Synthesis and Characterization of a Novel N-F Reagent derived from the Ethano-Tröger's Base: $^{1}J_{FN}$ Coupling Constant as Signature for the N-F Bond

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Supporting Information

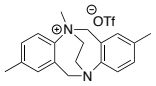
GENERAL

All reactions were performed in dried apparatus with magnetic stirring under an inert atmosphere of argon or nitrogen. All solvents and chemicals were used as purchased unless stated otherwise. All NMR spectra were recorded on Bruker AV400, AVIII400, AVIIIHD 500 or AVIIIHD 600 spectrometers. ^{1}H and ^{13}C NMR spectra are reported relative to external TMS as chemical shifts (δ) in parts per million (ppm). ^{15}N shifts are referenced relative to external NH_3 and the ^{19}F NMR shifts are referenced relative to external $CFCl_3$ at 0.0 ppm. ^{15}N-^{19}F HMQC spectra were recorded at 600 MHz (^{1}H) using a N_2-cooled broadband Prodigy cryoprobe with the ^{1}H channel tuned to ^{19}F. These HMQC experiments were optimised for $^{1}J_{FN}$ values of either 60 or 150 Hz. Coupling constants (*J*) are reported in units of hertz (Hz). The following abbreviations are used to describe multiplets: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), td (triplet of doublets), br (broad), aapd (apparent doublet), apt (apparent triplet). High-resolution mass spectra (HRMS, m/z) were recorded on a Bruker MicroTOF spectrometer using positive electrospray ionization (ESI) or on a Waters GC-TOF spectrometer using electron impact (EI). Infrared spectra were recorded as neat compounds using a Bruker Tensor 27 FT-IR spectrometer. Absorptions are reported in wavenumbers (cm^{-1}) and only peaks of interest are reported. Melting points of solids were measured on a Griffin apparatus and are uncorrected. IUPAC names were generated using ChemDraw Professional 15.0. All solvents were dried on a column of alumina prior to use. Thin layer chromatography (TLC) was performed using Merck aluminium-foil baked plates coated with Kieselgel 60 F245. The products were visualized using UV fluorescence (254 nm) or potassium permanganate stain. Flash column chromatography was performed over Merck silica gel C60 (40-60 µm) using eluent systems as described for each experiment.

SYNTHESIS

Compounds **3**,[1] **7**,[2] **8**[2] and **9**[2] were prepared according to published methods while **5**, **6**, **10** and **11** were bought from Sigma-Aldrich.

rac-2,5,8-trimethyl-5,12-dihydro-6*H*-5,11-ethanodibenzo[*b,f*][1,5]diazocin-5-ium trifluoromethanesulfonate **4**



Following a modified literature procedure[3] rac-2,8-Dimethyl-6,12-dihydro-5,11ethanodibenzo[b,f][1,5]diazocine, ethano-Tröger's base, **1** (5 g, 18.9 mmol) was stirred with CH_3I (14.7 g, 189.0 mmol, 10 equiv) in CH_2Cl_2 (20 mL) and CH_3OH (60 mL) for 24 hours at 25 °C. The solvents were removed under reduced pressure and the sticky residue was scratched with *n*-pentane (100 mL) until an off-white solid was formed. The solid was filtered-off and rinsed with acetone (50 mL × 3) to get rid off the unreacted **1**. The solvents were removed under reduced pressure to give a free flowing powder of 2,5,8-trimethyl-5,12-dihydro-6*H*-5,11-ethanodibenzo[*b,f*][1,5]diazocin-5-ium iodide[3] (5.45 g, 71%, 13.4 mmol) that was suspended in acetone (100 mL) and then treated in the dark with AgOTf (3.44 g, 13.4 mmol, 1.0 equiv) and stirred overnight. The silver iodide was filtered-off over a celite plug, and the filtrate was evaporated under reduced pressure to yield a sticky solid that was re-dissolved in acetonitrile and then evaporated to yield a stick solid that was scratched with *n*-pentane (100 mL) until an off-white solid formed which was filtered-off, finely powdered and then dried under high-vacuum overnight to yield **4** (5.67 g, 99%).

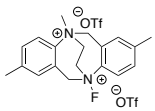
^{1}H NMR (500 MHz, CD_3CN): δ [ppm] = 2.15 (s, 3H, CH_3), 2.22 (s, 3H, CH_3), 3.68 (dd, *J* = 15.8, 5.1 Hz 1H, NCH_2CH$_2$N), 3.78 (td, *J* = 14.9, 12.8, 5.3 Hz, 1H, NCH_2CH$_2$N), 3.84 (s, 3H, NCH_3), 4.17 (dd, *J* = 14.1, 5.5 Hz, 1H, NCH$_2$CH_2N), 4.50 (d, *J* = 17.5 Hz, 1H, endo-CH_2N), 4.59 (td, *J* = 13.3, 12.8, 5.5 Hz, 1H, NCH$_2$CH_2N), 4.68 (d, *J* = 15.6 Hz, 1H, endo-CH_2NMe), 4.78 (d, *J* = 17.5 Hz, 1H, exo-CH_2N), 5.45 (d, *J* = 15.5 Hz, 1H, exo-CH_2NMe), 6.79 (s, 1H, Ar-*H*), 6.97 (s, 1H, Ar-*H*), 7.05 (s, 2H, Ar-*H*), 7.17 (d, J = 8.7 Hz, 1H Ar-*H*), 7.62 (d, J = 8.7 Hz, 1H Ar-*H*).

^{13}C NMR (125 MHz, CD_3CN): δ [ppm] = 20.4, 20.6, 49.6, 59.7, 60.3, 69.8, 71.2, 122.4, 128.2, 128.9, 130.4, 131.0, 131.8, 132.6, 134.9, 136.5, 141.9, 142.4, 146.3.

^{19}F NMR (125 MHz, CD_3CN): δ [ppm] = -79.3.

MP = 152 °C

rac-5-fluoro-2,8,11-trimethyl-5,6,11,12-tetrahydro-5,11-ethanodibenzo[b,f][1,5]diazocine-5,11-diium trifluoromethanesulfonate **2**



In a dry vial fitted with a stirring bar and rubber septum under nitrogen, **4** (42.8 mg, 1.0 mmol) was dissolved in dry CD_3CN (1.0 mL) and then cooled to -35 °C. To this was added a cooled (0-5 °C) slurry of 2,3,4,5,6-pentachloro-1-fluoropyridin-1-ium trifluoromethanesulfonate **7** (44.0 mg, 1.05 mmol, 1.05 equiv) in dry CD_3CN (1.0 mL) keeping the reaction temperature below -35 °C. The reaction was allowed to reach room temperature over 15 minutes and then the clear pale yellow solution was utilized in reactions or for ^{1}H, ^{13}C, ^{15}N and ^{19}F NMR and high-resolution mass spectrometry analyses.

^{1}H NMR (500 MHz, CD_3CN): δ [ppm] = 2.27 (s, 3H, CH_3), 2.31 (s, 3H, CH_3), 4.10 (s, 3H, NCH_3), 4.74 (appd, *J* = 15.7 Hz, 1H, FNCH$_2$CH_2NMe), 4.94 (m, 1H, FNCH$_2$CH_2NMe), 5.13 (d, *J* = 16.0 Hz, 1H, endo-CH_2NMe), 5.45 (m, 2H, FNCH_2CH$_2$NMe), 5.69 (d, *J* = 16.0 Hz, 1H, exo-CH_2NMe), 5.81 (appdd, *J* = 17.6, 15.1 Hz, 1H, endo-CH_2NF), 6.44 (d, *J* = 14.5 Hz, 1H, exo-CH_2NF), 7.15 (s, 1H, *Ar*-H), 7.16 (s, 1H, *Ar*-H), 7.46 (d, *J* = 8.7 Hz, 1H, *Ar*-H), 7.53 (d, *J* = 8.7 Hz, 1H, *Ar*-H), 7.80 (d, *J* = 8.7 Hz, 1H, *Ar*-H), 7.89 (d, *J* = 8.7 Hz, 1H, *Ar*-H).

^{13}C NMR (100 MHz, CD_3CN): δ [ppm] = 20.5, 21.0, 59.9, 60.05 (d, *J* = 8.6 Hz), 65.7 (d, *J* = 18.2 Hz), 70.9, 75.4 (d, *J* = 23.0 Hz), 121.5 (d, *J* = 12.2 Hz), 122.6 (d, *J* = 6.5 Hz), 123.3, 123.4, 132.9, 133.79, 133.87, 134.3, 139.5 (d, *J* = 18.7 Hz), 140.6, 143.9, 146.7.

^{19}F NMR (377 MHz, CD_3CN): δ [ppm] = +103.6 (N–F), -79.3 (OTf).

HRMS (ESI); m/z [M-2OTf]2+ calcd. for $C_{19}H_{23}FN_2$: 149.0917; found:149.0917.

$^{14}N/^{15}N$ ONE-BOND ISOTOPE SHIFT [^{19}F $^{1}\Delta\delta(^{14}N-^{15}N)$]

No	Compound	^{19}F $^{1}\Delta\delta(^{14}N-^{15}N)$
1	**2**	0.27 ppm
2	**5**	0.21 ppm
3	**8**	0.20 ppm
4	**9**	0.20 ppm
5	**7**	0.18 ppm
6	**6**	0.12 ppm
7	**10**	0.19 ppm
8	**11**	0.18 ppm

Conditions: ^{15}N-^{19}F HMQC [^{15}N (60.8 MHz) & ^{19}F (565.2 MHz) CD3CN, 298K]

FLUORINATION OF AROMATICS

General Procedure

Following a literature protocol[4] the aromatic compound (0.4 mmol) as a co-solvent in CH_3CN (1.0 mL), and to this solution was added a stock solution of the fluorinating reagent **2** (2mL, 0.15 mmol, 0.15 mmol) at 0°C and then run at the indicated temperature and time after which (0.1 mmol, 0.1 equiv, 0.2 mL) of a stock solution of 1-Fluoro-4-nitrobenzene (143.1 mg) in CD_3CN (2.0 mL) was added. The crude reaction (0.4 mL) was diluted with 0.2 mL CD_3CN was analyzed *via* ^{19}F NMR (using 1-Fluoro-4-nitrobenzene as an internal standard) and high-resolution GCMS.

Fluoroanisole

Deviating from the general procedure **2** (1.0 equiv) was used and the reaction was run at 0 °C for 1 hour.

^{19}F NMR (377 MHz, CH_3CN/CD_3CN): δ [ppm] = -137.4 (55%)[*o*-fluoroanisole (lit. 136.3 in $CDCl_3$)[4]], -126.3 (30%) [*p*-fluoroanisole (lit. 125.1 in $CDCl_3$)[4]].

HRMS (EI); m/z $[M]^+$ calcd. for C_7H_7FO: 126.0481; found: 126.0480.

Fluorobenzene

Following the general procedure, the reaction was run at 40 °C for 6 hours.

^{19}F NMR (377 MHz, CH_3CN/CD_3CN): δ [ppm] = -114.8 ppm (85%)[monofluorobenzene (lit. -113.7 in $CDCl_3$);[4] Authentic sample from Sigma-Aldrich -114.8 ppm in CD_3CN].

HRMS (EI); m/z $[M]^+$ calcd. for C_6H_5F: 96.0375 found: 96.0401.

Difluorobenzene

Following the general procedure, the reaction was run at 40 °C for 6 hours.

^{19}F NMR (377 MHz, CH_3CN/CD_3CN): δ [ppm] = -140.7 ppm (29%) [1,2-difluorobenzene (lit. -139.2 in $CDCl_3$)[4]], -121.1 (60%) [1,4-difluorobenzene (lit. -120.3 in $CDCl_3$)[4]].

HRMS (EI); m/z $[M]^+$ calcd. for $C_6H_4F_2$: 114.0281 found: 114.0306.

FLUORO-ACETOXYLATION OF OLEFINS

2-fluoro-1-phenylethyl acetate **13**

A dry 50 mL flask was charged with **4** (428.5mg, 1.0 mmol) and dry CH_3CN (8.0 mL) and stirred at -35 °C. To this was added **7** (419.4mg, 1.0 mmol, 1.0 equiv) in dry CH_3CN (8.0 mL) and stirred at -35 °C for 10 minutes under argon. The turbid suspension was then allowed to reach 0 °C and upon doing so the suspension turned into a clear pale yellow solution which was then added over 15 minutes into a solution of styrene (104 mg, 1.0 mmol, 1.0 equiv) in glacial acetic acid (40 mL) at 10 °C. The reaction was stirred at 10 °C for 30 minutes and then quenched into a saturated solution of sodium bicarbonate, extracted with diethyl ether (75 mL × 3). The organic phase was rinsed with water (30 mL × 2) and then with brine (30 mL) before being dried over $MgSO_4$. The compound was purified *via* column chromatography [silica gel (20g), diethyl ether/pentane (1:10)] to yield 2-fluoro-1-phenylethyl acetate (141 mg, 77%) as a clear oil. The spectral data (^1H and ^{19}F) match a literature precedent.[5]

^1H NMR (400 MHz, $CDCl_3$): δ [ppm] = 2.14 (s, 3H, OC*H*$_3$), 4.58 (dm, *J* = 48.0 Hz, 2H, C*H*$_2$F), 4.73 (ddd, *J* = 16.5, 7.5, 3.4 Hz, 1H, C*H*OAc), 7.37 (m, 5H, Ar-*H*).

^{13}C NMR (100 MHz, $CDCl_3$): δ [ppm] = 21.1, 74.1 (d, *J* = 20 Hz), 84.2 (d, *J* = 179 Hz), 126.9, 128.79, 128.85, 135.4 (d, *J* = 20 Hz), 170.1.

^{19}F NMR (377 MHz, $CDCl_3$): δ [ppm] = -223.8 (td, *J* = 48.0, 16.5 Hz).

IR (ATR, neat): ν [cm^{-1}] = 1736 (C=O).

MS (ESI): m/z $[M+Na]^+$ calcd. for $C_{10}H_{11}FO_2Na$: 205.06; found: 205.1.

2-fluoro-1-(*p*-tolyl)ethyl acetate **14**

A dry 50 mL flask was charged with **4** (428.5mg, 1.0 mmol) and dry CH_3CN (8.0 mL) and stirred at -35 °C. To this was added **7** (419.4mg, 1.0 mmol, 1.0 equiv) in dry CH_3CN (8.0 mL) and stirred at -35 °C for 10 minutes under argon. The turbid suspension was then allowed to reach 0 °C and upon doing so the suspension turned into a clear pale yellow solution which was then added over 15 minutes into a solution of 4-methylstyrene (118.1 mg, 1.0 mmol, 1.0 equiv) in glacial acetic acid (40 mL) at 10 °C. The reaction was stirred at 10 °C for 30 minutes and then quenched into a saturated solution of sodium bicarbonate, extracted with diethyl ether (75 mL × 3). The organic phase was rinsed with water (30 mL × 2) and then with brine (30 mL) before being dried over $MgSO_4$. The compound was purified *via* column chromatography [silica gel (20g), diethyl ether/pentane (1:10)] to yield 2-fluoro-1-(*p*-tolyl)ethyl acetate (159 mg, 81%) as a clear oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 2.10 (s, 3H, OCH_3), 2.32 (s, 3H, CH_3), 4.52 (dm, *J* = 47.3 Hz, 2H, CH_2F), 5.98 (ddd, *J* = 16.0, 7.6, 3.4 Hz, 1H, C*H*OAc), 7.15 (d, *J* = 8.0 Hz, 2H, Ar-*H*), 7.22 (d, *J* = 8.0 Hz, 2H, Ar-*H*).

^{13}C NMR (100 MHz, $CDCl_3$): δ [ppm] = 21.2, 21.3, 74.1 (d, *J* = 20.0 Hz), 84.3 (d, *J* = 179.1 Hz), 126.9, 129.5, 132.5 (d, *J* = 7.0 Hz), 138.8, 170.1.

^{19}F NMR (376 MHz, $CDCl_3$): δ [ppm] = -223.47 (td, *J* = 47.3, 16.0 Hz).

IR (ATR, neat): ν [cm^{-1}] = 1742 (C=O).

HRMS (ESI): m/z $[M+Na]^+$ calcd. for $C_{11}H_{13}FNaO_2$: 219.0791; found: 219.0793.

1-(4-bromophenyl)-2-fluoroethyl acetate **15**

A dry 50 mL flask was charged with **4** (428.5 mg, 1.0 mmol) and dry CH_3CN (8.0 mL) and stirred at -35 °C. To this was added **7** (419.4 mg, 1.0 mmol, 1.0 equiv) in dry CH_3CN (8.0 mL) and stirred at -35 °C for 10 minutes under argon. The turbid suspension was then allowed to reach 0 °C and upon doing so the suspension turned into a clear pale yellow solution which was then added over 15 minutes into a solution of 4-bromostyrene (183.1 mg, 1.0 mmol, 1.0 equiv) in glacial acetic acid (40 mL) at 10 °C. The reaction was stirred at 10 °C for 30 minutes and then quenched into a saturated solution of sodium bicarbonate, extracted with diethyl ether (75 mL × 3). The organic phase was rinsed with water (30 mL × 2) and then with brine (30 mL) before being dried over $MgSO_4$. The compound was purified *via* column chromatography [silica gel (15g), diethyl ether/pentane (1:10)] to yield 1-(4-bromophenyl)-2-fluoroethyl acetate (196mg, 75%) as a clear oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 2.10 (s, 3H, OCH_3), 4.51 (dm, *J* = 47 Hz, 2H, CH_2F), 5.92 (ddd, *J* = 16.9, 6.9, 3.7 Hz, 1H, C*H*OAc), 7.20 (m, 2H, Ar-*H*), 7.47 (m, 2H, Ar-*H*).

^{13}C NMR (100 MHz, $CDCl_3$): δ [ppm] = 21.1, 73.5 (d, *J* = 20.0 Hz), 83.8 (d, *J* = 179.0 Hz), 123.0, 128.7, 132.1, 134.6 (d, *J* = 6.5 Hz), 170.1.

^{19}F NMR (377 MHz $CDCl_3$): δ [ppm] = -224.9 (td, *J* = 47.1, 16.9 Hz).

IR (ATR, neat): ν [cm^{-1}] = 1738 (C=O).

HRMS (ESI): m/z $[M+Na]^+$ calcd. for $C_{10}H_{10}BrFNaO_2$: 282.97404; found: 282.97416.

1-(2-chlorophenyl)-2-fluoroethyl acetate **16**

A dry 50 mL flask was charged with **4** (428.5mg, 1.0 mmol) and dry CH_3CN (8.0 mL) and stirred at -35 °C. To this was added **7** (419.4mg, 1.0 mmol, 1.0 equiv) in dry CH_3CN (8.0 mL) and stirred at -35 °C for 10 minutes under argon. The turbid suspension was then allowed to reach 0 °C and upon doing so the suspension turned into a clear pale yellow solution which was then added over 15 minutes into a solution of 2-chlorostyrene (138.6 mg, 1.0 mmol, 1.0 equiv) in glacial acetic acid (40 mL) at 10 °C. The reaction was stirred at 10 °C for 30 minutes and then quenched into a saturated solution of sodium bicarbonate, extracted with diethyl ether (75 mL × 3). The organic phase was rinsed with water (30 mL × 2) and then with brine (30 mL) before being dried over $MgSO_4$. The compound was purified *via* column chromatography [silica gel (20g), diethyl ether/pentane (1:10)] to yield 1-(2-chlorophenyl)-2-fluoroethyl acetate (100 mg, 46%) as a clear oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 2.11 (s, 3H, OC*H*$_3$), 4.52 (m, 2H, C*H*$_2$F), 6.35 (ddd, *J* = 18.6, 6.8, 2.8 Hz, 1H, C*H*OAc), 7.21 (m, 2H, Ar-*H*), 7.31 (m, 1H, Ar-*H*), 7.37 (m, 1H, Ar-*H*).

^{13}C NMR (100 MHz $CDCl_3$): δ [ppm] = 21.1, 71.3 (d, *J* = 19.9 Hz), 82.9 (d, *J* = 179.6 Hz), 127.2, 128.1, 129.8, 132.4, 133.2 (d, *J* = 6.5 Hz), 169.80.

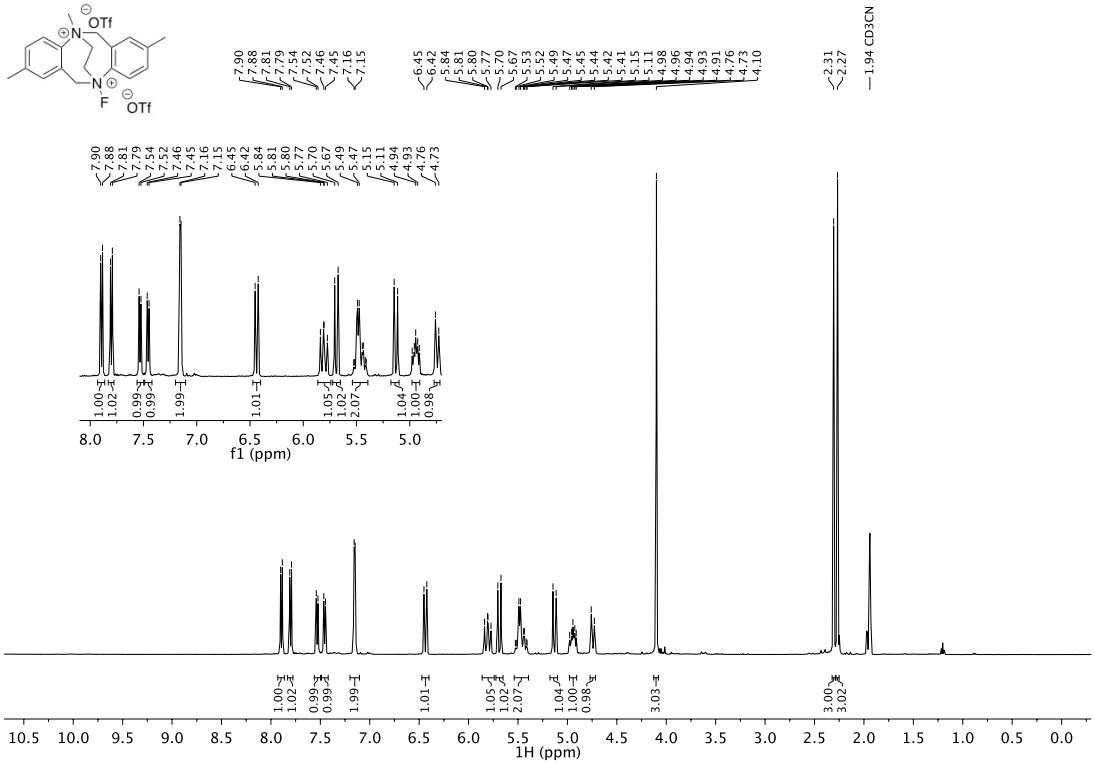
^{19}F NMR (377 MHz, $CDCl_3$): δ [ppm] = -224.27 (td, *J* = 47.0, 18.6 Hz).

IR (ATR, neat): ν [cm^{-1}] = 1743 (C=O).

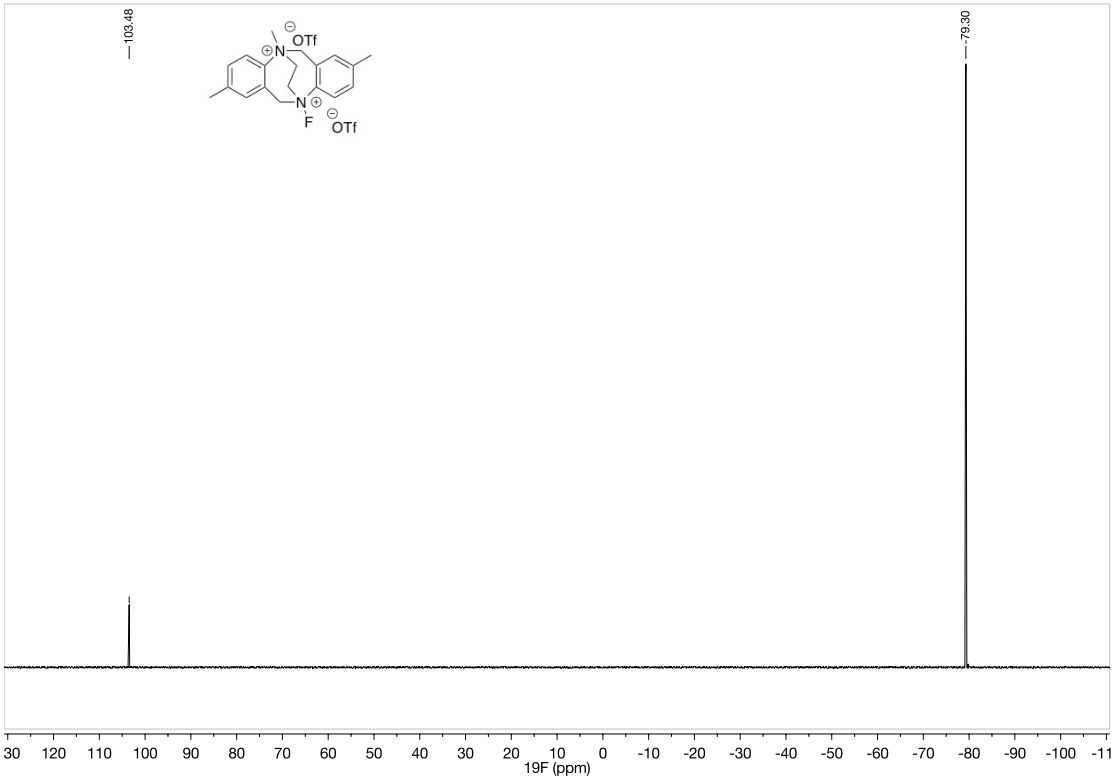
HRMS (ESI): m/z $[M+Na]^+$ calcd. for $C_{10}H_{10}ClFNaO_2$: 239.0245; found: 239.0247.

NMR SPECTRA

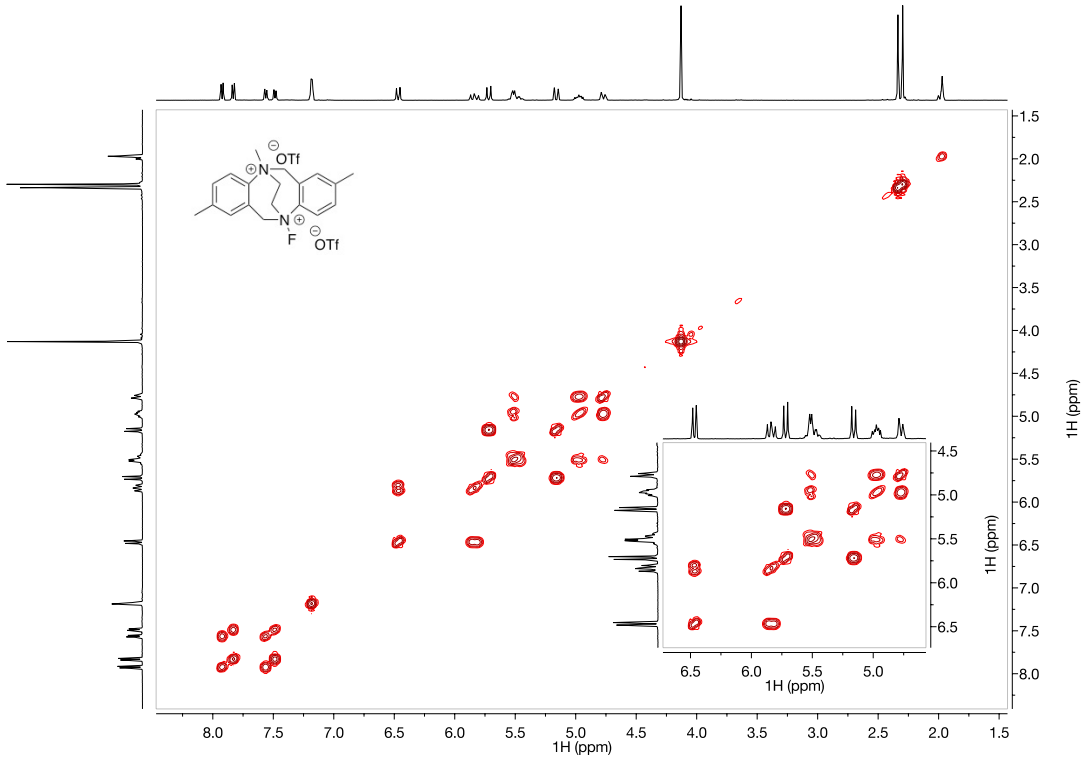
^{1}H NMR (500 MHz, CD_3CN, 298K) of **2**



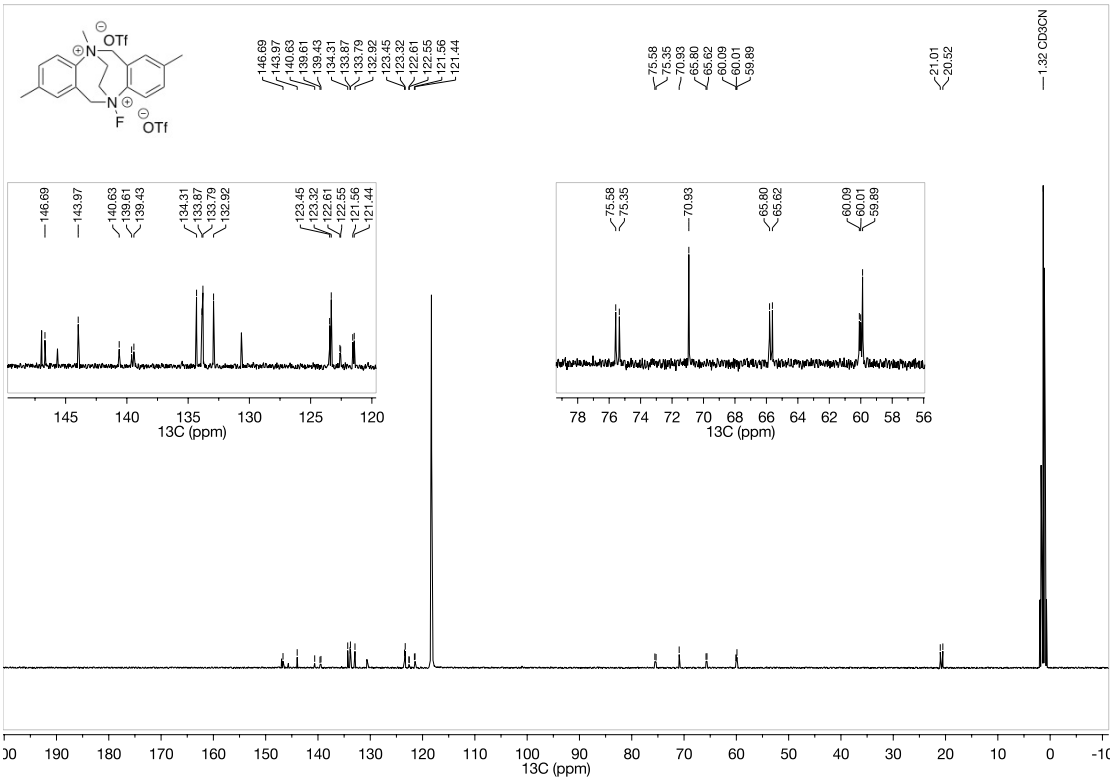
^{19}F NMR (377 MHz, CD_3CN, 298K) of **2**



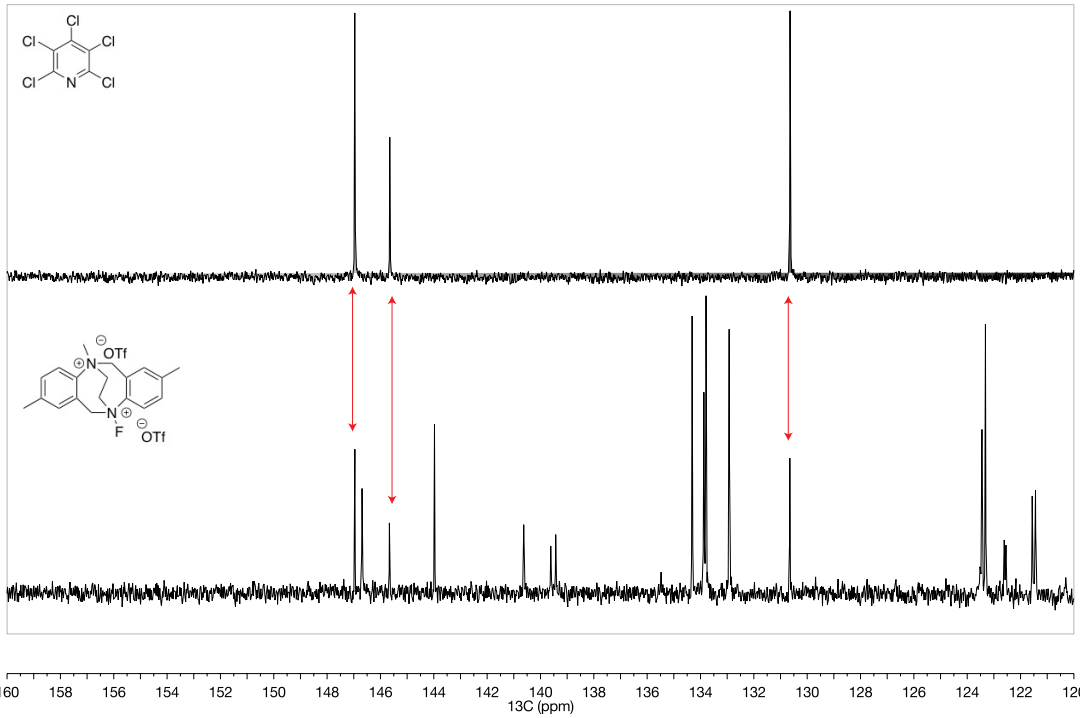
^{1}H-^{1}H COSY (500 MHz, CD_3CN, 298K) of **2**



^{13}C NMR (100 MHz, CD_3CN, 298K) of **2**



Note: Since 3 was generated in situ; there are three residual peaks of pentachloropyridine in the ^{13}C NMR (100 MHz, CD_3CN, 298K) spectrum (see below for a comparison).


Cl
Cl
Cl
Cl
N
Cl
OTf
N
F
OTf

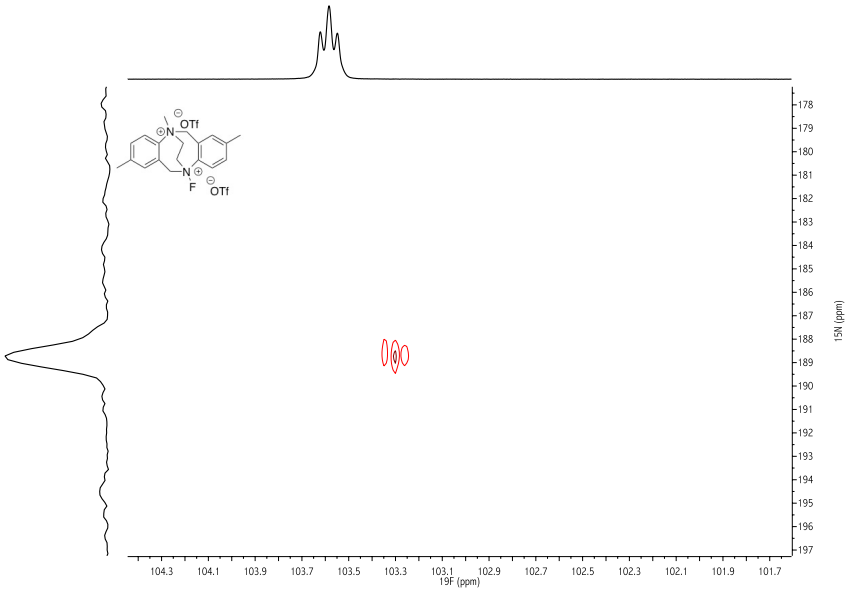
160
158
156
154
152
150
148
146
144
142
140
138
136
134
132
130
128
126
124
122
120
13C (ppm)

^{15}N-^{19}F HMQC Spectra

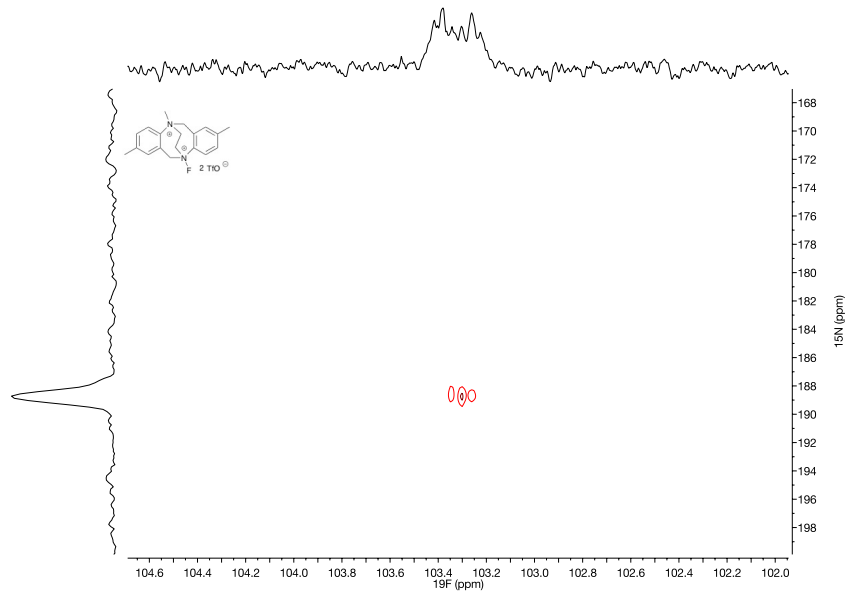
All 2D ^{15}N-^{19}F HMQC spectra were recorded in the presence of ^{19}F decoupling (the use of HMQC over HSQC was favoured as this avoids potential signal loss through the use of inversion pulses on ^{19}F). In the figures below these are shown in trace (a) with the conventional ^{1}H-coupled ^{19}F spectra shown above. 1D versions of the ^{15}N-^{19}F HMQC experiment were also collected in the absence of ^{19}F decoupling to enable measurement of the one-bond ^{19}F-^{15}N coupling constants ($^{1}J_{FN}$) with high resolution. Traces (b) show the 2D HMQC again but with the corresponding 1D HMQC spectrum shown above, thus revealing the reported $^{1}J_{FN}$ doublets and subject to the one-bond isotope shifts defined above.

^{15}N-^{19}F HMQC [^{15}N (60.8 MHz) & ^{19}F (565.2 MHz) CD_3CN, 298K] of **2**

a) Without showing the splitting of the ^{19}F peak by ^{15}N

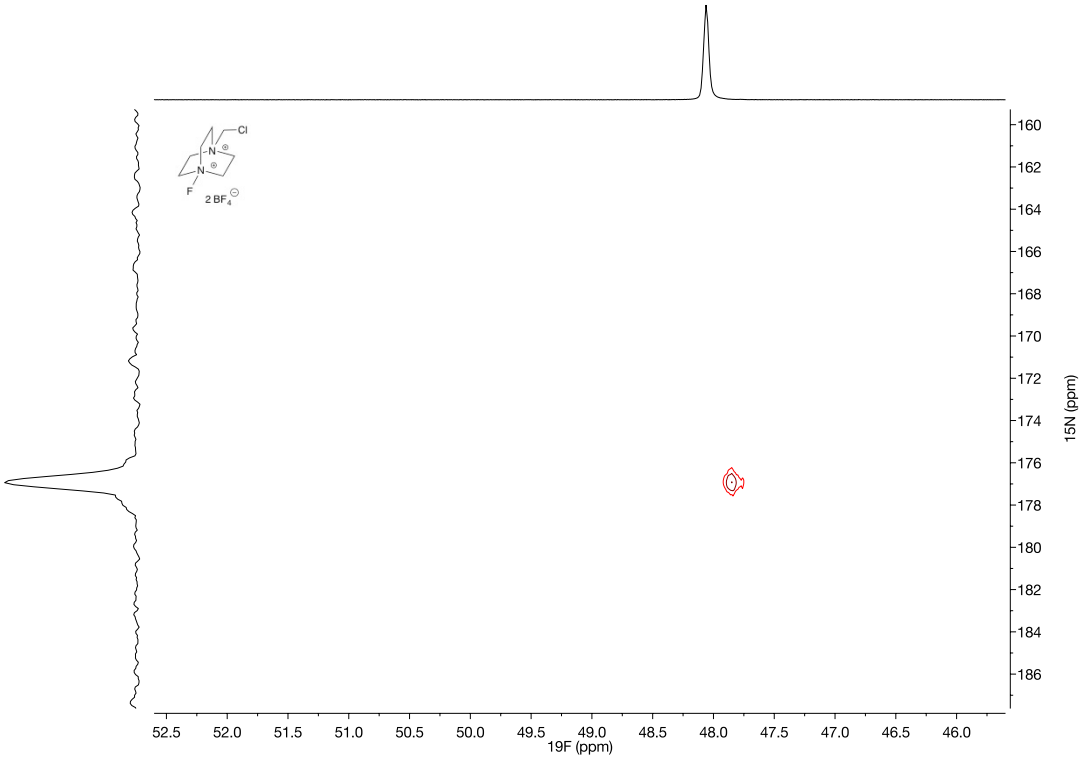


b) Showing the splitting of the ^{19}F peak by ^{15}N

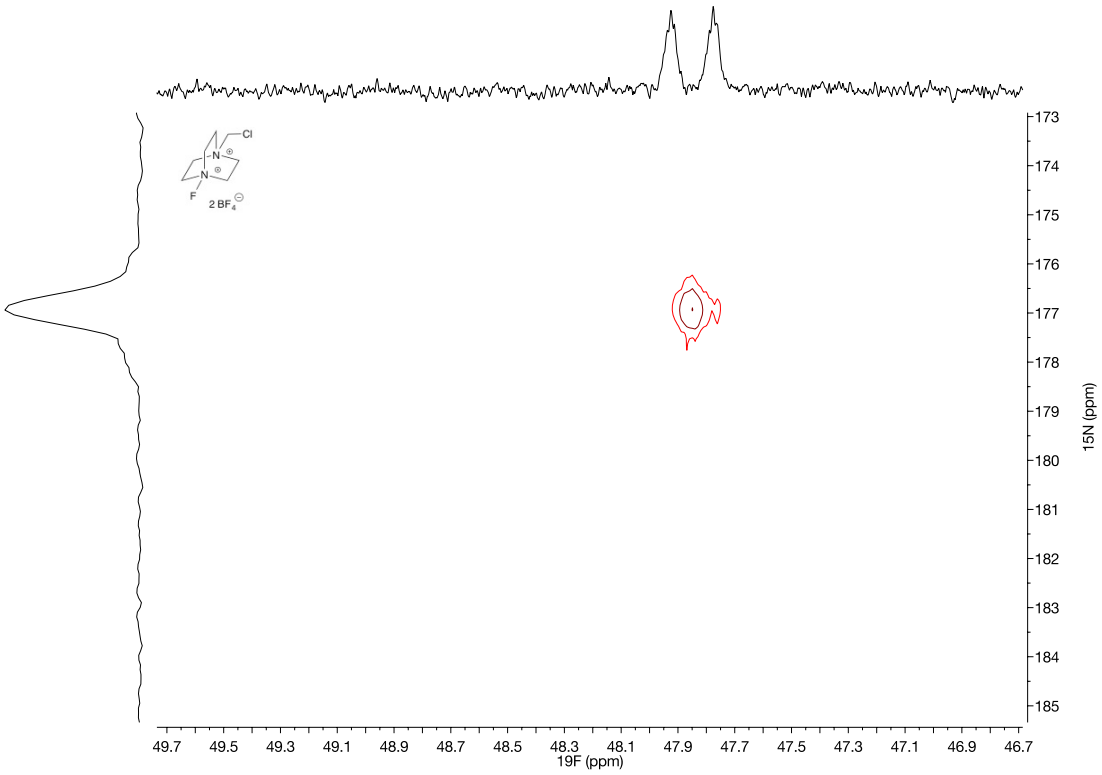


^{15}N-^{19}F HMQC [^{15}N (60.8 MHz) & ^{19}F (565.2 MHz) CD_3CN, 298K] of **5**

a) Without showing the splitting of the ^{19}F peak by ^{15}N

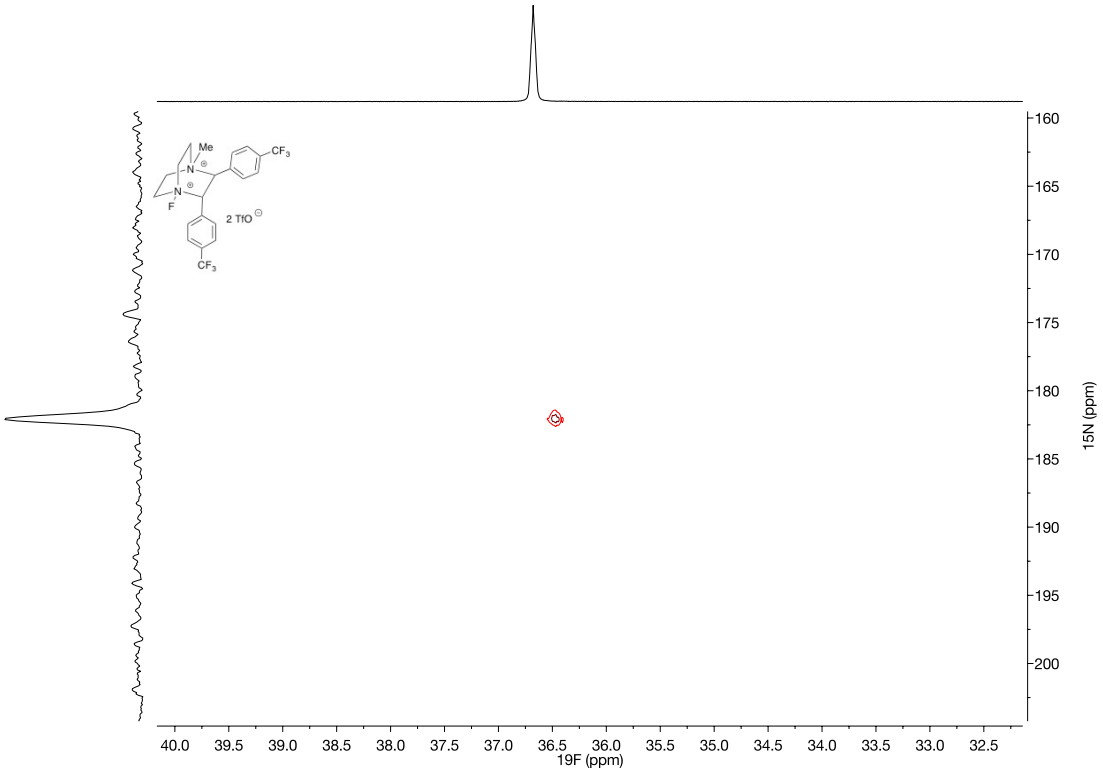


b) Showing the splitting of the ^{19}F peak by ^{15}N

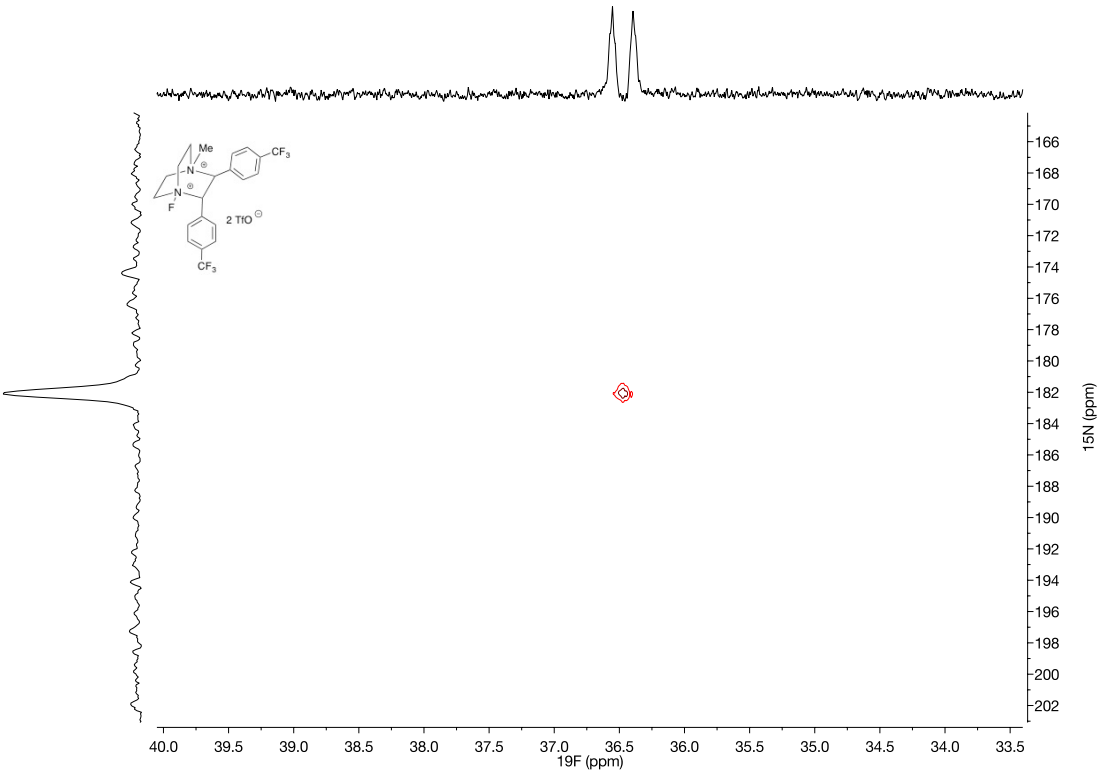


^{15}N-^{19}F HMQC [^{15}N (60.8 MHz) & ^{19}F (565.2 MHz) CD_3CN, 298K] of **8**

a) Without showing the splitting of the ^{19}F peak by ^{15}N

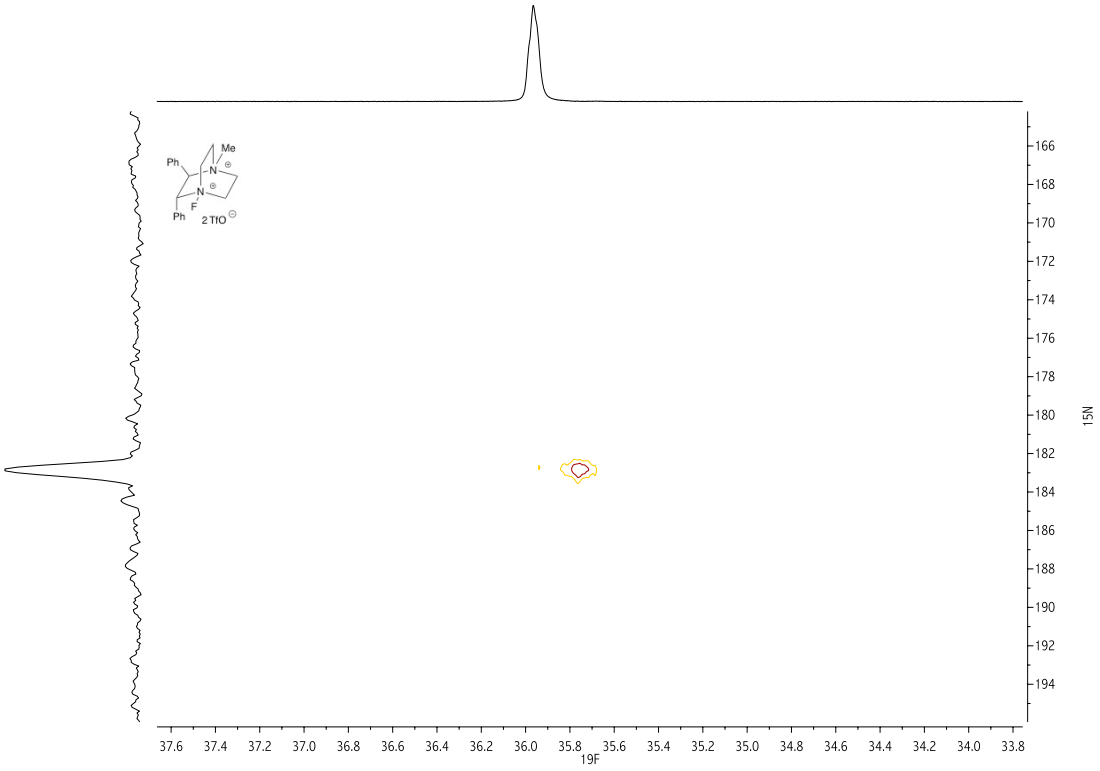


b) Showing the splitting of the ^{19}F peak by ^{15}N

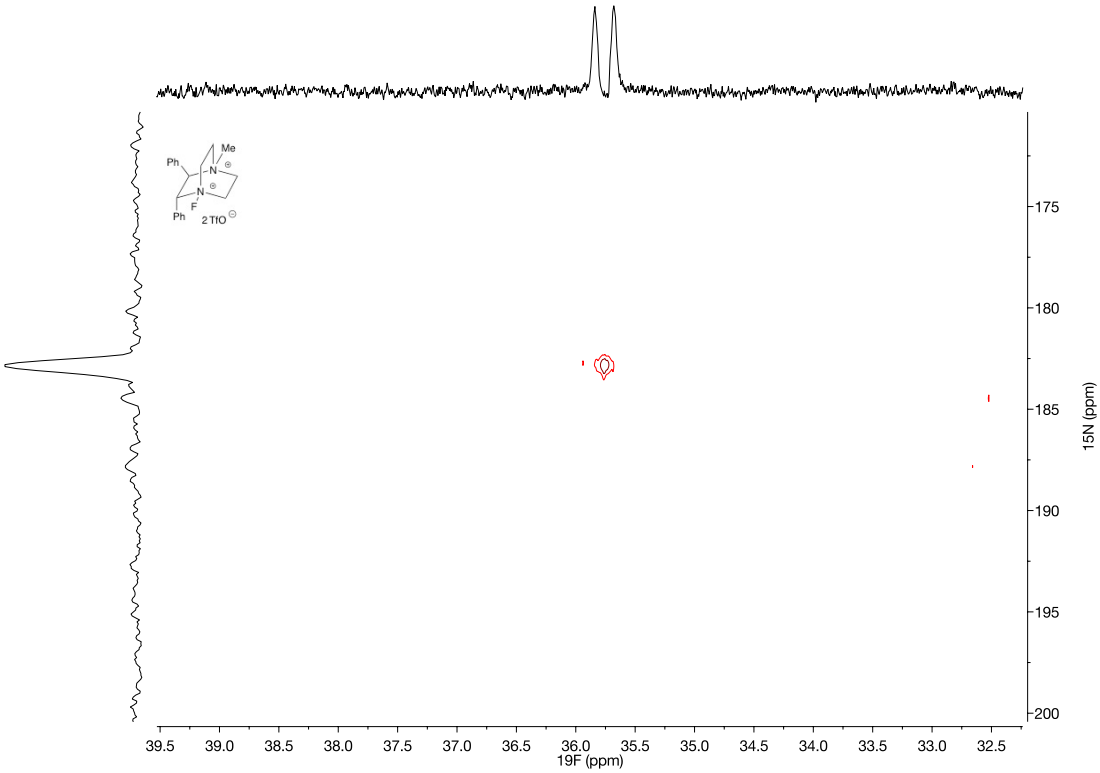


^{15}N-^{19}F HMQC [^{15}N (60.8 MHz) & ^{19}F (565.2 MHz) CD_3CN, 298K] of **9**

a) Without showing the splitting of the ^{19}F peak by ^{15}N

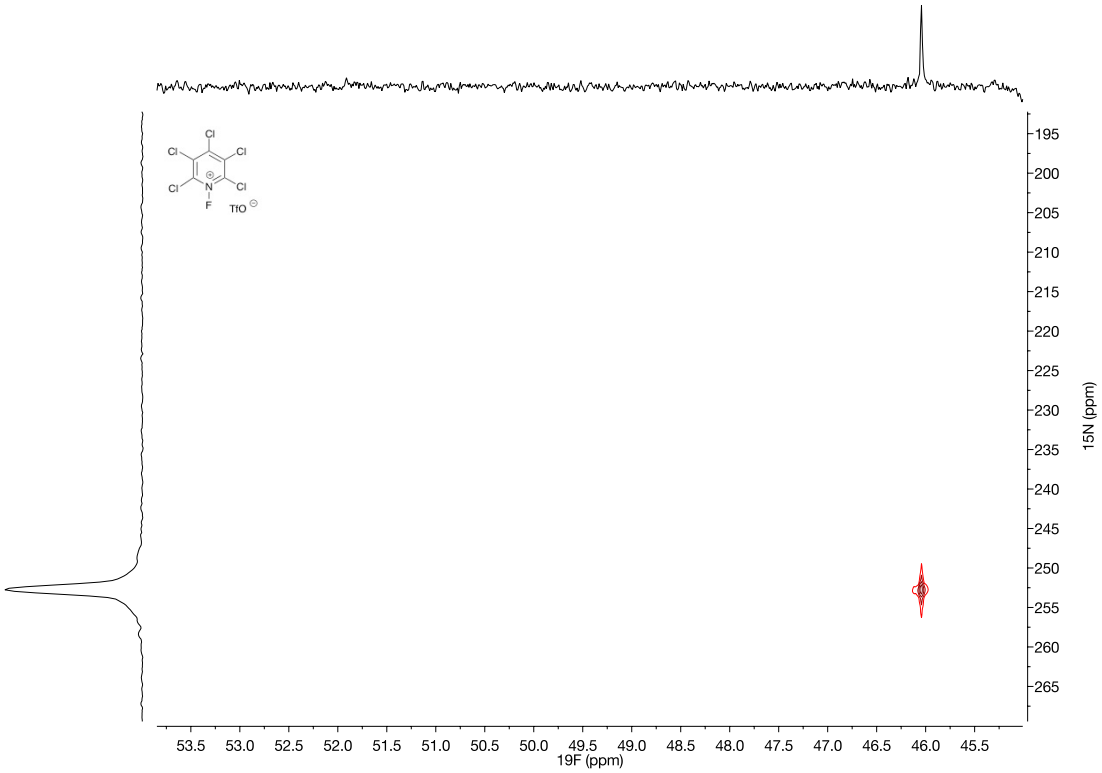


b) Showing the splitting of the ^{19}F peak by ^{15}N

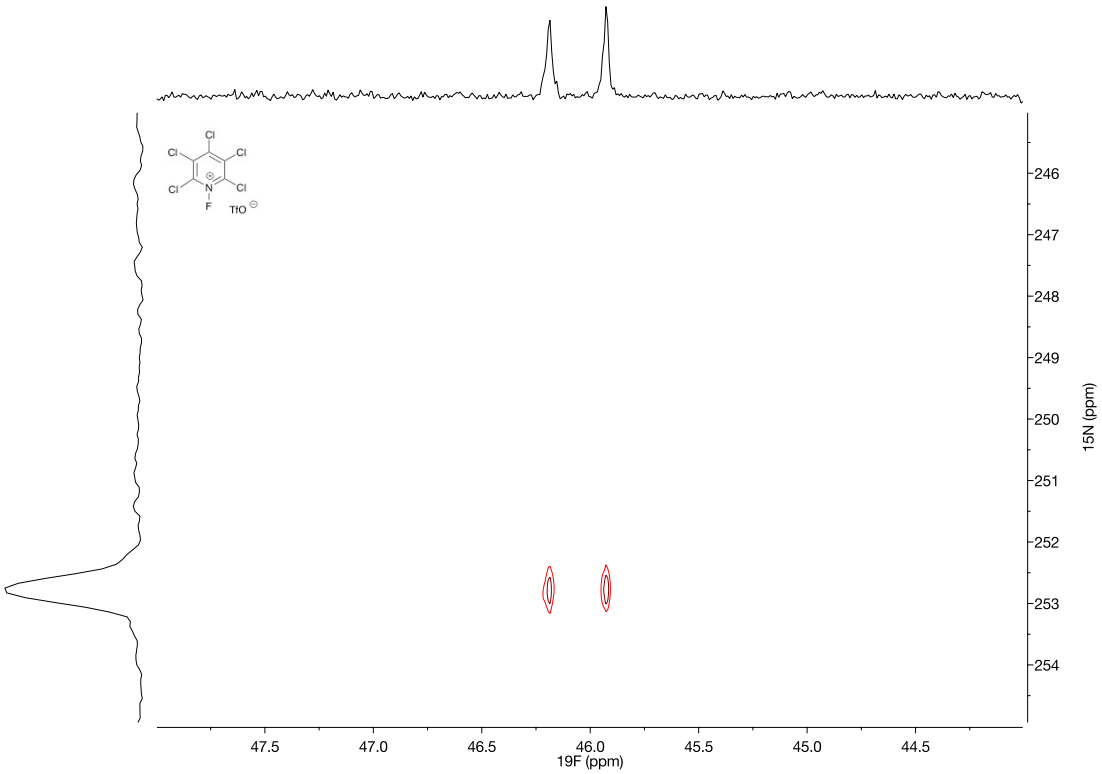


^{15}N-^{19}F HMQC [^{15}N (60.8 MHz) & ^{19}F (565.2 MHz) CD_3CN, 298K] of **7**

a) Without showing the splitting of the ^{19}F peak by ^{15}N

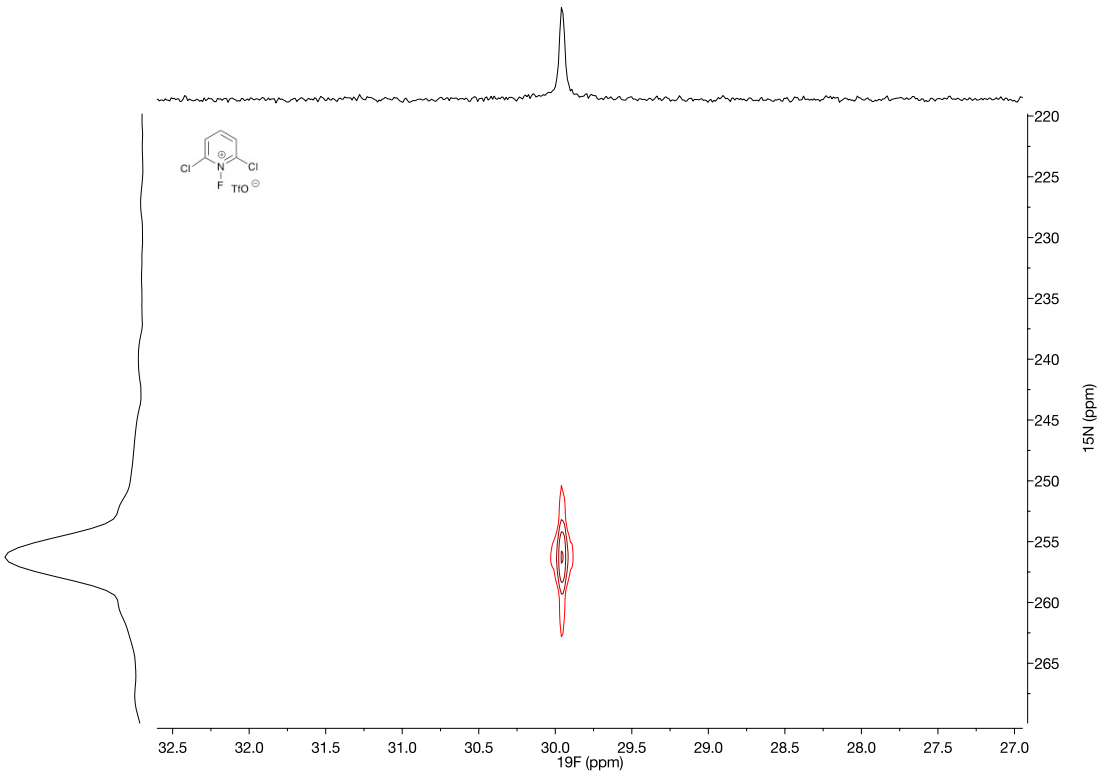


b) Showing the splitting of the ^{19}F peak by ^{15}N

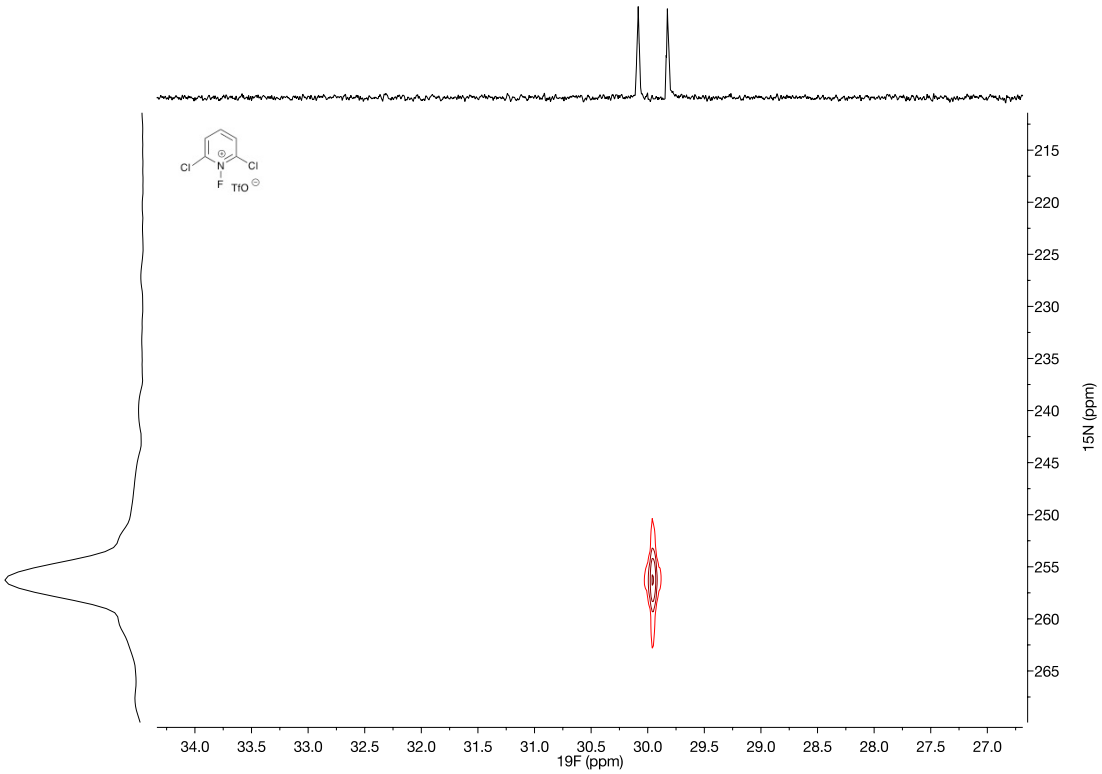


^{15}N-^{19}F HMQC [^{15}N (60.8 MHz) & ^{19}F (565.2 MHz) CD_3CN, 298K] of **6**

a) Without showing the splitting of the ^{19}F peak by ^{15}N

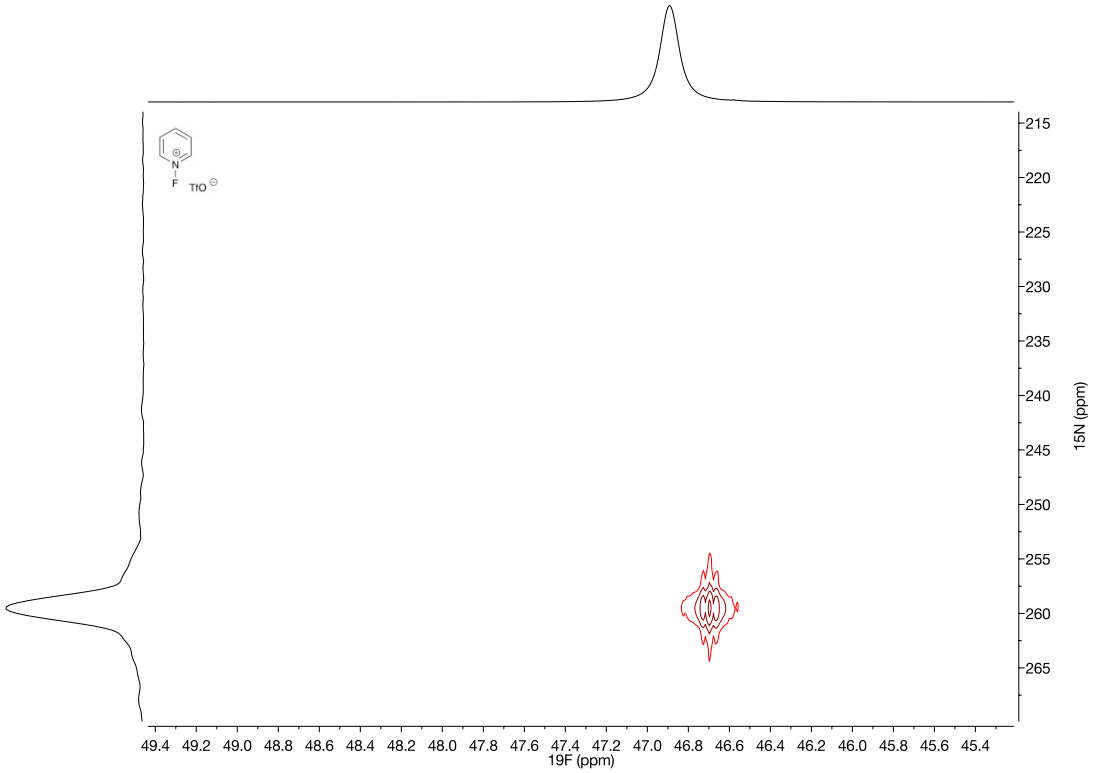


b) Showing the splitting of the ^{19}F peak by ^{15}N

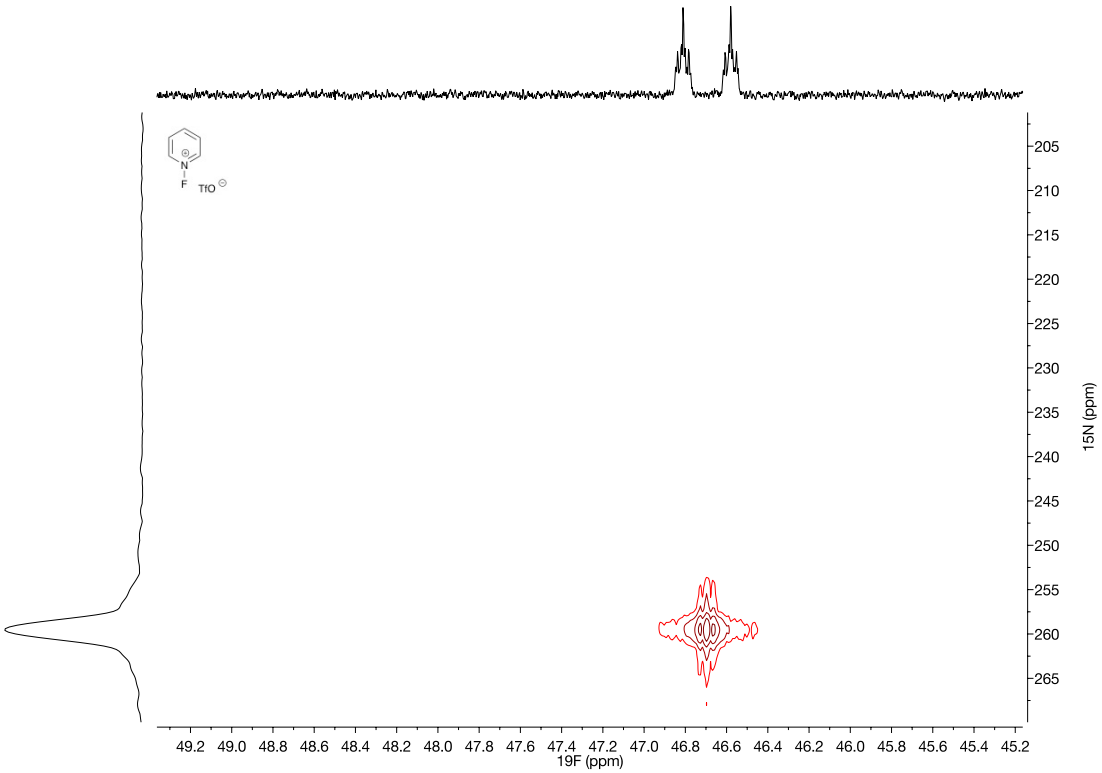


^{15}N-^{19}F HMQC [^{15}N (60.8 MHz) & ^{19}F (565.2 MHz) CD_3CN, 298K] of **10**

a) Without showing the splitting of the ^{19}F peak by ^{15}N

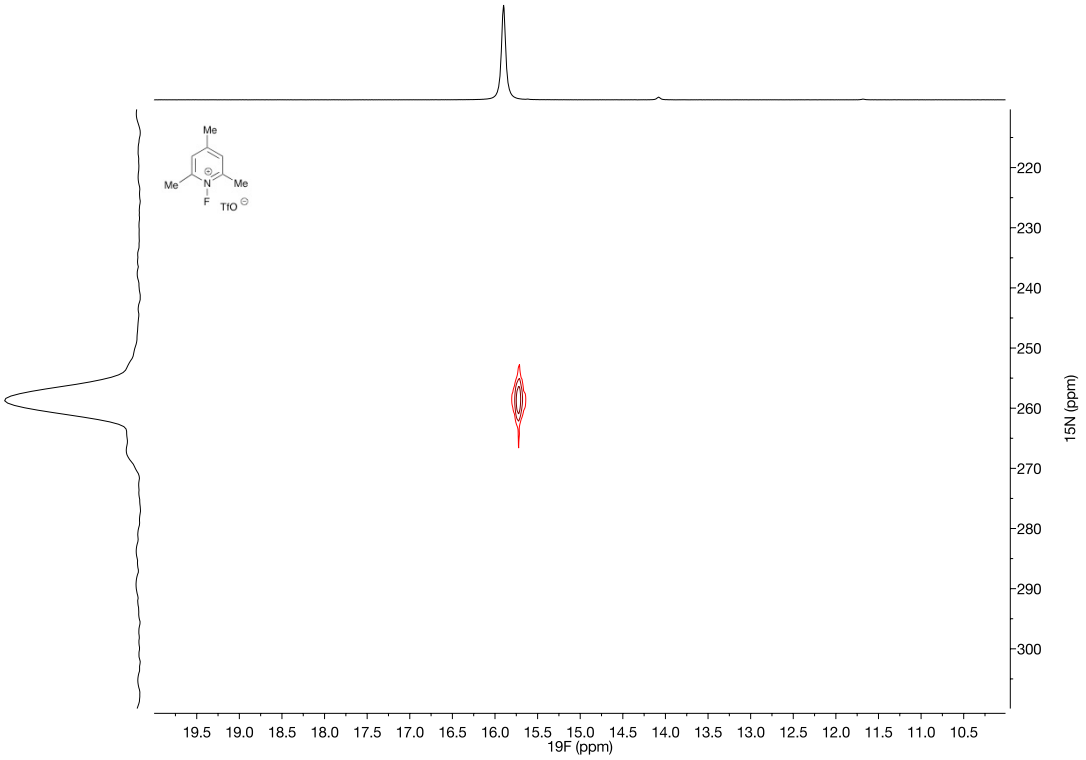


b) Showing the splitting of the ^{19}F peak by ^{15}N

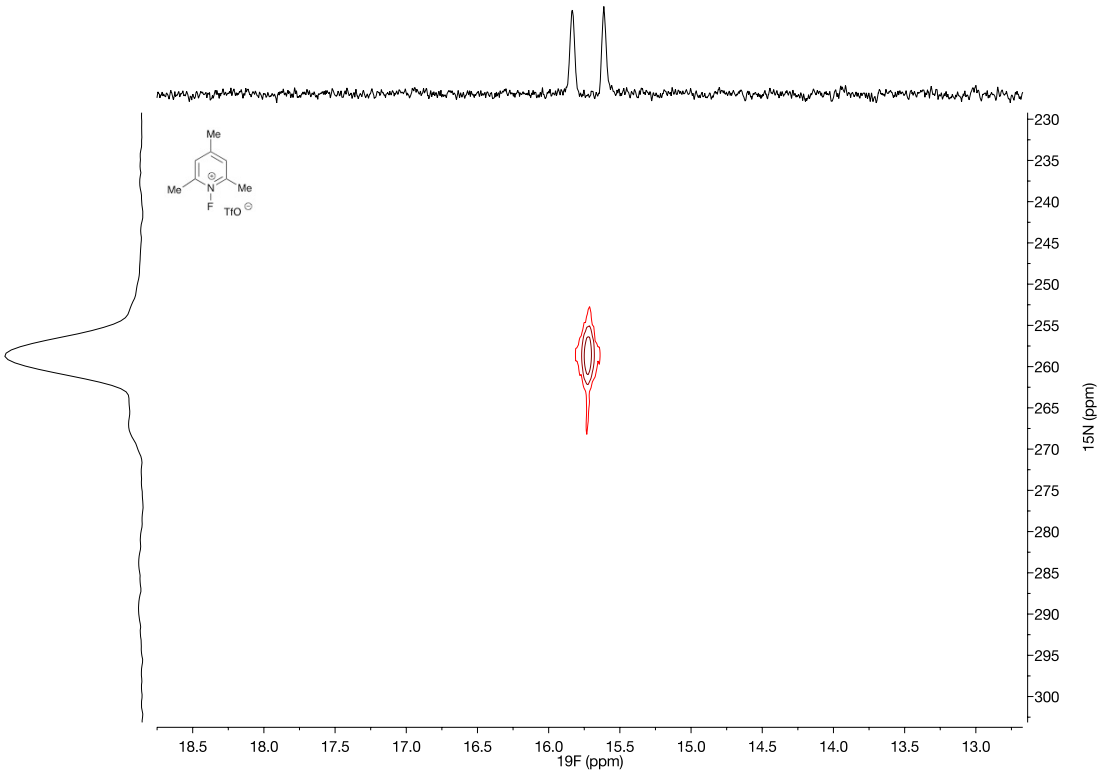


^{15}N-^{19}F HMQC [^{15}N (60.8 MHz) & ^{19}F (565.2 MHz) CD_3CN, 298K] of **11**

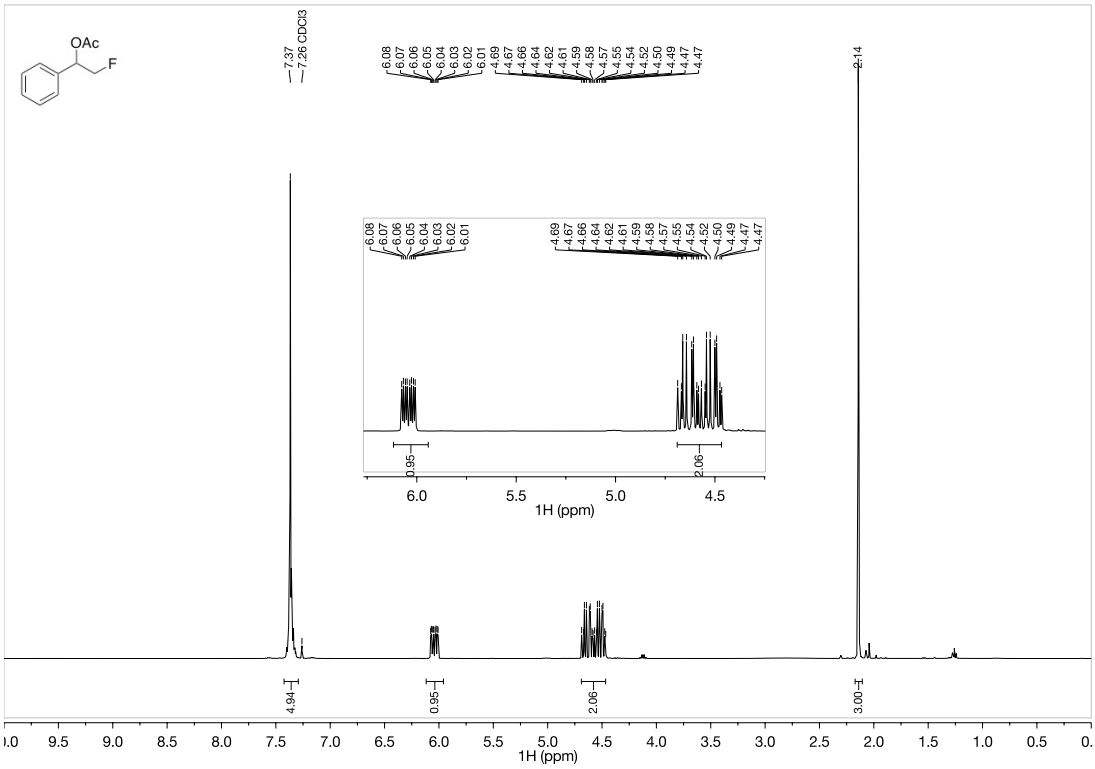
a) Without showing the splitting of the ^{19}F peak by ^{15}N



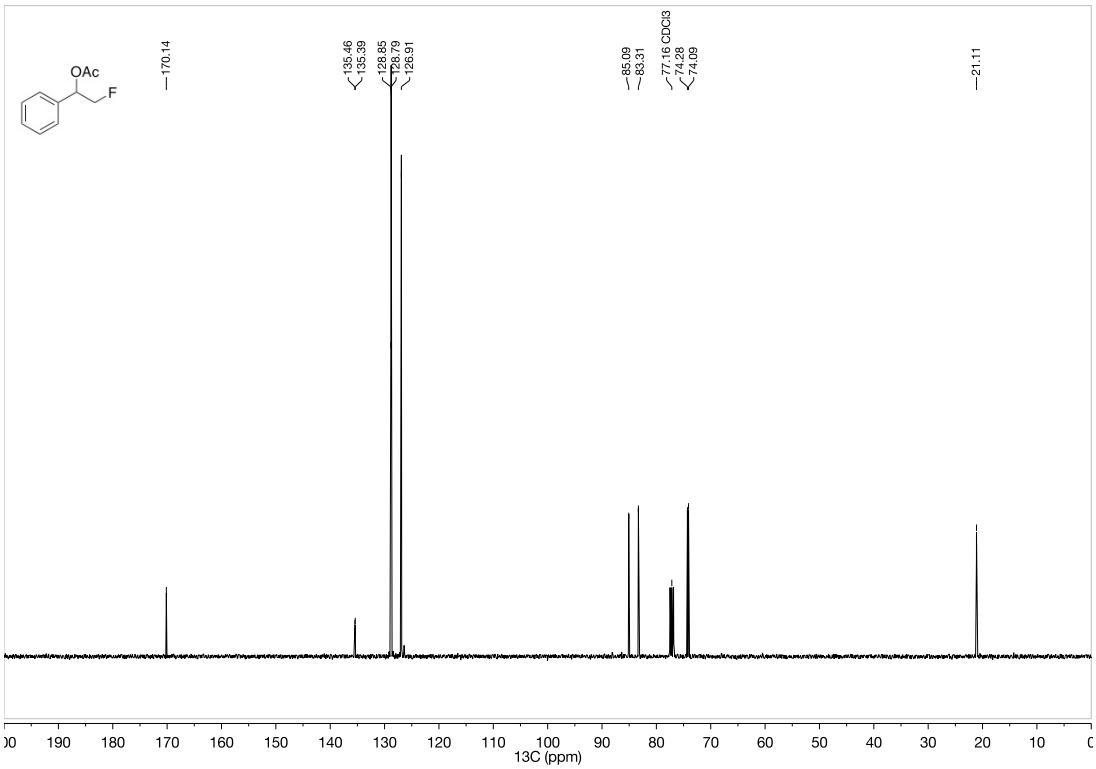
b) Showing the splitting of the ^{19}F peak by ^{15}N



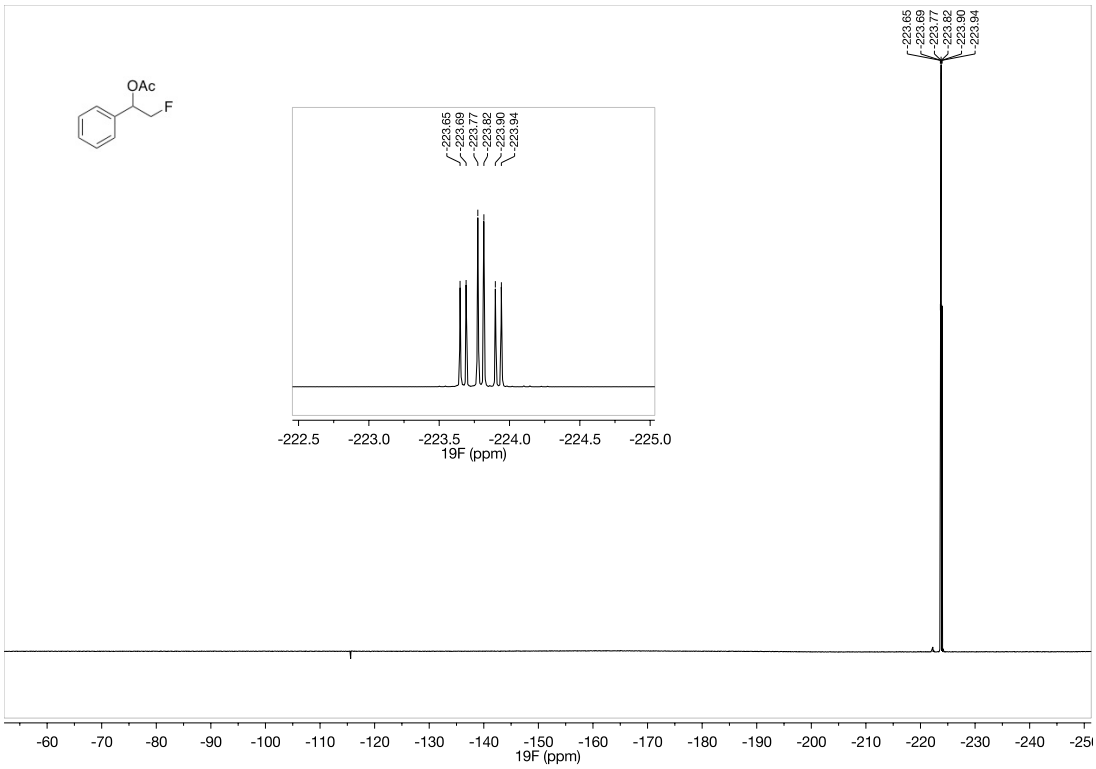
^{1}H NMR (400 MHz, $CDCl_3$, 298K) of **13**



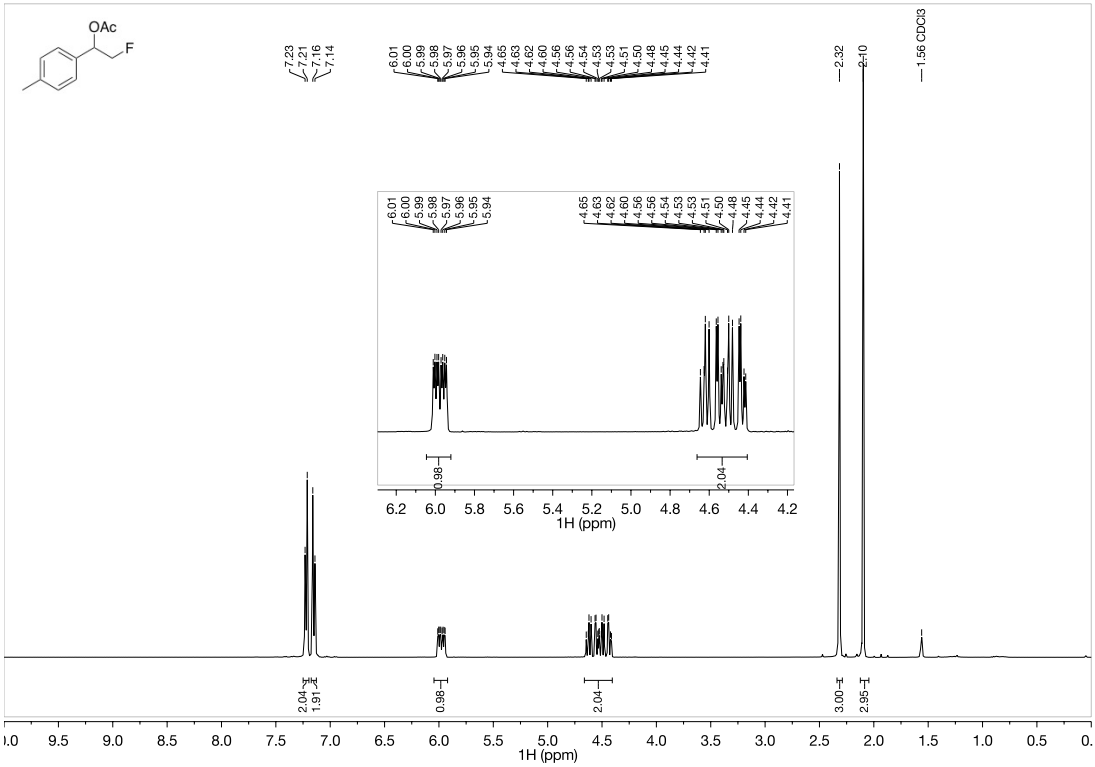
^{13}C NMR (100 MHz, $CDCl_3$, 298K) of **13**



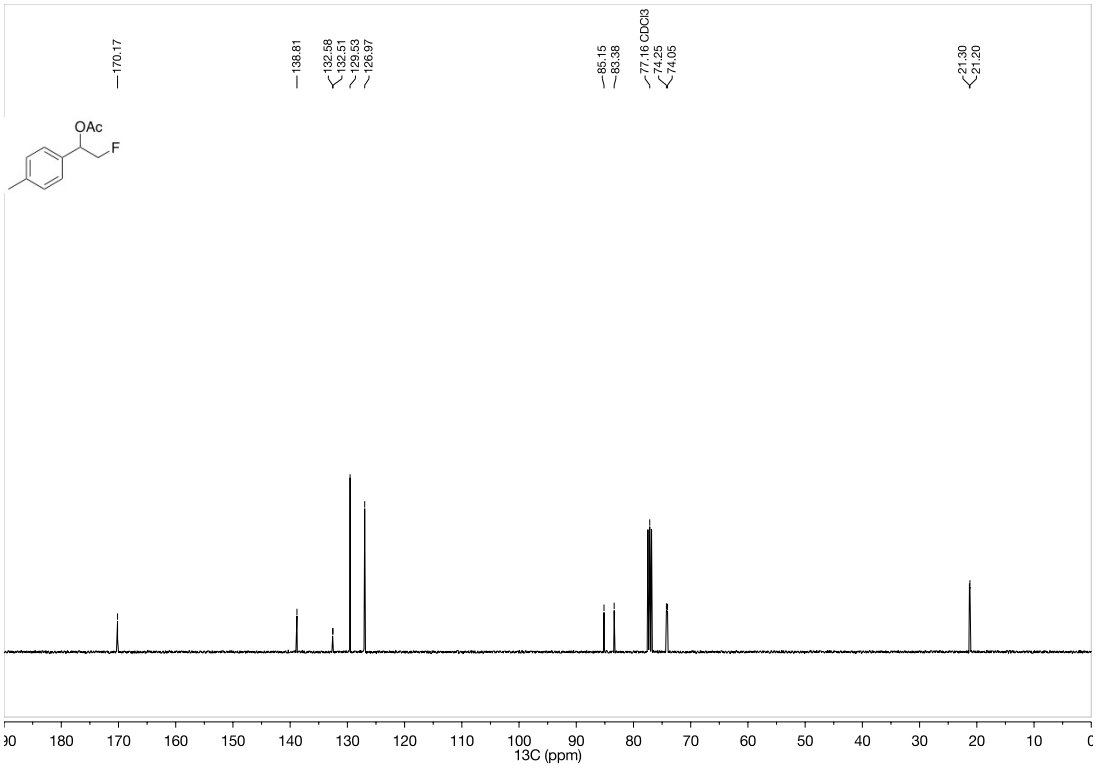
^{19}F NMR (377 MHz, $CDCl_3$, 298K) of **13**



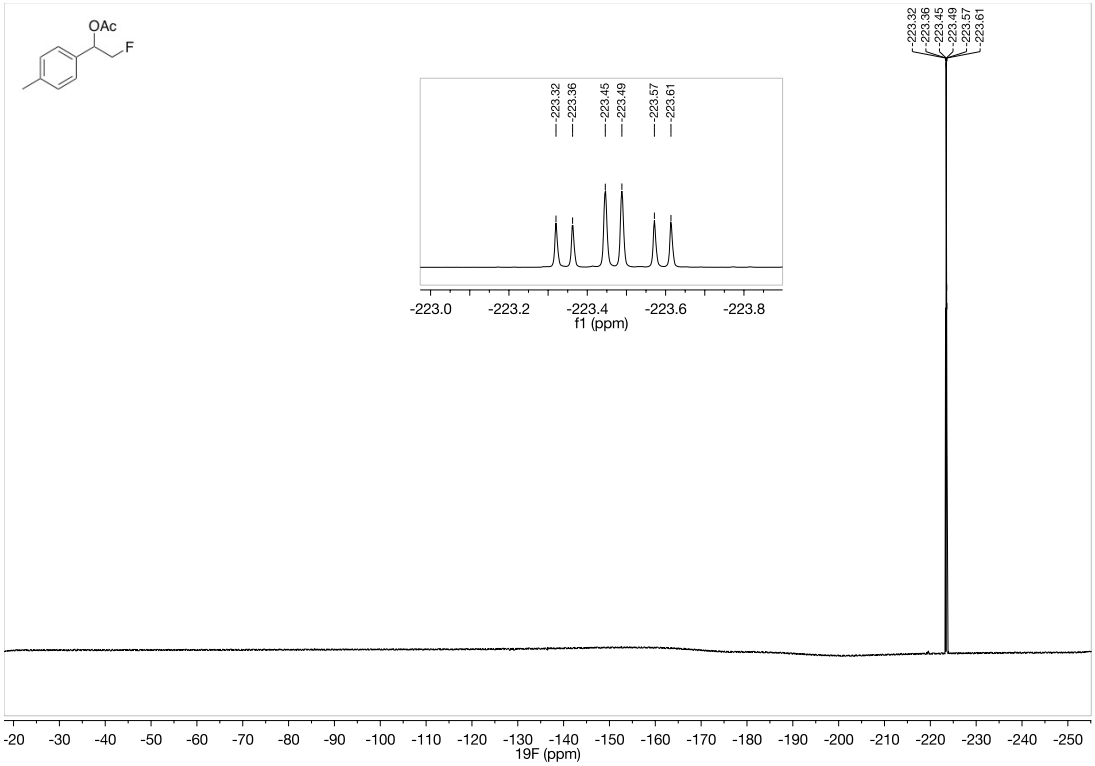
^{1}H NMR (400 MHz, $CDCl_3$, 298K) of **14**



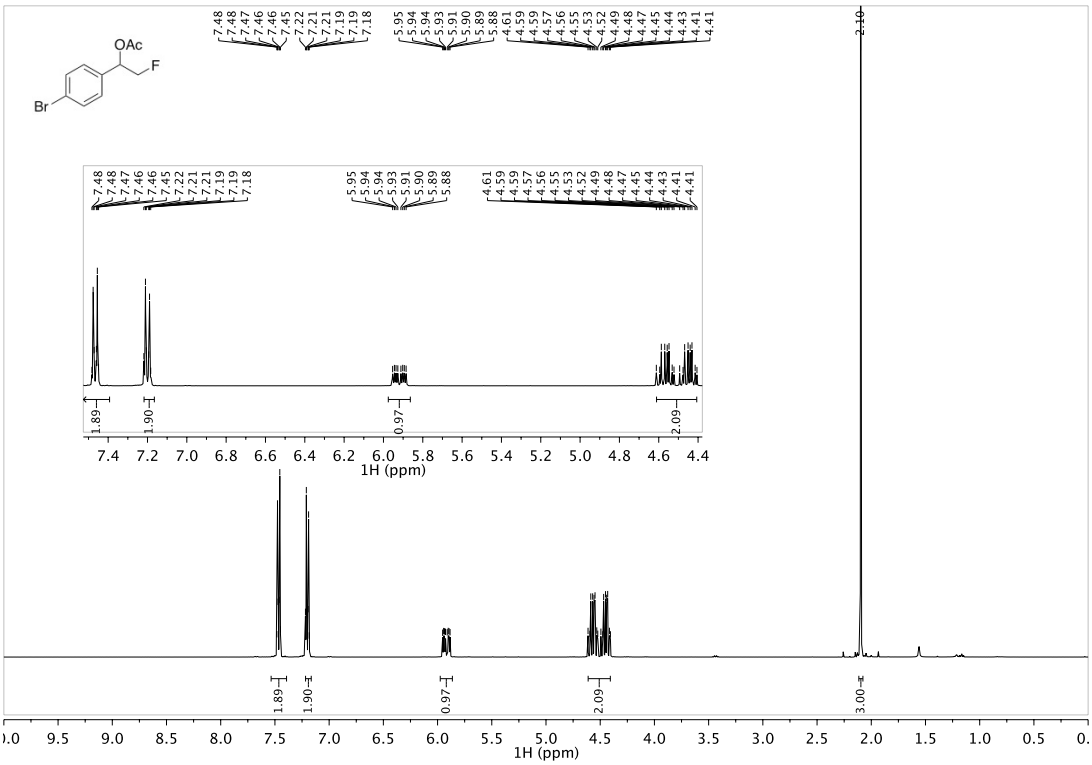
^{13}C NMR (100 MHz, $CDCl_3$, 298K) of **14**



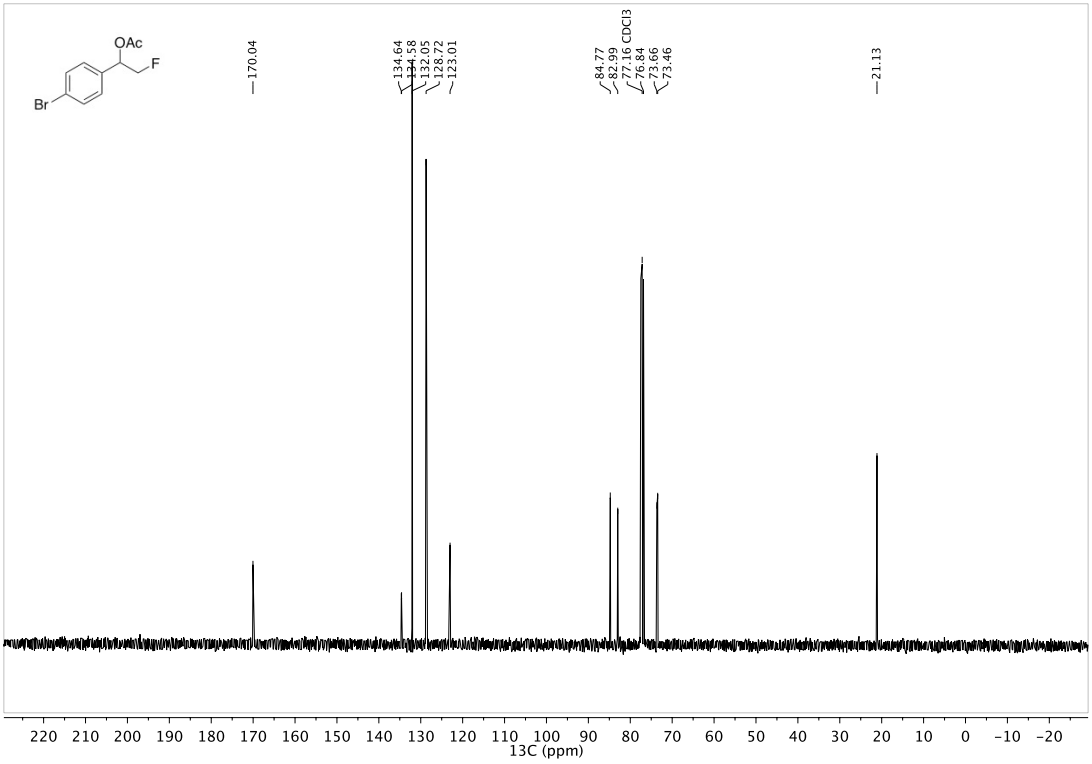
^{19}F NMR (377 MHz, $CDCl_3$, 298K) of **14**



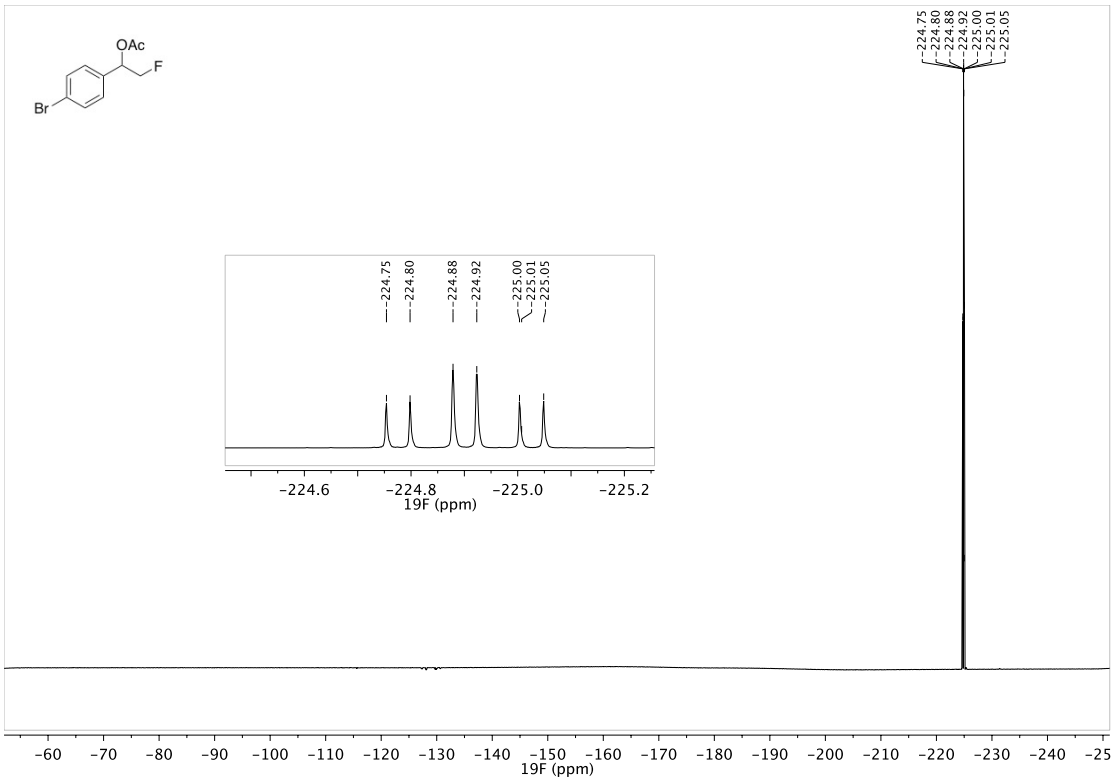
^{1}H NMR (400 MHz, $CDCl_3$, 298K) of **15**



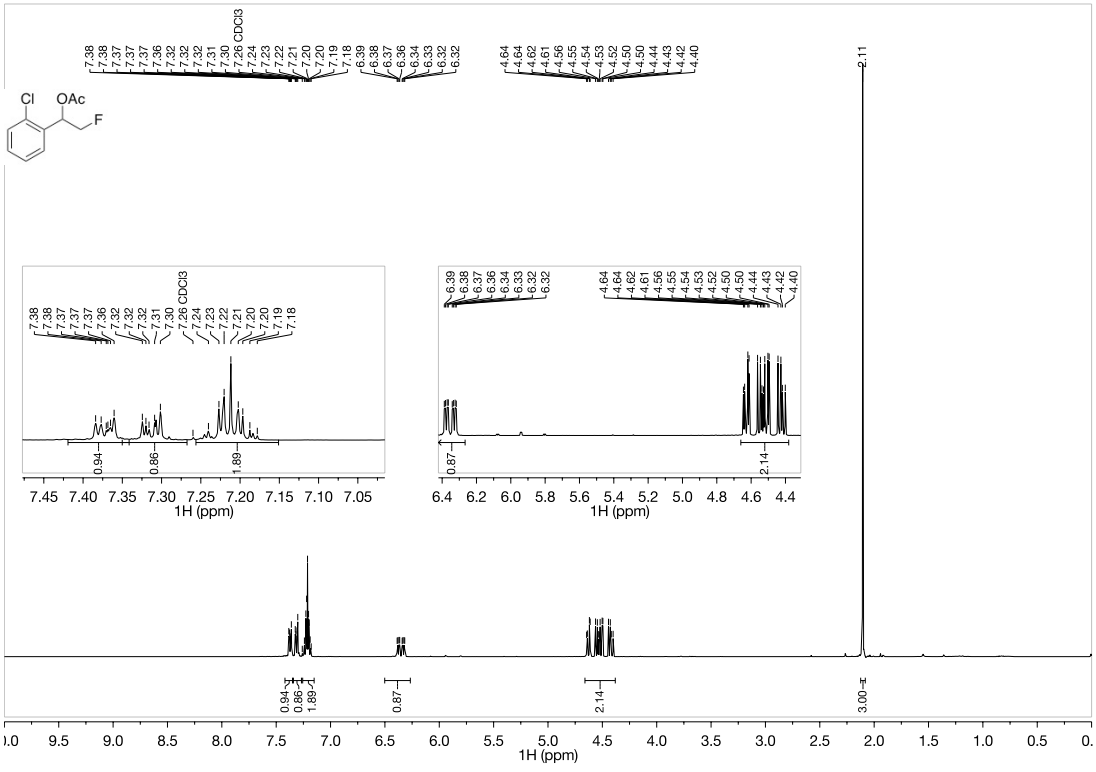
^{13}C NMR (100 MHz, $CDCl_3$, 298K) of **15**



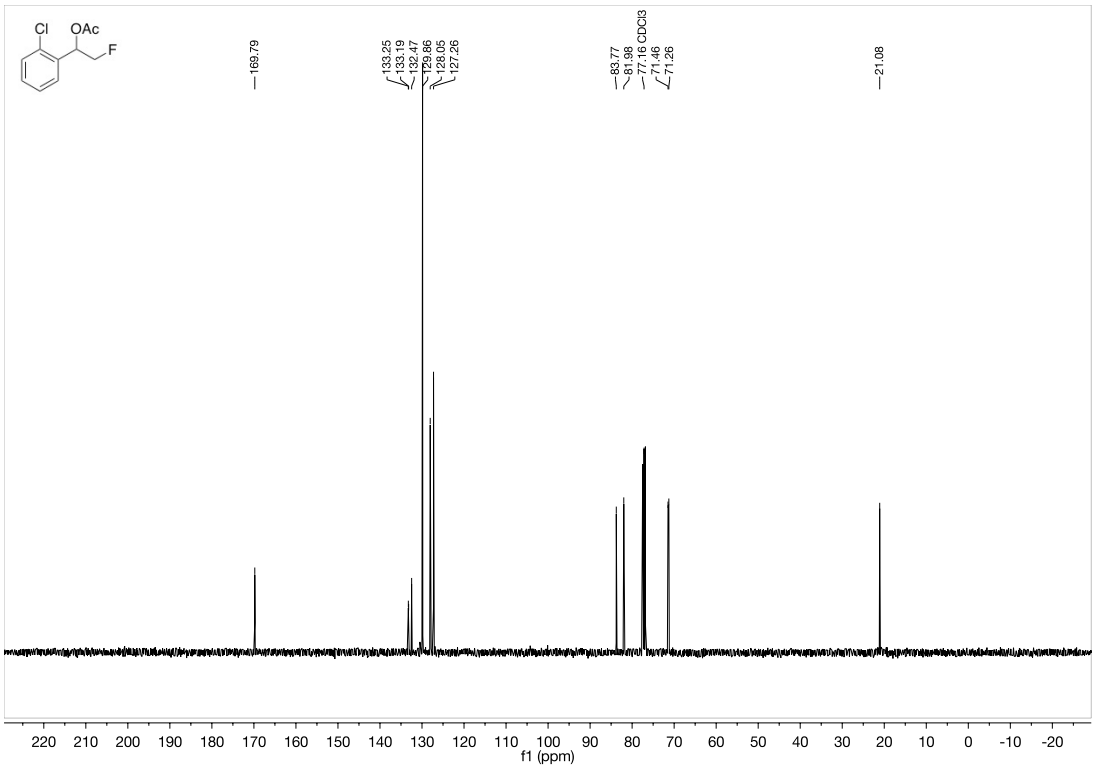
^{19}F NMR (377 MHz, $CDCl_3$, 298K) of **15**



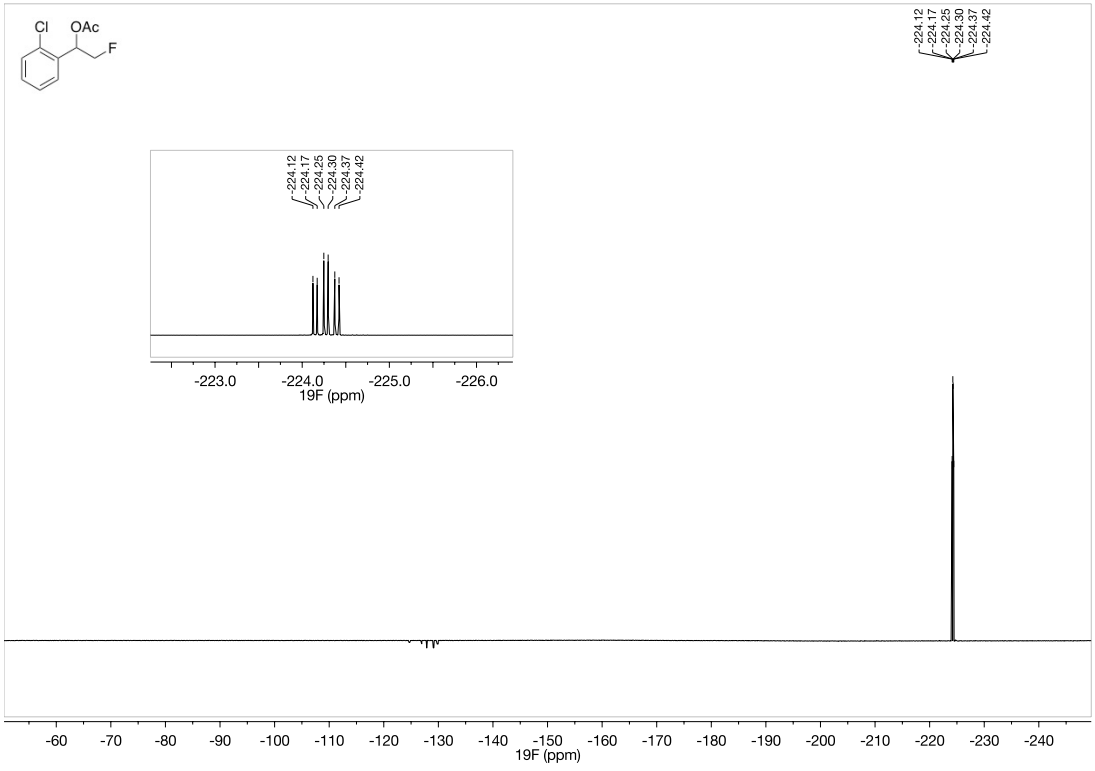
^{1}H NMR (400 MHz, $CDCl_3$, 298K) of **16**



^{13}C NMR (100 MHz, $CDCl_3$, 298K) of **16**



^{19}F NMR (377 MHz, $CDCl_3$, 298K) of **16**



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