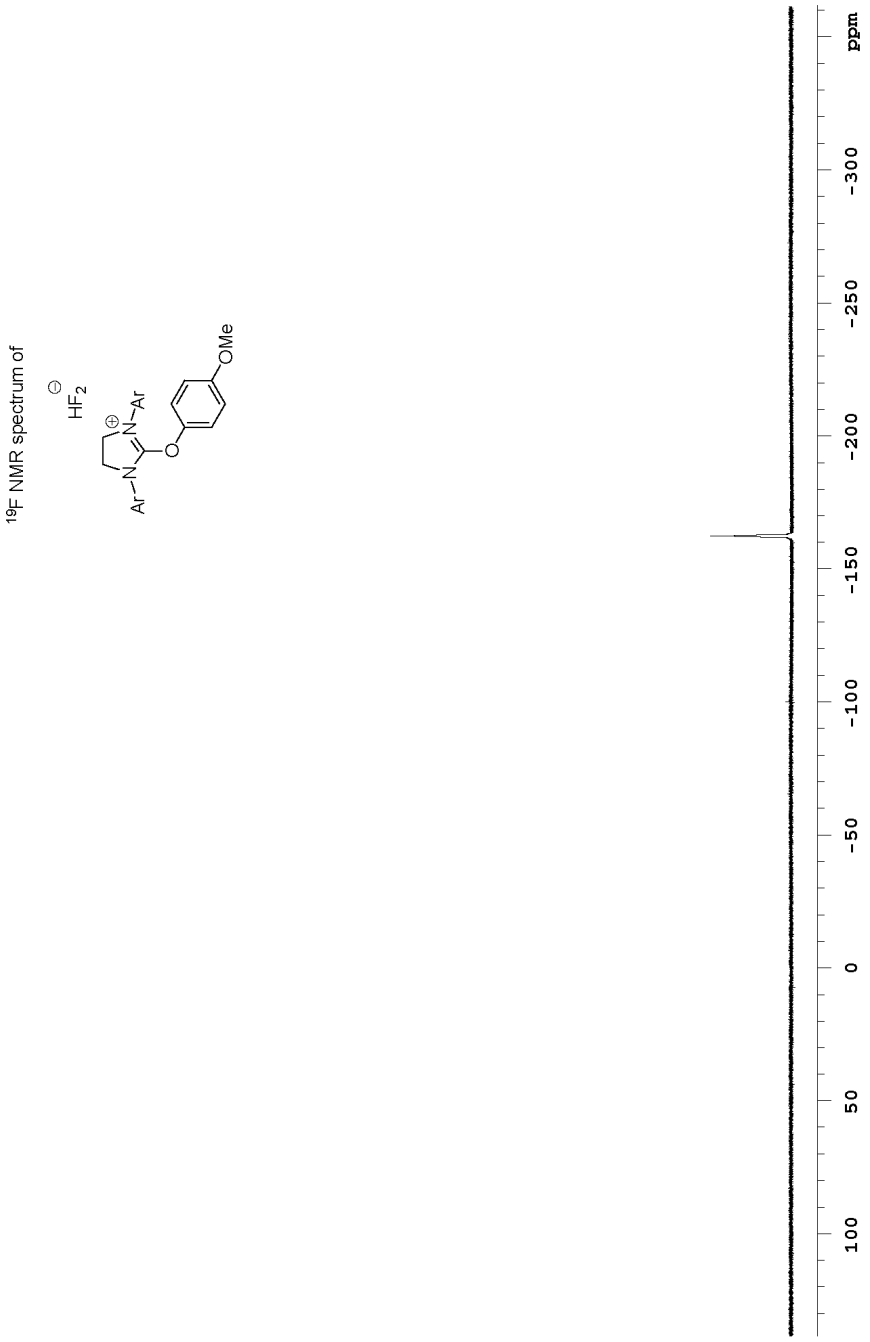
^{1}H NMR spectrum (500 MHz, $CDCl_3$, 23 ºC) of **32**



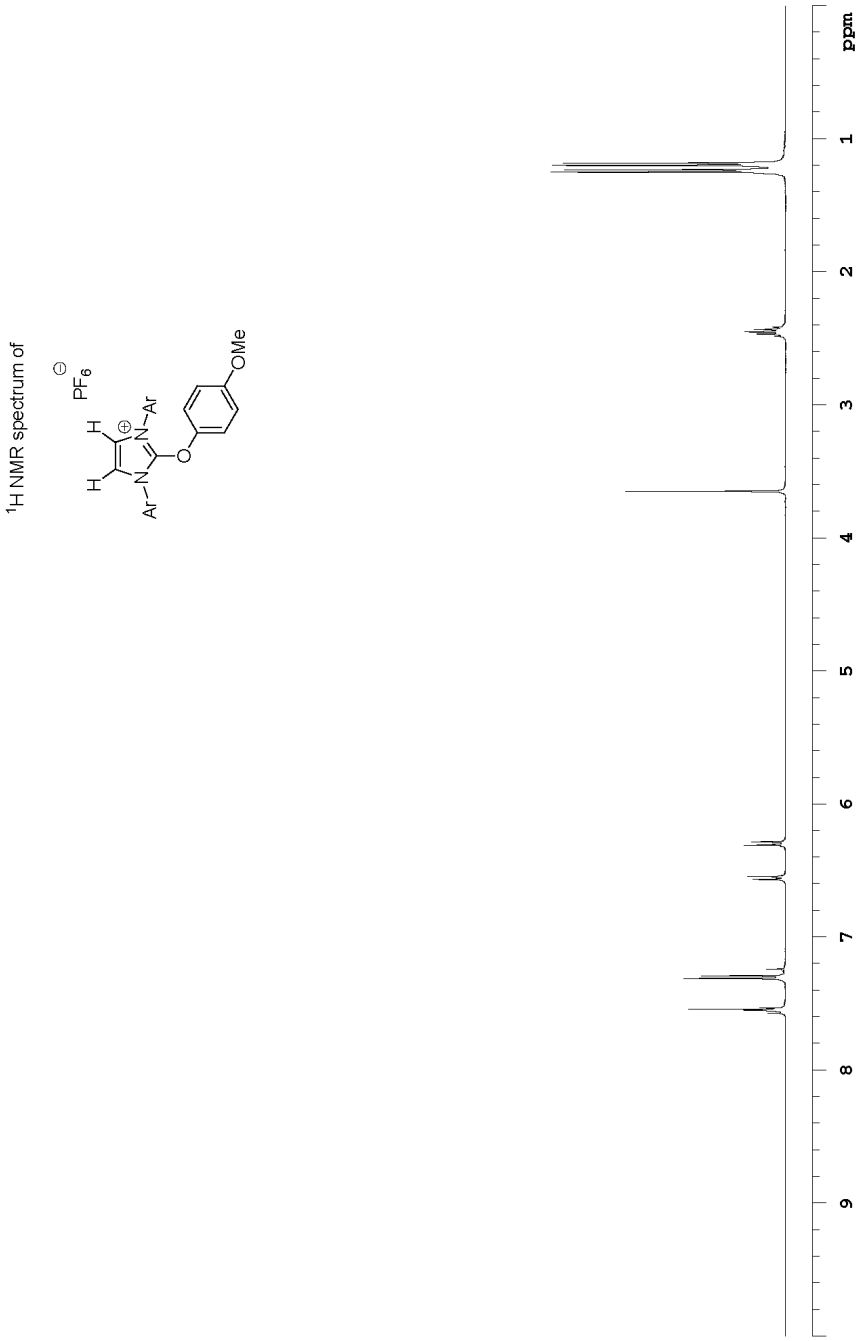
^{13}C NMR spectrum (125 MHz, $CDCl_3$, 23 ºC) of **32**



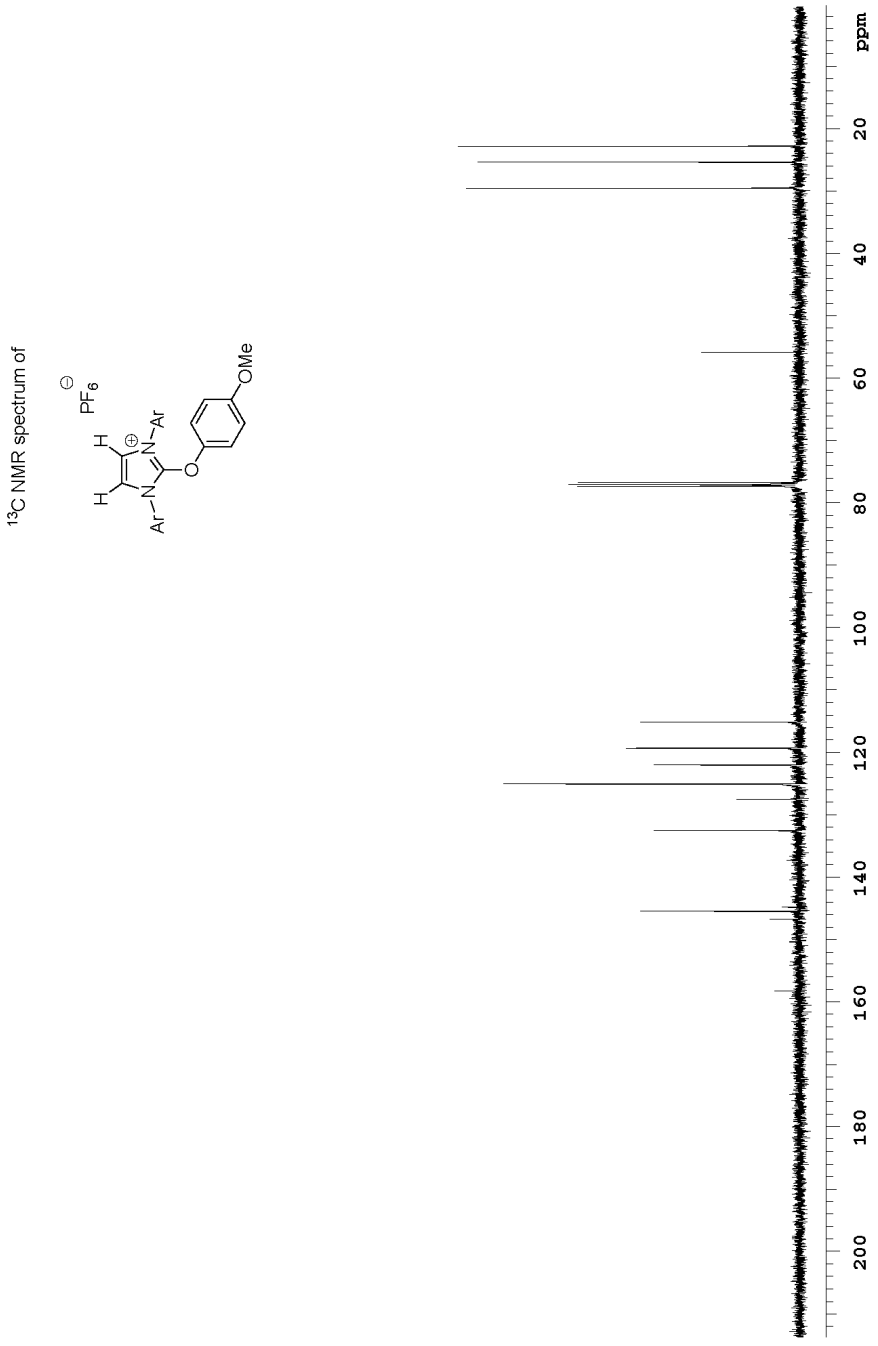
^{19}F NMR spectrum (375 MHz, $CDCl_3$, 23 ºC) of **32**



^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of **33**



^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ºC) of **33**



^{19}F NMR spectrum (375 MHz, $CDCl_3$, 23 ºC) of **33**