

Supporting Information

**PhenoFluorMix: Practical Chemoselective Deoxyfluorination of Phenols**

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## Materials and Methods

All air- and moisture-insensitive reactions were carried out under an ambient atmosphere, magnetically stirred, and monitored by thin layer chromatography (TLC) using EMD TLC plates pre-coated with 250  $\mu\text{m}$  thickness silica gel 60 F254 plates and visualized by fluorescence quenching under UV light. Flash chromatography was performed on Dynamic Adsorbents Silica Gel 40–63  $\mu\text{m}$  particle size using a forced flow of eluent at 0.3–0.5 bar pressure.<sup>1</sup> Toluene, dioxane and THF were distilled from deep purple sodium benzophenone ketyl. Methylene chloride- $d_2$  was dried over  $\text{CaH}_2$  and vacuum-distilled. Acetonitrile was dried over  $\text{P}_2\text{O}_5$  and vacuum-distilled. Chloroform- $d_1$  and all other chemicals were used as received. All deuterated solvents were purchased from Cambridge Isotope Laboratories. 1-Acetyl-4-(4-hydroxyphenyl)piperazine and 4-hydroxycoumarin were purchased from Acros. CsF (99.99%), 4-(methylsulfonyl)phenol, 3-bromo-4-hydroxybenzaldehyde, 3-(4-morpholinyl)phenol, 4-(1-imidazolyl)phenol and 4-hydroxy-2-methylquinoline were purchased from Alfa Aesar. Methyl 5-hydroxynicotinate and 4-methoxy-2(1H)-pyridone were purchased from Ark Pharm. 4-hydroxy-*N,N*-dimethylbenzamide was purchased from Combi Blocks. 2-(Methylthio)pyrimidine was purchased from Oxchem. 4-Phenoxyphenol, 2-phenylphenol, 6-hydroxy-2-methylbenzoxazole, 5-hydroxyisoquinoline, 8-hydroxyquinoline, estrone, 3,4-dimethoxyphenol and 2,6-dichlorophenol were purchased from Sigma-Aldrich. 4-hydroxy-3-methoxycinnamate was purchased from TCI. NMR spectra were recorded on either a Varian Unity/Inova 600 spectrometer operating at 600 MHz for  $^1\text{H}$  acquisitions, a Varian Unity/Inova 500 spectrometer operating at 500 MHz, 125 MHz and 470 MHz for  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{19}\text{F}$  acquisitions, respectively, or a Varian Mercury 400 spectrometer operating at 375 MHz for  $^{19}\text{F}$  acquisitions. Chemical shifts were referenced to the residual proton solvent peaks ( $^1\text{H}$ :  $\text{CDCl}_3$ ,  $\delta$  7.26;  $\text{CD}_3\text{CN}$ ,  $\delta$  1.94;  $\text{CD}_2\text{Cl}_2$ ,  $\delta$  5.32), solvent  $^{13}\text{C}$  signals ( $\text{CDCl}_3$ ,  $\delta$  77.16;  $\text{CD}_3\text{CN}$ ,  $\delta$  1.32, 118.26;  $\text{CD}_2\text{Cl}_2$ ,  $\delta$  53.84).<sup>2</sup> Signals are listed in ppm, and multiplicity identified as s = singlet, br = broad, d = doublet, t = triplet, q = quartet, quin = quintet, m = multiplet; br = broad; coupling constants in Hz; integration. High resolution mass spectra were obtained using an Agilent 6210 TOF LC/MS or a Bruker Maxis Impact LC-q-TOF. Concentration under reduced pressure was performed by rotary evaporation at 25–30  $^\circ\text{C}$  at appropriate pressure. Yields refer to purified and spectroscopically pure compounds.

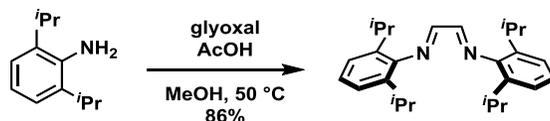
## Experimental Data

### General procedure for deoxyfluorination with PhenoFluorMix

Experiment was performed on the bench. An oven-dried vial was charged with PhenoFluorMix (1.10 g, corresponding to 1.50 equiv of the chloroimidazolium chloride to a substrate). PhenoFluorMix was heated at 140 °C for 1 hour under vacuum (~0.1 Torr). After the mixture was cooled to 23 °C, a phenol or a heterocycle (0.500 mmol, 1.00 equiv) was quickly added. The vial was evacuated and backfilled with N<sub>2</sub> gas, then toluene or xylene (5.0 mL) was added *via* syringe. The mixture was stirred at 23 °C for 30 min and subsequently heated at 110 °C or 140 °C for 24 hours. The reaction mixture was cooled to 23 °C, then filtered through a pad of Celite eluting with CH<sub>2</sub>Cl<sub>2</sub> (3 × 3 mL). The filtrate was concentrated *in vacuo* and the residue was purified by flash silica gel column chromatography to afford the fluorinated compound.

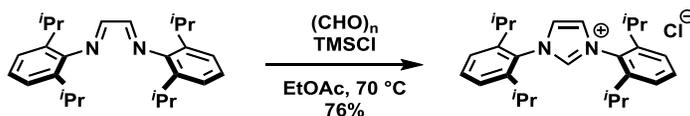
### Preparation of PhenoFluorMix

#### *N,N'*-1,4-Bis(2,6-diisopropylphenyl)-1,4-diazabutadiene<sup>3</sup>



In air, to a solution of 2,6-diisopropylaniline (197 g, 1.00 mol, 2.0 equiv) and AcOH (1.00 mL, 17.5 mmol, 0.035 equiv) in MeOH (250 mL) was added a solution of glyoxal (40% in water) (73 g, 0.50 mol, 1.0 equiv) in MeOH (250 mL). The mixture was stirred at 50 °C for 15 min, then stirred at 23 °C for 10 hours. The reaction mixture was filtered, then the filter cake was washed with MeOH (3 × 200 mL) and dried *in vacuo* to afford 162 g of the title compound as a yellow solid (86% yield). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 23 °C, 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). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, 23 °C, δ): 163.2, 148.2, 136.9, 125.3, 123.3, 28.2, 23.5.

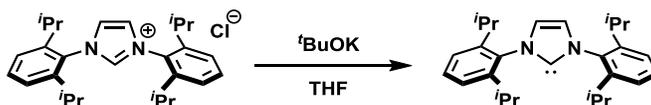
#### *N,N'*-1,3-Bis(2,6-diisopropylphenyl)imidazolium chloride<sup>3</sup>



In air, to a solution of *N,N'*-1,4-bis(2,6-diisopropylphenyl)-1,4-diazabutadiene (84.8 g, 225 mmol, 1.00 equiv) and paraformaldehyde (6.96 g, 232 mmol, 1.03 equiv) in EtOAc (2.0 L) was added a solution of TMSCl (29.4 mL, 232 mmol, 1.03 equiv) in EtOAc (30 mL) at 70 °C dropwise over 45 min. The mixture was stirred at 70 °C for 2 hours, then cooled to 10 °C. The reaction mixture was filtered, then the filter cake was washed with EtOAc (3 × 150 mL) and dried *in vacuo* to

afford 72.5 g of the title compound as a colorless solid (76% yield).  $^1\text{H}$  NMR (500 MHz,  $\text{CD}_3\text{CN}$ , 23 °C,  $\delta$ ): 10.36 (s, 1H), 7.94 (s, 2H), 7.68 (t,  $J = 7.5$  Hz, 2H), 7.50 (t,  $J = 7.5$  Hz, 4H), 2.49–2.41 (m, 4H), 1.31 (d,  $J = 7.0$  Hz, 12H), 1.25 (t,  $J = 7.0$  Hz, 12H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CD}_3\text{CN}$ , 23 °C,  $\delta$ ): 145.6, 139.8, 132.2, 126.0, 124.9, 29.2, 23.9, 23.0.

### ***N,N'*-1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene<sup>3</sup> (inside a glovebox)**

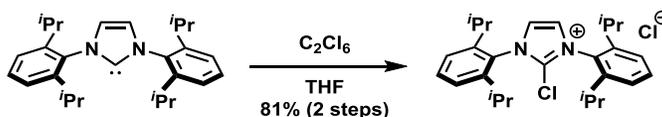


In an  $\text{N}_2$ -filled glovebox, *N,N'*-1,3-bis(2,6-diisopropylphenyl)imidazolium chloride (50.0 g, 118 mmol, 1.00 equiv) and *t*-BuOK (14.0 g, 125 mmol, 1.06 equiv) were placed in an oven-dried round-bottom flask. THF (240 mL) was added and the flask was capped with a rubber septum, then removed from the glovebox. The mixture was stirred at 23 °C for 3.5 hours, then the solvent was evaporated *in vacuo*. The residue was dissolved in toluene (450 mL) with gentle heating (50–60 °C) and the hot solution was filtered through a pad of Celite eluting with toluene (50 mL). The filtrate was concentrated and dried *in vacuo* to afford 39.1 g of the title compound as an off-white solid. The material was used in the next step without any further purification.

### ***N,N'*-1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene<sup>3</sup> (outside a glovebox)**

In air, *N,N'*-1,3-bis(2,6-diisopropylphenyl)imidazolium chloride (10.0 g, 23.5 mmol, 1.00 equiv) and *t*-BuOK (2.64 g, 23.5 mmol, 1.00 equiv) were placed in an oven-dried round-bottom flask. The flask was evacuated and backfilled with  $\text{N}_2$  gas, then THF (47 mL) was added. The mixture was stirred at 23 °C for 3.5 hours, then the solvent was evaporated *in vacuo*. The residue was dissolved in toluene (100 mL) with gentle heating (50–60 °C) and the hot solution was filtered through a pad of Celite eluting with toluene. The filtrate was concentrated and dried *in vacuo* to afford 7.80 g of the title compound as an off-white solid. The material was used in the next step without any further purification.

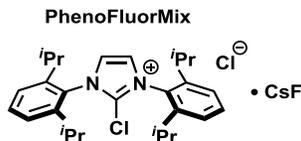
### ***N,N'*-1,3-Bis(2,6-diisopropylphenyl)-2-chloroimidazolium chloride<sup>3</sup>**



In air, to a mixture of *N,N'*-1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (39.1 g) in THF (240 mL) was added 1,1,1,2,2,2-hexachloroethane (26.2 g, 111 mmol) at  $-45$  °C. The mixture was warmed to 23 °C and stirred for 20 hours. The reaction mixture was filtered, then the filter cake was washed with THF ( $3 \times 100$  mL) and toluene ( $2 \times 100$  mL) and dried *in vacuo* to afford 44.0 g of the title compound as a white solid (81% yield, 2 steps).  $^1\text{H}$  NMR (600 MHz,  $\text{CD}_2\text{Cl}_2$ , 23 °C,  $\delta$ ): 8.87 (s, 2H), 7.67 (t,  $J = 7.8$  Hz, 2H), 7.45 (d,  $J = 7.8$  Hz, 4H), 2.36 (m, 4H), 1.32 (d,  $J = 7.0$

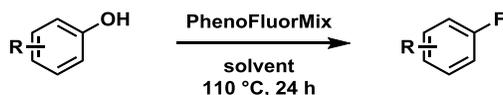
Hz, 12H), 1.22 (d,  $J = 7.0$  Hz, 12H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CD}_2\text{Cl}_2$ , 23 °C,  $\delta$ ): 145.5, 133.9, 133.1, 128.9, 128.4, 125.6, 29.7, 24.4, 23.5.

### PhenoFluorMix



In air, an oven-dried vial was charged with *N,N'*-1,3-bis(2,6-diisopropylphenyl)imidazolium chloride (5.52 g, 12.0 mmol) and CsF (12.2 g, 80.0 mmol). The mixture was shaken well to afford 17.7 g of PhenoFluorMix. The vial was flashed with  $\text{N}_2$  gas and stored on the bench.

### Evaluation of deoxyfluorination in different solvents



In an  $\text{N}_2$ -filled glovebox, an oven-dried vial was charged with *N,N'*-1,3-bis(2,6-diisopropylphenyl)imidazolium chloride (68.9 mg, 0.150 mmol, 1.50 equiv), previously dried (200 °C, 24 hours) CsF (152 mg, 1.00 mmol, 10.0 equiv) and a phenol (0.100 mmol, 1.00 equiv). Solvent (1.0 mL) was added and the vial was sealed, then removed from the glovebox. The mixture was stirred at 23 °C for 30 min and subsequently heated at 100 °C, 110 °C or 140 °C for 24 hours. The reaction mixture was cooled to 23 °C, then 1-fluoro-3-nitrobenzene (10.0  $\mu\text{L}$ , 0.0939 mmol, 0.939 equiv) was added to the mixture. The yields were determined by comparing the integration of the  $^{19}\text{F}$  NMR (470 MHz, 23 °C) resonance of 4-fluoro-1,1'-biphenyl (−117.2 ppm), 1-fluoro-4-methoxybenzene (−126.8 ppm) or 1-fluoro-2-methoxybenzene (−137.1 ppm) with that of 1-fluoro-3-nitrobenzene (−112.0 ppm). The yields are reported in Table S1.

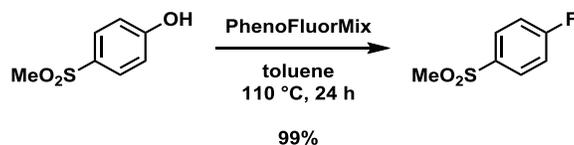
Table S1: Solvent effect on deoxyfluorination of phenols

Solvent	R = <i>p</i> -Ph: Yield (%)	R = <i>p</i> -OMe: Yield (%)	R = <i>o</i> -OMe: Yield (%)
EtOAc	99 (100 °C)	<1 (100 °C)	–
MeCN	83 (100 °C)	<1 (100 °C)	–
DMF	90	3	–
DMSO	70	<1	–
DME	91 (100 °C)	53 (100 °C)	–

dioxane	94	43	12
diglyme	–	78	12
toluene	96	34	14
<i>o</i> -xylene	94	87	66 (140 °C)
anisole	97	91	27 (140 °C)

## Deoxyfluorination of phenols and heterocycles

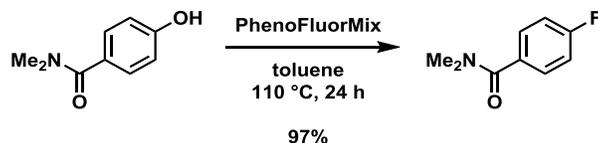
### 1-Fluoro-4-methylsulfonylbenzene (1)



A mixture of 4-(methylsulfonyl)phenol (88.8 mg, 0.500 mmol) and PhenoFluorMix (1.10 g) in toluene (5.0 mL) was stirred at 23 °C for 30 min, then at 110 °C for 24 hours. Purification by flash silica gel column chromatography (EtOAc in hexanes = 10–30%) afforded 86.4 mg of the title compound as a colorless solid (99% yield).

$R_f$  = 0.15 (EtOAc in hexanes = 20%). NMR Spectroscopy:  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , 23 °C,  $\delta$ ): 7.96 (dd,  $J$  = 7.4, 5.4 Hz, 2H), 7.24 (t,  $J$  = 7.9 Hz, 2H), 3.05 (s, 3H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ , 23 °C,  $\delta$ ): 165.9 (d,  $J$  = 256.6 Hz), 136.7 (d,  $J$  = 3.8 Hz), 130.4 (d,  $J$  = 10.5 Hz), 116.8 (d,  $J$  = 22.9 Hz), 44.8.  $^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ , 23 °C,  $\delta$ ): –106.5. HRMS-FIA( $m/z$ ) calc'd for  $\text{C}_7\text{H}_8\text{FO}_2\text{S}$   $[\text{M}+\text{H}]^+$ , 175.0224; found, 175.0227.

### 4-Fluoro-*N,N*-dimethylbenzamide (2)

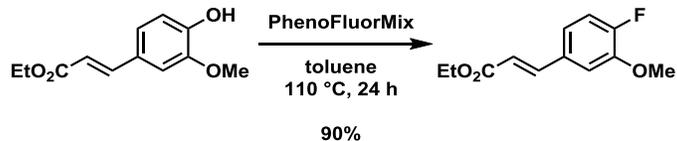


A mixture of 4-hydroxy-*N,N*-dimethylbenzamide (84.3 mg, 0.500 mmol) and PhenoFluorMix (1.10 g) in toluene (5.0 mL) was stirred at 23 °C for 30 min, then at 110 °C for 24 hours. Purification by flash silica gel column chromatography (EtOAc in hexanes = 20–50%) afforded 81.1 mg of the title compound as a colorless solid (97% yield).

$R_f$  = 0.20 (EtOAc in hexanes = 50%). NMR Spectroscopy:  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , 23 °C,  $\delta$ ): 7.41 (dd,  $J$  = 8.8, 5.4 Hz, 2H), 7.06 (t,  $J$  = 8.8 Hz, 2H), 3.08 (br s, 3H), 2.97 (br s, 3H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ , 23 °C,  $\delta$ ): 170.8, 163.3 (d,  $J$  = 249.9 Hz), 132.4 (d,  $J$  = 3.8 Hz), 129.5 (d,  $J$  =

8.6 Hz), 115.5 (d,  $J = 21.9$  Hz), 39.7, 35.6.  $^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ , 23 °C,  $\delta$ ): -113.7. HRMS-FIA( $m/z$ ) calc'd for  $\text{C}_9\text{H}_{11}\text{FNO}$  [ $\text{M}+\text{H}$ ] $^+$ , 168.0819; found, 168.0832.

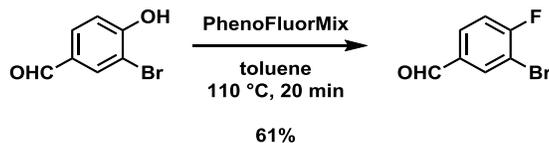
### 3-(4-Fluoro-3-methoxyphenyl)-2-propenoic acid ethyl ester (3)



A mixture of ethyl 4-hydroxy-3-methoxycinnamate (111 mg, 0.500 mmol) and PhenoFluorMix (1.10 g) in toluene (5.0 mL) was stirred at 23 °C for 30 min, then at 110 °C for 24 hours. Purification by flash silica gel column chromatography ( $\text{Et}_2\text{O}$  in hexanes = 5–10%) afforded 101 mg of the title compound as a colorless solid (90% yield).

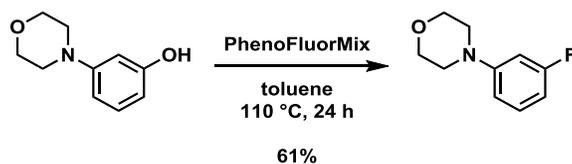
$R_f = 0.14$  ( $\text{Et}_2\text{O}$  in hexanes = 10%). NMR Spectroscopy:  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , 23 °C,  $\delta$ ): 7.61 (d,  $J = 16.1$  Hz, 1H), 7.12–7.04 (m, 3H), 6.34 (d,  $J = 16.1$  Hz, 1H), 4.25 (q,  $J = 7.1$  Hz, 2H), 3.91 (s, 3H), 1.33 (q,  $J = 7.1$  Hz, 3H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ , 23 °C,  $\delta$ ): 166.9, 153.8 (d,  $J = 250.8$  Hz), 148.1 (d,  $J = 10.5$  Hz), 143.7, 131.2 (d,  $J = 3.8$  Hz), 121.6 (d,  $J = 6.7$  Hz), 118.2 (d,  $J = 1.9$  Hz), 116.5 (d,  $J = 19.1$  Hz), 112.3 (d,  $J = 1.9$  Hz), 60.7, 56.3, 14.4.  $^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ , 23 °C,  $\delta$ ): -134.3. HRMS-FIA( $m/z$ ) calc'd for  $\text{C}_{12}\text{H}_{14}\text{FO}_3$  [ $\text{M}+\text{H}$ ] $^+$ , 225.0921; found, 225.0926.

### 3-Bromo-4-fluorobenzaldehyde (4)



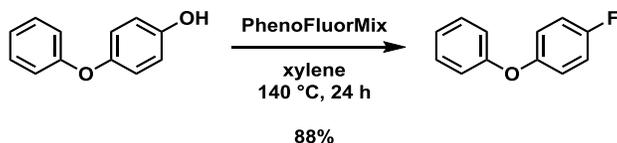
A mixture of 3-bromo-4-hydroxybenzaldehyde (104 mg, 0.500 mmol) and PhenoFluorMix (1.10 g) in toluene (5.0 mL) was stirred at 23 °C for 30 min, then at 110 °C for 20 min. Purification by flash silica gel column chromatography ( $\text{Et}_2\text{O}$  in hexanes = 5–10%) afforded 61.6 mg of the title compound as a colorless solid (61% yield).

$R_f = 0.37$  ( $\text{Et}_2\text{O}$  in hexanes = 10%). NMR Spectroscopy:  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , 23 °C,  $\delta$ ): 9.92 (s, 1H), 8.12 (dd,  $J = 6.4, 2.0$  Hz, 1H), 7.85 (ddd,  $J = 8.3, 4.9, 2.0$  Hz, 1H), 7.29 (t,  $J = 8.3$  Hz, 1H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ , 23 °C,  $\delta$ ): 189.3, 160.9 (d,  $J = 232.7$  Hz), 135.3 (d,  $J = 1.9$  Hz), 134.0, 130.9 (d,  $J = 8.6$  Hz), 117.4 (d,  $J = 22.9$  Hz), 110.7 (d,  $J = 22.8$  Hz).  $^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ , 23 °C,  $\delta$ ): -99.7. HRMS-FIA( $m/z$ ) calc'd for  $\text{C}_7\text{H}_5\text{BrFO}$  [ $\text{M}+\text{H}$ ] $^+$ , 202.9502; found, 202.9498.

**4-(3-Fluorophenyl)morpholine (5)**

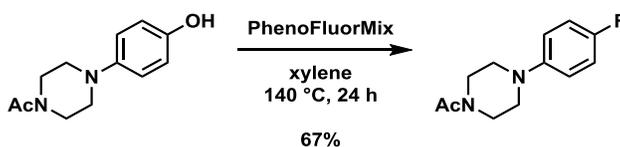
A mixture of 3-(4-morpholinyl)phenol (91.4 mg, 0.500 mmol) and PhenoFluorMix (1.10 g) in toluene (5.0 mL) was stirred at 23 °C for 30 min, then at 110 °C for 24 hours. Purification by flash silica gel column chromatography (Et<sub>2</sub>O in hexanes = 5%) afforded 55.4 mg of the title compound as a colorless oil (61% yield).

R<sub>f</sub> = 0.19 (Et<sub>2</sub>O in hexanes = 10%). NMR Spectroscopy: <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 23 °C, δ): 7.21 (dd, *J* = 15.2, 7.8 Hz, 1H), 6.67 (dd, *J* = 8.3, 2.0 Hz, 1H), 6.58 (dt, *J* = 17.1, 2.5 Hz, 1H), 6.56 (dd, *J* = 15.1, 2.0 Hz, 1H), 3.85 (t, *J* = 4.9 Hz, 4H), 3.16 (t, *J* = 4.9 Hz, 4H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, 23 °C, δ): 163.9 (d, *J* = 243.2 Hz), 153.1 (d, *J* = 9.5 Hz), 130.3 (d, *J* = 10.5 Hz), 110.9 (d, *J* = 2.9 Hz), 106.3 (d, *J* = 21.9 Hz), 102.5 (d, *J* = 24.8 Hz), 66.8, 48.9. <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>, 23 °C, δ): -115.2. HRMS-FIA(*m/z*) calc'd for C<sub>10</sub>H<sub>13</sub>FNO [M+H]<sup>+</sup>, 182.0976; found, 182.0985.

**1-Fluoro-4-phenoxybenzene (6)**

A mixture of 4-phenoxyphenol (94.0 mg, 0.500 mmol) and PhenoFluorMix (1.10 g) in xylene (5.0 mL) was stirred at 23 °C for 30 min, then at 140 °C for 24 hours. Purification by flash silica gel column chromatography (Et<sub>2</sub>O in hexanes = 5%) afforded 82.4 mg of the title compound as a colorless oil (88% yield).

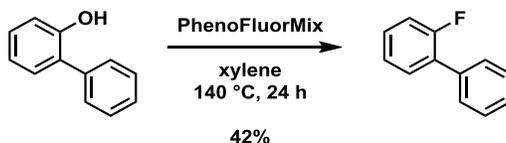
R<sub>f</sub> = 0.62 (Et<sub>2</sub>O in hexanes = 10%). NMR Spectroscopy: <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 23 °C, δ): 7.33 (dd, *J* = 8.8, 7.3 Hz, 2H), 7.09 (tt, *J* = 7.3, 1.0 Hz, 1H), 7.06–6.95 (m, 6H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, 23 °C, δ): 158.9 (d, *J* = 238.4 Hz), 157.8, 153.0, 129.9, 123.3, 120.7 (d, *J* = 8.6 Hz), 118.4, 116.4 (d, *J* = 22.9 Hz). <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>, 23 °C, δ): -123.2. HRMS-FIA(*m/z*) calc'd for C<sub>12</sub>H<sub>10</sub>FO [M+H]<sup>+</sup>, 189.0710; found, 189.0710.

**1-[4-(4-Fluorophenyl)-1-piperazinyl]ethanone (7)**

A mixture of 1-acetyl-4-(4-hydroxyphenyl)piperazine (112 mg, 0.500 mmol) and PhenoFluorMix (1.10 g) in xylene (5.0 mL) was stirred at 23 °C for 30 min, then at 140 °C for 24 hours. Purification by flash silica gel column chromatography (EtOAc in hexanes = 50–100%) afforded 74.8 mg of the title compound as a colorless solid (67% yield).

$R_f$  = 0.14 (EtOAc = 100%). NMR Spectroscopy:  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , 23 °C,  $\delta$ ): 6.97 (t,  $J$  = 8.3 Hz, 2H), 6.87 (dd,  $J$  = 8.8, 5.0 Hz, 2H), 3.75 (t,  $J$  = 5.0 Hz, 2H), 3.60 (t,  $J$  = 5.0 Hz, 2H), 3.07 (t,  $J$  = 5.0 Hz, 2H), 3.04 (t,  $J$  = 5.0 Hz, 2H), 2.12 (s, 3H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ , 23 °C,  $\delta$ ): 169.1, 157.7 (d,  $J$  = 240.3 Hz), 147.7 (d,  $J$  = 1.9 Hz), 118.7 (d,  $J$  = 7.6 Hz), 115.8 (d,  $J$  = 21.9 Hz), 50.8, 50.5, 46.4, 41.5, 21.4.  $^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ , 23 °C,  $\delta$ ): -126.2. HRMS-FIA( $m/z$ ) calc'd for  $\text{C}_{12}\text{H}_{16}\text{FN}_2\text{O}$  [ $\text{M}+\text{H}$ ] $^+$ , 223.1241; found, 223.1247.

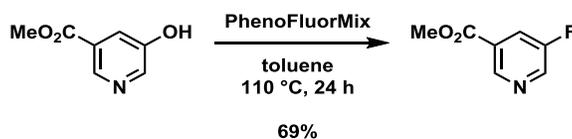
### 2-Fluoro-1-1'-biphenyl (9)



A mixture of 2-phenylphenol (84.2 mg, 0.500 mmol) and PhenoFluorMix (1.10 g) in xylene (5.0 mL) was stirred at 23 °C for 30 min, then at 140 °C for 24 hours. Purification by flash silica gel column chromatography ( $\text{Et}_2\text{O}$  in hexanes = 5%) afforded 35.8 mg of the title compound as a colorless solid (42% yield).

$R_f$  = 0.59 ( $\text{Et}_2\text{O}$  in hexanes = 10%). NMR Spectroscopy:  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , 23 °C,  $\delta$ ): 7.60–7.55 (m, 2H), 7.50–7.43 (m, 3H), 7.39 (t,  $J$  = 7.3 Hz, 1H), 7.33 (m, 1H), 7.23 (dt,  $J$  = 7.3, 1.5 Hz, 1H), 7.17 (m, 1H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ , 23 °C,  $\delta$ ): 159.9 (d,  $J$  = 247.0 Hz), 136.0, 130.9 (d,  $J$  = 3.8 Hz), 129.0 (d,  $J$  = 2.9 Hz), 128.9 (d,  $J$  = 7.6 Hz), 128.8 (d,  $J$  = 21.0 Hz), 128.4, 127.7, 124.3 (d,  $J$  = 3.8 Hz), 116.1 (d,  $J$  = 21.9 Hz).  $^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ , 23 °C,  $\delta$ ): -121.1. HRMS-FIA( $m/z$ ) calc'd for  $\text{C}_{12}\text{H}_{10}\text{F}$  [ $\text{M}+\text{H}$ ] $^+$ , 173.0761; found, 173.0753.

### 5-Fluoro-3-pyridinecarboxylic acid methyl ester (12)

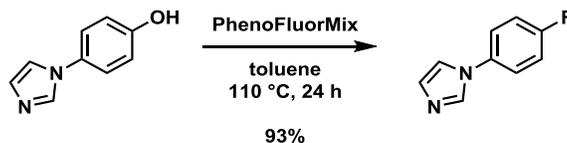


A mixture of methyl 5-hydroxynicotinate (80.6 mg, 0.500 mmol) and PhenoFluorMix (1.10 g) in toluene (5.0 mL) was stirred at 23 °C for 30 min, then at 110 °C for 24 hours. Purification by flash silica gel column chromatography ( $\text{Et}_2\text{O}$  in hexanes = 5%) afforded 53.6 mg of the title compound as a colorless solid (69% yield).

$R_f$  = 0.15 ( $\text{Et}_2\text{O}$  in hexanes = 10%). NMR Spectroscopy:  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , 23 °C,  $\delta$ ): 9.04 (s, 1H), 8.64 (d,  $J$  = 2.9 Hz, 1H), 7.99 (ddd,  $J$  = 8.3, 2.9, 2.0 Hz, 1H), 3.97 (s, 3H).  $^{13}\text{C}$  NMR

(125 MHz, CDCl<sub>3</sub>, 23 °C,  $\delta$ ): 164.8, 159.2 (d,  $J = 258.5$  Hz), 146.8 (d,  $J = 4.8$  Hz), 142.2 (d,  $J = 23.8$  Hz), 127.5 (d,  $J = 3.8$  Hz), 123.7 (d,  $J = 20.0$  Hz), 52.9. <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>, 23 °C,  $\delta$ ): -128.9. HRMS-FIA( $m/z$ ) calc'd for C<sub>7</sub>H<sub>7</sub>FNO<sub>2</sub> [M+H]<sup>+</sup>, 156.0455; found, 156.0463.

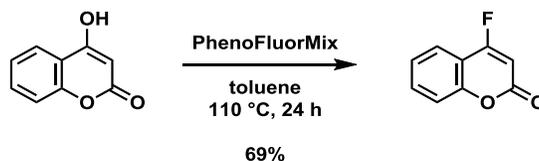
#### 1-(4-Fluorophenyl)-1H-imidazole (14)



A mixture of 4-(1-imidazolyl)phenol (82.6 mg, 0.500 mmol) and PhenoFluorMix (1.10 g) in toluene (5.0 mL) was stirred at 23 °C for 30 min, then at 110 °C for 24 hours. Purification by flash silica gel column chromatography (EtOAc in hexanes = 20–80%) afforded 75.5 mg of the title compound as a yellow oil (93% yield).

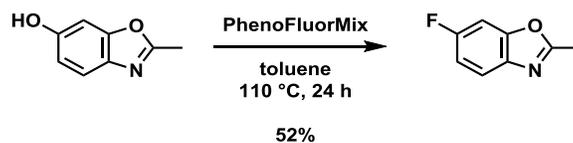
$R_f = 0.45$  (EtOAc = 100%). NMR Spectroscopy: <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 23 °C,  $\delta$ ): 7.78 (s, 1H), 7.37–7.31 (m, 2H), 7.22–7.13 (m, 4H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, 23 °C,  $\delta$ ): 161.8 (d,  $J = 247.0$  Hz), 135.9, 133.7 (d,  $J = 3.8$  Hz), 130.6, 123.5 (d,  $J = 8.6$  Hz), 118.6, 116.7 (d,  $J = 22.9$  Hz). <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>, 23 °C,  $\delta$ ): -117.0. HRMS-FIA( $m/z$ ) calc'd for C<sub>9</sub>H<sub>8</sub>FN<sub>2</sub> [M+H]<sup>+</sup>, 163.0666; found, 163.0673.

#### 4-Fluoro-2H-benzopyran-2-one (15)



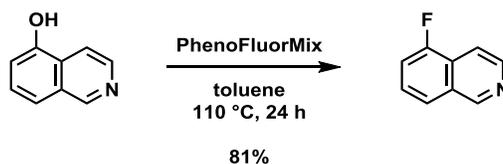
A mixture of 4-hydroxycoumarin (82.7 mg, 0.500 mmol) and PhenoFluorMix (1.10 g) in toluene (5.0 mL) was stirred at 23 °C for 30 min, then at 110 °C for 24 hours. Purification by flash silica gel column chromatography (Et<sub>2</sub>O in hexanes = 5%–10%) afforded 56.7 mg of the title compound as a colorless solid (69% yield).

$R_f = 0.18$  (Et<sub>2</sub>O in hexanes = 10%). NMR Spectroscopy: <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 23 °C,  $\delta$ ): 7.74 (d,  $J = 7.8$  Hz, 1H), 7.64 (t,  $J = 7.8$  Hz, 1H), 7.39 (d,  $J = 8.3$  Hz, 1H), 7.36 (t,  $J = 7.8$  Hz, 1H), 6.12 (d,  $J = 10.3$  Hz, 1H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, 23 °C,  $\delta$ ): 168.9 (d,  $J = 280.4$  Hz), 161.8 (d,  $J = 21.9$  Hz), 153.7 (d,  $J = 8.6$  Hz), 133.6, 124.6, 122.2 (d,  $J = 3.8$  Hz), 117.0 (d,  $J = 3.8$  Hz), 113.5 (d,  $J = 21.9$  Hz), 98.0 (d,  $J = 17.2$  Hz). <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>, 23 °C,  $\delta$ ): -104.9. HRMS-FIA( $m/z$ ) calc'd for C<sub>9</sub>H<sub>6</sub>FO<sub>2</sub> [M+H]<sup>+</sup>, 165.0346; found, 165.0353.

**6-Fluoro-2-methylbenzoxazole (16)**

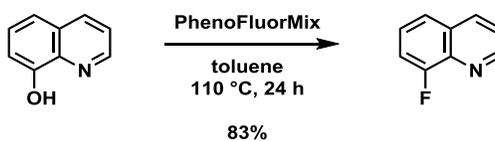
A mixture of 6-hydroxy-2-methylbenzoxazole (74.6 mg, 0.500 mmol) and PhenoFluorMix (1.10 g) in toluene (5.0 mL) was stirred at 23 °C for 30 min, then at 110 °C for 24 hours. Purification by flash silica gel column chromatography (Et<sub>2</sub>O in hexanes = 5%–10%) afforded 39.4 mg of the title compound as a yellow oil (52% yield).

R<sub>f</sub> = 0.16 (Et<sub>2</sub>O in hexanes = 10%). NMR Spectroscopy: <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 23 °C, δ): 7.56 (dd, *J* = 8.8, 4.9 Hz, 1H), 7.19 (dd, *J* = 7.8, 2.0 Hz, 1H), 7.39 (td, *J* = 8.8, 2.5 Hz, 1H), 2.62 (s, 3H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, 23 °C, δ): 164.5, 160.4 (d, *J* = 242.6 Hz), 151.0 (d, *J* = 14.4 Hz), 137.9, 119.7 (d, *J* = 9.6 Hz), 112.1 (d, *J* = 24.0 Hz), 98.5 (d, *J* = 27.8 Hz), 14.6. <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>, 23 °C, δ): -119.4. HRMS-FIA(*m/z*) calc'd for C<sub>8</sub>H<sub>7</sub>FNO [M+H]<sup>+</sup>, 152.0506; found, 152.0511.

**5-Fluoroisoquinoline (17)**

A mixture of 5-hydroxyisoquinoline (80.6 mg, 0.500 mmol) and PhenoFluorMix (1.10 g) in toluene (5.0 mL) was stirred at 23 °C for 30 min, then at 110 °C for 24 hours. Purification by flash silica gel column chromatography (EtOAc in hexanes = 5%–15%) afforded 59.9 mg of the title compound as a yellow oil (81% yield).

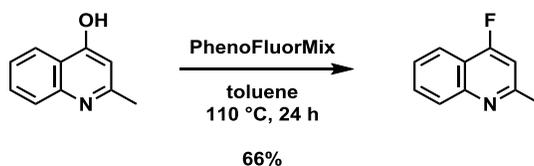
R<sub>f</sub> = 0.22 (EtOAc in hexanes = 20%). NMR Spectroscopy: <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 23 °C, δ): 9.28 (s, 1H), 8.59 (d, *J* = 5.9 Hz, 1H), 7.87 (d, *J* = 5.4 Hz, 1H), 7.77 (d, *J* = 7.8 Hz, 1H), 7.53 (td, *J* = 7.8, 5.4 Hz, 1H), 7.35 (dd, *J* = 9.8, 7.8 Hz, 1H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, 23 °C, δ): 157.6 (d, *J* = 253.7 Hz), 152.1 (d, *J* = 2.9 Hz), 143.5, 129.7 (d, *J* = 4.8 Hz), 127.3 (d, *J* = 6.7 Hz), 126.5 (d, *J* = 17.2 Hz), 123.5 (d, *J* = 4.8 Hz), 114.0 (d, *J* = 19.1 Hz), 113.5 (d, *J* = 2.9 Hz). <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>, 23 °C, δ): -126.2. HRMS-FIA(*m/z*) calc'd for C<sub>9</sub>H<sub>7</sub>FN [M+H]<sup>+</sup>, 148.0557; found, 148.0562.

**8-Fluoroquinoline (18)**

A mixture of 8-hydroxyquinoline (73.3 mg, 0.500 mmol) and PhenoFluorMix (1.10 g) in toluene (5.0 mL) was stirred at 23 °C for 30 min, then at 110 °C for 24 hours. Purification by flash silica gel column chromatography (EtOAc in hexanes = 10%–30%) afforded 61.4 mg of the title compound as a colorless oil (83% yield).

$R_f$  = 0.26 (EtOAc in hexanes = 30%). NMR Spectroscopy:  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , 23 °C,  $\delta$ ): 8.95 (d,  $J$  = 3.9 Hz, 1H), 8.16 (dd,  $J$  = 8.3, 1.5 Hz, 1H), 7.58 (d,  $J$  = 8.3 Hz, 1H), 7.49–7.41 (m, 2H), 7.38 (t,  $J$  = 9.3 Hz, 1H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ , 23 °C,  $\delta$ ): 158.1 (d,  $J$  = 256.6 Hz), 150.6 (d,  $J$  = 1.9 Hz), 138.6 (d,  $J$  = 11.5 Hz), 135.9 (d,  $J$  = 3.8 Hz), 129.9, 126.5 (d,  $J$  = 8.6 Hz), 123.5 (d,  $J$  = 4.8 Hz), 122.1, 113.6 (d,  $J$  = 18.1 Hz).  $^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ , 23 °C,  $\delta$ ): –128.7. HRMS-FIA( $m/z$ ) calc'd for  $\text{C}_9\text{H}_7\text{FN}$  [ $\text{M}+\text{H}$ ] $^+$ , 148.0557; found, 148.0563.

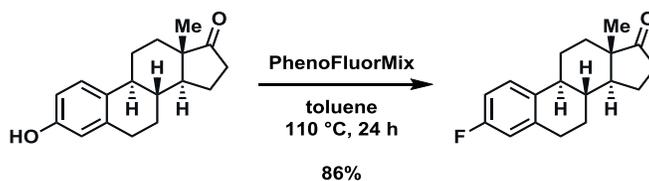
#### 4-Fluoro-2-methylquinoline (19)



A mixture of 4-hydroxy-2-methylquinoline (81.2 mg, 0.500 mmol) and PhenoFluorMix (1.10 g) in toluene (5.0 mL) was stirred at 23 °C for 30 min, then at 110 °C for 24 hours. Purification by flash silica gel column chromatography (EtOAc in hexanes = 5%–10%) afforded 53.3 mg of the title compound as a colorless oil (66% yield). The product was highly volatile.

$R_f$  = 0.22 (EtOAc in hexanes = 10%). NMR Spectroscopy:  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , 23 °C,  $\delta$ ): 8.05–8.01 (m, 2H), 7.74 (t,  $J$  = 8.3 Hz, 1H), 7.54 (d,  $J$  = 7.8 Hz, 1H), 6.99 (d,  $J$  = 10.3 Hz, 1H), 2.74 (s, 3H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ , 23 °C,  $\delta$ ): 165.5 (d,  $J$  = 267.6 Hz), 160.8 (d,  $J$  = 7.7 Hz), 150.1 (d,  $J$  = 4.8 Hz), 130.7, 128.5 (d,  $J$  = 3.8 Hz), 126.1 (d,  $J$  = 1.9 Hz), 120.5 (d,  $J$  = 4.8 Hz), 118.2, 106.3 (d,  $J$  = 14.4 Hz), 25.8 (d,  $J$  = 2.9 Hz).  $^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ , 23 °C,  $\delta$ ): –117.3. HRMS-FIA( $m/z$ ) calc'd for  $\text{C}_{10}\text{H}_9\text{FN}$  [ $\text{M}+\text{H}$ ] $^+$ , 162.0714; found, 162.0721.

#### 3-Fluoroestra-1,3,5(10)-trien-17-one (20)

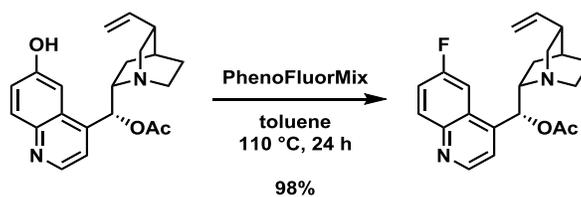


A mixture of estrone (135 mg, 0.500 mmol) and PhenoFluorMix (1.10 g) in toluene (5.0 mL) was stirred at 23 °C for 30 min, then at 110 °C for 24 hours. Purification by flash silica gel column chromatography ( $\text{Et}_2\text{O}$  in hexanes = 5%) afforded 117 mg of the title compound as a colorless solid (86% yield).

$R_f$  = 0.31 (EtOAc in hexanes = 10%). NMR Spectroscopy:  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , 23 °C,  $\delta$ ):

7.23 (dd,  $J = 8.3, 5.8$  Hz, 1H), 6.83 (td,  $J = 8.3, 2.6$  Hz, 1H), 6.78 (dd,  $J = 9.6, 2.6$  Hz, 1H), 2.92–2.86 (m, 2H), 2.51 (dd,  $J = 19.2, 8.3$  Hz, 1H), 2.39 (m, 1H), 2.25 (br t,  $J = 10.3$  Hz, 1H), 2.15 (quin,  $J = 9.0$  Hz, 1H), 2.09–1.93 (m, 3H), 1.67–1.40 (m, 6H), 0.91 (s, 3H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ , 23 °C,  $\delta$ ): 220.8, 161.1 (d,  $J = 244.2$  Hz), 138.8 (d,  $J = 7.6$  Hz), 135.5 (d,  $J = 2.9$  Hz), 126.9 (d,  $J = 8.6$  Hz), 115.2 (d,  $J = 20.0$  Hz), 112.6 (d,  $J = 21.0$  Hz), 50.5, 48.0, 44.1, 38.2, 36.0, 31.7, 29.6, 26.4, 26.0, 21.7, 13.9.  $^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ , 23 °C,  $\delta$ ): -121.1. HRMS-FIA( $m/z$ ) calc'd for  $\text{C}_{18}\text{H}_{22}\text{FO}$  [ $\text{M}+\text{H}$ ] $^+$ , 273.1649; found, 273.1652.

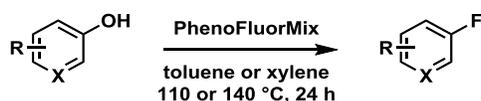
### Gram scale synthesis of (8 $\alpha$ , 9R)-6'-fluorocinchonan-9-ol acetate



An oven-dried flask was charged with PhenoFluorMix (6.23 g). PhenoFluorMix was heated at 140 °C for 1 hour under vacuum (~0.1 Torr). After the mixture was cooled to 23 °C, *O*-acetyl (8 $\alpha$ , 9R)-cinchonan-6',9-diol 9-acetate<sup>4</sup> (1.00 g, 2.83 mmol) was quickly added. The flask was evacuated and backfilled with  $\text{N}_2$  gas, then toluene (28 mL) was added *via* syringe. The mixture was stirred at 23 °C for 30 min and subsequently heated at 110 °C for 24 hours. The reaction mixture was cooled to 23 °C, then filtered through a pad of Celite eluting with  $\text{CH}_2\text{Cl}_2$  (3  $\times$  15 mL). The filtrate was concentrated *in vacuo* and the residue was purified by flash silica gel column chromatography (MeOH in EtOAc = 0%–10%) to afford 998 mg of the title compound as a light yellow oil (98% yield).

$R_f = 0.24$  (MeOH in EtOAc = 5%). NMR Spectroscopy:  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , 23 °C,  $\delta$ ): 8.84 (d,  $J = 4.4$  Hz, 1H), 8.11 (dd,  $J = 9.3, 5.4$  Hz, 1H), 7.86 (dd,  $J = 10.3, 2.5$  Hz, 1H), 7.48 (td,  $J = 8.3, 2.9$  Hz, 1H), 7.41 (d,  $J = 4.9$  Hz, 1H), 6.33 (d,  $J = 8.3$  Hz, 1H), 5.85 (m, 1H), 5.04–4.98 (m, 2H), 3.35 (q,  $J = 8.3$ , 1H), 3.07 (m, 1H), 3.00 (dd,  $J = 13.7, 9.8$ , 1H), 2.62 (m, 1H), 2.54 (m, 1H), 2.26 (br s, 1H), 2.10 (s, 3H), 1.96 (m, 1H), 1.85 (m, 1H), 1.71 (m, 1H), 1.55 (m, 1H), 1.45 (dd,  $J = 13.7, 7.3$  Hz, 1H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ , 23 °C,  $\delta$ ): 170.2, 160.7 (d,  $J = 248.0$  Hz), 149.4 (d,  $J = 1.9$  Hz), 146.0, 145.0 (d,  $J = 5.7$  Hz), 141.8, 133.1 (d,  $J = 9.5$  Hz), 127.0 (d,  $J = 9.5$  Hz), 119.9, 119.6 (d,  $J = 25.8$  Hz), 114.7, 107.4 (d,  $J = 22.9$  Hz), 74.3, 59.6, 56.7, 42.3, 39.8, 27.9, 27.6, 25.2, 21.1.  $^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ , 23 °C,  $\delta$ ): -114.6. HRMS-FIA( $m/z$ ) calc'd for  $\text{C}_{21}\text{H}_{24}\text{FN}_2\text{O}_2$  [ $\text{M}+\text{H}$ ] $^+$ , 355.1816; found, 355.1832.

### General procedure for volatile compound

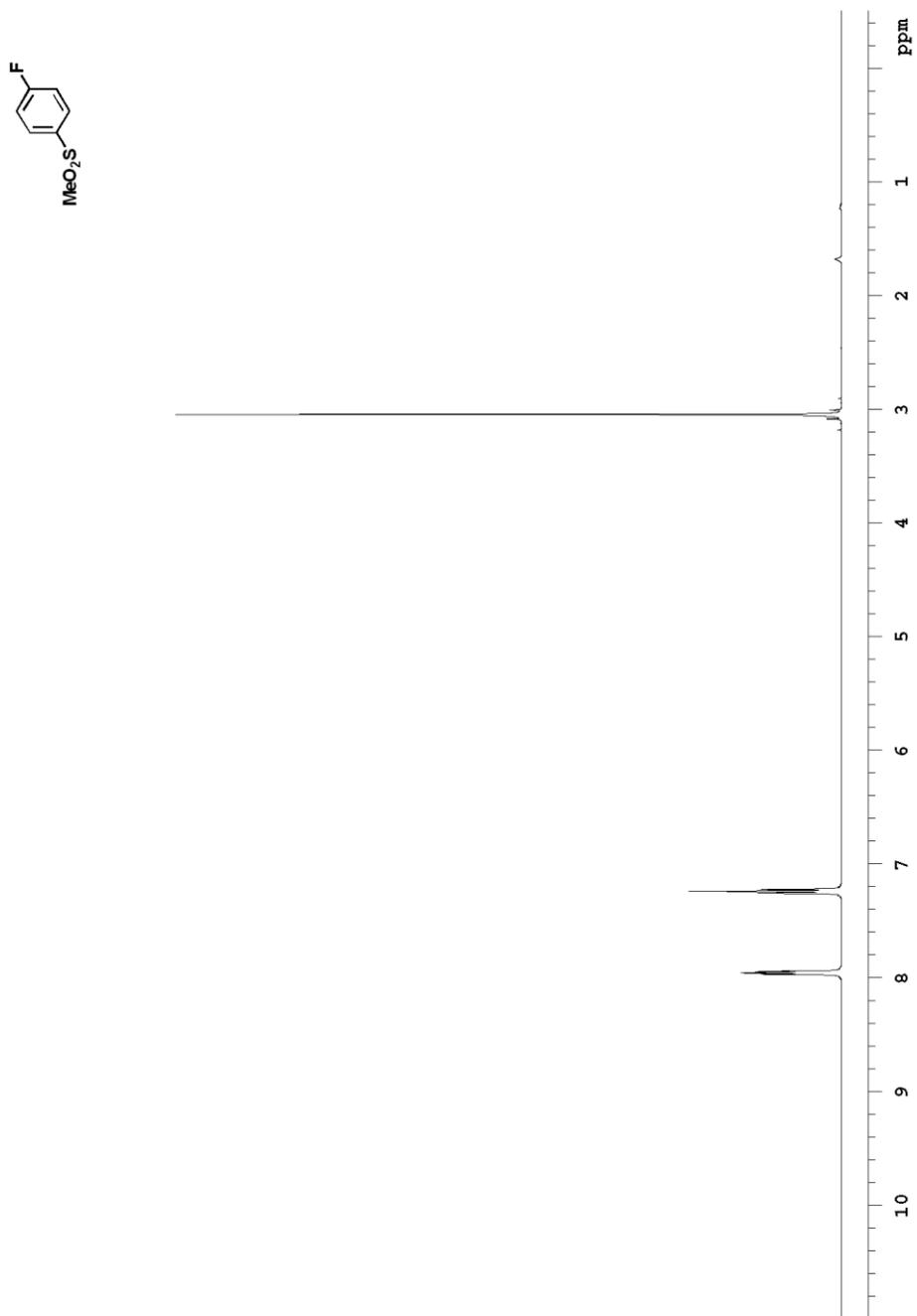


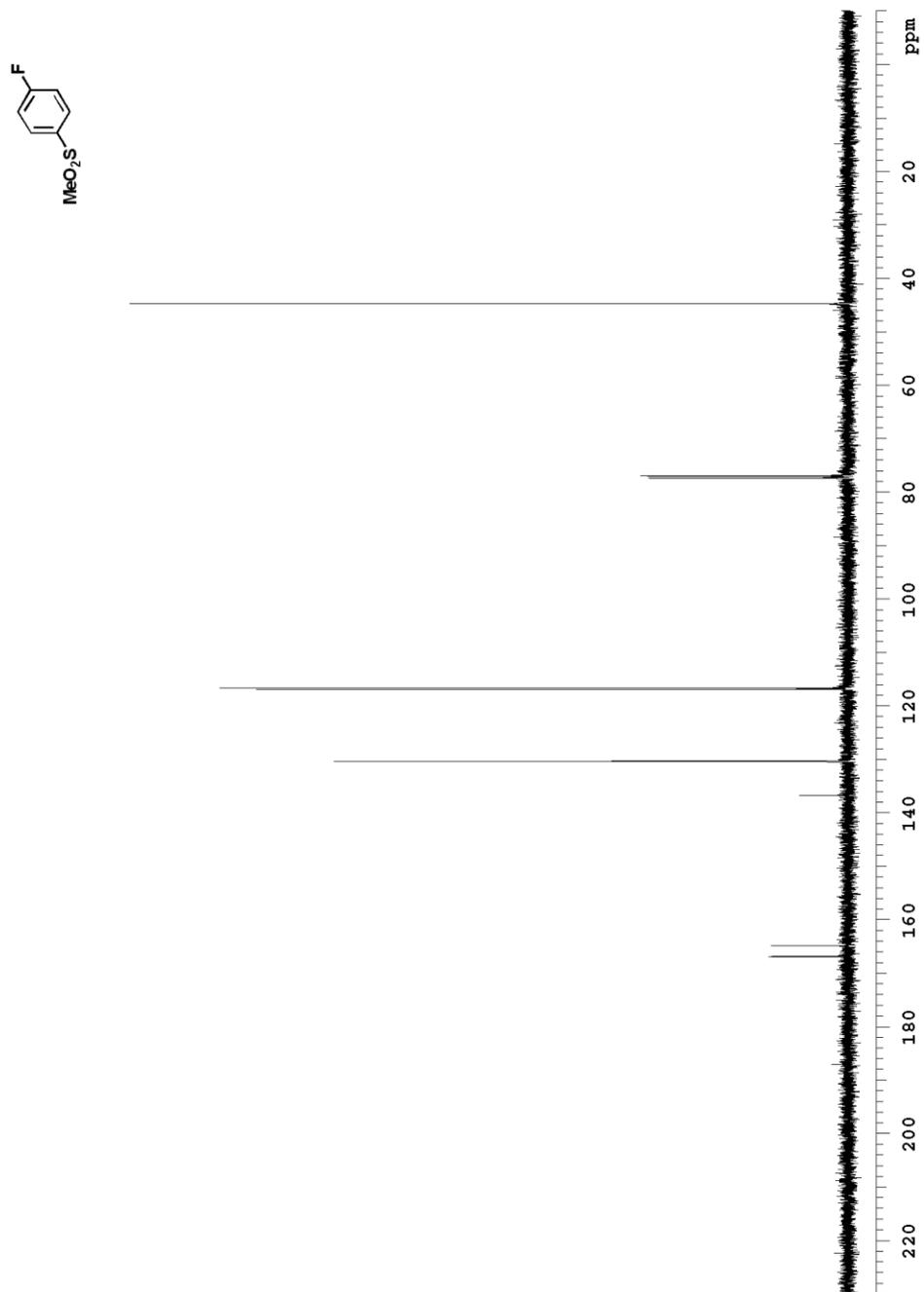
An oven-dried vial was charged with PhenoFluorMix (220 mg, corresponding to 1.50 equiv of the chloroimidazolium chloride to a substrate). PhenoFluorMix was heated at 140 °C for 1 hour under vacuum (~0.1 Torr). After the mixture was cooled to 23 °C, a phenol or a heterocycle (0.100 mmol, 1.00 equiv) was quickly added. The vial was evacuated and backfilled with N<sub>2</sub> gas, then toluene or xylene (1.0 mL) was added *via* syringe. The mixture was stirred at 23 °C for 30 min and subsequently heated at 110 °C or 140 °C for 24 hours. The reaction mixture was cooled to 23 °C, then 1-fluoro-3-nitrobenzene (10.0 μL, 0.0939 mmol, 0.939 equiv) was added to the mixture. The yields were determined by comparing the integration of the <sup>19</sup>F NMR (470 MHz, 23 °C, toluene or xylene) resonance of the fluorinated product with that of 1-fluoro-3-nitrobenzene (-112.0 ppm). The yields are reported in Table S2.

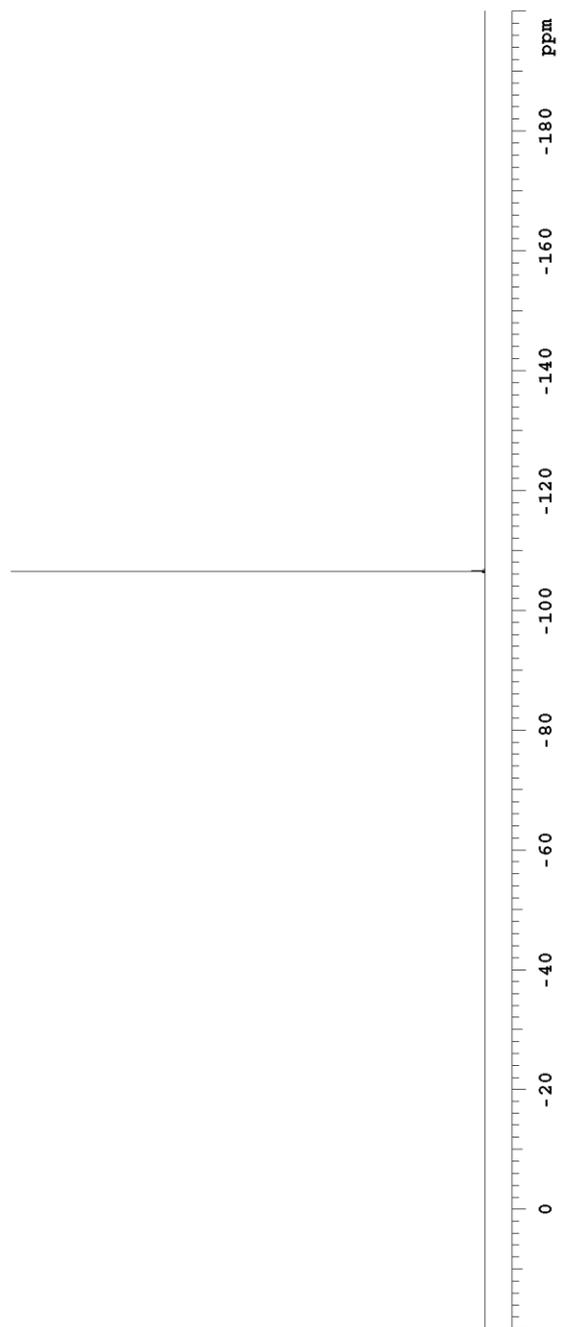
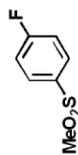
Table S2: Synthesis of volatile aryl fluoride

Product	Solvent Temp	<sup>19</sup> F NMR (ppm)	Yield (%)
4-fluoro-1,2-dimethoxybenzene ( <b>8</b> )	xylene 140 °C	-123.5	79
1,3-dichloro-2-fluorobenzene ( <b>10</b> )	xylene 140 °C	-118.2	47
2-fluoro-4-methoxypyridine ( <b>11</b> )	xylene 140 °C	-68.4	55
5-fluoro-2-(methylthio)pyrimidine ( <b>13</b> )	toluene 110 °C	-148.4	90

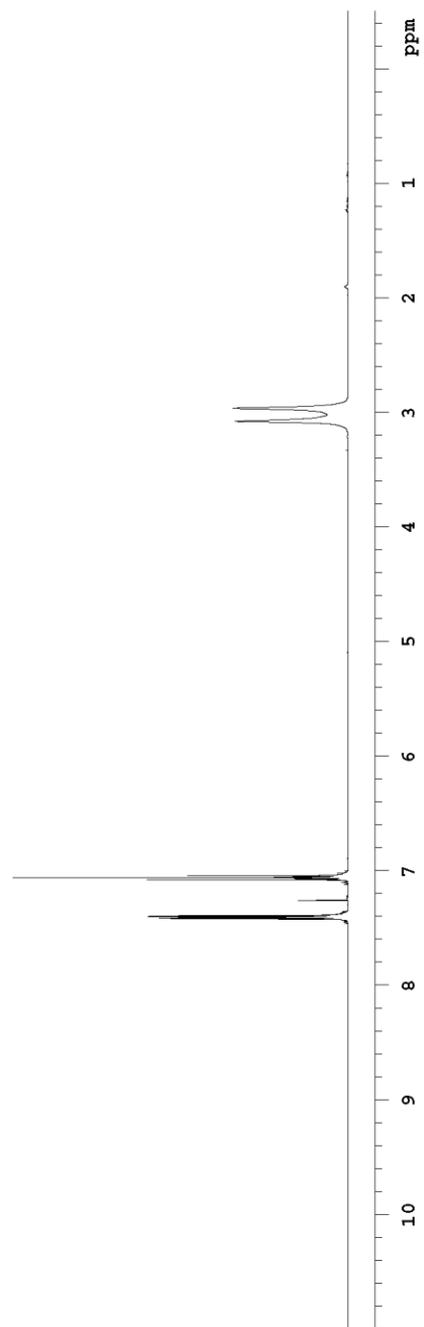
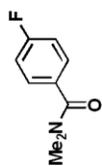
## Spectroscopic Data

 $^1\text{H}$  NMR (CDCl<sub>3</sub>, 23 °C) of **1**

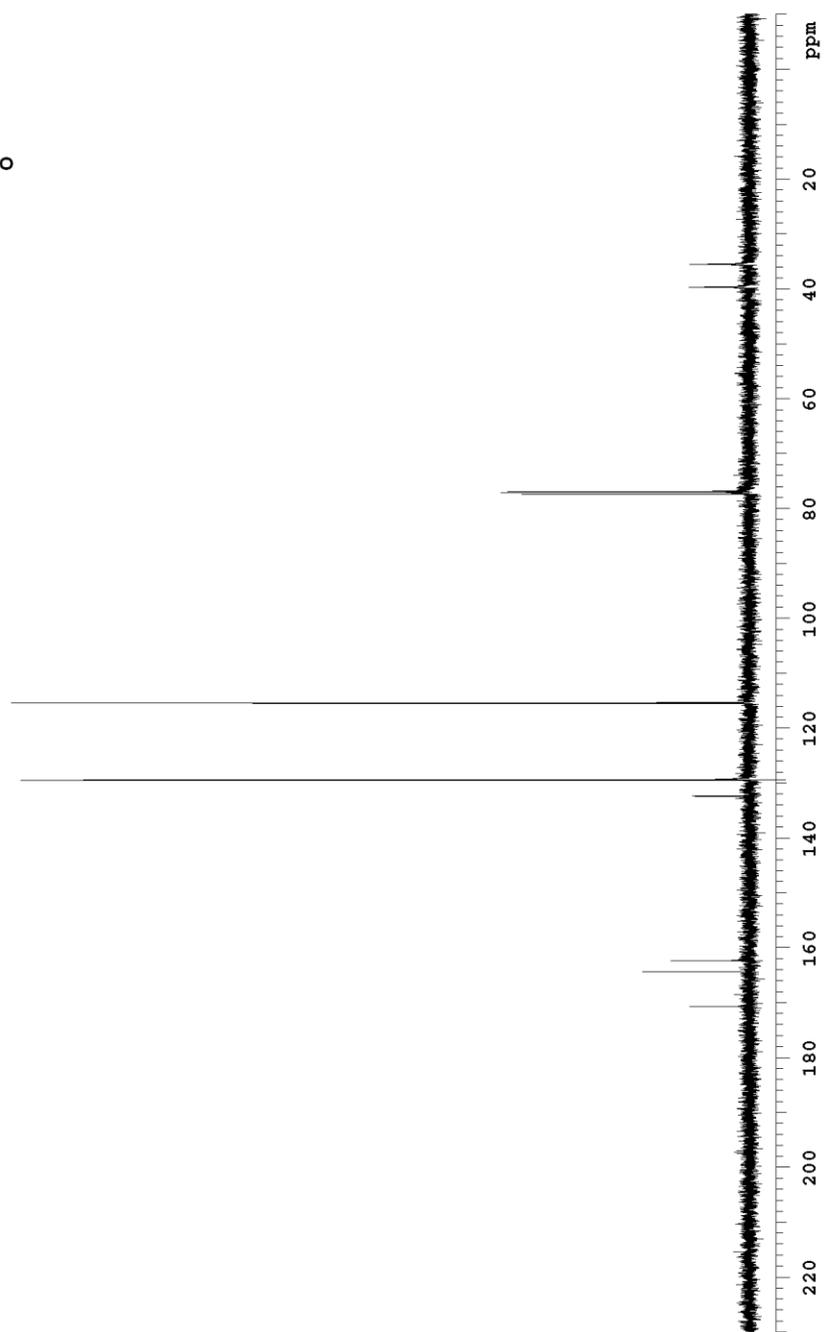
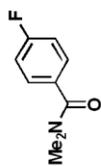
 $^{13}\text{C}$  NMR (CDCl<sub>3</sub>, 23 °C) of 1



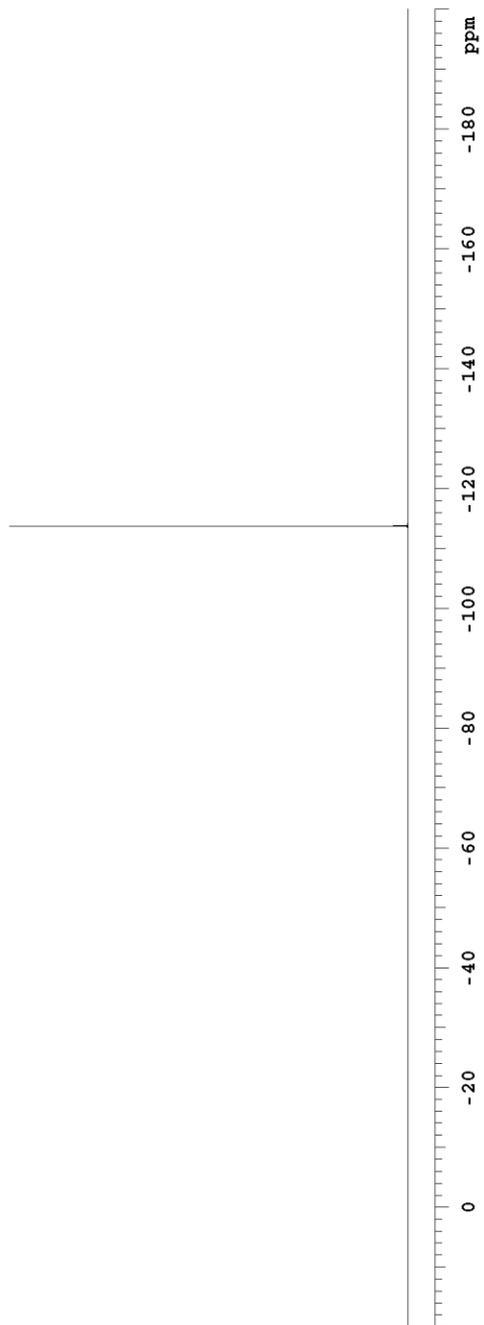
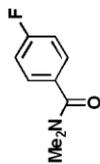
$^{19}\text{F}$  NMR (CDCl<sub>3</sub>, 23 °C) of **1**



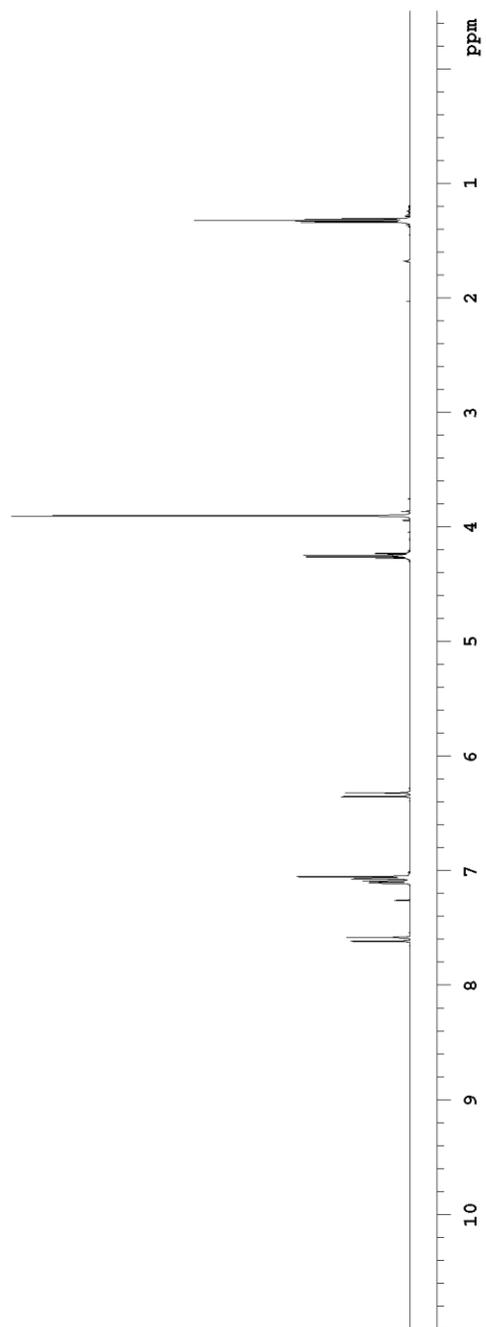
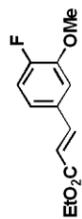
$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 23 °C) of **2**



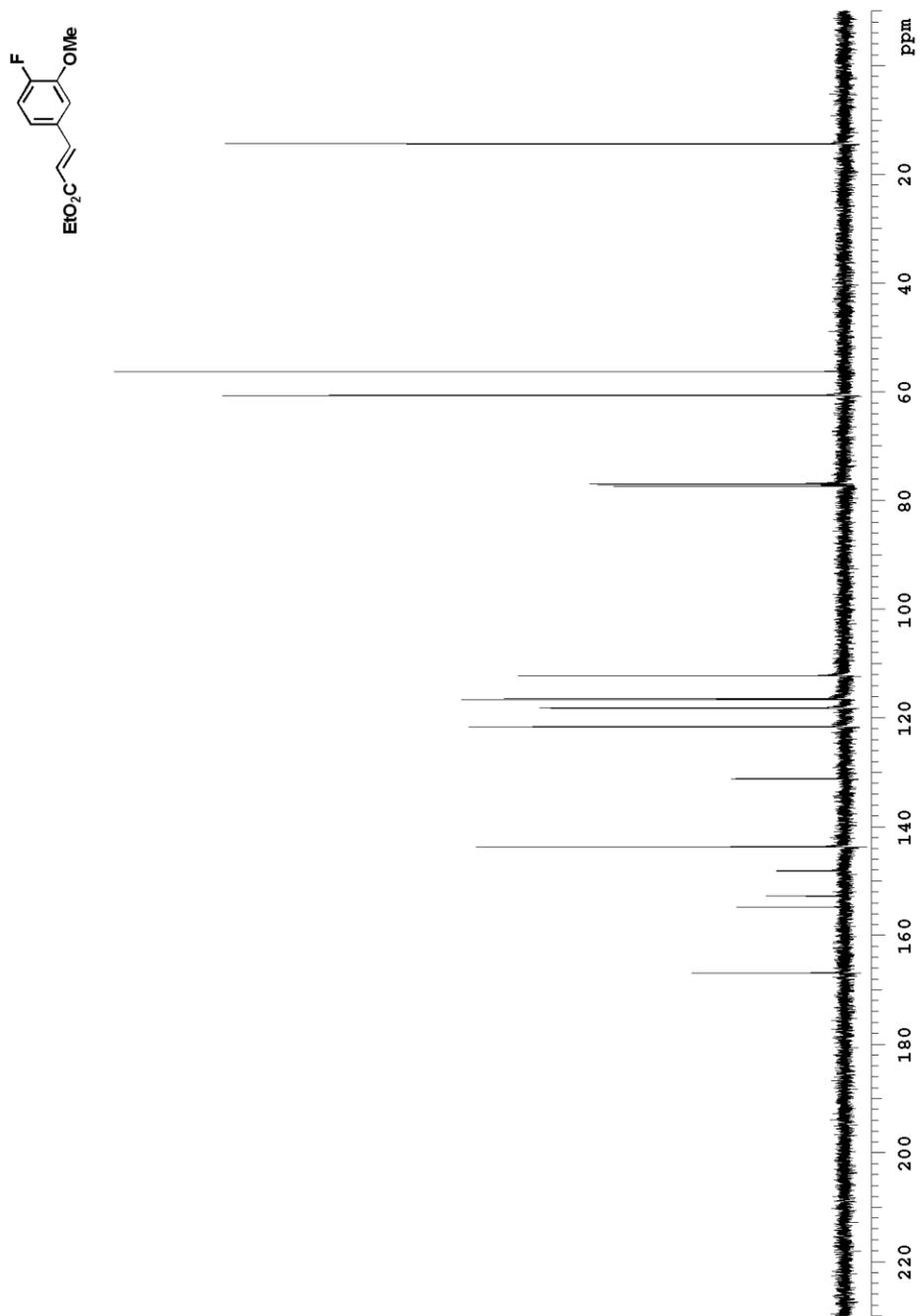
$^{13}\text{C}$  NMR (CDCl<sub>3</sub>, 23 °C) of **2**



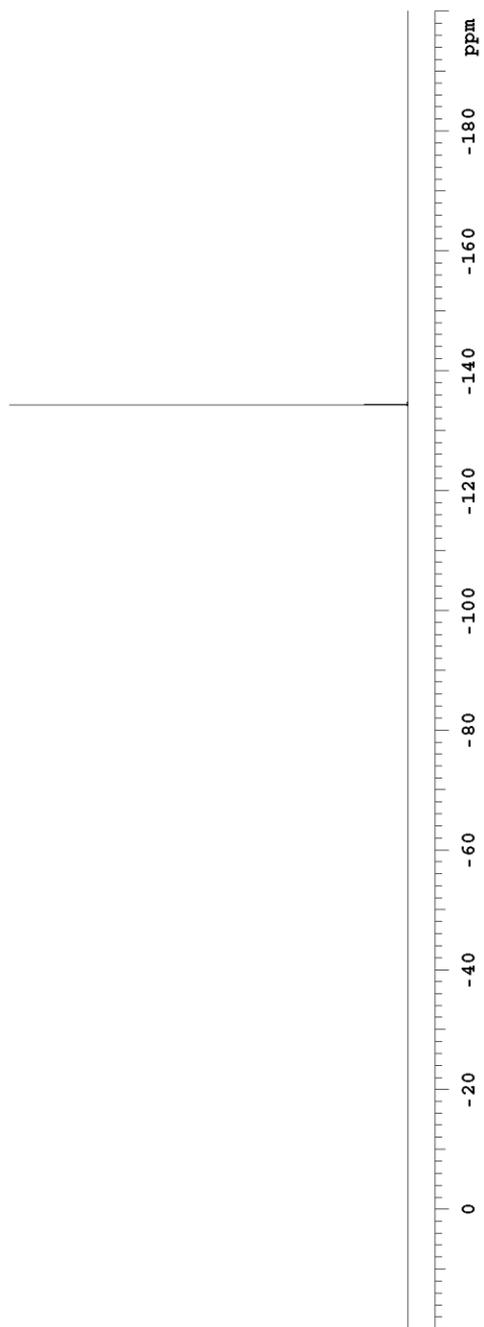
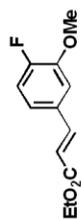
$^{19}\text{F}$  NMR (CDCl<sub>3</sub>, 23 °C) of **2**



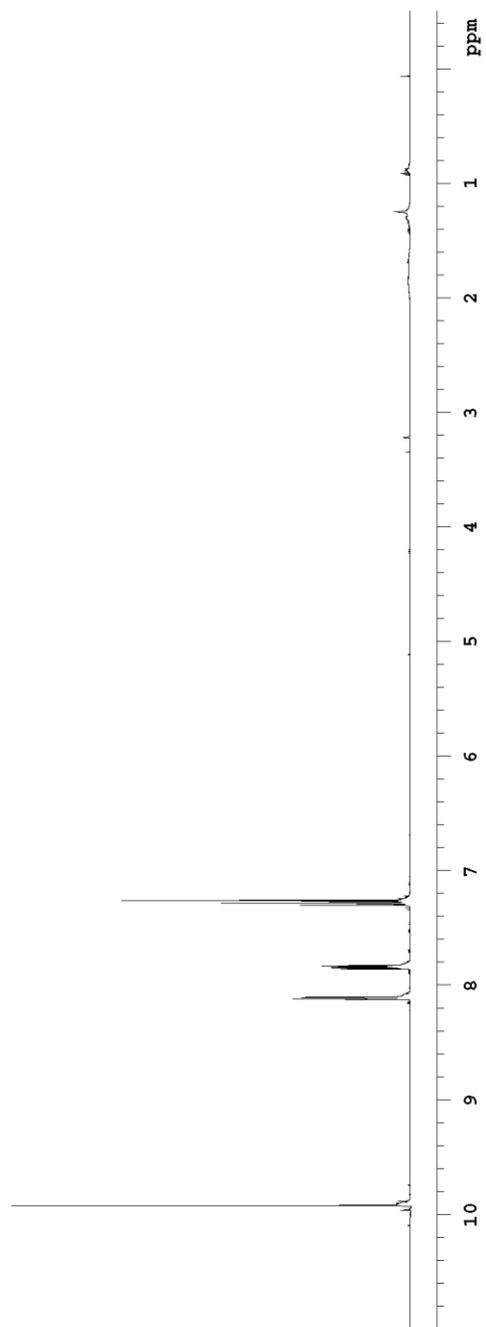
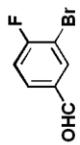
$^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $23\text{ }^\circ\text{C}$ ) of **3**



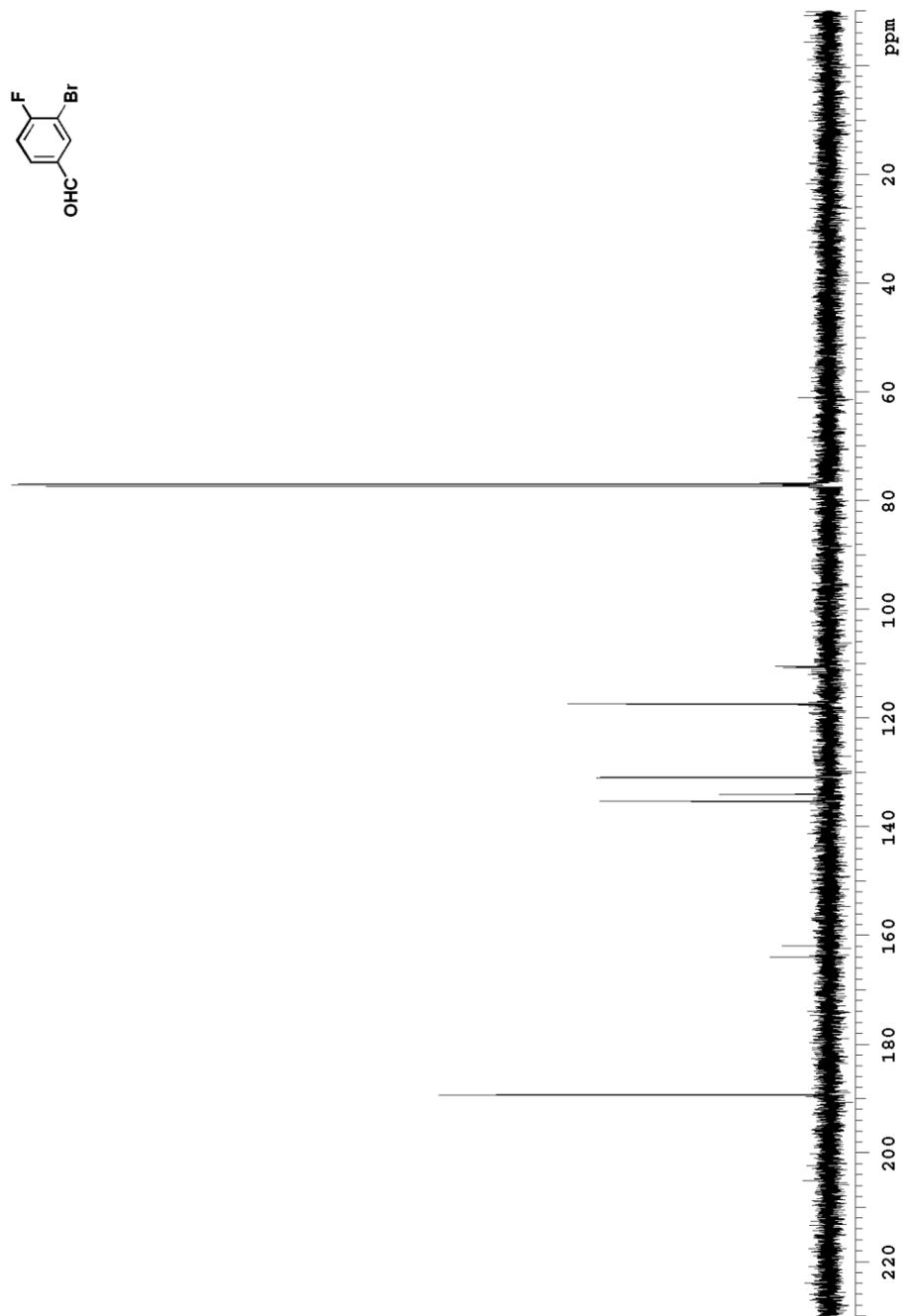
$^{13}\text{C}$  NMR (CDCl<sub>3</sub>, 23 °C) of **3**



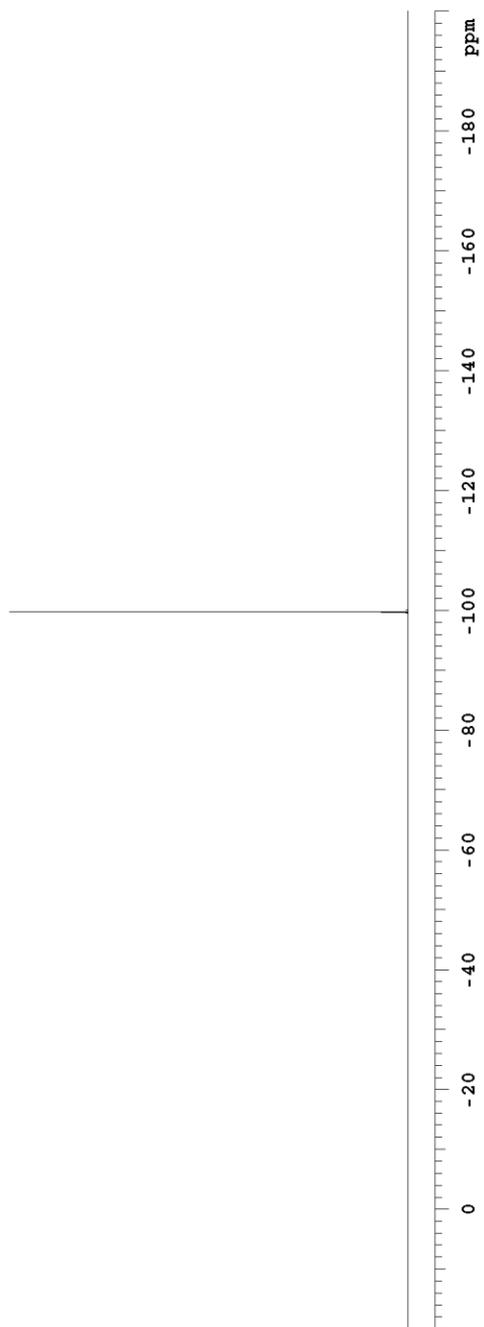
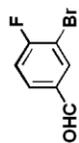
$^{19}\text{F}$  NMR ( $\text{CDCl}_3$ , 23 °C) of **3**



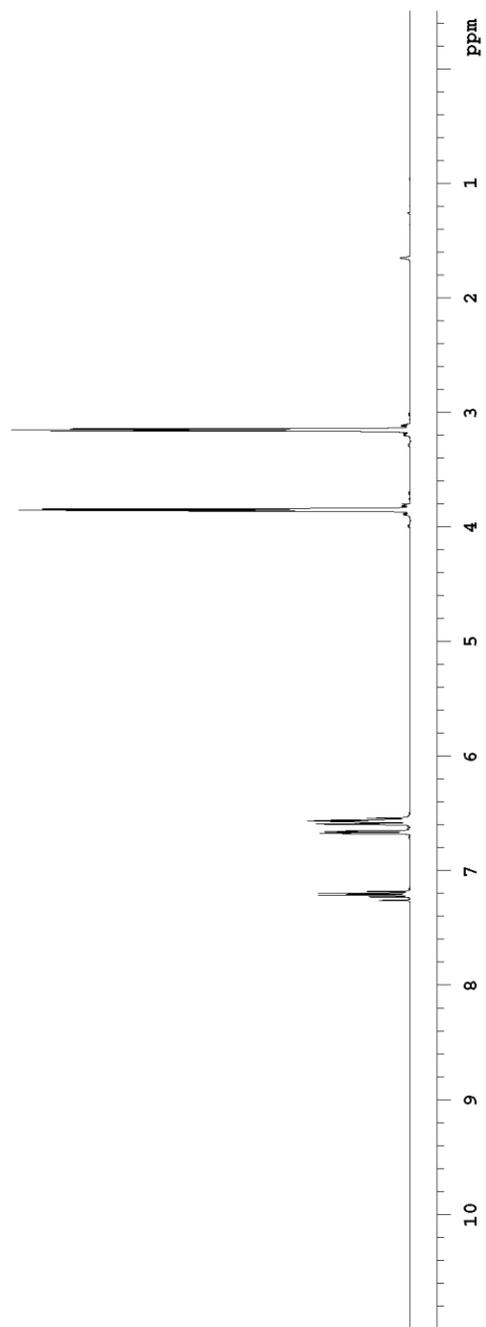
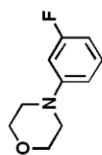
$^1\text{H}$  NMR (CDCl<sub>3</sub>, 23 °C) of **4**



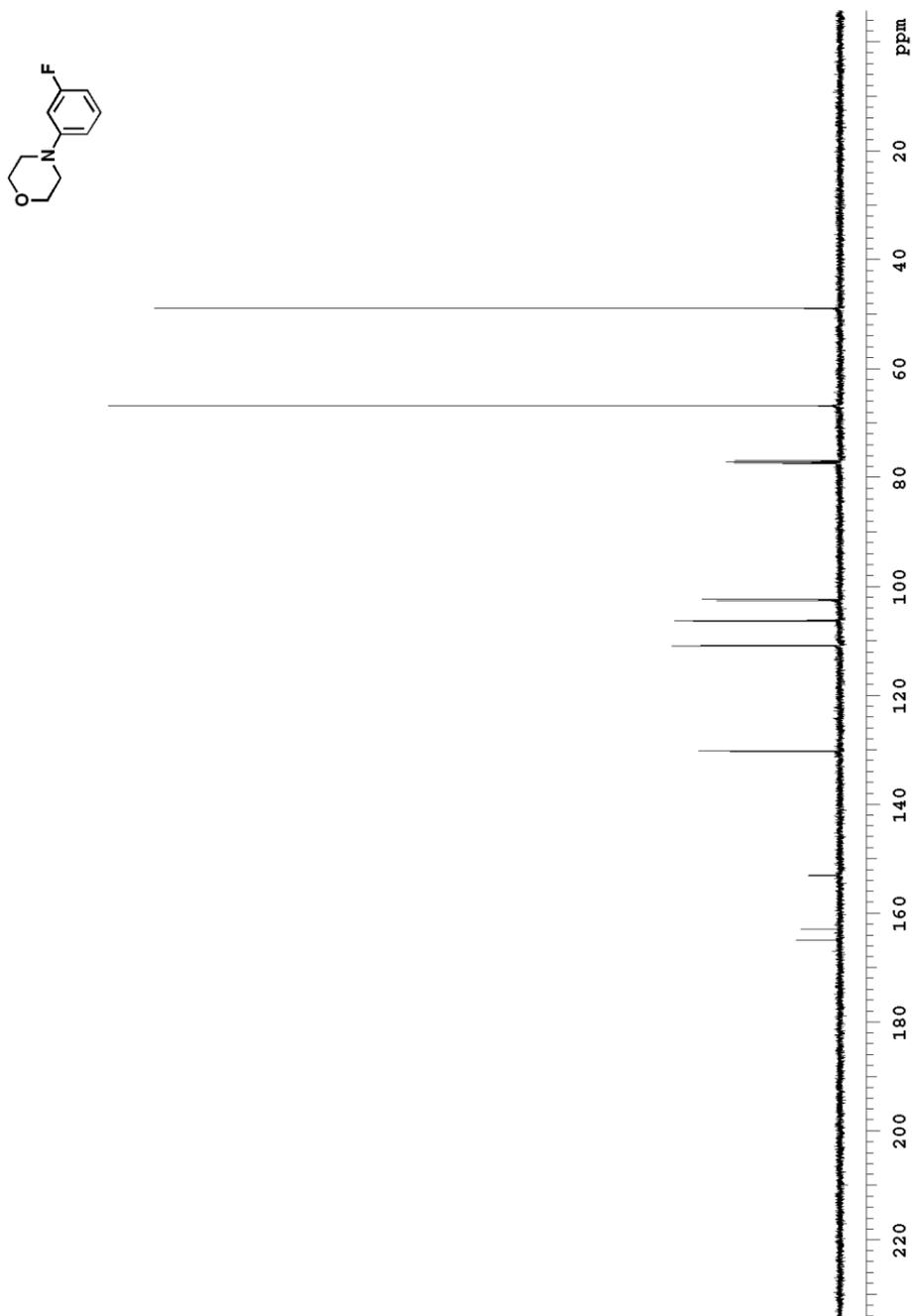
$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 23 °C) of **4**

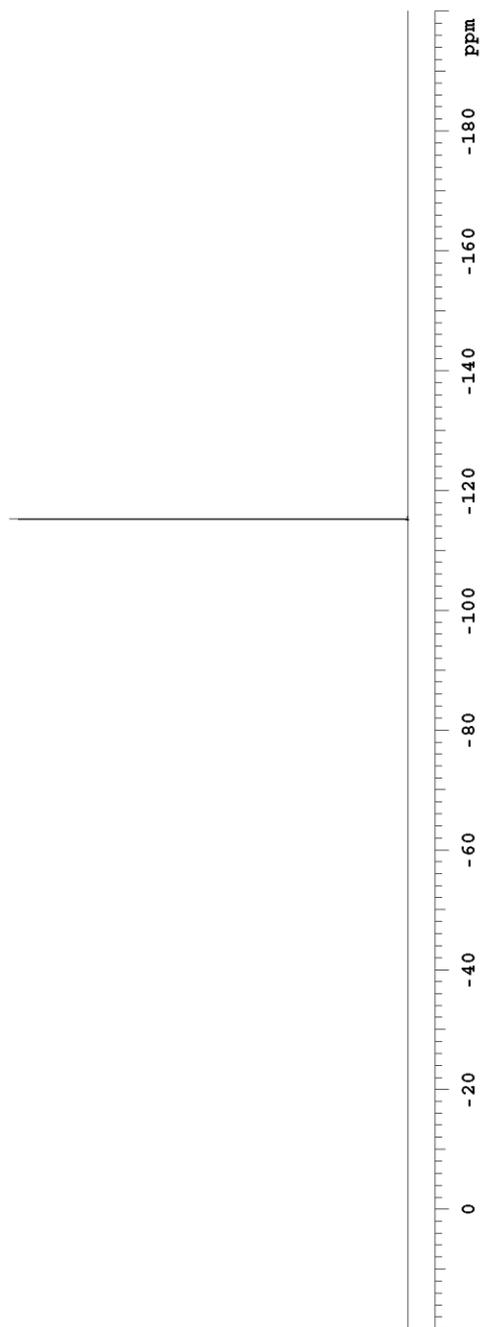
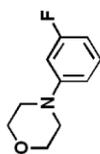


$^{19}\text{F}$  NMR (CDCl<sub>3</sub>, 23 °C) of **4**

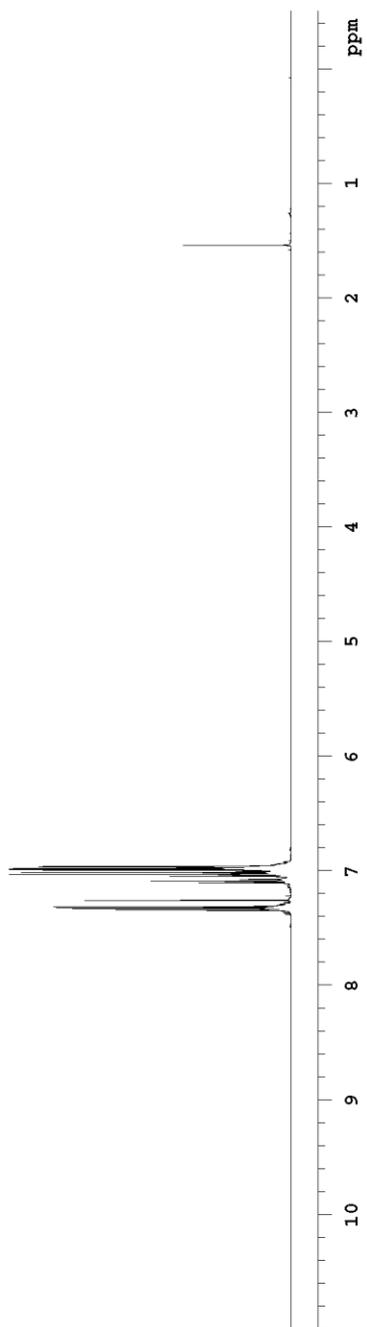
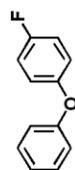


$^1\text{H}$  NMR (CDCl<sub>3</sub>, 23 °C) of **5**

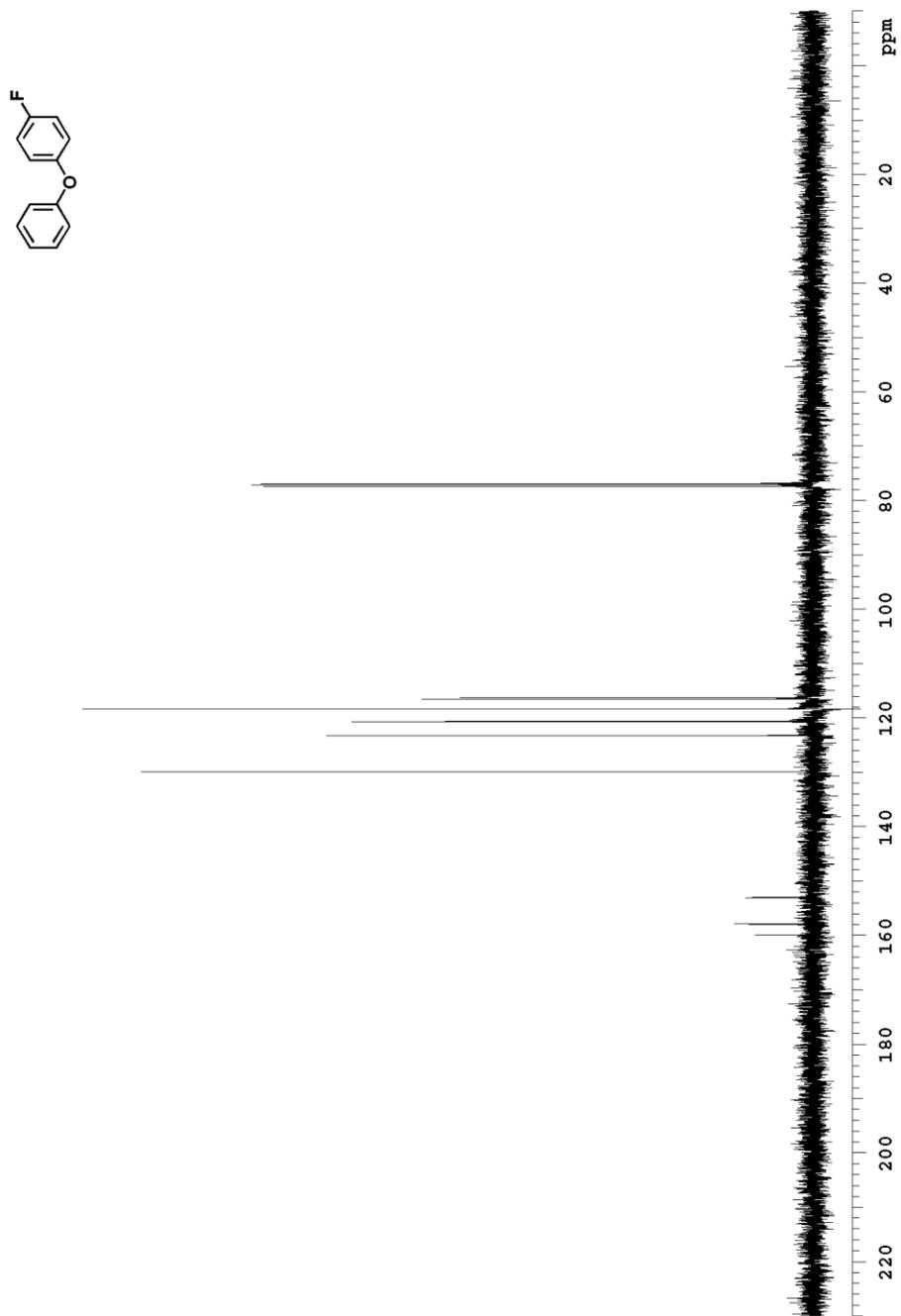
 $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 23 °C) of **5**



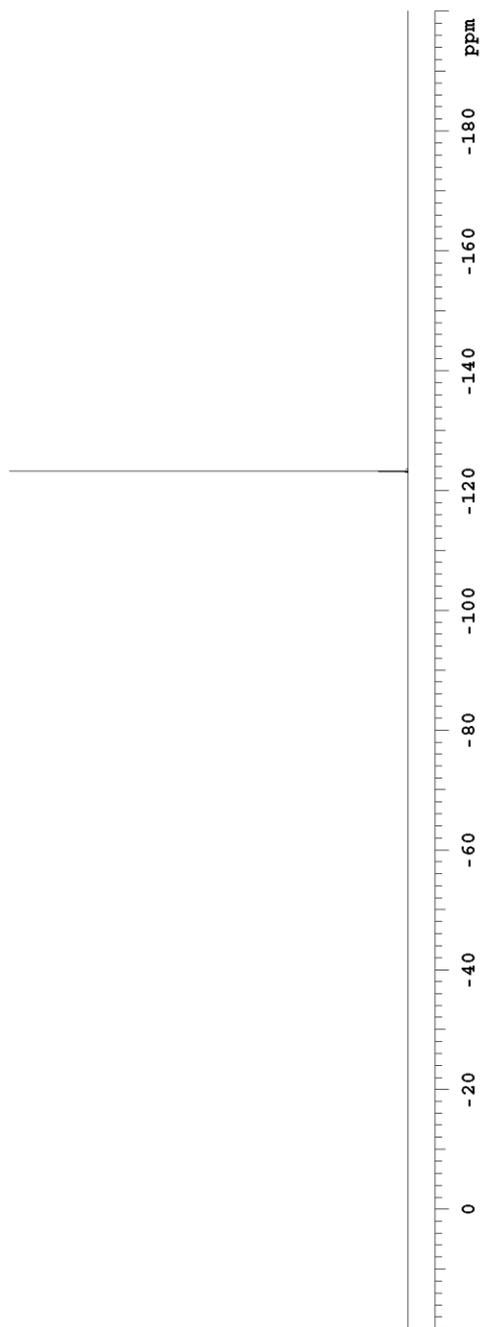
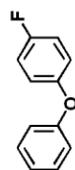
$^{19}\text{F}$  NMR ( $\text{CDCl}_3$ , 23 °C) of **5**



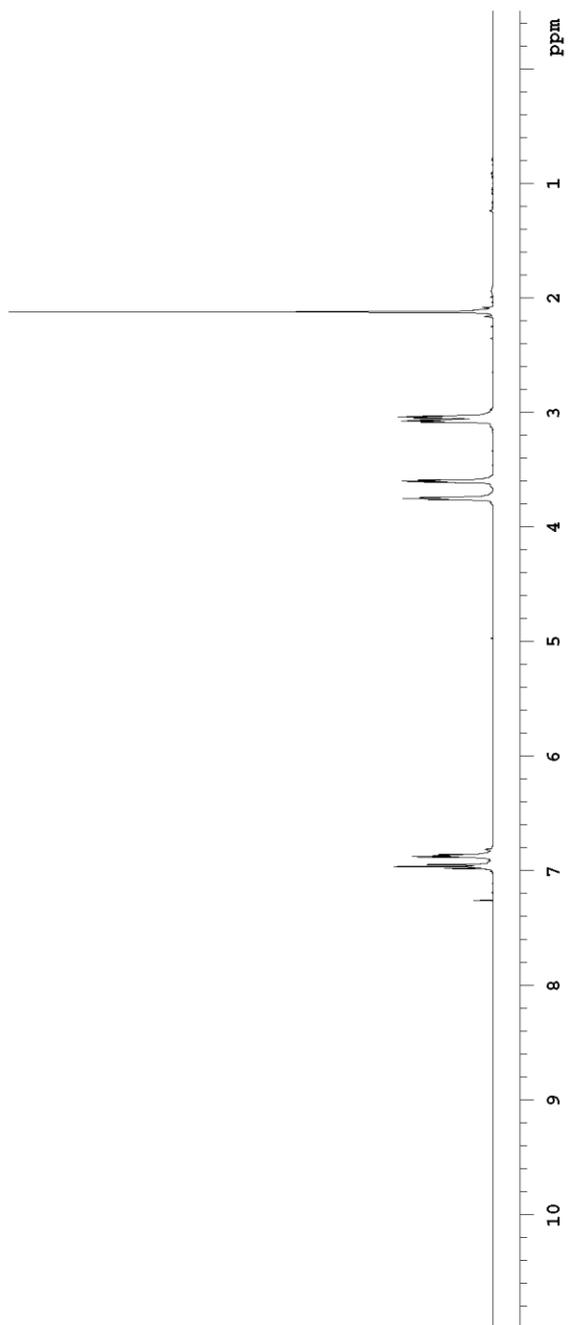
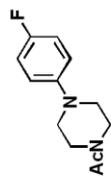
$^1\text{H}$  NMR (CDCl<sub>3</sub>, 23 °C) of **6**



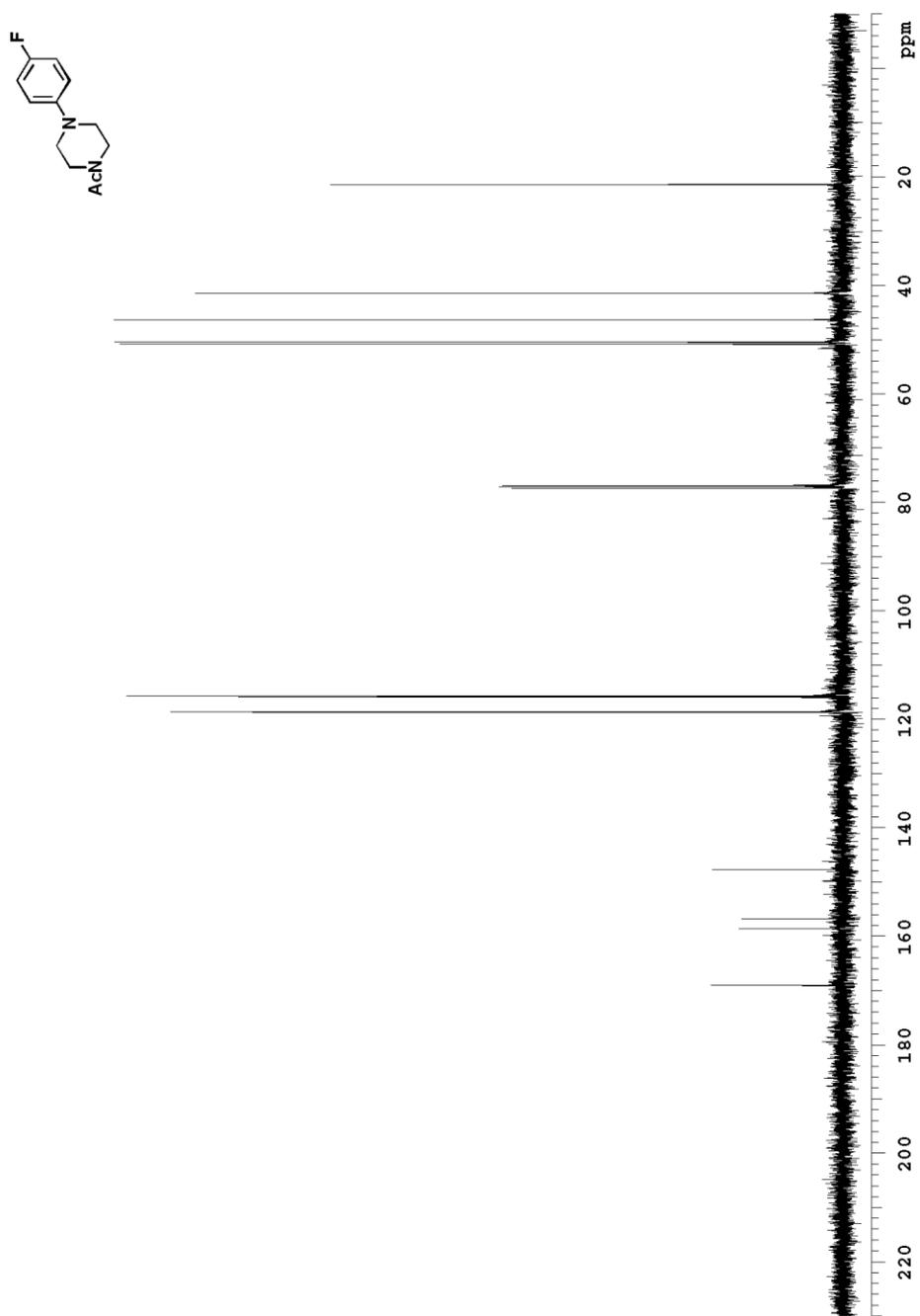
$^{13}\text{C}$  NMR (CDCl<sub>3</sub>, 23 °C) of **6**

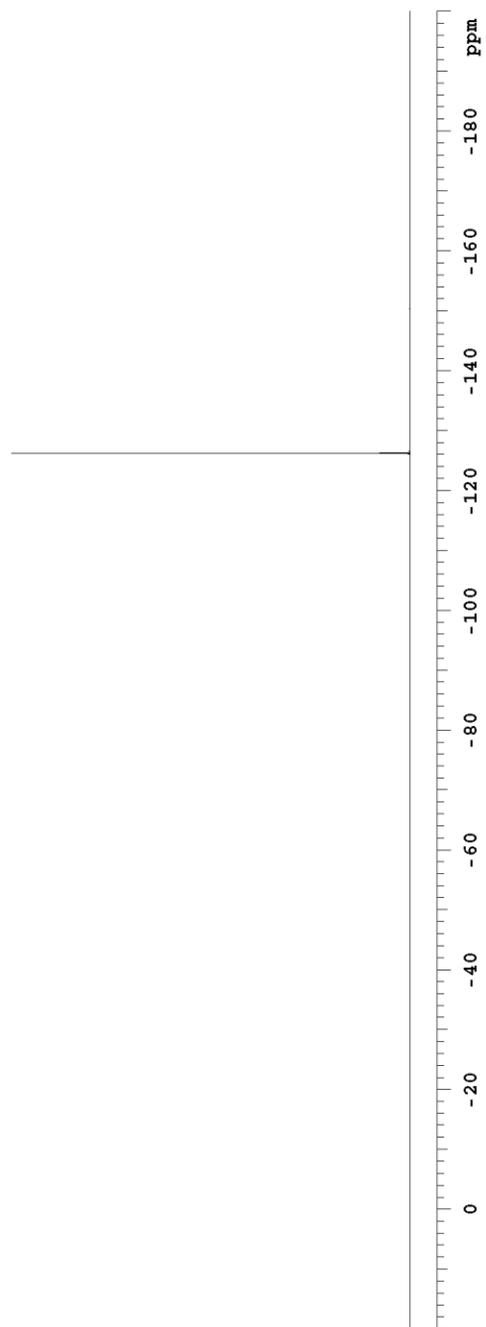
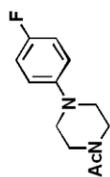


$^{19}\text{F}$  NMR ( $\text{CDCl}_3$ , 23 °C) of **6**

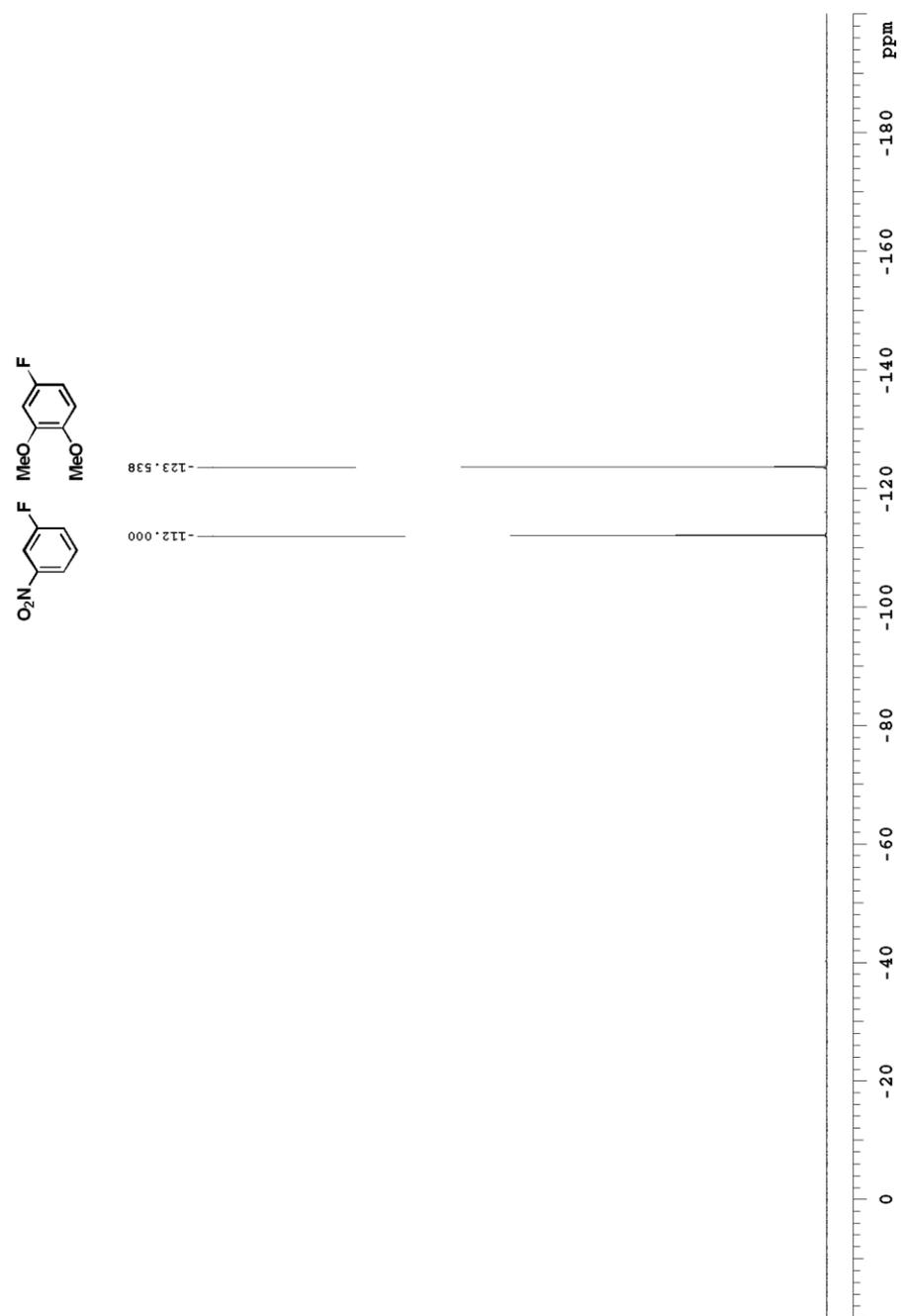


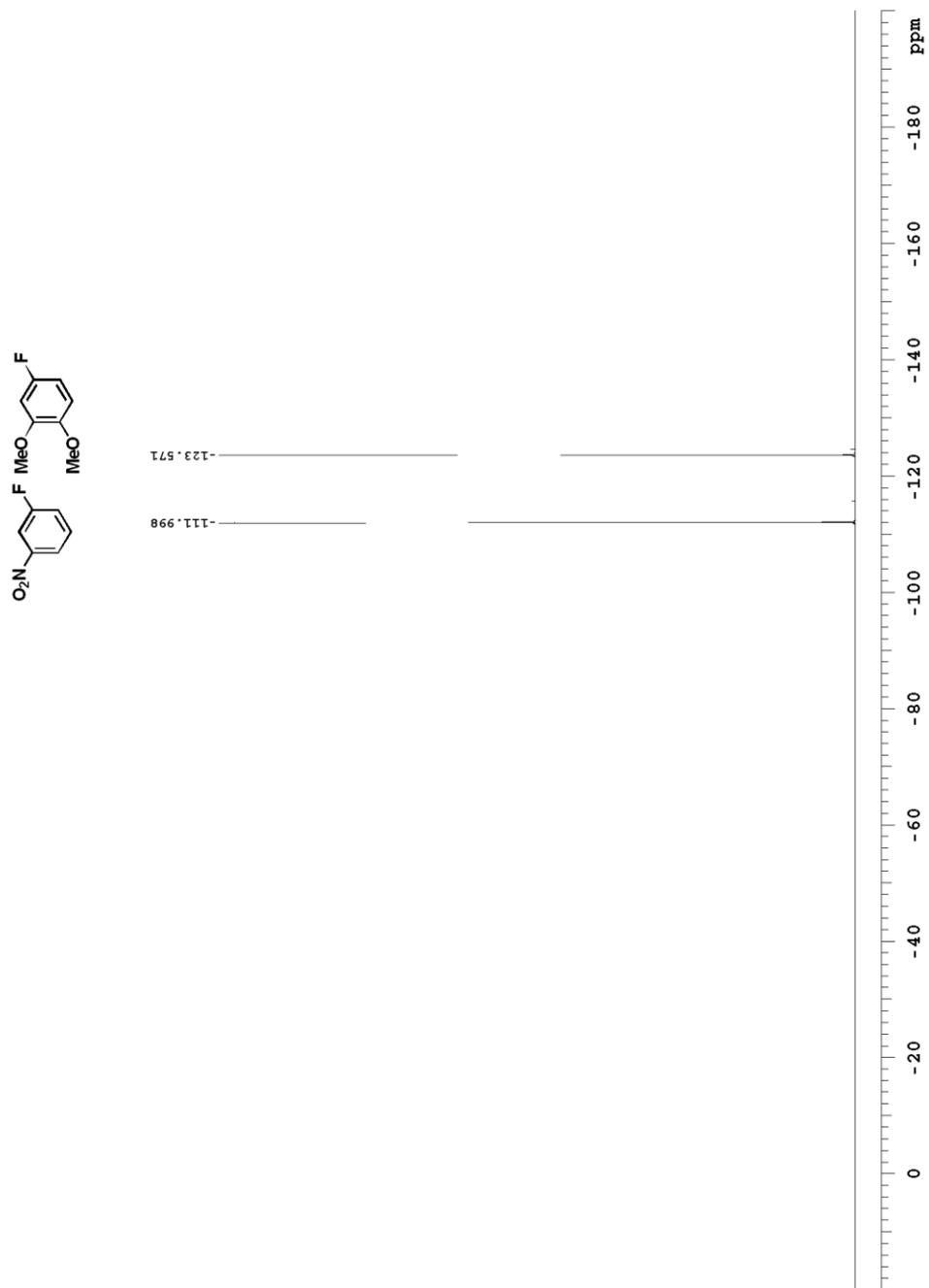
$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 23 °C) of **7**

 $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ,  $23\text{ }^\circ\text{C}$ ) of **7**

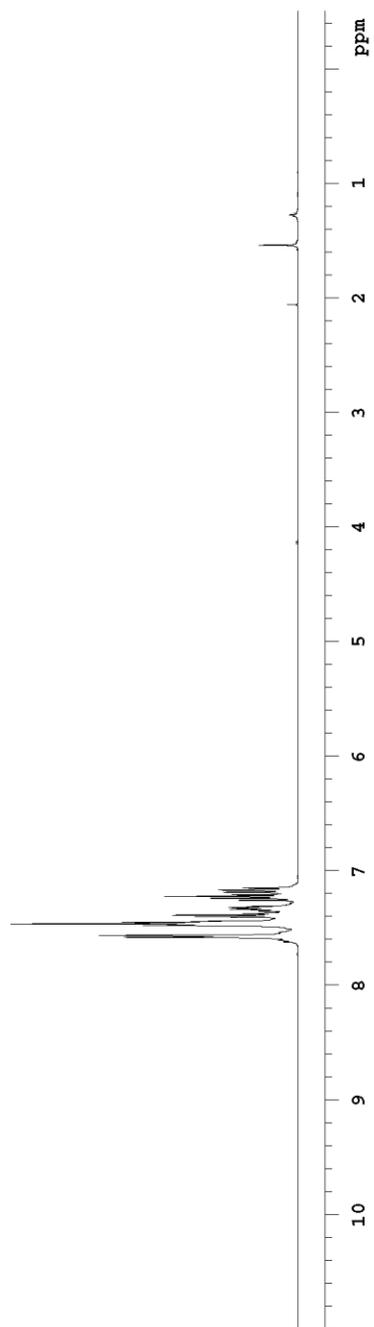
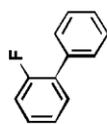


$^{19}\text{F}$  NMR ( $\text{CDCl}_3$ , 23 °C) of **7**

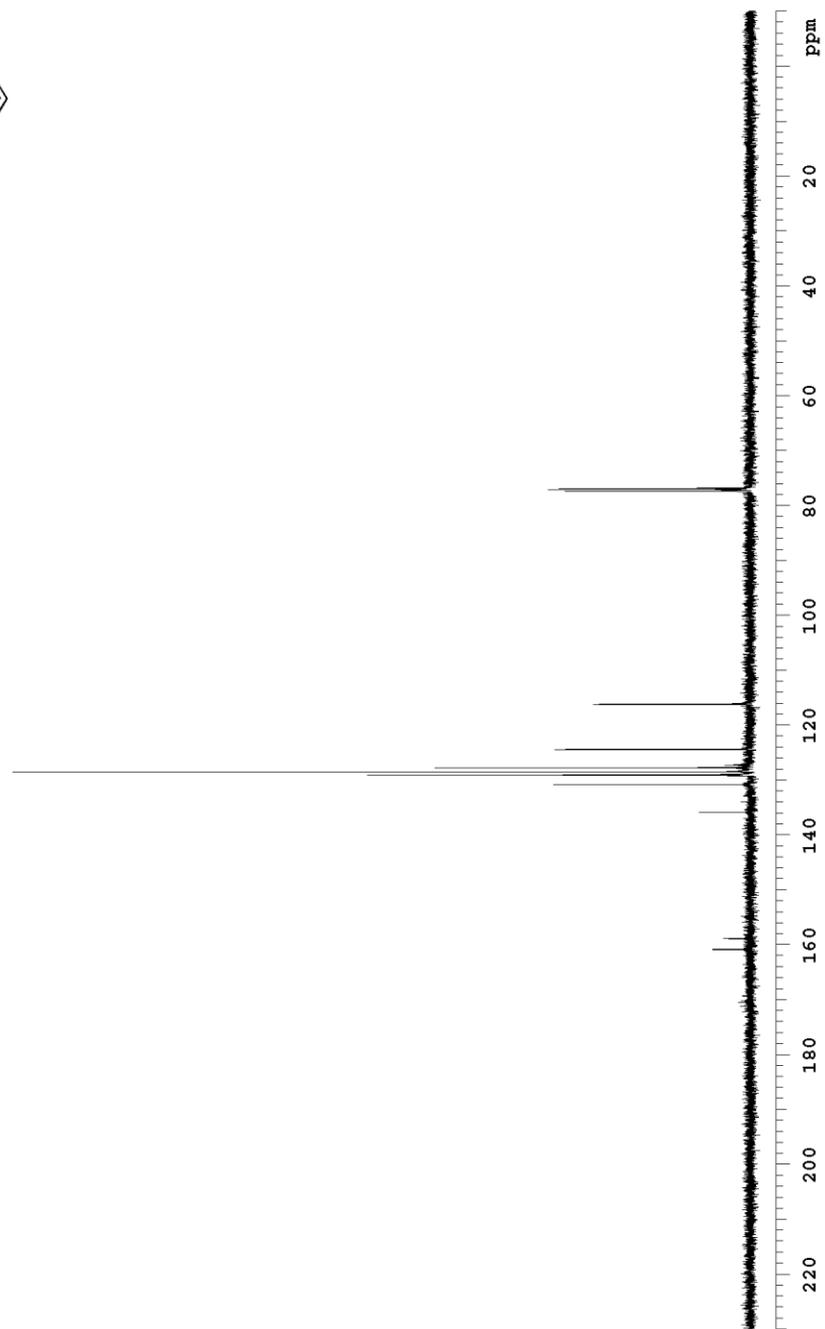
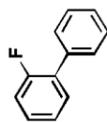
 $^{19}\text{F}$  NMR (xylene, 23 °C) of **8**



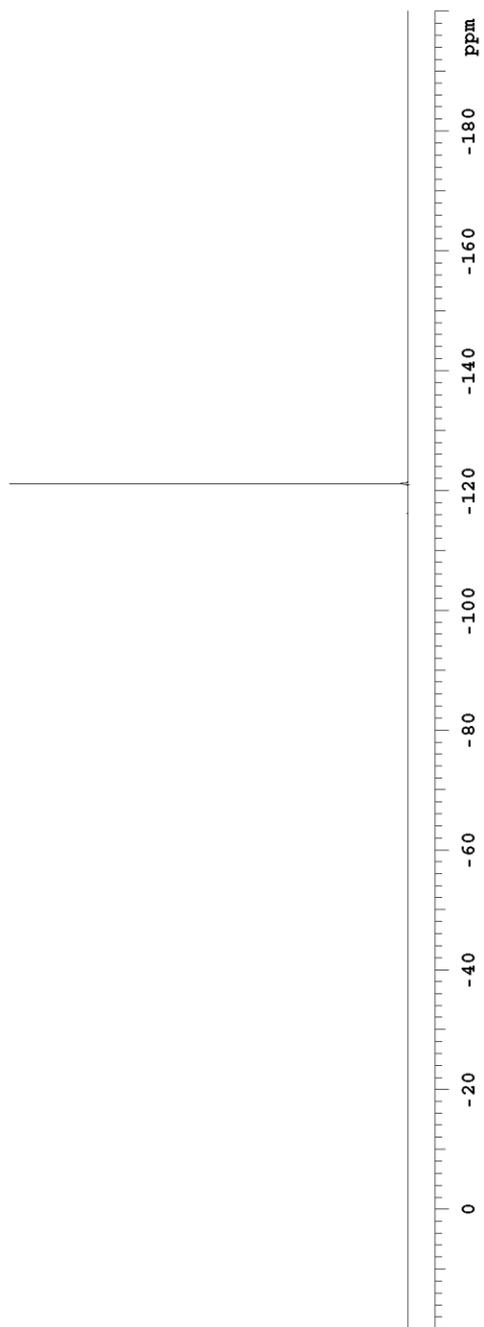
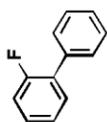
$^{19}\text{F}$  NMR (xylene, 23 °C) of commercial sample **8**



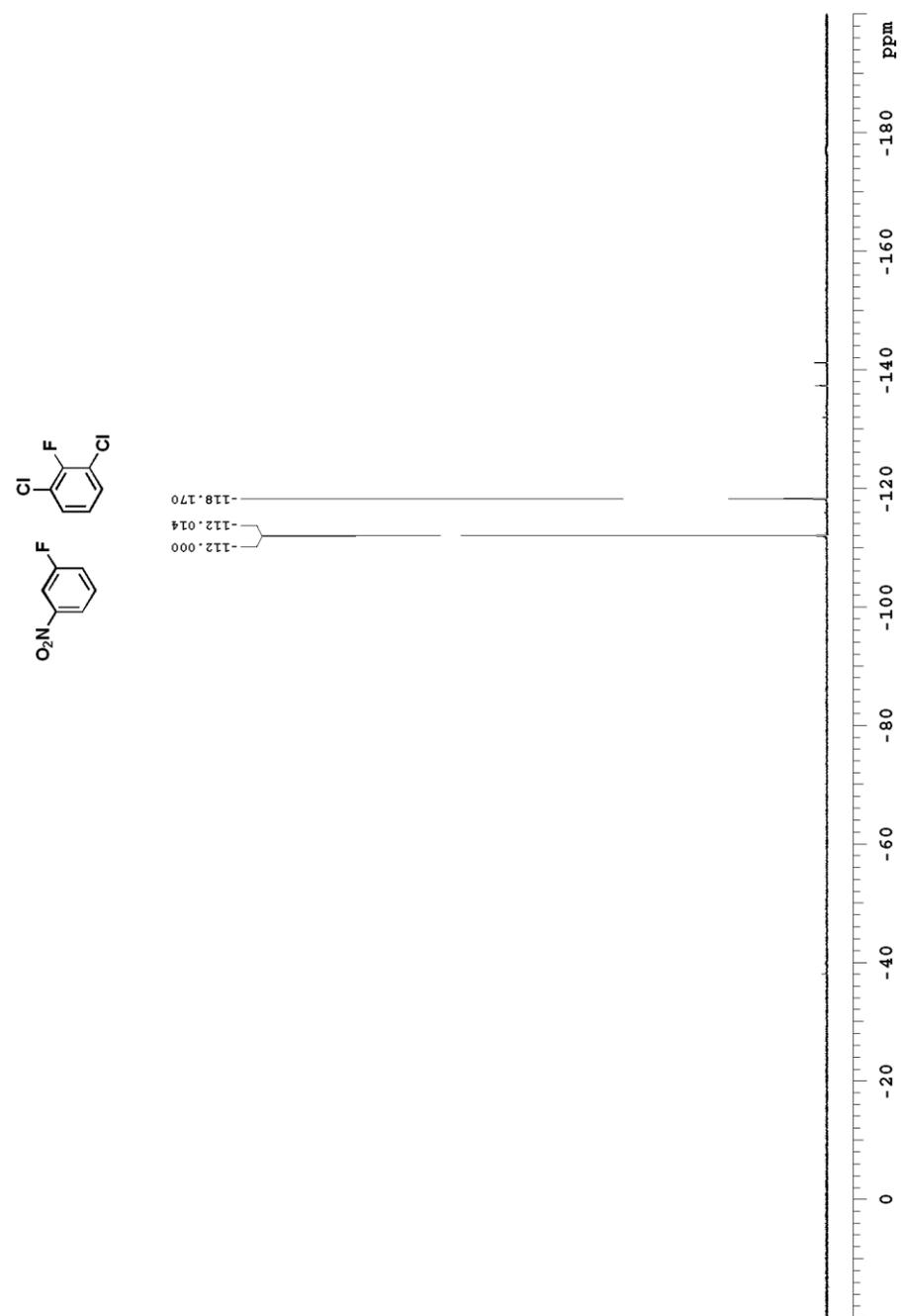
$^1\text{H}$  NMR (CDCl<sub>3</sub>, 23 °C) of **9**

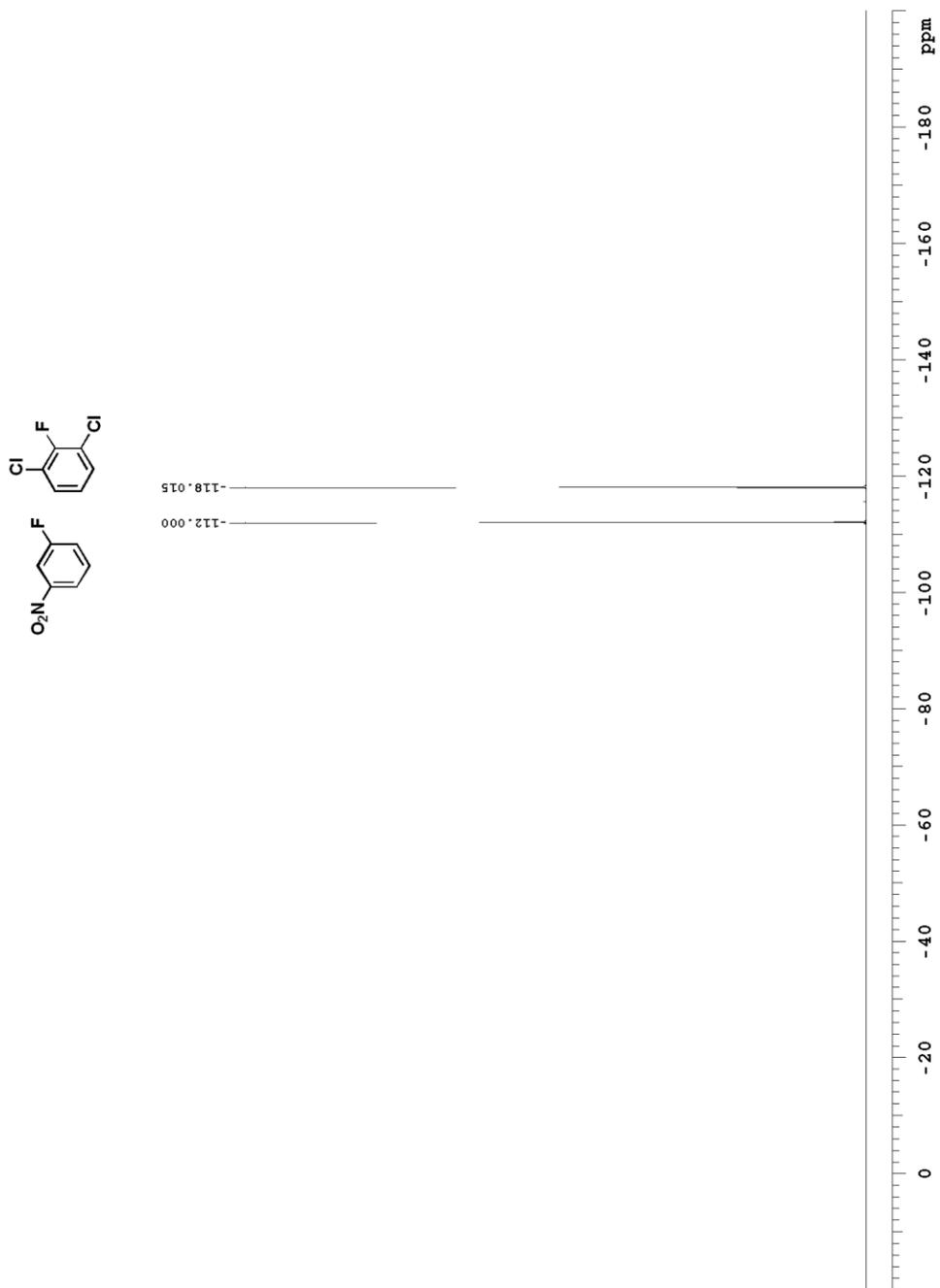


$^{13}\text{C}$  NMR (CDCl<sub>3</sub>, 23 °C) of **9**

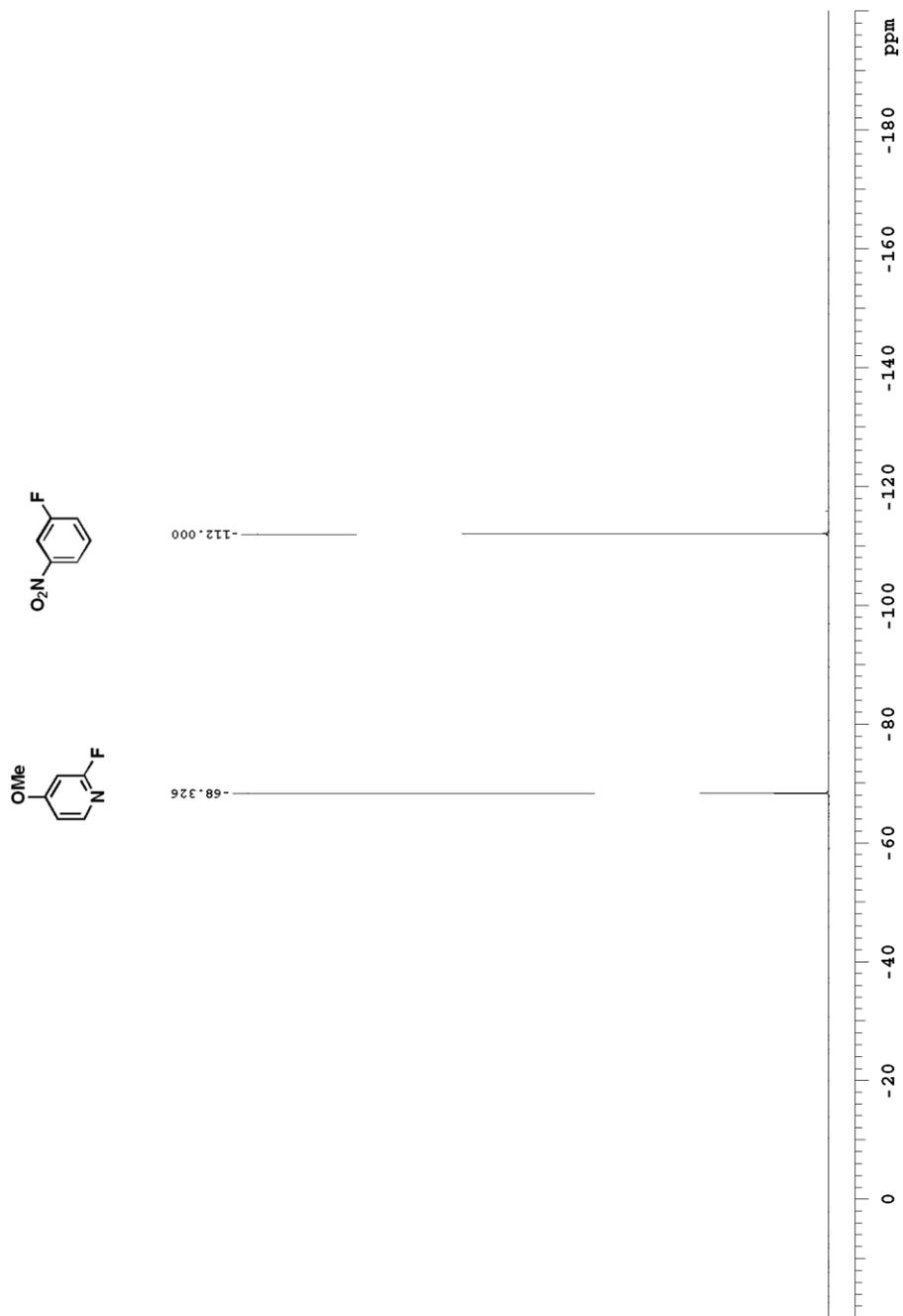


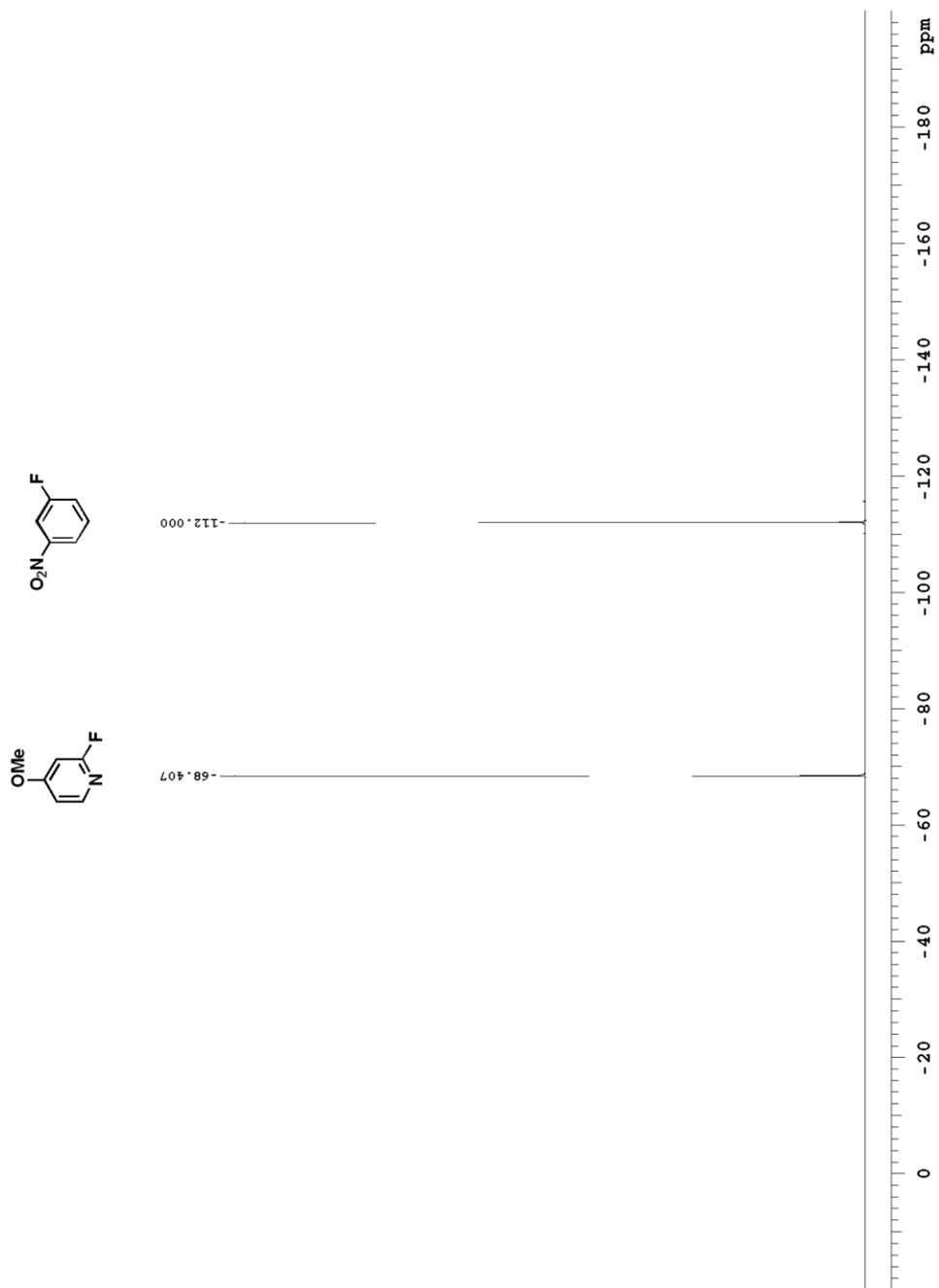
$^{19}\text{F}$  NMR ( $\text{CDCl}_3$ , 23 °C) of **9**

 $^{19}\text{F}$  NMR (xylene, 23 °C) of **10**

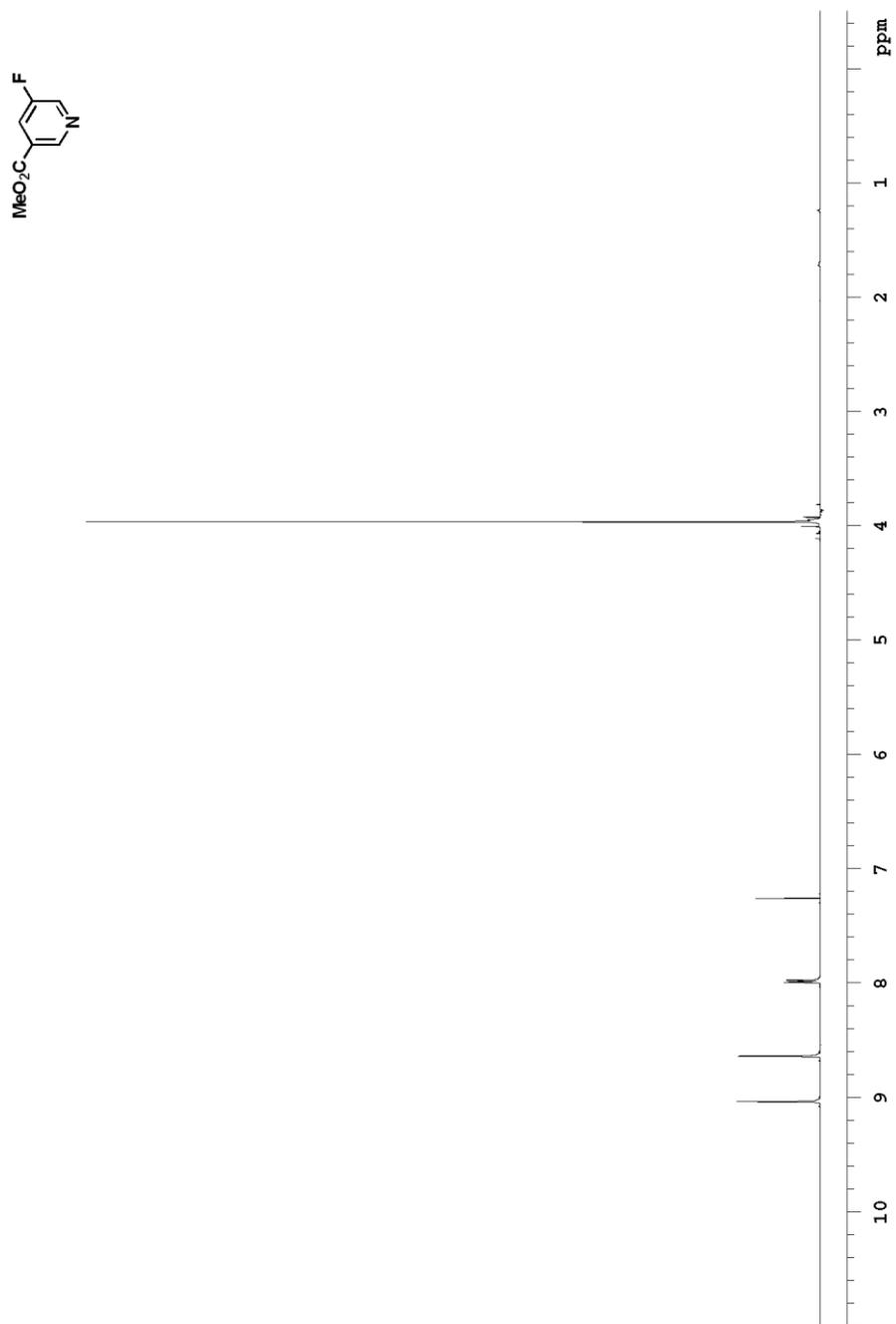


$^{19}\text{F}$  NMR (xylene, 23 °C) of commercial sample **10**

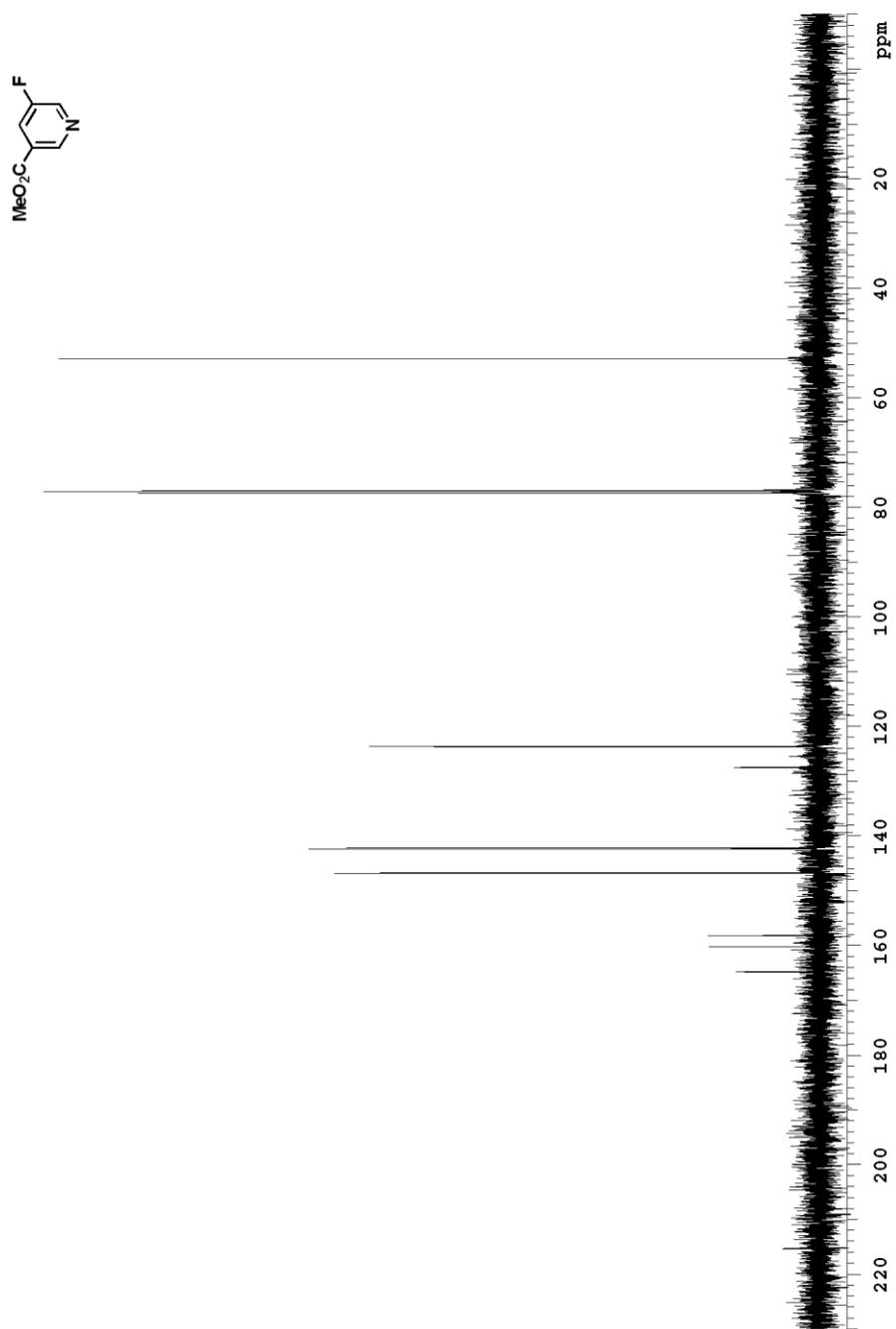
 $^{19}\text{F}$  NMR (xylene, 23 °C) of **11**

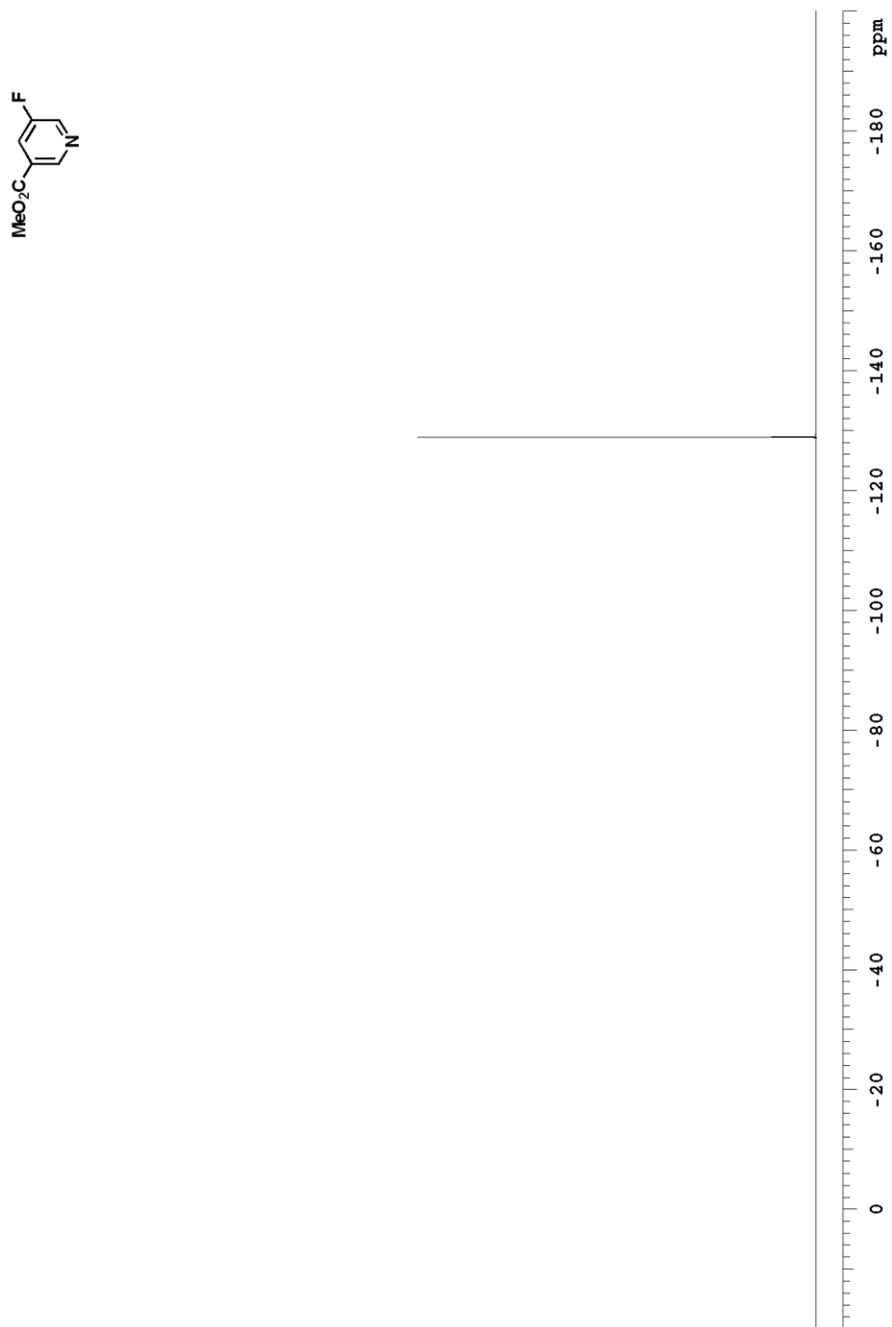


$^{19}\text{F}$  NMR (xylene, 23 °C) of commercial sample **11**

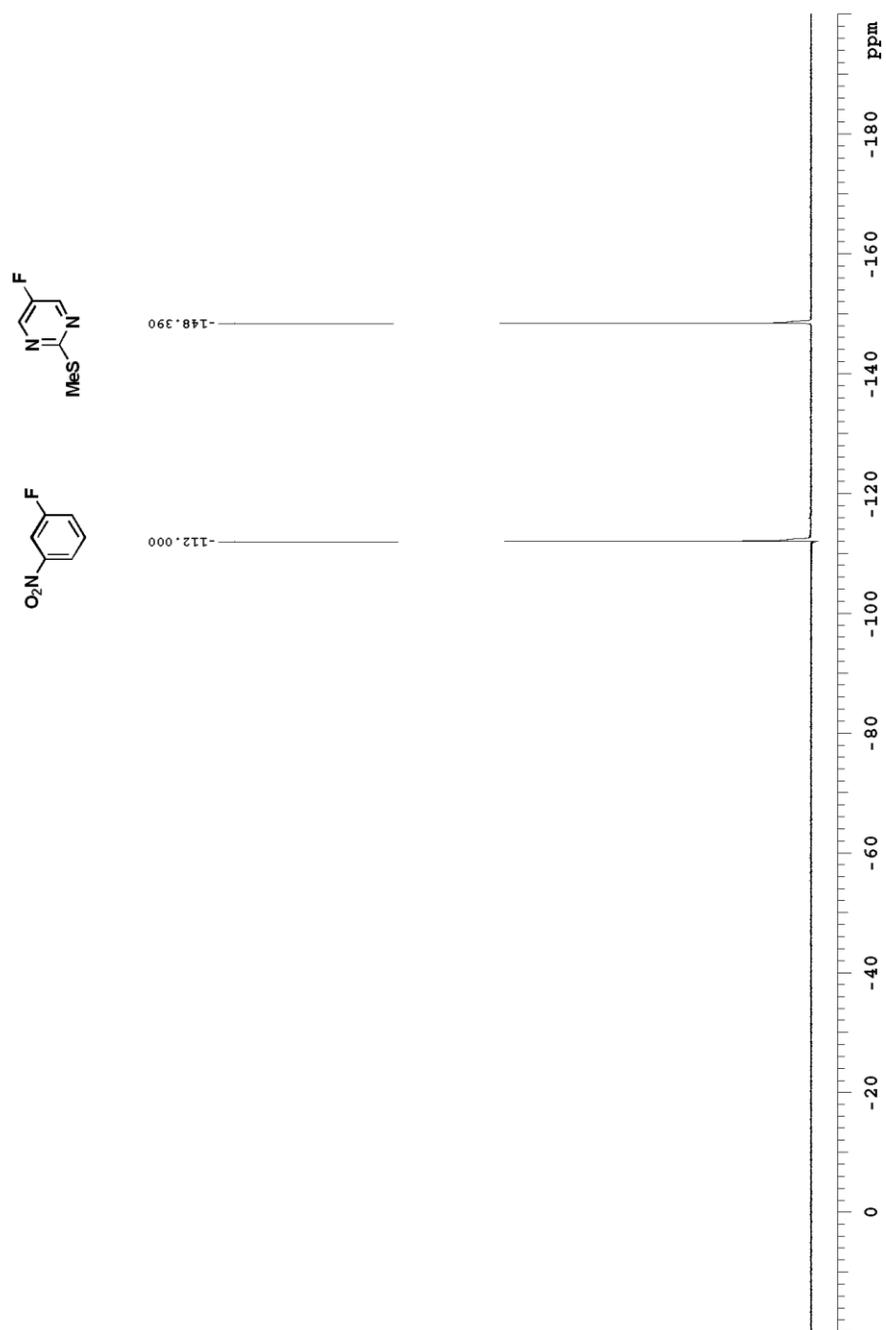


$^1\text{H NMR}$  (CDCl<sub>3</sub>, 23 °C) of **12**

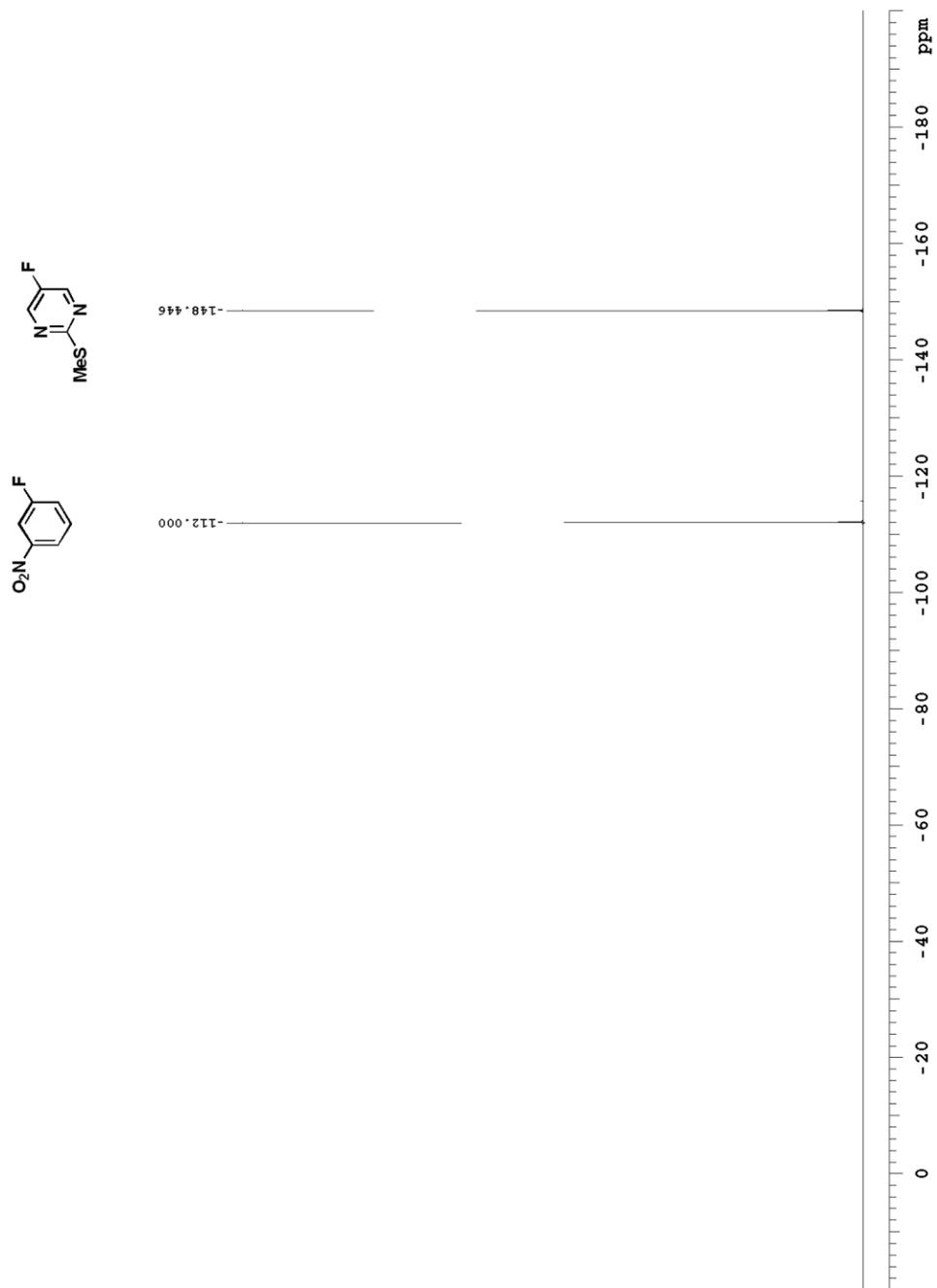
 $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ,  $23^\circ\text{C}$ ) of **12**



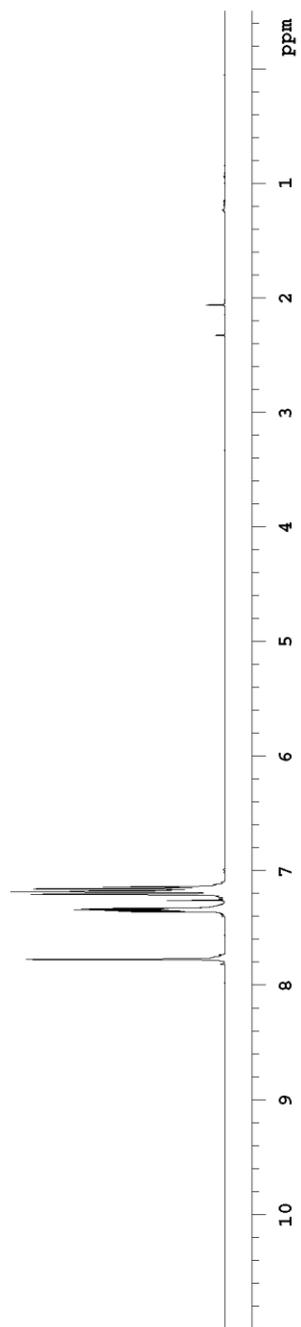
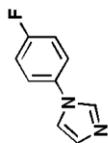
<sup>19</sup>F NMR (CDCl<sub>3</sub>, 23 °C) of **12**



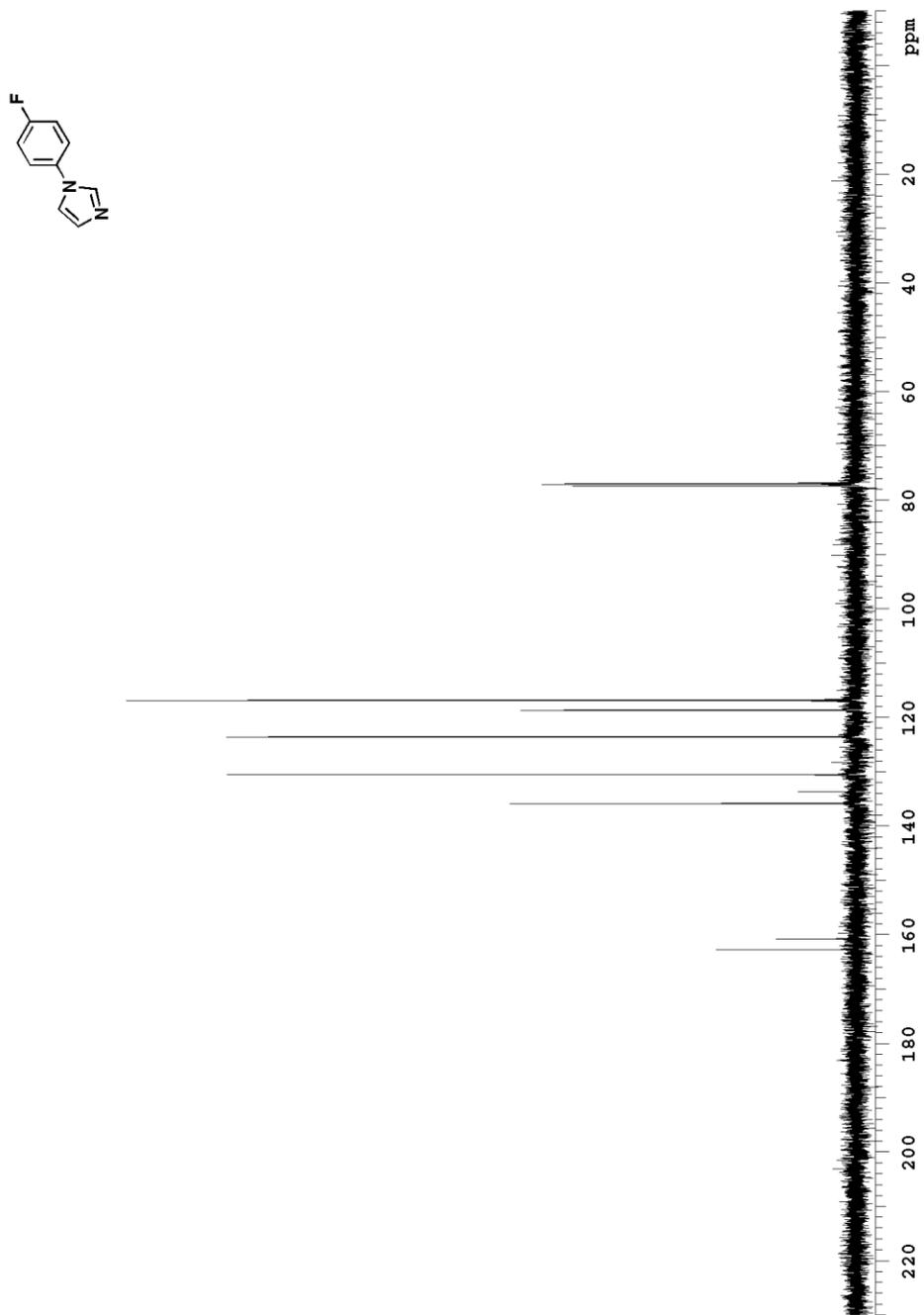
$^{19}\text{F}$  NMR (toluene, 23 °C) of **13**



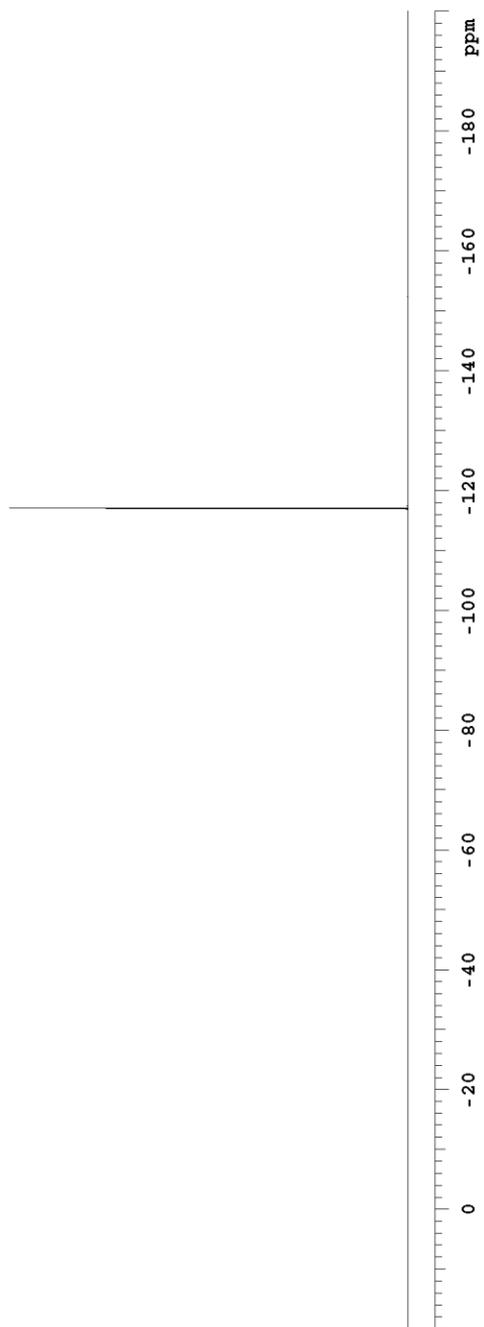
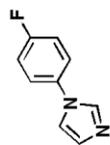
$^{19}\text{F}$  NMR (toluene, 23 °C) of commercial sample 13



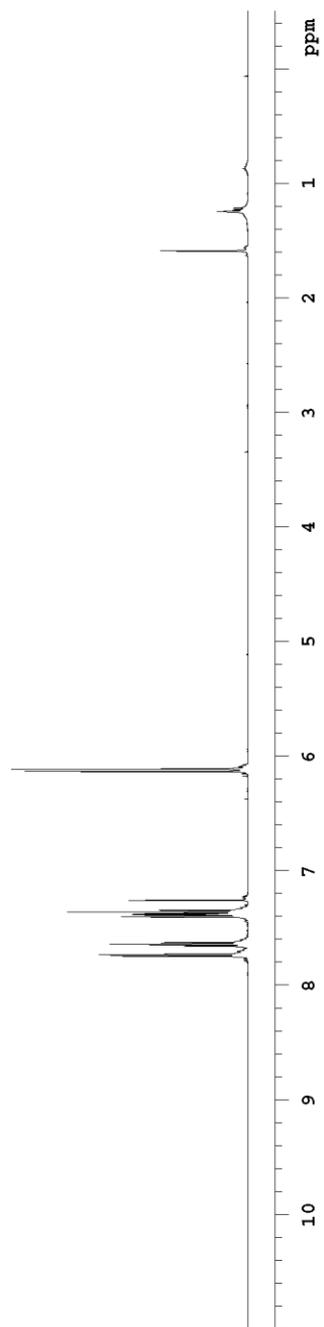
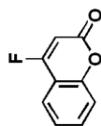
$^1\text{H}$  NMR (CDCl<sub>3</sub>, 23 °C) of **14**



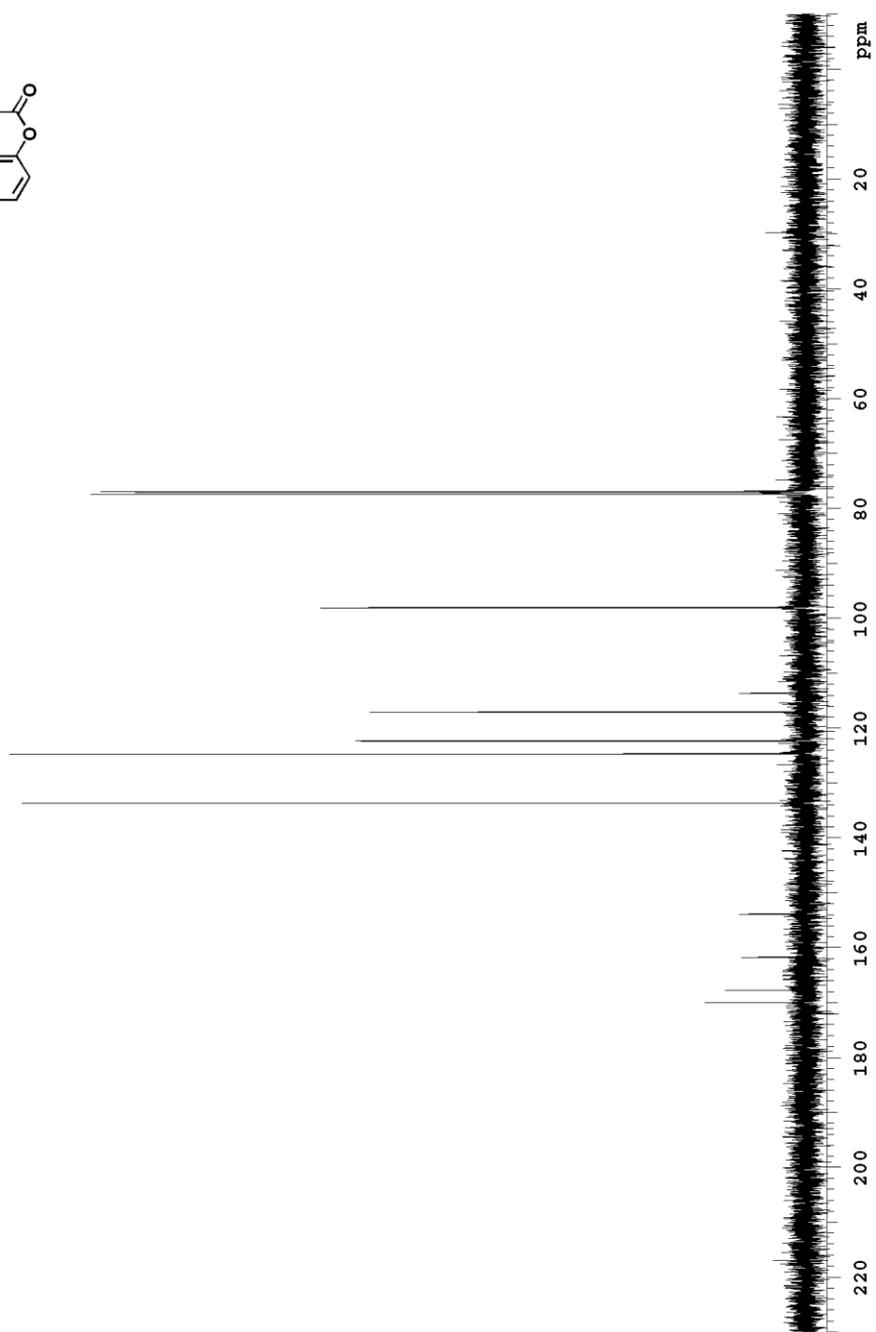
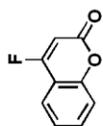
$^{13}\text{C}$  NMR (CDCl<sub>3</sub>, 23 °C) of 14



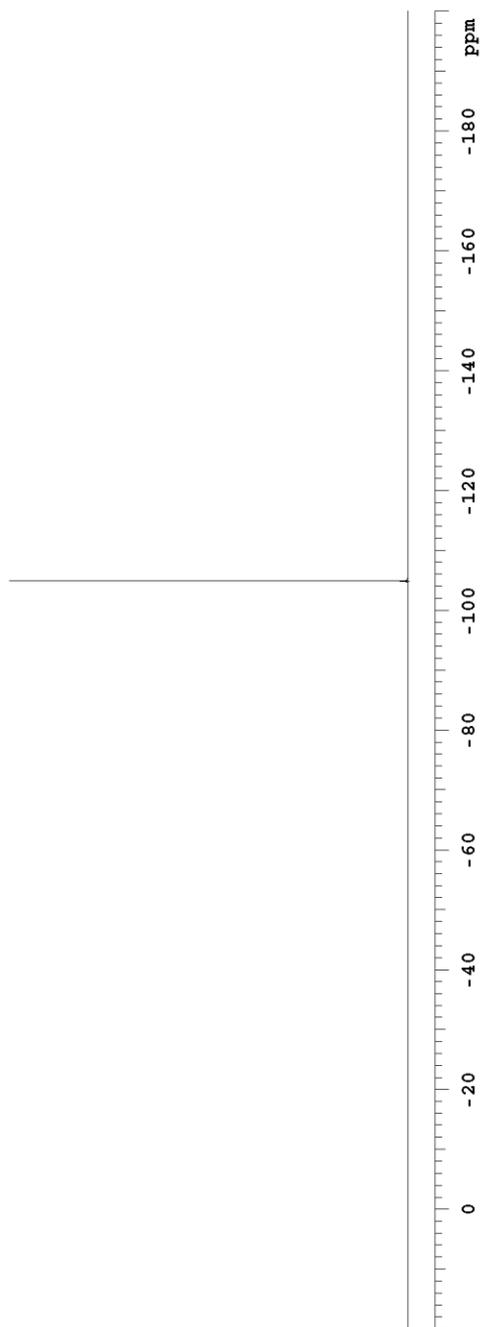
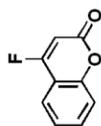
$^{19}\text{F}$  NMR ( $\text{CDCl}_3$ , 23 °C) of **14**



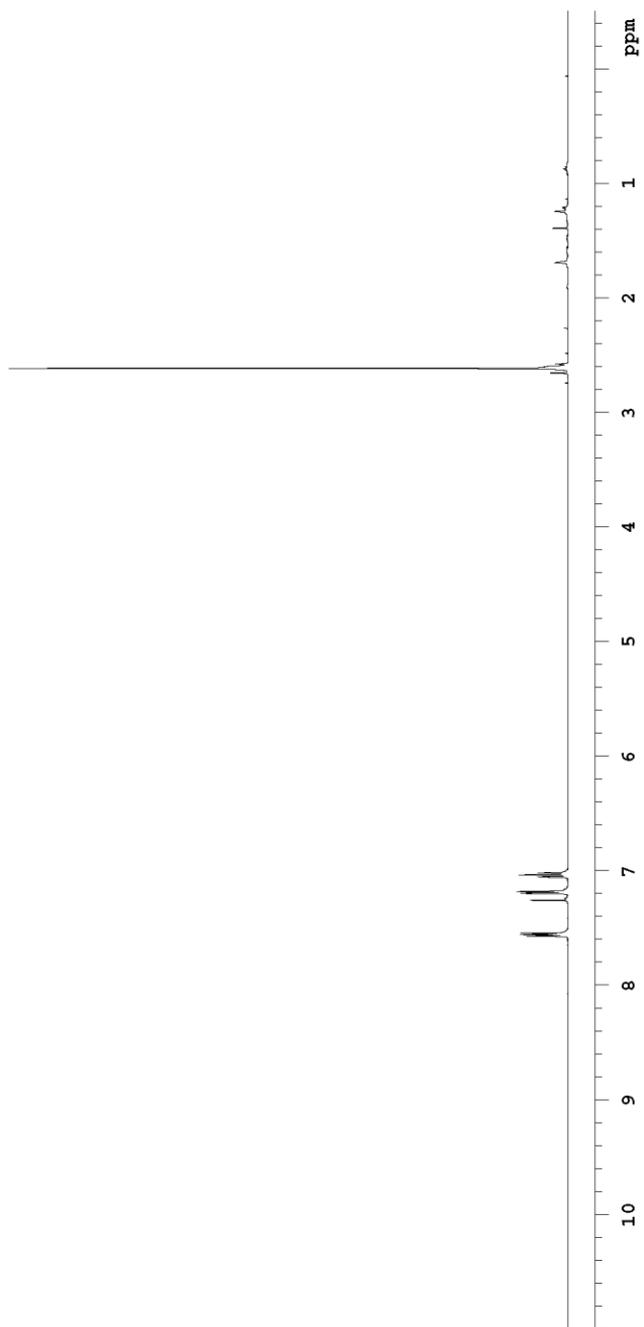
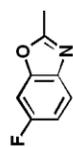
$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 23 °C) of **15**



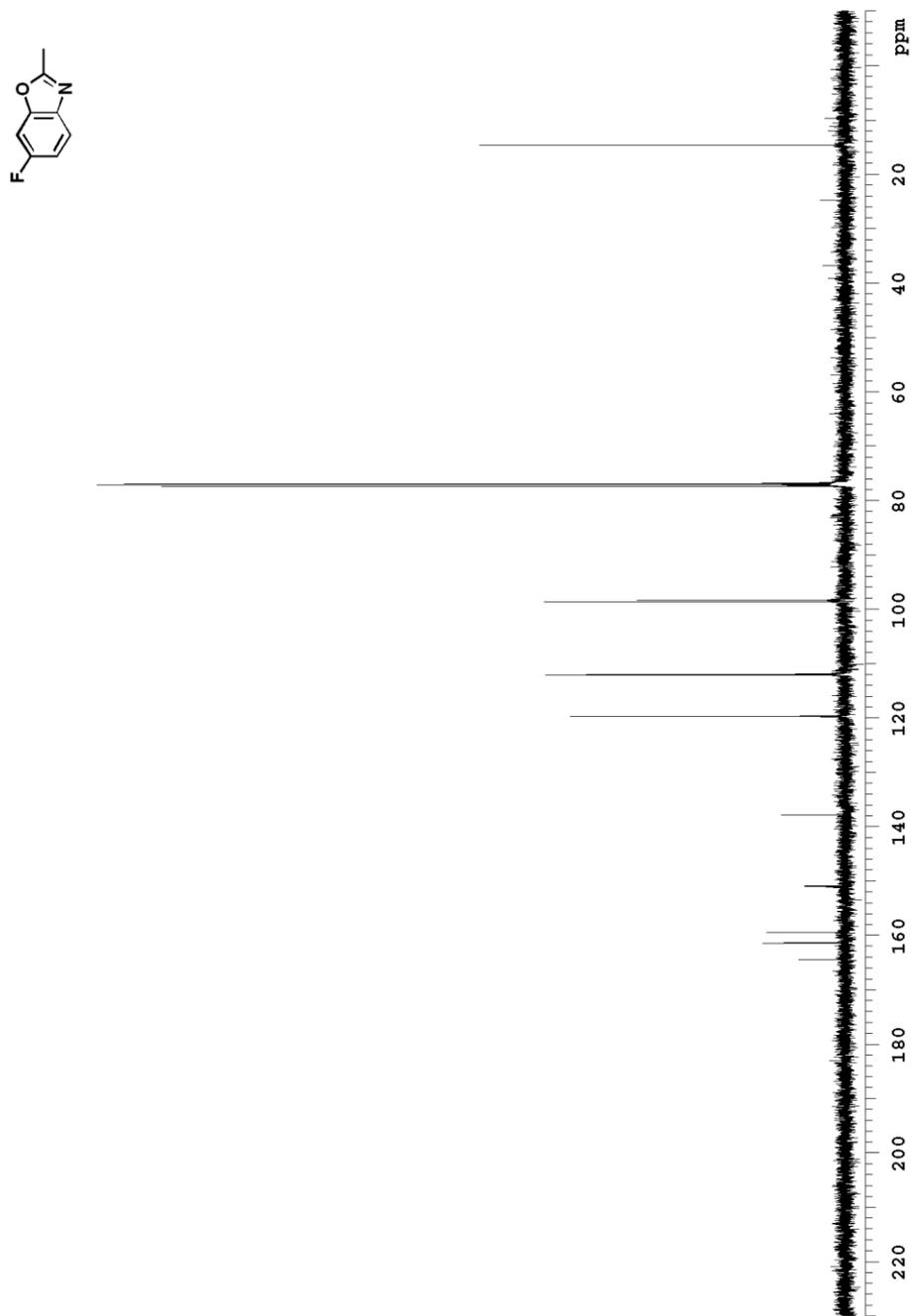
$^{13}\text{C}$  NMR (CDCl<sub>3</sub>, 23 °C) of **15**



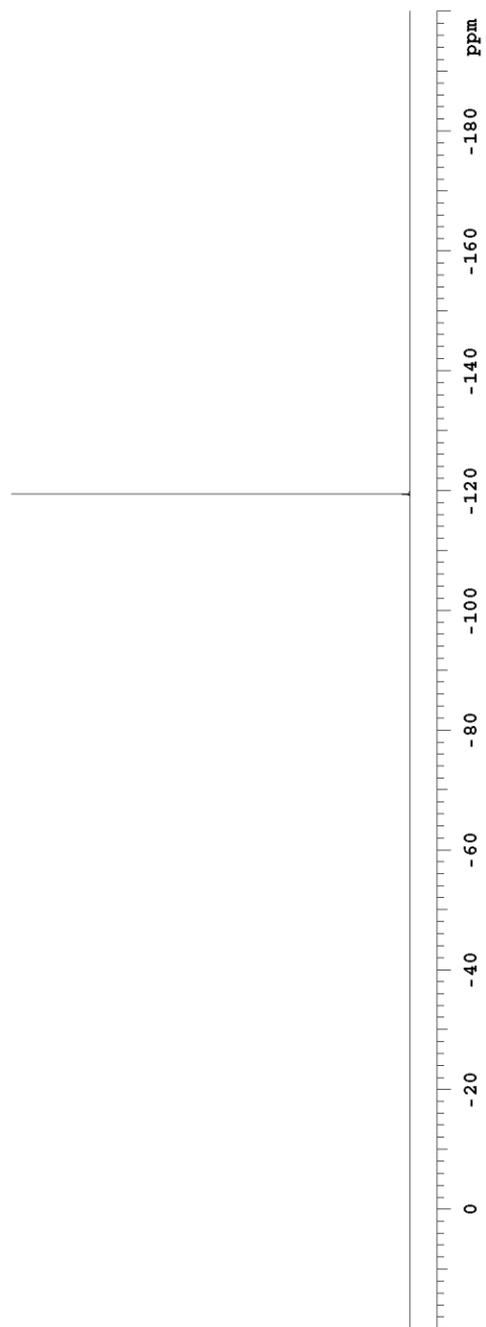
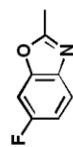
$^{19}\text{F}$  NMR ( $\text{CDCl}_3$ , 23 °C) of **15**



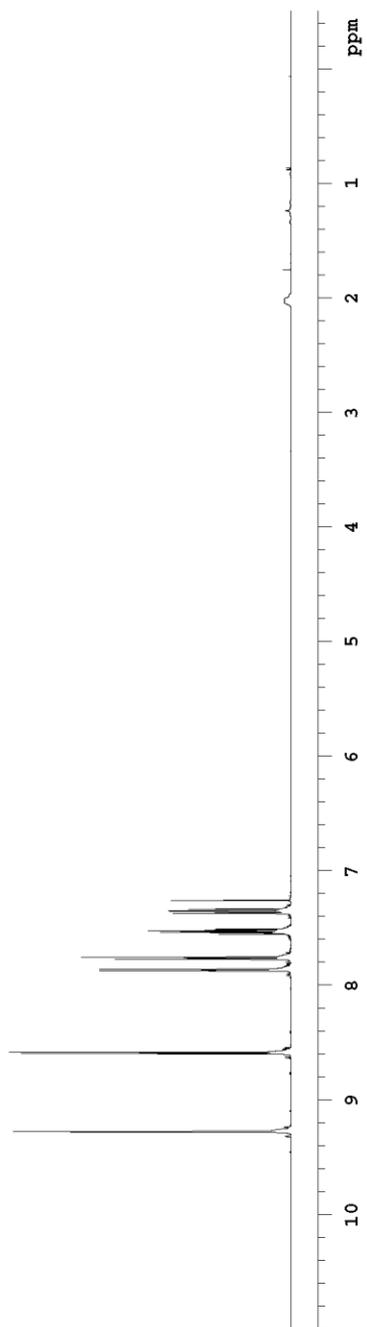
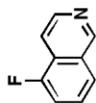
$^1\text{H}$  NMR (CDCl<sub>3</sub>, 23 °C) of **16**



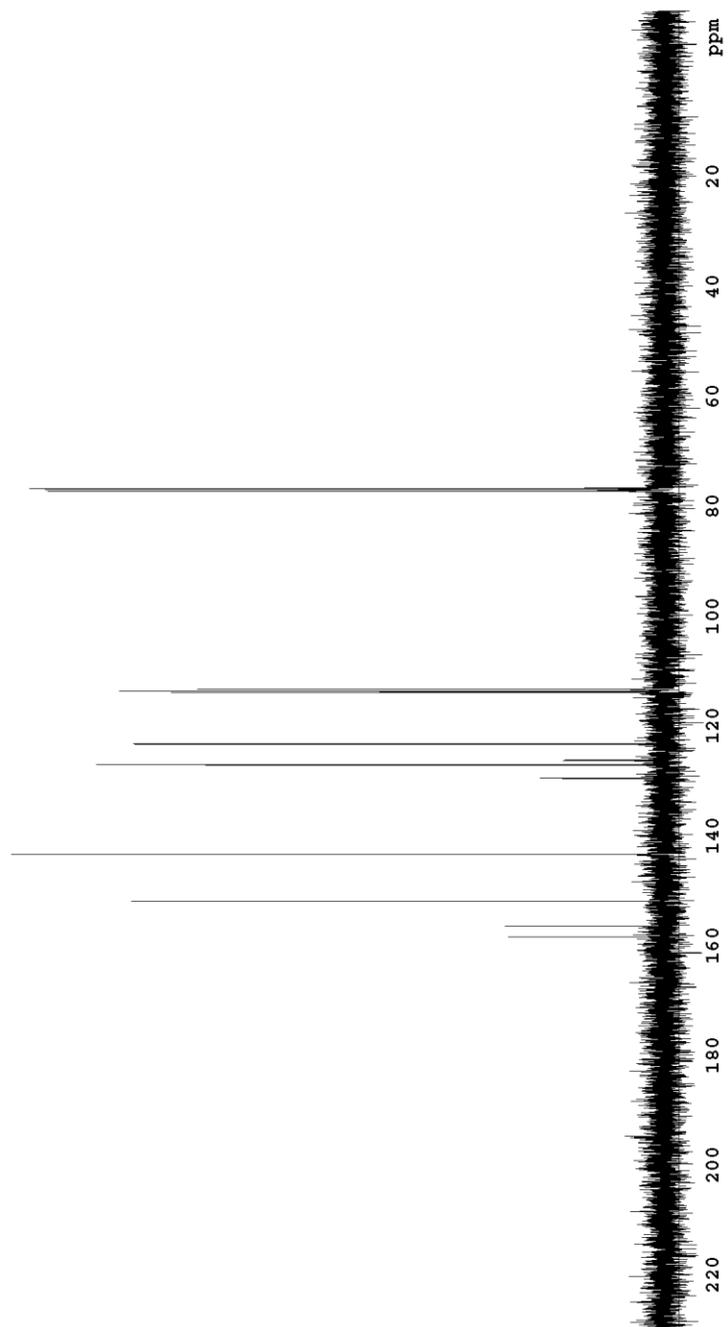
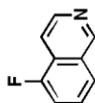
$^{13}\text{C}$  NMR (CDCl<sub>3</sub>, 23 °C) of **16**



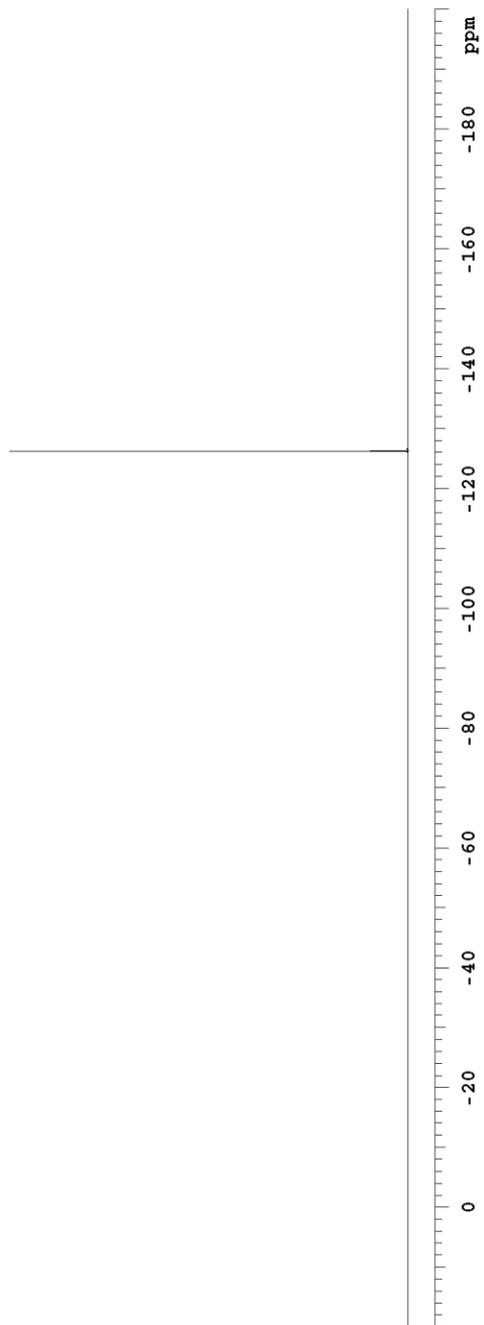
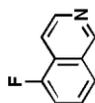
$^{19}\text{F}$  NMR ( $\text{CDCl}_3$ , 23 °C) of **16**



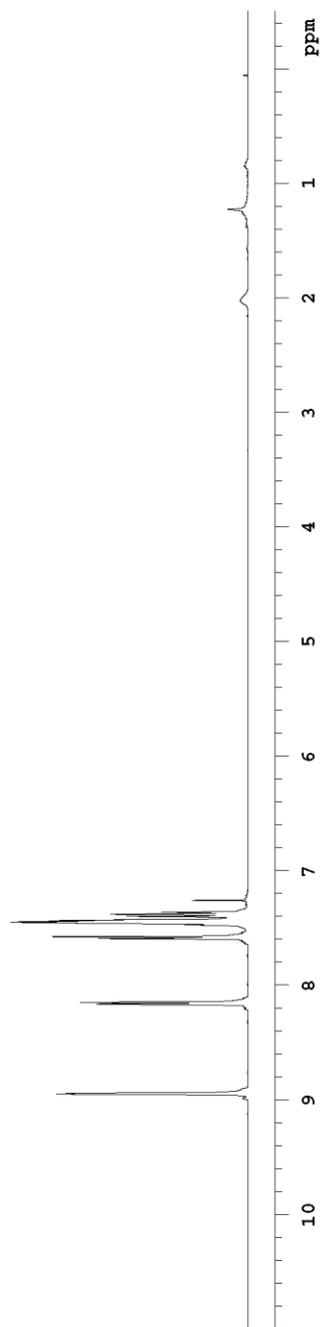
$^1\text{H}$  NMR (CDCl<sub>3</sub>, 23 °C) of **17**



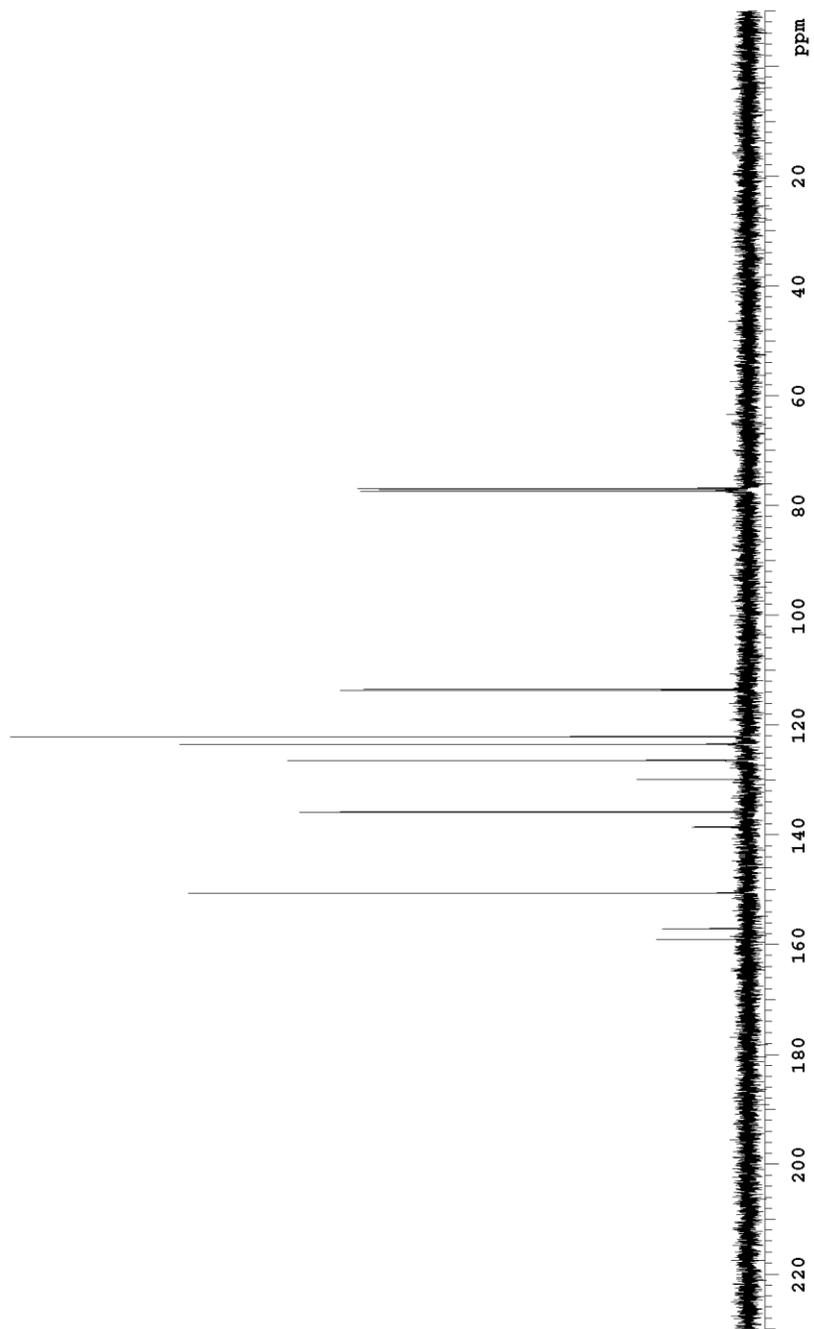
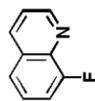
$^{13}\text{C}$  NMR (CDCl<sub>3</sub>, 23 °C) of **17**



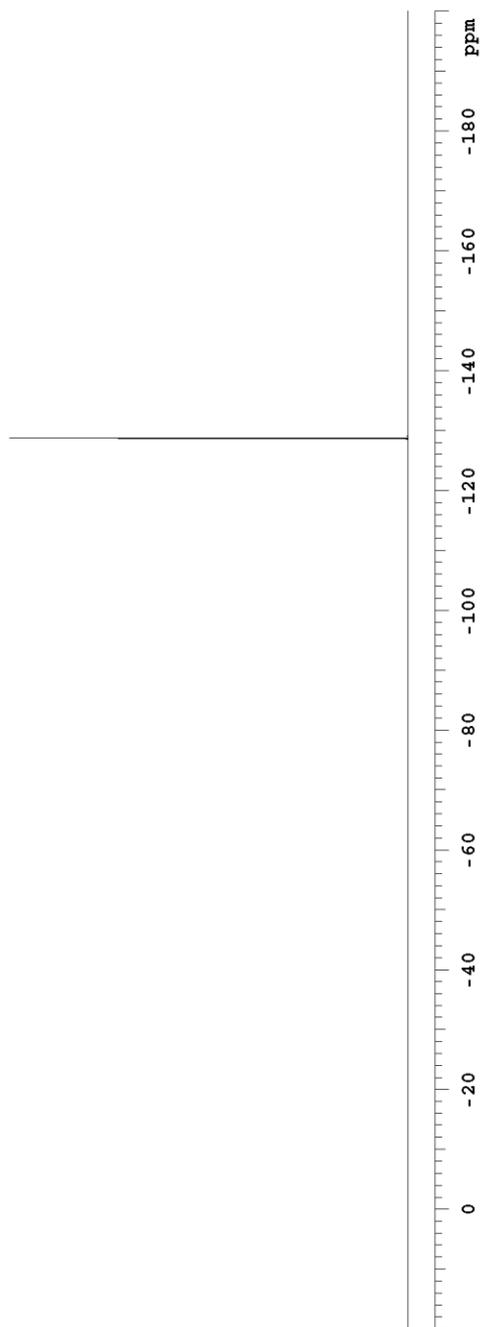
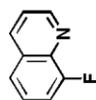
$^{19}\text{F}$  NMR ( $\text{CDCl}_3$ , 23 °C) of **17**



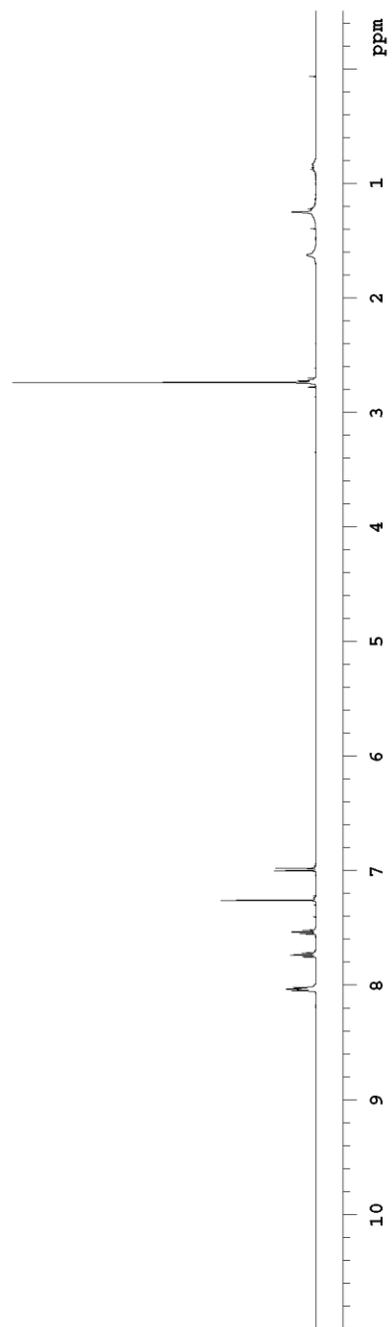
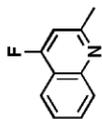
$^1\text{H}$  NMR (CDCl<sub>3</sub>, 23 °C) of **18**



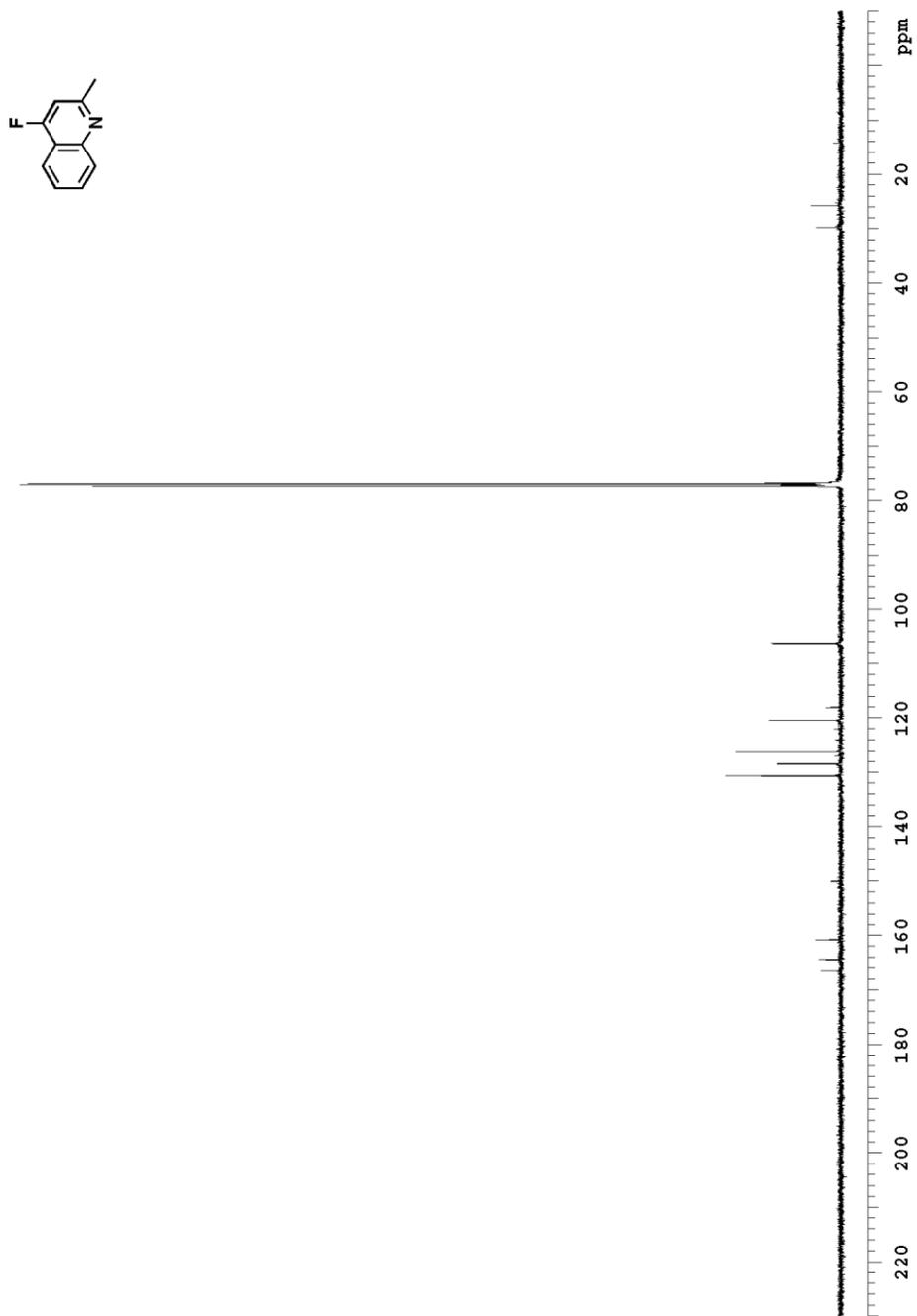
$^{13}\text{C}$  NMR (CDCl<sub>3</sub>, 23 °C) of **18**

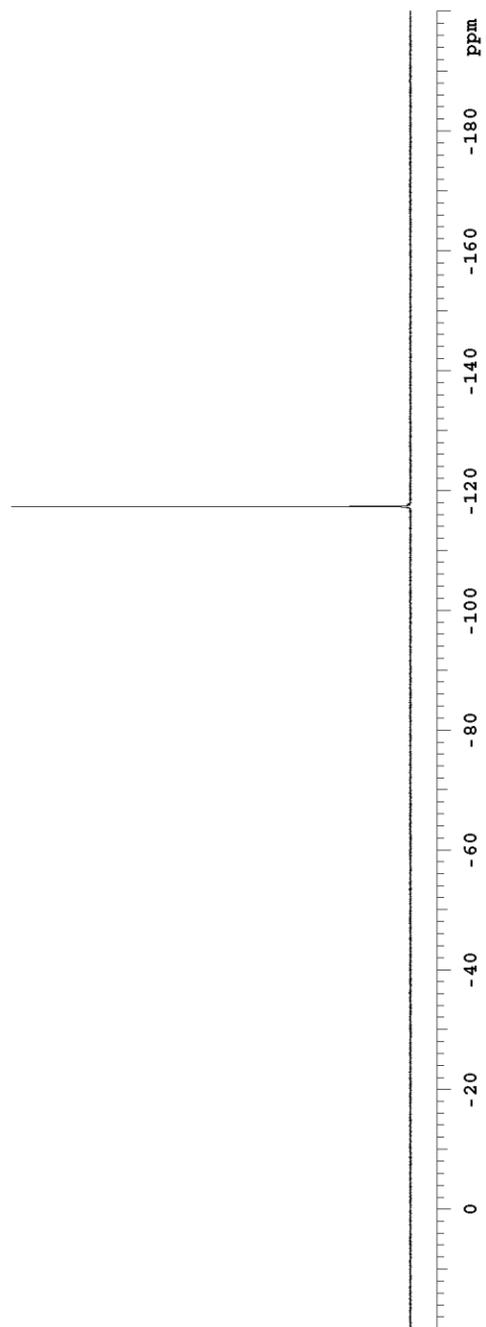
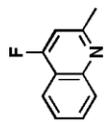


$^{19}\text{F}$  NMR ( $\text{CDCl}_3$ , 23 °C) of **18**

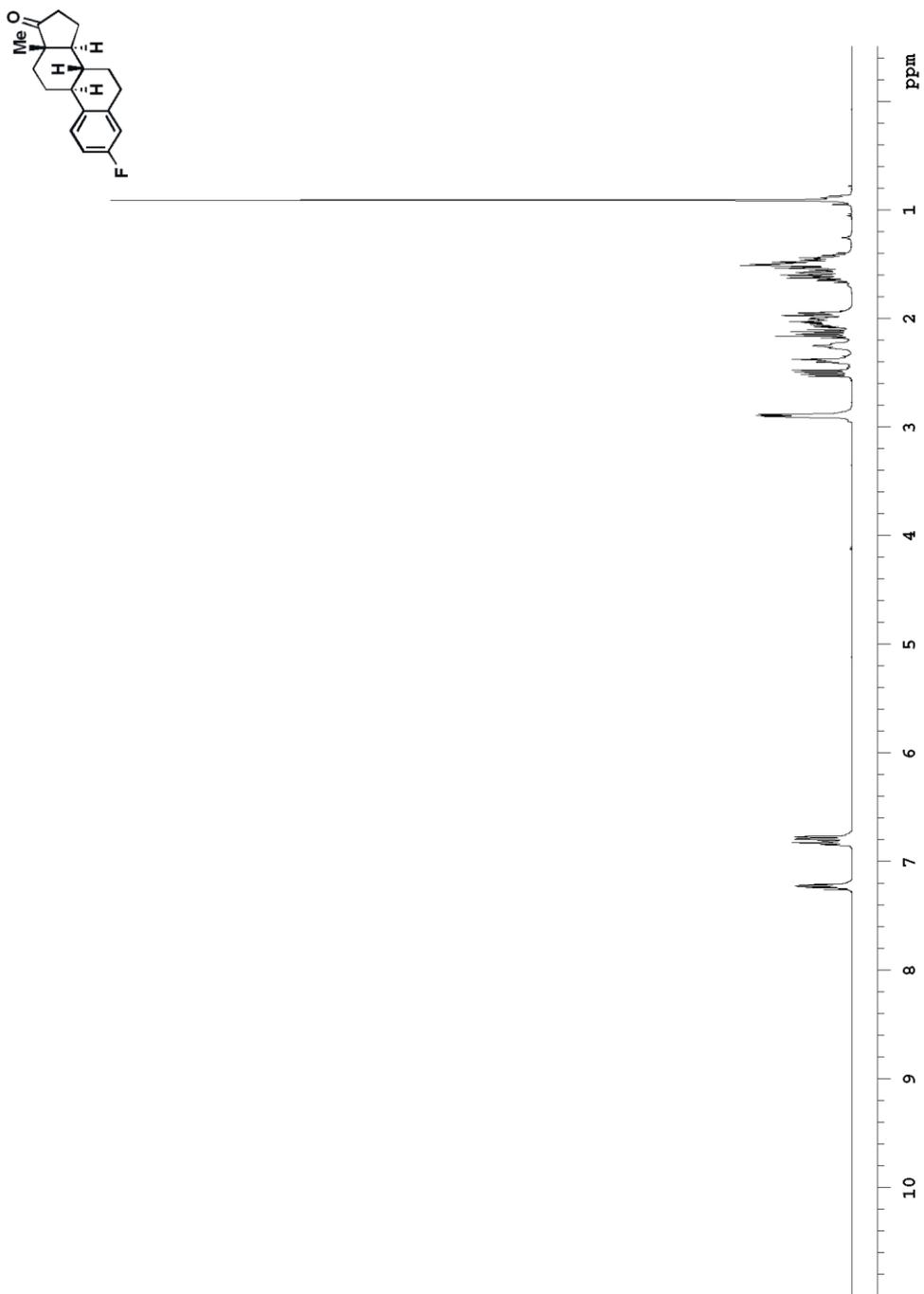


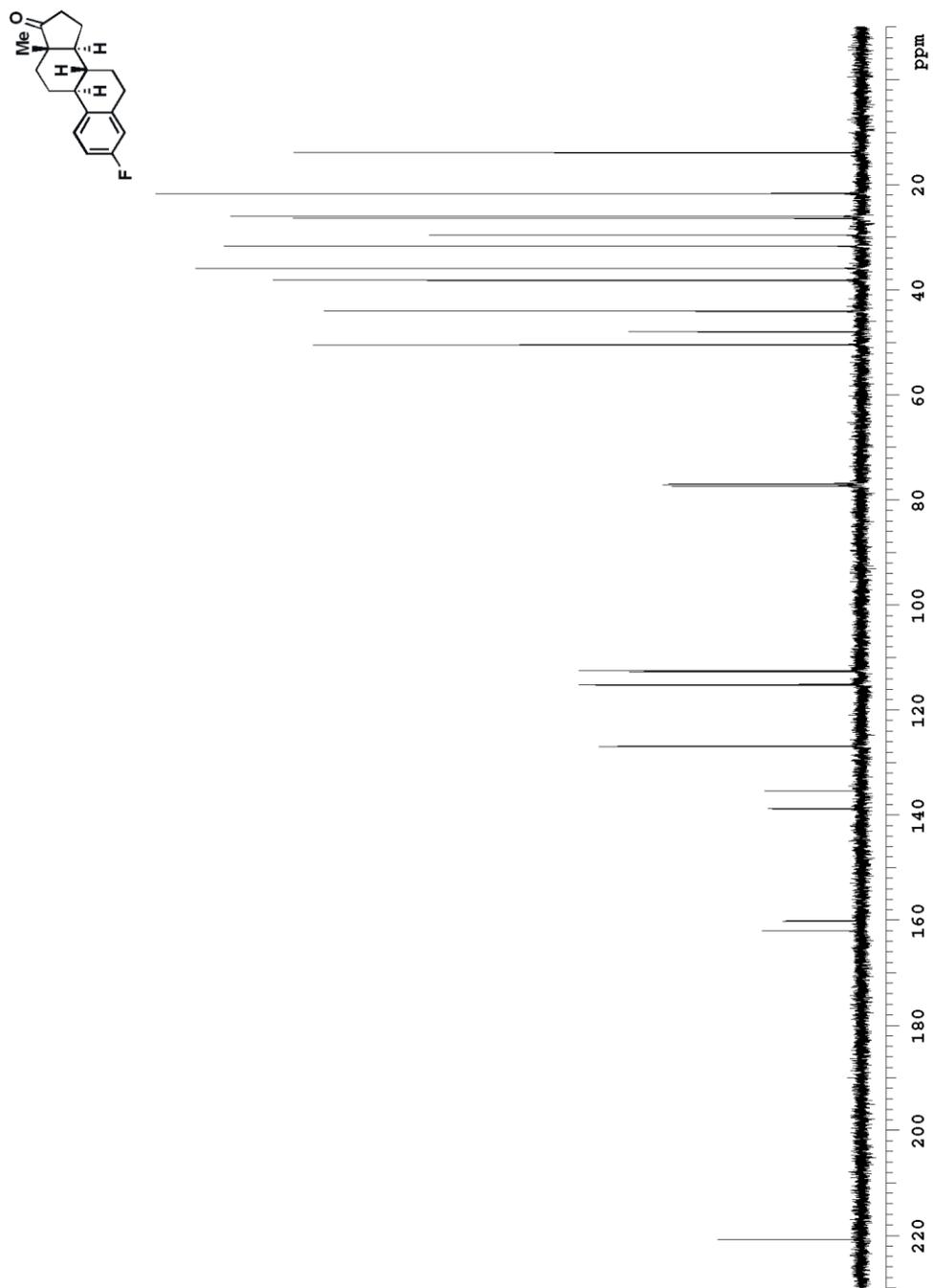
$^1\text{H}$  NMR (CDCl<sub>3</sub>, 23 °C) of **19**

 $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ,  $23^\circ\text{C}$ ) of **19**

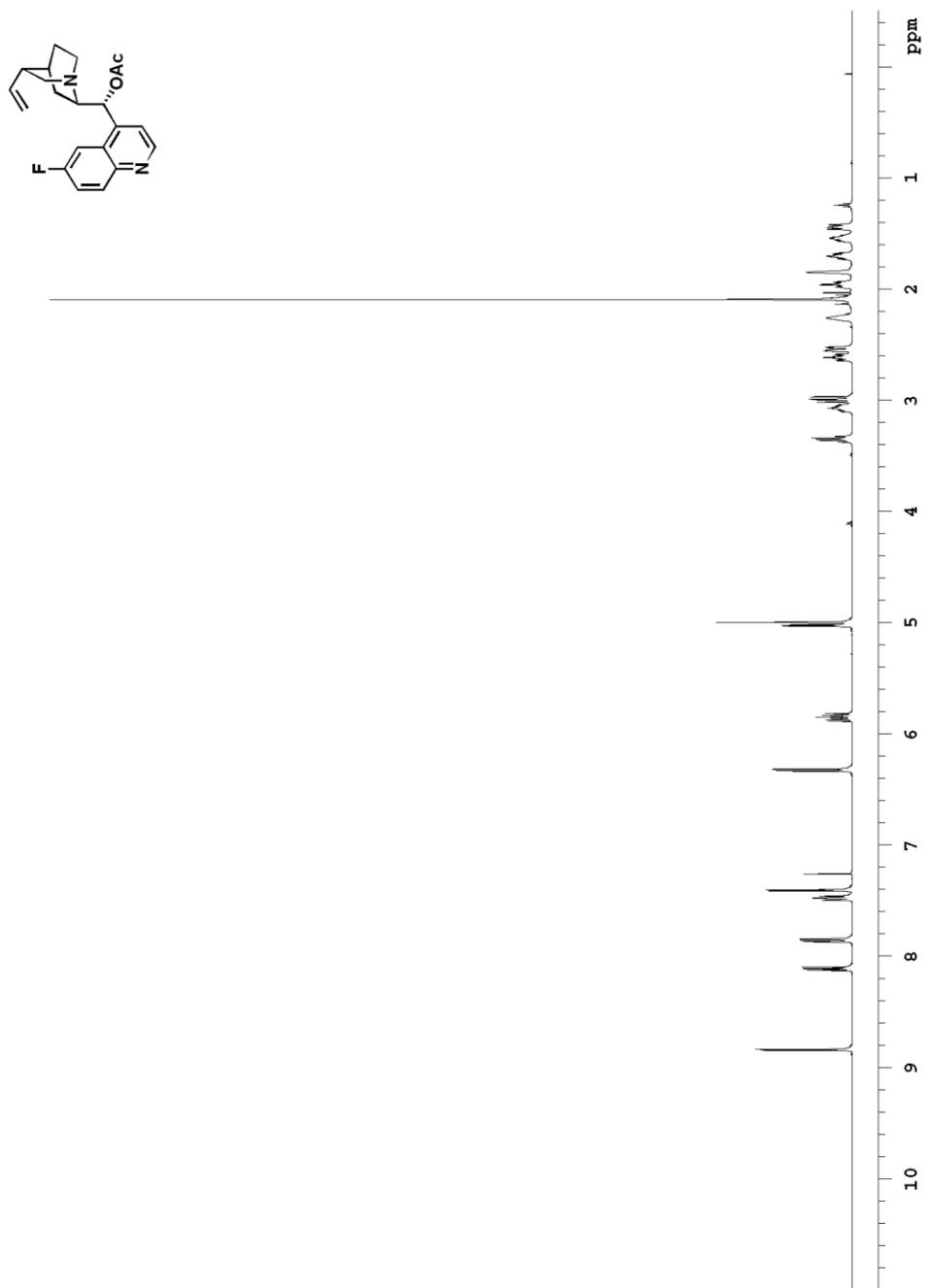


$^{19}\text{F}$  NMR ( $\text{CDCl}_3$ , 23 °C) of **19**

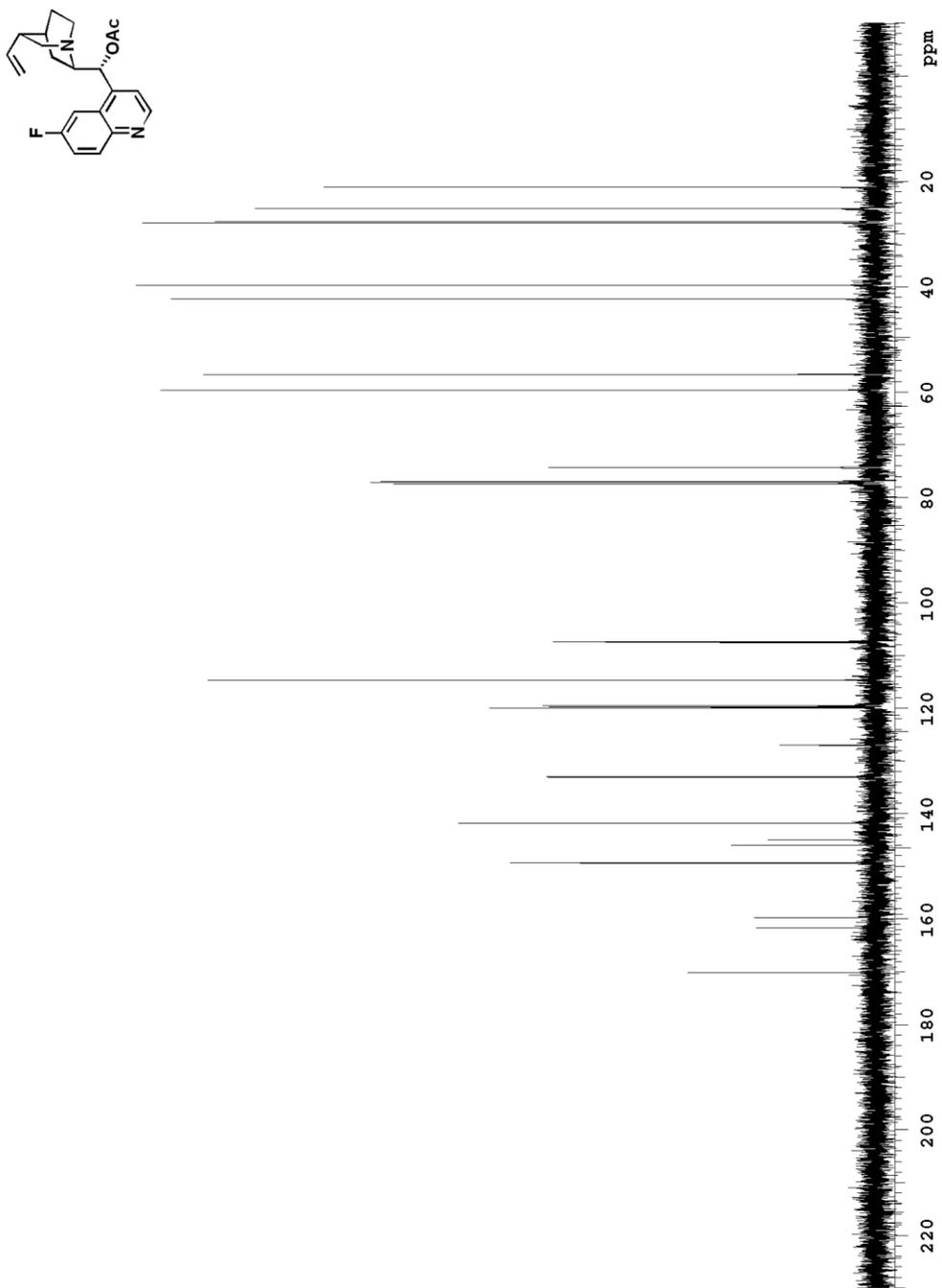
 $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $23\text{ }^\circ\text{C}$ ) of **20**

 $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 23 °C) of **20**

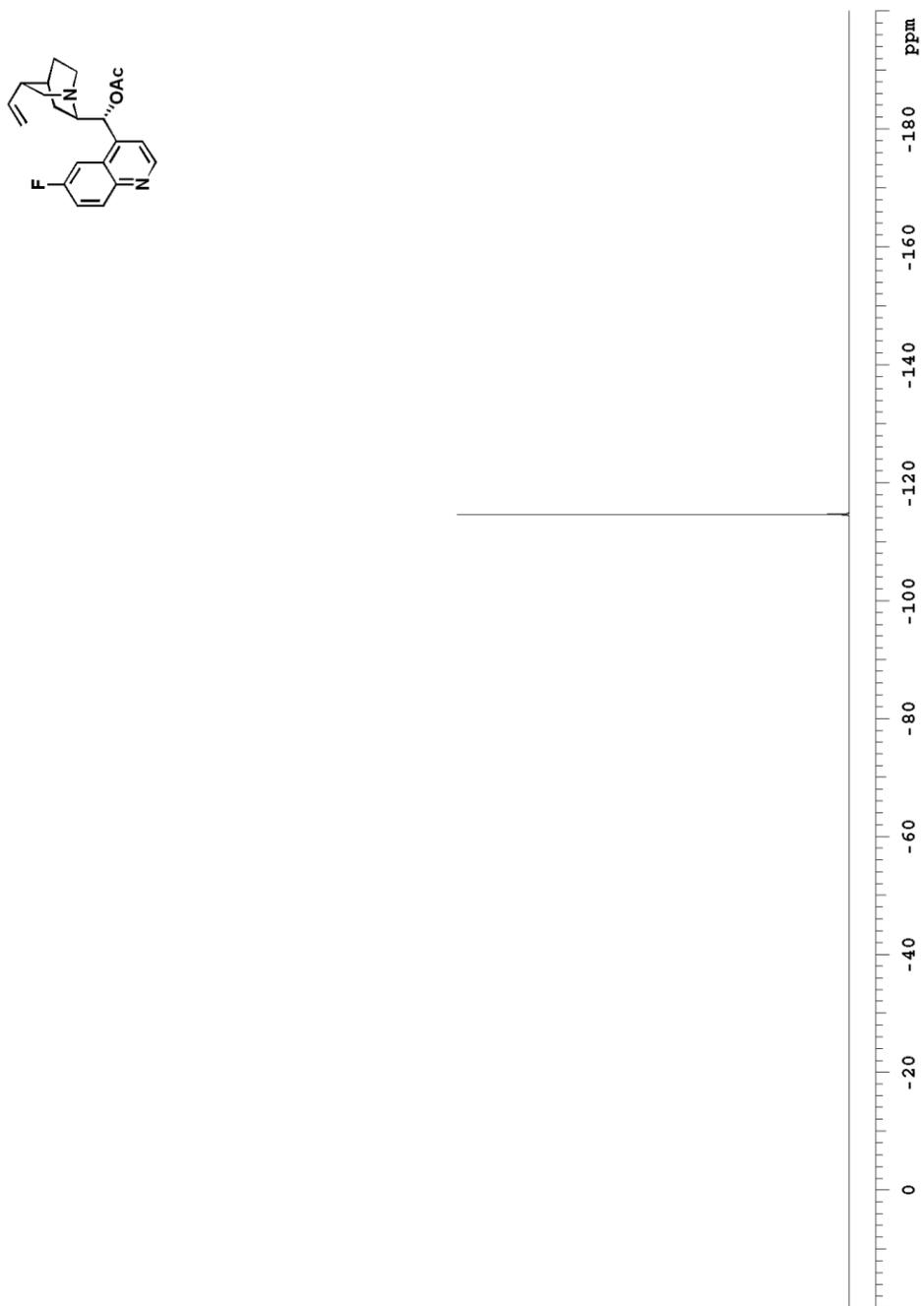
 $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ , 23 °C) of **20**



<sup>1</sup>H NMR (CDCl<sub>3</sub>, 23 °C) of (8 $\alpha$ , 9R)-6'-fluorocinchonan-9-yl acetate



<sup>13</sup>C NMR (CDCl<sub>3</sub>, 23 °C) of (8 $\alpha$ , 9R)-6'-fluorocinchonan-9-yl acetate



$^{19}\text{F}$  NMR (CDCl<sub>3</sub>, 23 °C) of (8 $\alpha$ , 9R)-6'-fluorocinchonan-9-yl acetate

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