Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Difluorination of Heterobenzylic C–H Bonds with *N*-Fluoro-*N*-(fluorosulfonyl)carbamate (NFC)

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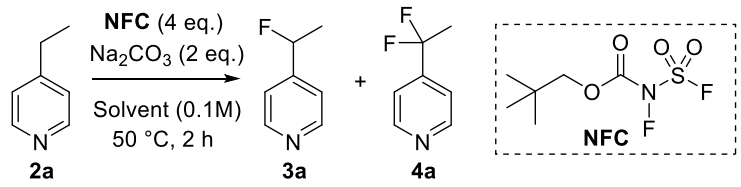
S1. General Information

^{1}H, ^{13}C, and ^{19}F NMR spectra were measured on JEOL JNM-ECZ400S (^{1}H NMR: 400 MHz, ^{13}C NMR: 100 MHz, ^{19}F NMR: 376 MHz) spectrometers at ambient temperature. Analytical thin layer chromatography (TLC) was performed on glass plates pre-coated with silica-gel (Merck Kieselgel 60 F_{254}, layer thickness 0.25 nm). Column chromatography was performed on KANTO Silica Gel 60N (spherical, neutral). High-resolution mass (HRMS) spectra were measured on a JEOL JMS-T100LP spectrometer in the electron spray ionization time-of-flight (ESI-TOF) mode. Gas chromatography-mass spectroscopy (GC-MS) analyses (using CI as ionization mode) were performed using a Shimadzu GC-MS QP2020 gas chromatograph mass spectrometer equipped with an HP-5 capillary column (0.320 i.d.; 0.25 μm df; 30 m; Agilent Technologies) with helium as the carrier gas. *N*-Fluoro-*N*-(fluorosulfonyl)-neopentylcarbamate (NFC) as a fluorinating reagent was synthesized according to the previous synthetic method.[1]

S2. Screening of Reaction Conditions in Fluorination of Pyridine 2a

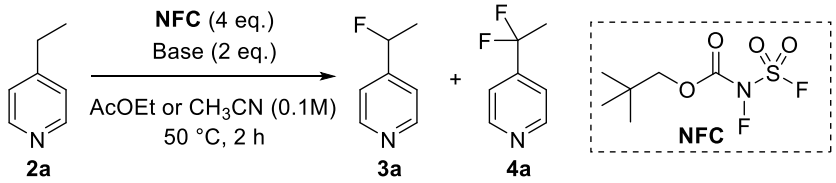
S2-1. Solvent



To a mixture of Na_2CO_3 (21.2 mg, 0.20 mmol, 2.0 equiv.) and **2a** (10.7 mg, 0.10 mmol) in solvent (0.1 M, 1.0 mL) was added **NFC** (92.5 mg, 0.40 mmol, 4.0 equiv.)[1] at room temperature under N_2 atmosphere. After stirring for 2 h at 50 ℃, the yield and selectivity were determined by ^{19}F NMR spectroscopy analysis using benzotrifluoride as an internal standard.

Entry	**solvent**	^{19}F NMR yield [%]	
		3a	**4a**
1	AcOEt	0	>99
2	CH_3CN	0	>99
3	Toluene	11	70
4	CH_2ClCH_2Cl	0	85
5	DMSO	<10	trace
6	DMF	56	12

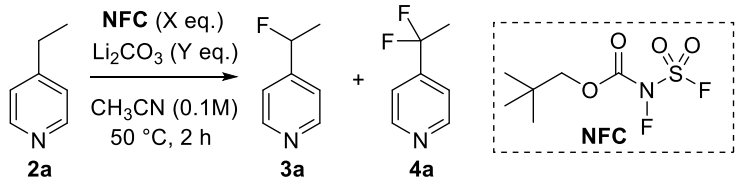
S2-2. Base



To a mixture of organic/inorganic base (0.20 mmol, 2.0 equiv.) and **2a** (10.7 mg, 0.10 mmol) in AcOEt or CH_3CN (0.1 M, 1.0 mL) was added **NFC** (92.5 mg, 0.40 mmol, 4.0 equiv.) at room temperature under N_2 atmosphere. After stirring for 2 h at 50 ℃, the yield and selectivity were determined by ^{19}F NMR spectroscopy analysis using benzotrifluoride as an internal standard.

Entry	**base**	**solvent**	^{19}F NMR yield [%]	
			3a	**4a**
1	Li_2CO_3	AcOEt	0	>99
2	Na_2CO_3	AcOEt	0	>99
3	K_2CO_3	AcOEt	0	98
4	Cs_2CO_3	AcOEt	0	93
5	$CaCO_3$	AcOEt	0	88
6	2,6-lutidine	AcOEt	0	98
7	*i*-Pr_2NEt	AcOEt	0	76
8	Li_2CO_3	CH_3CN	0	>99
9	Na_2CO_3	CH_3CN	0	>99

S2-3. Equivalence

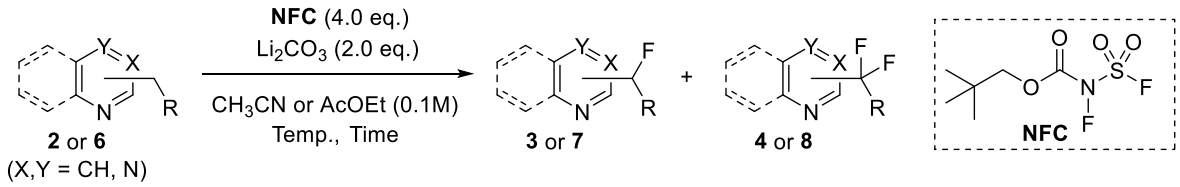


To a mixture of Li_2CO_3 (Y equiv.) and **2a** (10.7 mg, 0.10 mmol) in CH_3CN (0.1 M, 1.0 mL) was added **NFC** (X equiv.) at room temperature under N_2 atmosphere. After stirring for 2 h at 50 ℃, the yield and selectivity were determined by ^{19}F NMR spectroscopy analysis using benzotrifluoride as an internal standard.

Entry	**NFC** [eq.]	Li_2CO_3 [eq.]	^{19}F NMR yield [%]	
			3a	**4a**
1	4.0	2.0	0	>99
2	3.0	2.0	0	88
3	2.0	2.0	27	64
4	4.0	1.5	0	97
5	4.0	1.0	0	97

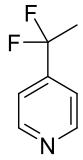
S3. Substrate Scope

S3-1. Direct Fluorination of *N*-Heterocycles using with NFC



To a mixture of Li_2CO_3 (14.8 mg, 0.20 mmol, 2.0 equiv.) and **2** (0.10 mmol) in CH_3CN or AcOEt (0.1 M, 1.0 mL) was added **NFC** (92.5 mg, 0.40 mmol, 4.0 equiv.) at room temperature under N_2 atmosphere. After stirring for 2-48 h at 50-75 ℃, the yield and selectivity were determined by ^{19}F NMR spectroscopy analysis using benzotrifluoride as an internal standard. The resulting crude mixture was purified by silica-gel column chromatography to give the products **3** or **7** and **4** or **8**.

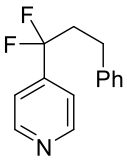
4-(1,1-Difluoroethyl)pyridine (4a)



The title compound was obtained from 4-ethylpyridine following the procedure above (CH_3CN, 50 ℃, 2 h). The yield and ratio of compounds (>99%, mono-F/di-F = <1/>99) were determined by ^{19}F NMR analysis using benzotrifluoride as an internal standard. Purification by silica-gel column chromatography (*n*-hexane/EtOAc = 7/1) gave the compound (12.6 mg, 88% yield) as a yellow oil. The product is known and the following data are identical to those given in corresponding literature.[2-3]

^1H NMR (400 MHz, $CDCl_3$) δ 8.69 (d, *J* = 4.8 Hz, 2H), 7.38 (d, *J* = 4.8 Hz, 2H), 1.89 (t, *J* = 18.0 Hz, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -91.1 (q, *J* = 17.3 Hz, 2F).

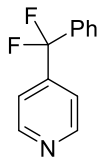
4-(1,1-Difluoro-2-phenylpropyl)pyridine (4b)



The title compound was obtained from 4-(3-phenylpropyl)pyridine following the procedure above (CH_3CN, 50 ℃, 10 h). The yield and ratio of compounds (93%, mono-F/di-F = <1/>99) were determined by ^{19}F NMR analysis using benzotrifluoride as an internal standard. Purification by silica-gel column chromatography (*n*-hexane/EtOAc = 3/1) gave the compound (16.7 mg, 72% yield) as a yellow oil.

^1H NMR (400 MHz, $CDCl_3$) δ 8.71 (t, *J* = 4.2 Hz, 2H), 7.39 (t, *J* = 4.2 Hz, 2H), 7.25 (d, *J* = 4.2 Hz, 2H), 7.20 (t, *J* = 8.0 Hz, 1H), 7.13 (d, *J* = 8.4 Hz), 2.75-2.80 (m, 2H), 2.33-2.47 (m, 2H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -99.19 (t, *J* = 17.3 Hz, 2F); ^{13}C NMR (100MHz, $CDCl_3$) δ 150.43, 145.32 (t, J_{C-F} = 28.0 Hz), 139.85, 128.72, 128.30, 126.51, 121.30 (t, J_{C-F} = 241.9 Hz), 119.66 (t, J_{C-F} = 5.5 Hz), 40.48 (t, J_{C-F} = 26.5 Hz), 28.52 (t, J_{C-F} = 4.0 Hz); HRMS (ESI-TOF) calcd for $C_{14}H_{14}F_2N$ $[M+H]^+$: 234.1094, found:234.1090.

4-(Difluoro(phenyl)methyl)pyridine (4c)

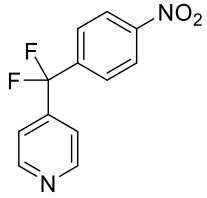


The title compound was obtained from 4-(benzyl)pyridine following the procedure above (CH_3CN, 50 ℃, 2 h). The yield and ratio of compounds (73%, mono-F/di-F = <1/>99) were determined by ^{19}F NMR analysis using benzotrifluoride as an internal standard. Purification by silica-gel column chromatography (CH_2Cl_2) gave the compound (13.1 mg, 64% yield) as a yellow oil. The product is

known and the following data are identical to those given in corresponding literature.[4]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (d, *J* = 5.6 Hz, 1H), 7.41-7.50 (m, 7H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -92.5 (s, 2F).

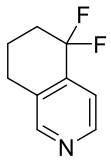
4-(1,1-Difluoro-1-(4'-nitrophenyl)methyl)pyridine (4d)



The title compound was obtained from 4-((4'-nitrophenyl)methyl)pyridine following the procedure above (CH_3CN, 50 °C, 2 h). The yield and ratio of compounds (99%, mono-F/di-F = <1/>99) were determined by ^{19}F NMR analysis using benzotrifluoride as an internal standard. Purification by silica-gel column chromatography (*n*-hexane/EtOAc =5/1) gave the compound (18.4 mg, 86% yield) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (d, *J* = 5.8 Hz, 2H), 8.31 (d, *J* = 9.0 Hz, 2H), 7.71 (d, *J* = 9.0 Hz, 2H), 7.12 (d, *J* = 5.8 Hz, 2H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -93.63 (s, 2F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.68, 149.22, 144.47 (t, *J* = 29.8 Hz), 142.28 (t, *J* = 28.8 Hz), 126.97 (t, *J* = 5.8 Hz), 124.12, 119.90 (t, *J* = 5.3 Hz), 118.42 (t, *J* = 243.4 Hz); HRMS (ESI-TOF) calcd for $C_{12}H_8F_2N_2NaO_2$ $[M+Na]^+$: 273.04515, found: 273.04410.

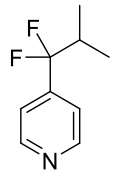
5,5-Difluoro-5,6,7,8-tetrahydroisoquinoline (4e)



The title compound was obtained from 5,6,7,8-tetrahydroisoquinoline following the procedure above (CH_3CN, 50 °C, 2 h). The yield and ratio of compounds (99%, mono-F/di-F = <1/>99) were determined by ^{19}F NMR analysis using benzotrifluoride as an internal standard. Purification by silica-gel column chromatography (*n*-hexane/EtOAc =2/1) gave the compound (14.0 mg, 83% yield) as a yellow oil. **4e** was not identified through ESI-MS (TOF, HRMS), but was identified through GC-MS (CI, LRMS).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (d, *J* = 4.8 Hz, 1H), 8.48 (s, 1H), 7.50 (d, *J* = 4.8 Hz, 1H), 2.81 (s, 2H), 2.22-2.32 (m, 2H), 1.98-2.05 (m, 2H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -87.7 (t, *J* = 11.3 Hz, 2F); ^{13}C NMR (100MHz, $CDCl_3$) δ 150.69, 148.15, 139.95 (t, $J_{C\text{-}F}$ = 26.7 Hz), 132.84 (t, $J_{C\text{-}F}$ = 5.7 Hz), 119.38, 118.57 (t, $J_{C\text{-}F}$ = 237.4 Hz), 33.08 (t, $J_{C\text{-}F}$ = 23.3 Hz), 25.55, 19.70 (t, $J_{C\text{-}F}$ = 4.8 Hz); LRMS (CI) calcd for $C_9H_{10}F_2N$ $[M+H]^+$: 170.08, found: 170.00.

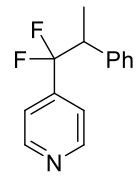
4-(1,1-Difluoro-2-methylpropyl)pyridine (4f)



The title compound was obtained from 4-(2-methylpropyl)pyridine following the procedure above (CH_3CN, 50 °C, 10 h). The yield and ratio of compounds (74%, mono-F/di-F = <1/>99) were determined by ^{19}F NMR analysis using benzotrifluoride as an internal standard. Purification by silica-gel column chromatography (*n*-hexane/EtOAc =4/1) gave the compound (8.0 mg, 48% yield) as a colorless oil. **4f** was not identified through ESI-MS (TOF, HRMS), but was identified through GC-MS (CI, LRMS).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.76 (d, *J* = 4.4 Hz, 2H), 7.42 (d, *J* = 4.6 Hz, 2H), 2.30 (m, 1H), 0.98 (d, *J* = 6.8 Hz, 6H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -106.56 (d, *J* = 13.9 Hz, 2F); ^{13}C NMR (100MHz, $CDCl_3$) δ 149.68, 145.27 (t, *J* = 28.5 Hz), 123.19 (t, *J* = 245.6 Hz), 120.56 (t, *J* = 5.7 Hz), 36.19 (t, *J* = 25.6 Hz), 15.65 (t, *J* = 4.3 Hz); LRMS (CI) calcd for $C_9H_{12}F_2N$ $[M+H]^+$: 172.09, found: 172.00.

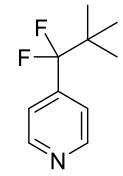
4-(1,1-Difluoro-2-phetnylpropyl)pyridine (4g)



The title compound was obtained from 4-(2-phenylpropyl)pyridine following the procedure above (CH_3CN, 50 °C, 10 h). The yield and ratio of compounds (69%, mono-F/di-F = <1/>99) were determined by ^{19}F NMR analysis using benzotrifluoride as an internal standard. Purification by silica-gel column chromatography (CH_2Cl_2) gave the compound (14.0 mg, 60% yield) as a yellow oil. The product is known in the literature.[5]

^1H NMR (400 MHz, $CDCl_3$) δ 8.56 (d, *J* = 6.4 Hz, 2H), 7.22-7.24 (m, 3H), 7.04-7.10 (m, 4H), 3.35-3.44 (m, 1H), 1.47 (d, *J* = 6.8 Hz, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -101.03 (dd, *J* = 242.5, 11.7 Hz, 1F), -106.36 (dd, *J* = 242.9, 85.0 Hz, 1F).

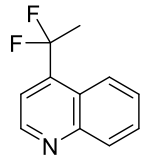
4-(1,1-Difluoro-2,2-dimethylpropyl)pyridine (4h)



The title compound was obtained from 4-(2,2-dimethylpropyl)pyridine following the procedure above (0.050 mmol, AcOEt, 50 °C, 18 h). The yield and ratio of compounds (65%, mono/di-F = 13/87) were determined by ^{19}F NMR analysis using benzotrifluoride as an internal standard. Purification by silica-gel column chromatography (*n*-hexane/EtOAc =4/1) solely gave the difluorinated compound (4.2 mg, 45% yield) as a yellow oil. **4h** was not identified through ESI-MS (TOF, HRMS), but was identified through GC-MS (CI, LRMS).

^1H NMR (400 MHz, $CDCl_3$) δ 8.68 (d, *J* = 4.0 Hz, 2H), 7.33 (d, *J* = 4.4 Hz, 2H), 1.03 (s, 9H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -108.2 (s, 2F); LRMS (CI) calcd for $C_{10}H_{14}F_2N$ $[M+H]^+$: 186.11, found: 186.05.

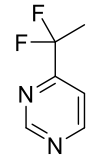
4-(1,1-Difluoroethyl)quinoline (4i)



The title compound was obtained from 4-ethylquinoline following the procedure above (0.050 mmol, AcOEt, 75 °C, 10 h). The yield and ratio of compounds (75%, mono-F/di-F = <1/>99) were determined by ^{19}F NMR analysis using benzotrifluoride as an internal standard. Purification by silica-gel column chromatography (*n*-hexane/EtOAc =8/1) gave the compound (5.2 mg, 45% yield) as a yellow oil.

^1H NMR (400 MHz, $CDCl_3$) δ 8.97 (brs, 1H), 8.20 (t, *J* = 7.6 Hz, 2H), 7.77 (t, *J* = 7.6 Hz, 1H), 7.63 (t, *J* = 7.6 Hz, 1H), 7.57 (d, *J* = 7.6 Hz, 1H), 2.13 (t, *J* = 18.6 Hz, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -86.51 (q, *J* = 18.4 Hz, 2F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.89, 149.01, 130.53, 129.67, 127.58, 124.75, 123.34, 121.62 (t, J_{C-F} = 235.5 Hz), 117.67, 117.38. 26.16 (t, J_{C-F} = 28.6 Hz); HRMS(ESI-TOF) calcd for $C_{11}H_{11}ClF_2N$ $[M+H]^+$: 230.0548, found: 230.0568.

4-(1,1-Difluoroethyl)pyrimidine (4j)

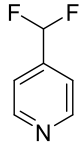


The title compound was obtained from 4-ethylpyrimidine following the procedure above (AcOEt, 75 °C, 10 h). The yield and ratio of compounds (71%, mono-F/di-F = <1/>99) were determined by ^{19}F NMR analysis using hexafluorobenzene (δ -163) as an internal standard. Purification by silica-gel column chromatography (*n*-pentane/Et_2O = 5/1) afforded volatile **4j** containing solvents and some impurities. **4j**

was not identified through ESI-MS (TOF, HRMS), but was identified through GC-MS (CI, LRMS).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.30 (s, 1H), 8.91 (d, *J* = 5.2 Hz, 1H), 7.65 (dd, *J* = 5.2, 1.6 Hz, 1H), 2.00 (t, *J* = 18.8 Hz, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -93.61 (q, *J* = 18.6 Hz, 2F); LRMS (CI) calcd for $C_6H_7F_2N_2$ $[M+H]^+$: 145.06, found: 145.10.

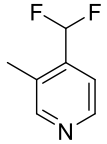
4-(Difluoromethyl)pyridine (4k)



The title compound was obtained from 4-picoline following the procedure above (CH_3CN, 75 °C, 10 h). The yield and ratio of compounds (60%, mono-F/di-F = <1/>99) were determined by ^{19}F NMR analysis using benzotrifluoride as an internal standard. Purification by silica-gel column chromatography (*n*-hexane/EtOAc =5/1) gave the compound (15.2 mg, 59% yield) as a yellow oil. The product is known and the following data are identical to those given in corresponding literature.[2]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (d, *J* = 4.8 Hz, 2H), 7.36 (d, *J* = 4.8 Hz, 2H), 6.59 (t, *J* = 55.8 Hz, 1H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.8 (d, *J* = 55.6 Hz, 2F).

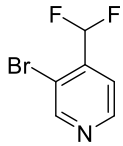
4-(Difluoromethyl)-3-methyl-pyridine (4l)



The title compound was obtained from 3,4-lutidine following the procedure above (CH_3CN, 75 °C, 24 h). The yield and ratio of compounds (32%, mono-F/di-F = <1/>99) were determined by ^{19}F NMR analysis using hexafluorobenzene (δ -163) as an internal standard. **4l** was volatile, therefore purification by silica-gel column chromatography was difficult.

^{19}F NMR (376 MHz, $CDCl_3$, crude) δ -119.47 (d, *J* = 57.9 Hz, 2F); LRMS (CI) calcd for $C_7H_8F_2N$ $[M+H]^+$: 144.06, found: 144.15.

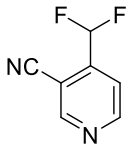
3-Bromo-4-(difluoromethyl)pyridine (4m)



The title compound was obtained from 3-bromo-4-picoline following the procedure above (CH_3CN, 75 °C, 10 h). The yield and ratio of compounds (90%, mono-F/di-F = <1/>99) were determined by ^{19}F NMR analysis using benzotrifluoride as an internal standard. Purification by silica-gel column chromatography (*n*-hexane/EtOAc =10/1) gave the compound (15.1 mg, 73% yield) as a yellow liquid. The product is known and the following data are identical to those given in corresponding literature.[2]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.78 (s, 1H), 8.64 (d, *J* = 5.2 Hz, 1H), 7.52 (t, *J* = 5.2 Hz, 1H), 6.81 (t, *J* = 54.0 Hz, 1H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -118.45 (d, *J* = 53.0 Hz, 2F).

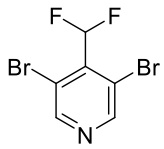
3-Cyano-4-(difluoromethyl)pyridine (4n)



The title compound was obtained from 3-cyano-4-(methyl)pyridine following the procedure above (CH_3CN, 75 °C, 10 h). The yield and ratio of compounds (75%, mono-F/di-F = <1/>99) were determined by ^{19}F NMR analysis using benzotrifluoride as an internal standard. Purification by silica-gel column chromatography (*n*-hexane/EtOAc =3/1) gave the compound (9.2 mg, 60% yield) as a yellow oil. The product is known and the following data are identical to those given in corresponding literature.[6]

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.01 (s, 1H), 8.97 (d, *J* = 3.6 Hz, 1H), 7.67 (d, *J* = 4.0 Hz, 1H), 6.88 (t, *J* = 42.8 Hz, 1H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -116.1 (d, *J* = 40.2 Hz, 2F).

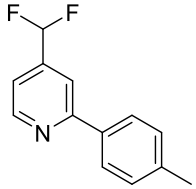
3,5-Dibromo-4-(difluoromethyl)pyridine (4o)



The title compound was obtained from 3,5-dibromo-4-methylpyridine following the procedure above (CH_3CN, 75 °C, 10 h). The yield and ratio of compounds (71%, mono-F/di-F = <1/>99) were determined by ^{19}F NMR analysis using benzotrifluoride as an internal standard. Purification by silica-gel column chromatography (*n*-hexane/EtOAc = 15/1) gave the compound (6.4 mg, 45% yield) as a colorless liquid, containing 10% of impurity at around -139 ppm in ^{19}F NMR spectra.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 (s, 2H), 7.10 (t, *J* = 52.8 Hz, 1H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -116.70 (d, *J* = 50.8 Hz, 2F); HRMS (ESI-TOF) calcd for $C_6H_3Br_2F_2NNa$ $[M+H]^+$: 307.8498, found: 307.8501.

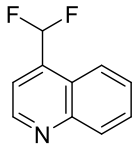
4-(Difluoromethyl)-2-(*p*-tolyl)pyridine (4p)



The title compound was obtained from 2-(*p*-tolyl)pyridine (0.20 mmol) following the procedure above (AcOEt, 75 °C, 24 h). The yield and the ratio of compounds (40%, mono-F/di-F = <1/>99) were determined by ^{19}F NMR analysis using benzotrifluoride as an internal standard. Purification by silica-gel column chromatography (*n*-hexane/EtOAc = 6/1) gave the compound (14.0 mg, 32% yield) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.79 (d, *J* = 4.8 Hz, 1H), 7.92 (d, *J* = 8.4 Hz, 2H), 7.81 (s, 1H), 7.26-7.32 (m, 3H), 6.69 (t, *J* = 56.0 Hz), 2.42 (s, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.47 (d, *J* = 57.5 Hz, 2F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.58, 150.43, 143.04 (t, J_{C-F} = 23.0 Hz), 139.86, 135.83, 129.78, 127.01, 118.04, 116.46, 113.33 (t, J_{C-F} = 238.6 Hz), 21.47; HRMS (ESI-TOF) calcd for $C_{13}H_{11}F_2NNa$ $[M+Na]^+$: 242.0757, found: 242.0758.

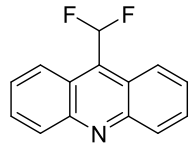
4-(Difluoromethyl)quinoline (4s)



The title compound was obtained from 4-lepidine following the procedure above (AcOEt, 75 °C, 18 h). The yield and ratio of compounds (71%, mono-F/di-F = <1/>99) were determined by ^{19}F NMR analysis using benzotrifluoride as an internal standard. Purification by silica-gel column chromatography (*n*-hexane/EtOAc = 8/1) gave the compound (5.5 mg, 58% yield) as a colorless oil. The product is known and the following data are identical to those given in corresponding literature.[7]

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.02 (d, *J* = 4.8 Hz, 1H), 8.20 (d, *J* = 8.4 Hz, 1H), 8.10 (d, *J* = 8.4 Hz, 1H), 7.80 (t, *J* = 7.2 Hz, 1H), 7.66 (t, *J* = 8.4 Hz, 1H), 7.60 (d, *J* = 4.4 Hz, 1H), 7.16 (t, *J* = 54.4 Hz, 1H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.0 (d, *J* = 53.4 Hz ,2F).

9-(Difluoromethyl)acridine (4t)

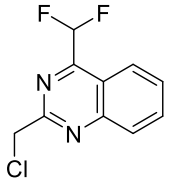


The title compound was obtained from 9-methylactidine following the procedure above (CH_3CN, 75 °C, 18 h). The yield and ratio of compounds (73%, mono-F/di-F = <1/>99) were determined by ^{19}F NMR analysis using benzotrifluoride as an internal standard. Purification by silica-gel column chromatography (*n*-hexane/EtOAc = 10/1) gave the compound (11.7 mg, 51%

yield) as a yellow powder.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (d, *J* = 8.8 Hz, 2H), 8.31 (d, *J* = 8.8 Hz, 2H), 7.95 (t, *J* = 54.0 Hz, 1H), 7.84 (t, *J* = 7.6 Hz, 2H), 7.67 (dd, *J* = 8.6, 6.6 Hz, 2H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -108.39 (d, *J* = 57.9 Hz , 2F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.91, 130.84, 130.69, 130.27, 123.48, 123.33, 112.85 (t, $J_{C\text{-}F}$ = 237.5 Hz); HRMS (ESI-TOF) calcd for $C_{14}H_{10}F_2N$ $[M+H]^+$: 230.0781, found: 230.0768.

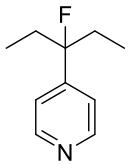
2-(Chloromethyl)-4-(difluoromethyl)quinazoline (4u)



The title compound was obtained from 2-(chloromethyl)-4-methylquinazoline (0.050 mmol) following the procedure above (AcOEt, 75 °C, 18 h). The yield and ratio of compounds (54%, mono-F/di-F = 37/63) were determined by ^{19}F NMR analysis using benzotrifluoride as an internal standard. Purification by silica-gel column chromatography (*n*-hexane/EtOAc =15/1) solely gave the difluorinated compound (3.6 mg, 31% yield) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (d, *J* = 8.4 Hz, 1H), 8.15 (d, *J* = 8.4 Hz, 1H), 8.02 (t, *J* = 7.6 Hz, 1H), 7.77 (t, *J* = 7.6 Hz, 1H), 6.90 (t, *J* = 54.0 Hz, 1H), 4.92 (s, 2H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -111.7 (d, *J* = 53.4 Hz ,2F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.80, 160.21 (t, J_{C-F} = 27.3 Hz), 151.99, 135.08, 129.26, 129.23, 125.05 (t, J_{C-F} = 3.3 Hz), 119.61, 116.44 (t, J_{C-F} = 242.9 Hz), 47.09; HRMS (ESI-TOF) calcd for $C_{10}H_8ClF_2N_2$ $[M+H]^+$: 229.0344, found: 229.0355.

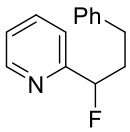
4-(3-Fluoro-3-pentyl)pyridine (5)



The title compound was obtained from 4-(3-pentyl)pyridine following the procedure above (CH_3CN, 50 °C, 2 h). The yield and ratio of compounds (92%) were determined by ^{19}F NMR analysis using benzotrifluoride as an internal standard. Purification by silica-gel column chromatography (-*n*-hexane/EtOAc =10/1) gave the compound (13.2 mg, 79% yield) as a yellow oil. **5** was not identified through ESI-MS (TOF, HRMS), but was identified through GC-MS (CI, LRMS).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (d, *J* = 5.2 Hz, 2H), 7.15 (d, *J* = 4.8 Hz, 2H), 1.76-2.01 (m, 4H), 0.75 (t, *J* = 7.2 Hz, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -167.99 (m, 1F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.92 (d, J_{C-F} = 19.2 Hz), 149.83, 120.06 (d, J_{C-F} = 7.7 Hz), 99.45 (d, J_{C-F} = 141.1 Hz), 32.98 (d, J_{C-F} = 19.2 Hz), 7.52 (d, J_{C-F} = 3.9 Hz); LRMS (CI) calcd for $C_{10}H_{15}FN$ $[M+H]^+$: 168.12, found: 168.10.

2-(1-Fluoro-2-phenylpropyl)pyridine (7a)

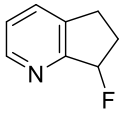


The title compound was obtained from 2-(2-phenylpropyl)pyridine following the procedure above (CH_3CN, 75 °C, 18 h). The yield and ratio of compounds (42%, mono-F/di-F = >99/<1) were determined by ^{19}F NMR analysis using benzotrifluoride as an internal standard. Purification by silica-gel column chromatography (CH_2Cl_2) gave the compound (6.5 mg, 30% yield) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (d, *J* = 5.2 Hz, 1H), 7.72 (t, *J* = 8.0 Hz, 1H), 7.46 (d, *J* = 7.6 Hz, 1H), 7.17-7.30 (m, 6H), 5.55 (ddd, *J* = 48.0, 8.0 ,4.0 Hz, 1H), 2.77-2.87 (m, 2H), 2.22-2.39 (m, 2H); ^{19}F-NMR (376 MHz, $CDCl_3$) δ -186.71 (m, 1F); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 159.73 (d, J_{C-F} = 240.0 Hz), 149.08 (d, J_{C-F} = 3.0 Hz), 141.22,

136.92, 128.62, 128.56, 126.12, 122.95, 119.82 (d, $J_{C–F}$ = 7.0 Hz), 94.02 (d, $J_{C–F}$ = 170.9 Hz), 37.69 (d, $J_{C–F}$ = 22.0 Hz), 31.25 (d, $J_{C–F}$ = 3.0 Hz); HRMS (ESI-TOF) calcd for $C_{14}H_{14}FNNa$ $[M+Na]^+$: 238.1008, found: 238.1035.

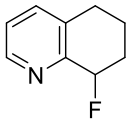
7-Fluoro-6,7-dihydro-5*H*-cyclopenta[*b*]pyridine (7b)



The title compound was obtained from 6,7-dihydro-5*H*-cyclopenta[*b*]pyridine (0.20 mmol) following the procedure above (CH_3CN, 50 °C, 24 h). The yield and ratio of compounds (55%, mono-F/di-F = 96/4) were determined by ^{19}F NMR analysis using benzotrifluoride as an internal standard. Purification by silica-gel column chromatography (*n*-hexane/EtOAc =4/1) solely gave the monofluorinated compound (11.2 mg, 41% yield) as a brown oil. The product is known and the following data are identical to those given in corresponding literature.[8]

^1H NMR (400 MHz, $CDCl_3$) δ 8.55 (d, *J* = 4.0 Hz, 1H), 7.65 (d, *J* = 6.0 Hz, 1H), 7.23-7.26 (m, 1H), 5.94 (ddd, *J* = 44.8, 5.2, 2.0 Hz, 1H), 3.15-3.22 (m, 1H), 2.87-2.94 (m, 1H), 2.32-2.53 (m, 2H); ^{19}F-NMR (376 MHz, $CDCl_3$) δ -167.54 (m, 1F).

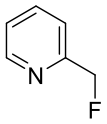
8-Fluoro-5,6,7,8-tetrahydroquinoline (7c)



The title compound was obtained from 5,6,7,8-tetrahydroquinoline following the procedure above (CH_3CN, 50 °C, 24 h). The yield and ratio of compounds (85%, mono-F/di-F = 95/5) were determined by ^{19}F NMR analysis using benzotrifluoride as an internal standard. Purification by silica-gel column chromatography (*n*-hexane/EtOAc =3/1) solely gave the monofluorinated compound (12.8 mg, 78% yield) as a yellow oil. The product is known and the following data are identical to those given in corresponding literature.[9]

^1H NMR (400 MHz, $CDCl_3$) δ 8.52 (d, *J* = 4.8 Hz, 1H), 7.47 (d, *J* = 8.0 Hz, 1H), 7.18-7.22 (m, 1H), 5.55 (d, *J* = 47.2 Hz, 1H), 2.69-2.88 (m, 2H), 2.35-2.40 (m, 1H), 1.92-2.08 (m, 2H), 1.81-1.91 (m, 1H); ^{19}F-NMR (376 MHz, $CDCl_3$) δ -163.00 (m, 1F).

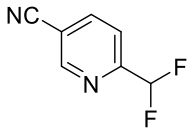
2-(Fluoromethyl)pyridine (7d)



The title compound was obtained from 2-picoline following the procedure above (CH_3CN, 75 °C, 18 h). The yield and ratio of compounds (87%, mono-F/di-F = 98/2) were determined by ^{19}F NMR analysis using benzotrifluoride (δ -63) as an internal standard. Purification by silica-gel column chromatography (*n*-hexane/CH_2Cl_2 =1/1 to 2/3) gave the compound including starting material. The product is known and the following peaks are found in correspond to the literature.[9]

^1H-NMR (400 MHz, $CDCl_3$) δ 8.56 (d, *J* = 4.4 Hz), 7.68-7.73 (m), 7.45 (d, *J* =7.6 Hz), 7.20-7.24 (m), 5.47 (d, *J* = 47.2 Hz); ^{19}F-NMR (376 MHz, $CDCl_3$) δ -221.41 (t, *J* = 46.2 Hz, 1F).

6-(Difluoromethyl)nicotinonitrile (8e)

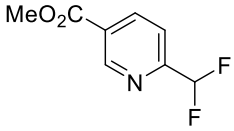


The title compound was obtained from 6-methylnicotinonitrile following the procedure above (CH_3CN, 75 °C, 24 h). The yield and ratio of compounds (89%, mono-F/di-F = 56/44) were determined by ^{19}F NMR analysis using benzotrifluoride as an internal standard. Purification by

silica-gel column chromatography (*n*-hexane/EtOAc =7/1) gave the difluorinated compound (5.4 mg, 35% yield) as a white powder. **8e** was not identified through ESI-MS (TOF, HRMS), but was identified through GC-MS (CI, LRMS).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.94 (s, 1H), 8.14 (m, 1H), 7.80 (m, 1H) , 6.67 (t, *J* = 55.2 Hz, 1H); ^{19}F-NMR (376 MHz, $CDCl_3$) δ -116.94 (d, *J* = 55.3 Hz, 2F); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 156.08 (t, J_{C-F} = 19.8 Hz), 152.27, 140.99, 120.43 (t, J_{C-F} = 3.1 Hz), 115.87, 112.95 (t, J_{C-F} = 242.0 Hz), 111.98; LRMS (CI) calcd for $C_7H_5F_2N_2$ $[M+H]^+$: 155.04, found: 155.00

Methyl 6-(difluoromethyl)nicotinate (8f)



The title compound was obtained from methyl 6-(methyl)nicotinate following the procedure above (CH_3CN, 75 °C, 24 h). The yield and ratio of compounds (93%, mono-F/di-F = 57/43) were determined by ^{19}F NMR analysis using benzotrifluoride as an internal standard. Purification by silica-gel column chromatography (*n*-hexane/EtOAc =3/1) gave the difluorinated compound (5.7 mg, 38% yield) as a white solid. The product is known and the following data are identical to those given in corresponding literature.[10]

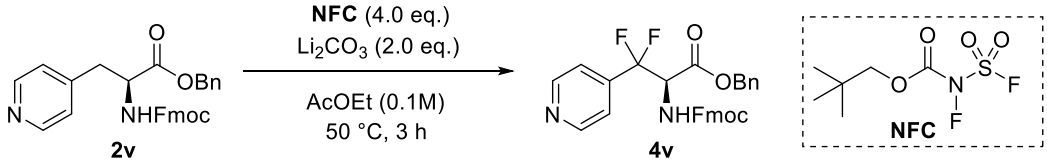
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.24 (s, 1H), 8.45 (d, *J* = 7.6 Hz, 1H), 7.74 (d, *J* = 8.0 Hz, 1H), 6.68 (t, *J* = 55.2 Hz, 1H), 3.99 (s, 3H); ^{19}F-NMR (376 MHz, $CDCl_3$) δ -116.52 (d, *J* = 57.9 Hz, 2F).

2-(Difluoromethyl)pyrazine (8h)

The title compound was obtained from 2-cyano-3-(methyl)pyridine following the procedure above (CH_3CN, 75 °C, 24 h). The yield and ratio of compounds (7%, mono-F/di-F = <1/>99) were determined by ^{19}F NMR analysis using hexafluorobenzene (δ -163) as an internal standard. **8h** was not identified through ESI-MS (TOF, HRMS), but was identified through GC-MS (CI, LRMS).

^{19}F-NMR (376 MHz, $CDCl_3$, crude) δ -96.47 (d, *J* = 46.2 Hz, 2F); LRMS (CI) calcd for $C_5H_5F_2N_2$ $[M+H]^+$: 131.04, found: 131.15.

S3-2. Direct Fluorination of Amino Acid Derivative 2v

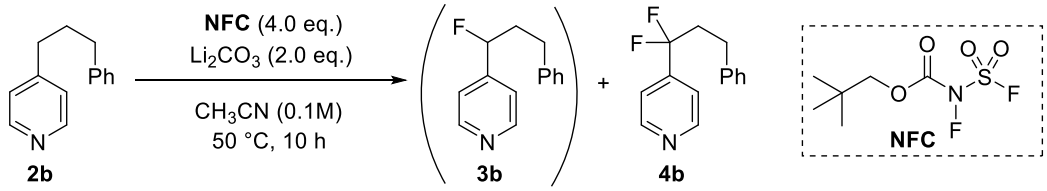


To a mixture of Li_2CO_3 (7.4 mg, 0.10 mmol, 2.0 equiv.) and **2v** (23.9 mg, 0.050 mmol) in AcOEt (0.1 M, 0.5 mL) was added **NFC** (46.2 mg, 0.40 mmol, 4.0 equiv.) at room temperature under N_2 atmosphere. After stirring for 3 h at 50 °C, the yield and selectivity were determined by ^{19}F NMR spectroscopy analysis using benzotrifluoride as an internal standard (89%, mono-F/di-F = <1/>99). The resulting crude mixture was purified by silica-gel column chromatography to give the products **4v** (15.4 mg, 60 % yield) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (d, *J* = 4.8 Hz, 2H), 7.77 (d, *J* = 7.6 Hz, 2H), 7.53 (d, *J* = 7.6 Hz, 2H), 7.41 (t, *J* = 7.4 Hz, 2H), 7.37 (t, *J* = 3.2 Hz, 3H), 7.31 (t, *J* = 7.2 Hz, 2H), 7.20-7.26 (m. 4H), 5.77 (d, *J* = 9.2 Hz, 1H),

5.07-5.22 (m, 3H), 4.41 (dd, *J* = 10.0 Hz, 7.6 Hz, 1H), 4.33 (dd, *J* = 10.0 Hz, 6.8 Hz, 1H), 4.10-4.18 (m, 1H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -103.78 (d, *J* = 251.9 Hz, 1F), -105.65 (d, *J* = 251.9 Hz, 1F); ^{13}C NMR (100 MHz, $CDCl_3$) δ166.11, 155.54, 150.28, 143.59, 141.44, 134.26, 129.04, 128.86, 128.80, 127.97, 127.26, 125.05, 120.19, 118.37 (t, *J* = 250.5 Hz), 68.50, 67.75, 59.06 (t, *J* = 29.0 Hz), 47.07, 21.18, 14.32; HRMS (ESI-TOF) calcd for $C_{30}H_{24}F_2N_2NaO_4$ [M+Na]$^+$: 537.1602, found: 537.1609.

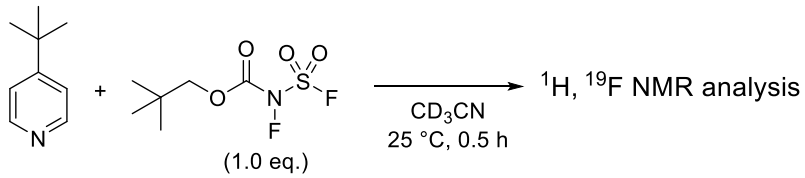
S3-3. Gram-Scale Synthesis



To a mixture of Li_2CO_3 (750 mg, 10.14 mmol, 2.0 equiv.) and **2b** (1.0 g, 5.07 mmol) in CH_3CN (0.1 M, 50 mL) was added **NFC** (4.69 g, 20.28 mmol, 4.0 equiv.) at room temperature under N_2 atmosphere. After stirring for 10 h at 50 ℃, the yield and selectivity (88%, mono-F/di-F = <1/>99) were determined by ^{19}F NMR spectroscopy analysis using benzotrifluoride as an internal standard. The resulting crude mixture was purified by silica-gel column chromatography to give the product **4b** (70%).

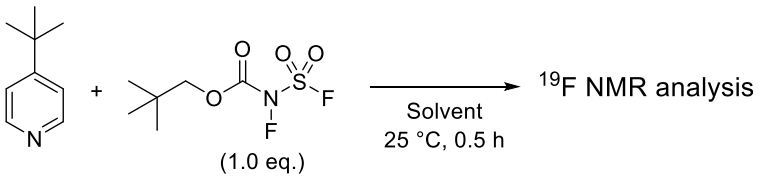
S4. Mechanistic Studies

S4-1. Observation of Intermediates from Pyridine Derivative and NFC (Scheme 2a)



To a mixture of 4-(*tert*-butyl)pyridine (13.5 mg, 0.10 mmol) in CD_3CN (0.1 M, 1.0 mL) was added to **NFC** (23.1 mg, 0.10 mmol, 1.0 equiv.) at 25 °C under N_2 atmosphere and stirred for 30 min. The resulting crude mixture was analyzed by ^{19}F NMR. The complete conversion from N-*F* of **NFC** (-47 ppm) to intermediate (-132 ppm) was observed, while RSO_2-*F* was almost not changed. Under the same conditions, NFSI instead of **NFC** gave no chemical shift.

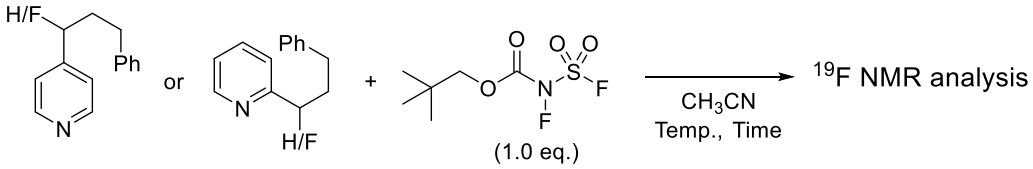
S4-2. Observation of intermediates from pyridine derivative and NFC in various solvents



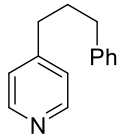
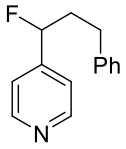
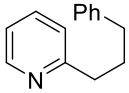
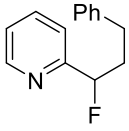
To a mixture of 4-(*tert*-butyl)pyridine (13.5 mg, 0.10 mmol) in solvent (0.1 M, 1.0 mL) was added to **NFC** (23.1 mg, 0.10 mmol, 1.0 equiv.) at 25 °C under N_2 atmosphere and stirred for 30 min. The resulting crude mixture was analyzed by ^{19}F NMR.

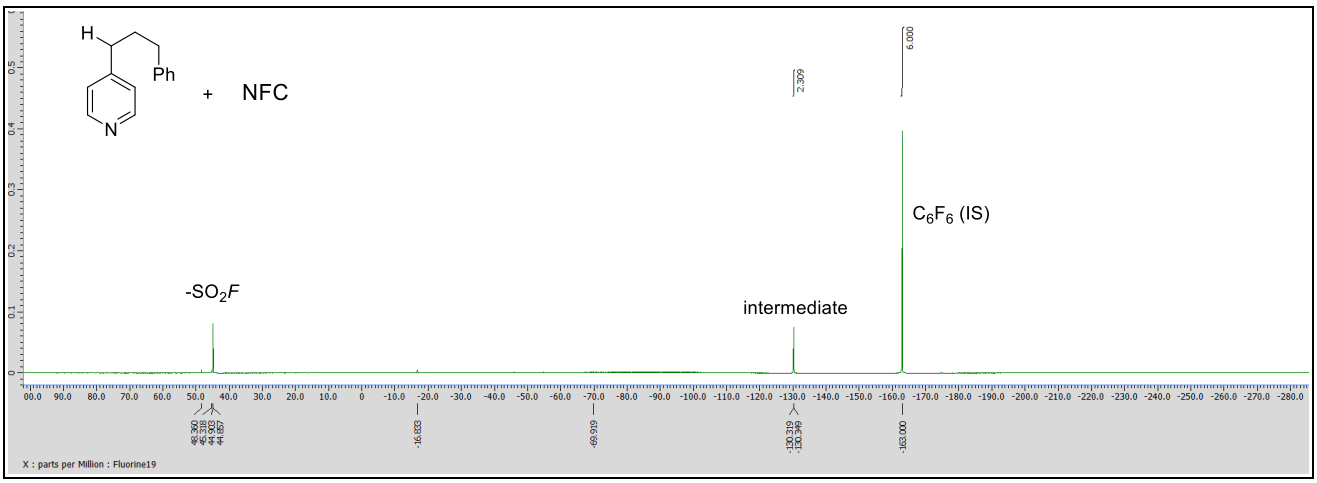
Entry	Solvent	Comments
1	CH_3CN	Intermediate was stable for >24 h (25 ˚C)
2	$CHCl_3$	Intermediate decomposed within 6 h (25 ˚C)
3	THF	Intermediate decomposed within 2 h (25 ˚C)

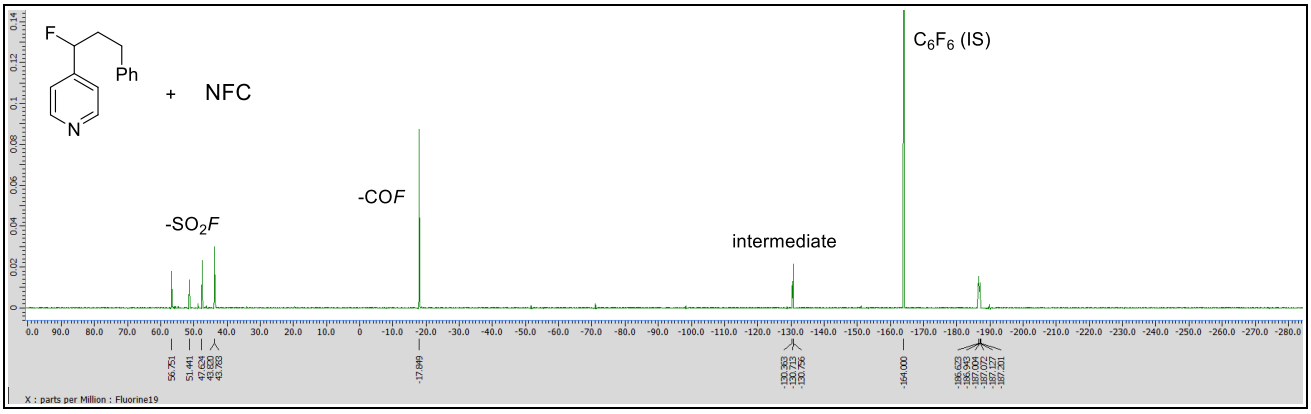
S4-3. Comparison in formation of intermediates from other pyridine derivatives

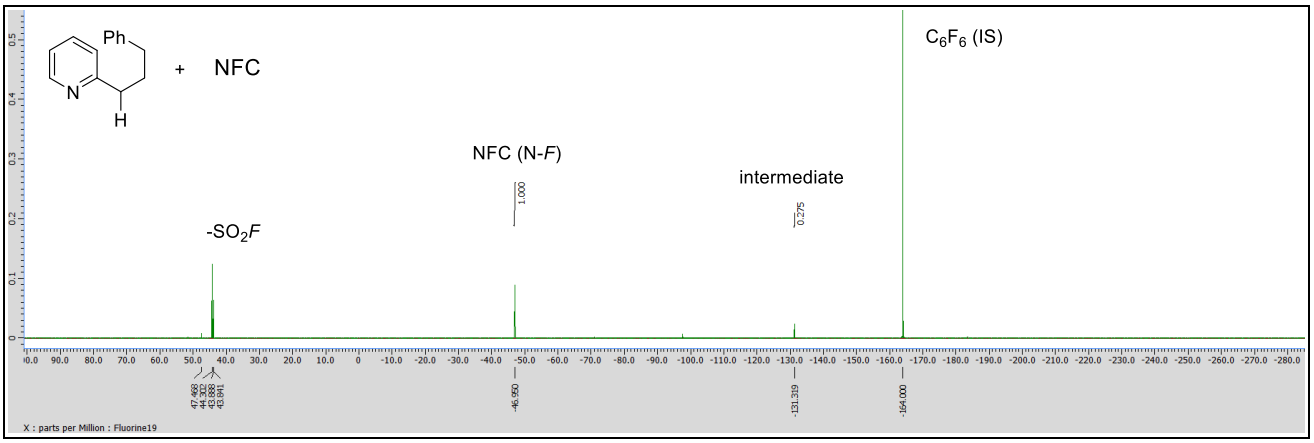


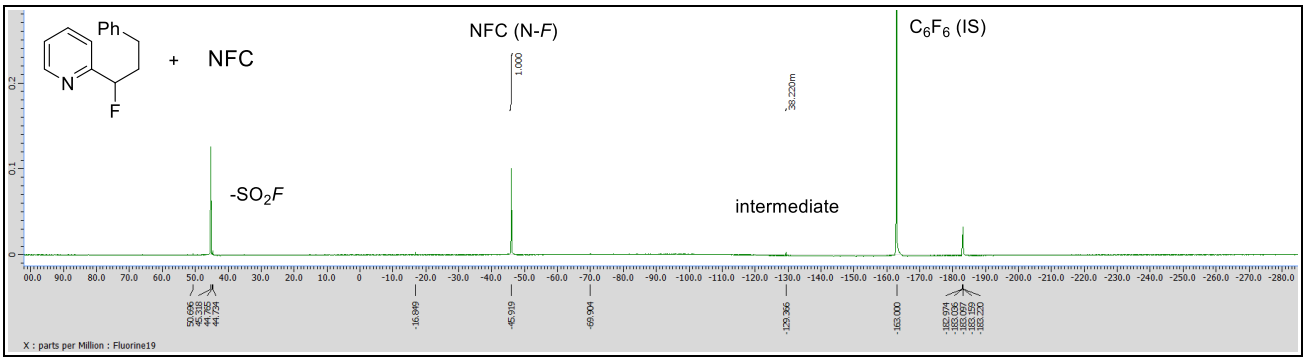
To a mixture of pyridines (0.050 mmol) in CH_3CN (0.1 M, 0.5 mL) was added **NFC** (0.050 mmol, 1.0 equiv.) at shown temperature under N_2 atmosphere and stirred for shown time. The resulting crude mixture was analyzed by ^{19}F NMR.

Entry	Pyridine derivatives	Temp. [˚C]	Time [h]	Ratio of **NFC** / intermediate in ^{19}F NMR
1		25	0.5	1 / >99
2		25	0.5	1 / >99
3		50	6	79 / 21
4		50	18	97 / 3

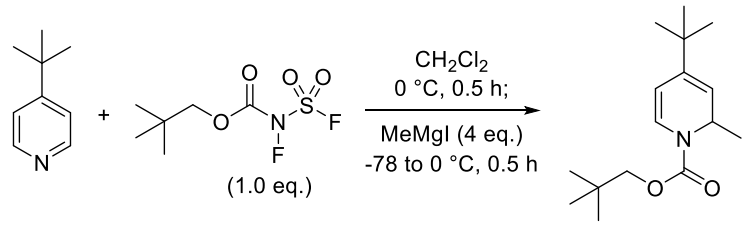

H
Ph
N
+ NFC
C_6F_6 (IS)
-SO_2F
intermediate
X : parts per Million : Fluorine19


F
Ph
N
+ NFC
C_6F_6 (IS)
-COF
-SO_2F
intermediate
X : parts per Million : Fluorine19


Ph
N
H
+ NFC
C_6F_6 (IS)
NFC (N-F)
intermediate
-SO_2F
X : parts per Million : Fluorine19

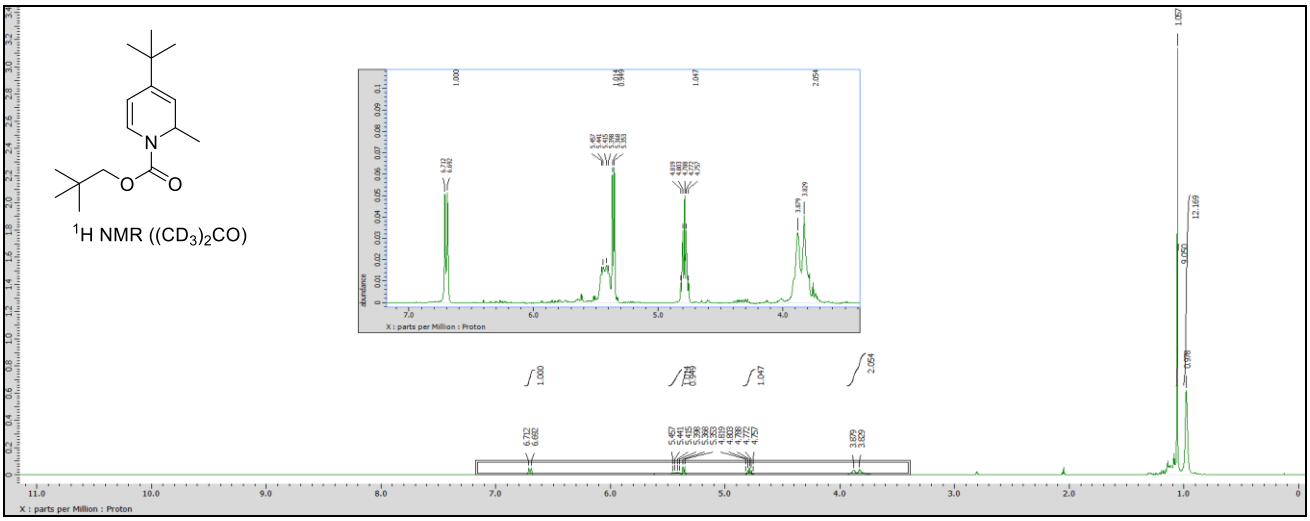

Ph
N
F
+ NFC
NFC (N-F)
C_6F_6 (IS)
-SO_2F
intermediate
X : parts per Million : Fluorine19

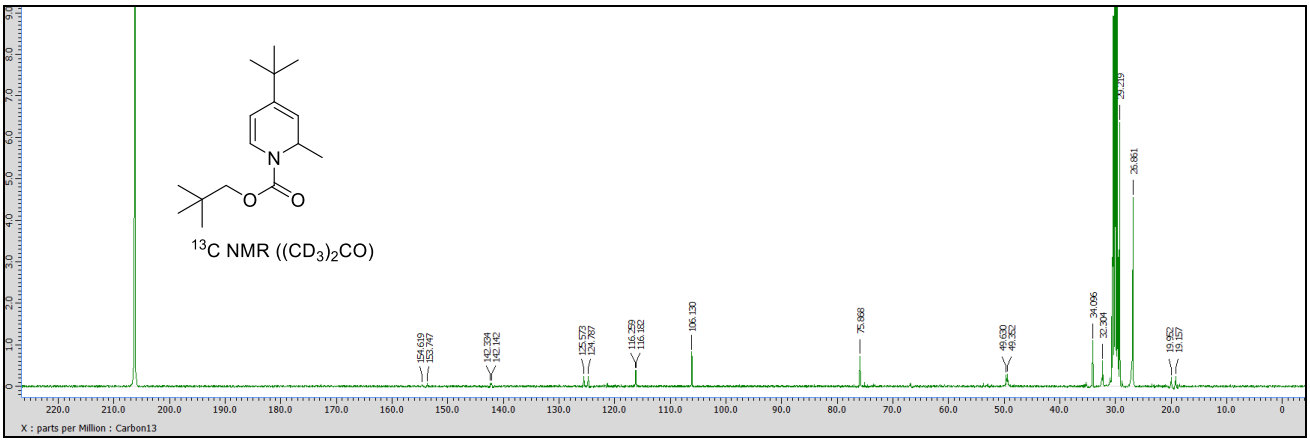
S4-4. Characterization as *N*-acylated dihydropyridine species (Scheme 2b)[11]



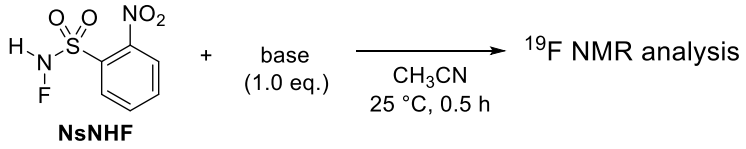
To a mixture of 4-(*tert*-buyl)pyridine (13.5 mg, 0.10 mmol) in CH_2Cl_2 (0.1 M, 1.0 mL) was added **NFC** (23.1 mg, 0.10 mmol, 1.0 equiv.) at 0 °C under N_2 atmosphere and stirred for 30 min. MeMgI (0.2 mL, 0.4 mmol, 4.0 equiv., 2M in diethyl ether) was added at -78 °C, stirred for 30 min in ice bath, subsequently analyzed by ^{19}F NMR using hexafluoro-*p*-xylene as internal standard (43% NMR yield). Resulting crude mixture was quenched by H_2O, extracted with CH_2Cl_2, combined organic layer was dried with Na_2SO_4, then evaporated under reduced pressure. Resulting crude mixture was purified by silica-gel column chromatography to give the product (31% yield).

^1H NMR (400 MHz, $(CD_3)_2CO$) δ 6.70 (d, *J* = 8.0 Hz, 1H), 5.40-5.46 (m, 1H), 5.36 (d, *J* = 6.0 Hz, 1H), 4.79 (quin, *J* = 6.4 Hz, 1H), 3.83 and 3.88 (brs, 2H, 2 rotamers), 1.06 (s, 9H), 0.98 (brs, 12H); ^{13}C-NMR (100 MHz, $(CD_3)_2CO$) δ 154.62 and 153.75 (2 rotamers), 142.33 and 142.14 (2 rotamers), 125.57 and 124.79 (2 rotamers), 116.26 and 116.18 (2 rotamers), 106.13, 75.87, 49.63 and 49.35 (2 rotamers), 34.10, 32.30, 29.22, 26.86, 19.95 and 19.16 (2 rotamers); HRMS (ESI-TOF) calcd for $C_{16}H_{27}NNaO_2$ $[M+Na]^+$: 288.1940, found: 288.1951.



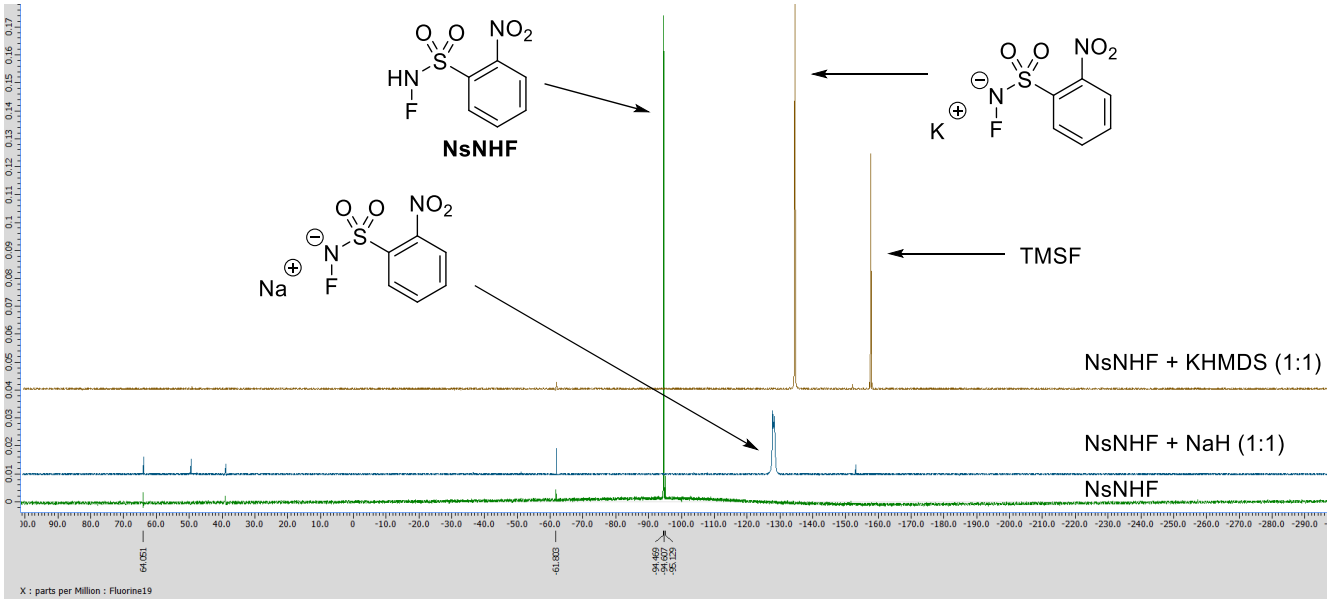


S4-5. Observation of *N*-Fluoro-sulfonamide anion species

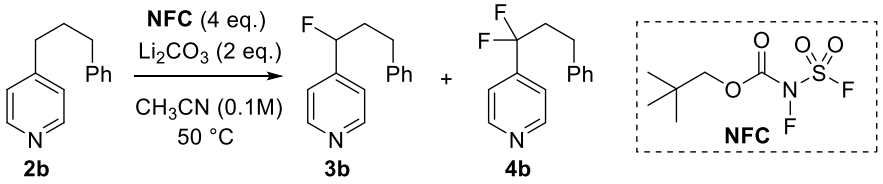


To a mixture of NsNHF (22.0 mg, 0.10 mmol)[12] in CH_3CN (0.1 M, 1.0 mL) was added base (0.10 mmol) at -78 °C under N_2 atmosphere and stirred for 30 min at 25 °C. The resulting crude mixture was analyzed by ^{19}F NMR.

Entry	Base	Comment
1	NaH (oil dispersion)	Chemical shift change (-93 → -134 ppm)
2	KHMDS (in 0.5 M toluene)	Chemical shift change (-93 → -127 ppm)

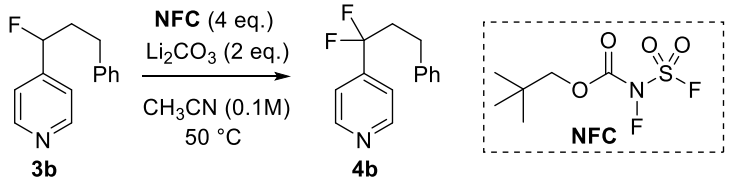


S4-6. Reaction ratio from non-/monofluorinated pyridine derivatives (Scheme 3)



0.5 h	0%	71%
4 h	0%	94%

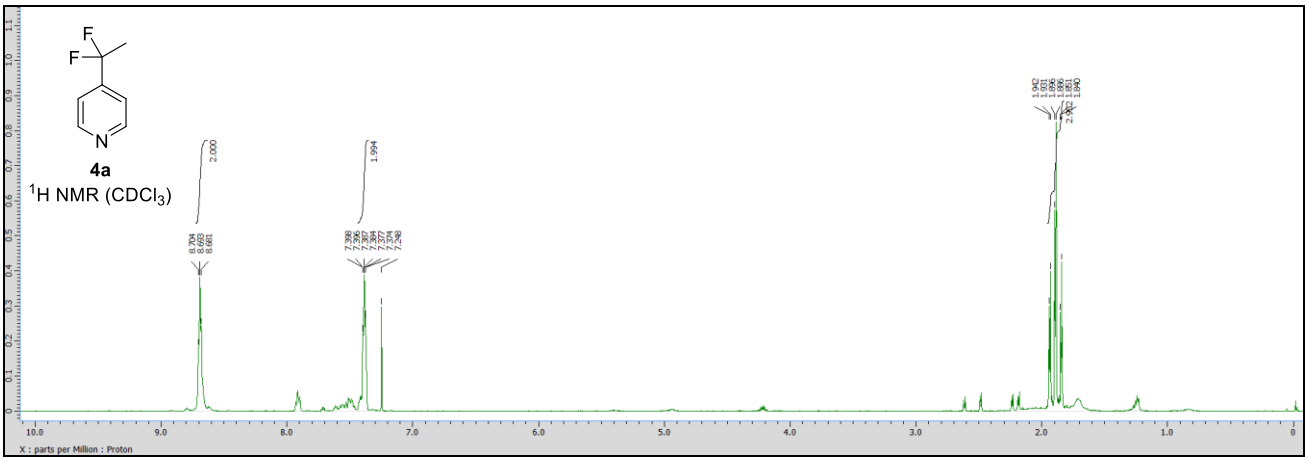
To a mixture of Li_2CO_3 (14.8 mg, 0.20 mmol, 2.0 equiv.) and **2b** (19.7 mg, 0.10 mmol) in CH_3CN (0.1 M, 1.0 mL) was added **NFC** (0.40 mmol) at room temperature under N_2 atmosphere. After stirring for shown time at 50 ℃, the yield and selectivity were monitored by ^{19}F NMR spectroscopy analysis using benzotrifluoride as an internal standard.

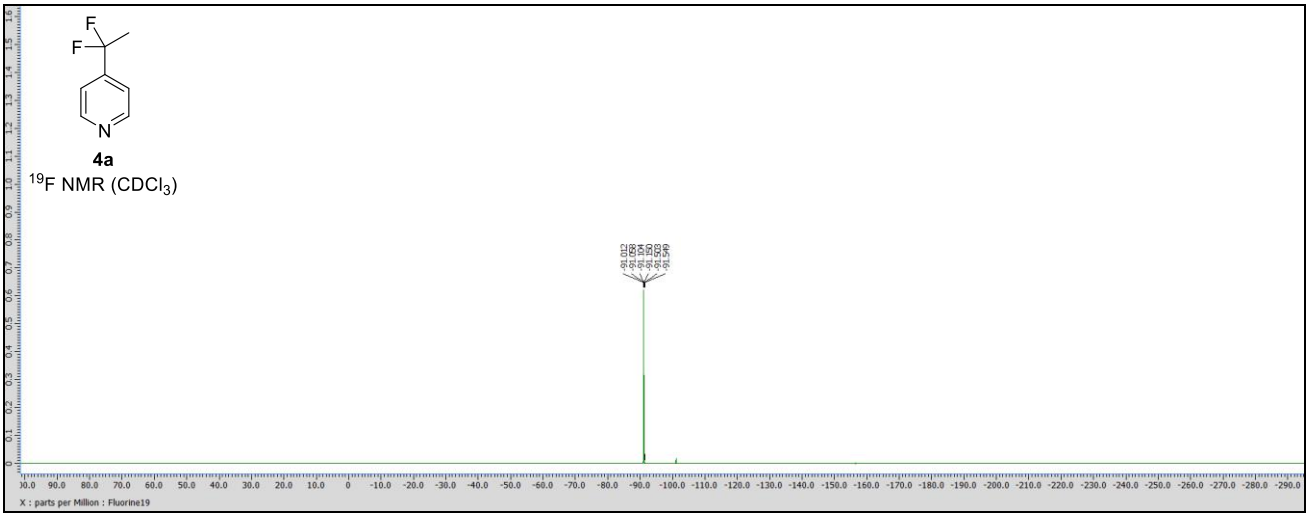


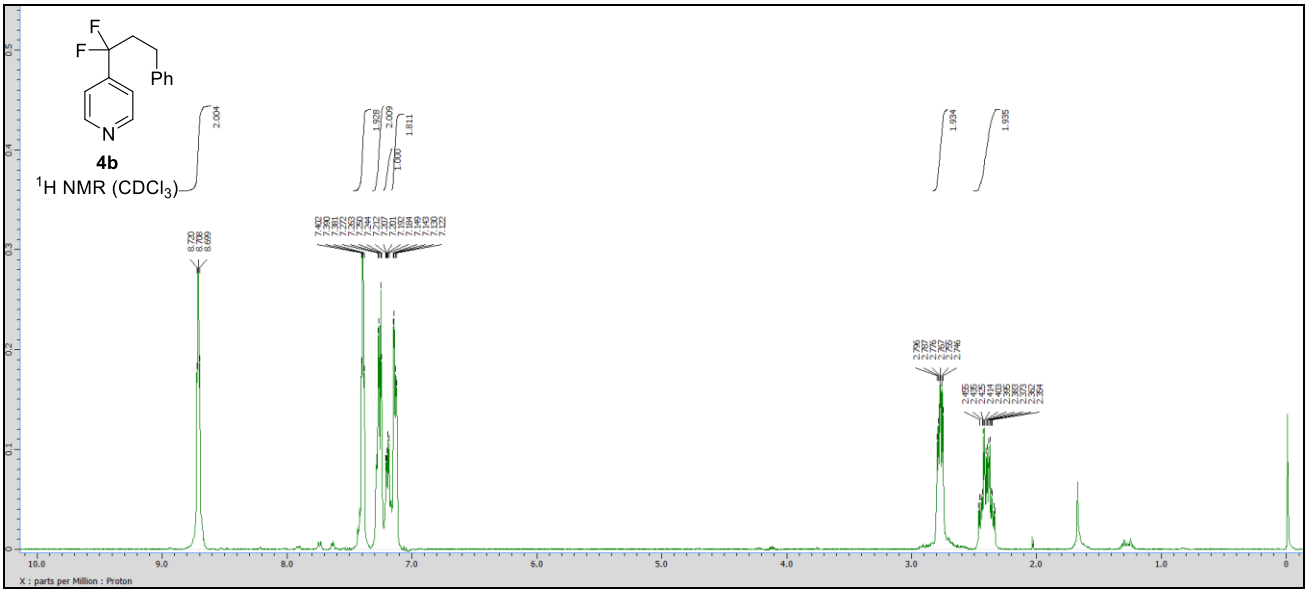
0.5 h	91%

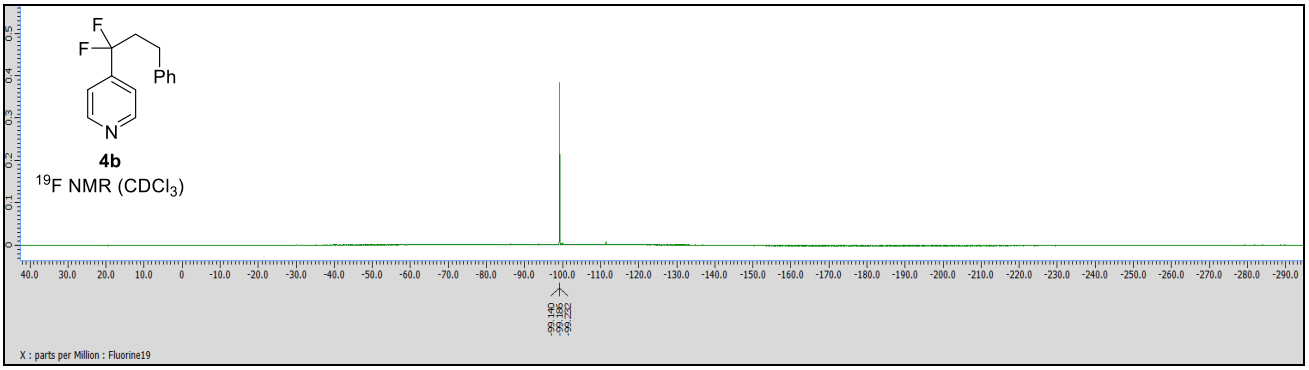
To a mixture of Li_2CO_3 (7.4 mg, 0.10 mmol, 1.0 equiv.) and **3b** (21.5 mg, 0.10 mmol) in CH_3CN (0.1 M, 1.0 mL) was added **NFC** (0.20 mmol) at room temperature under N_2 atmosphere. After stirring for 0.5 h at 50 ℃, the yield and selectivity were monitored by ^{19}F NMR spectroscopy analysis using benzotrifluoride as an internal standard.

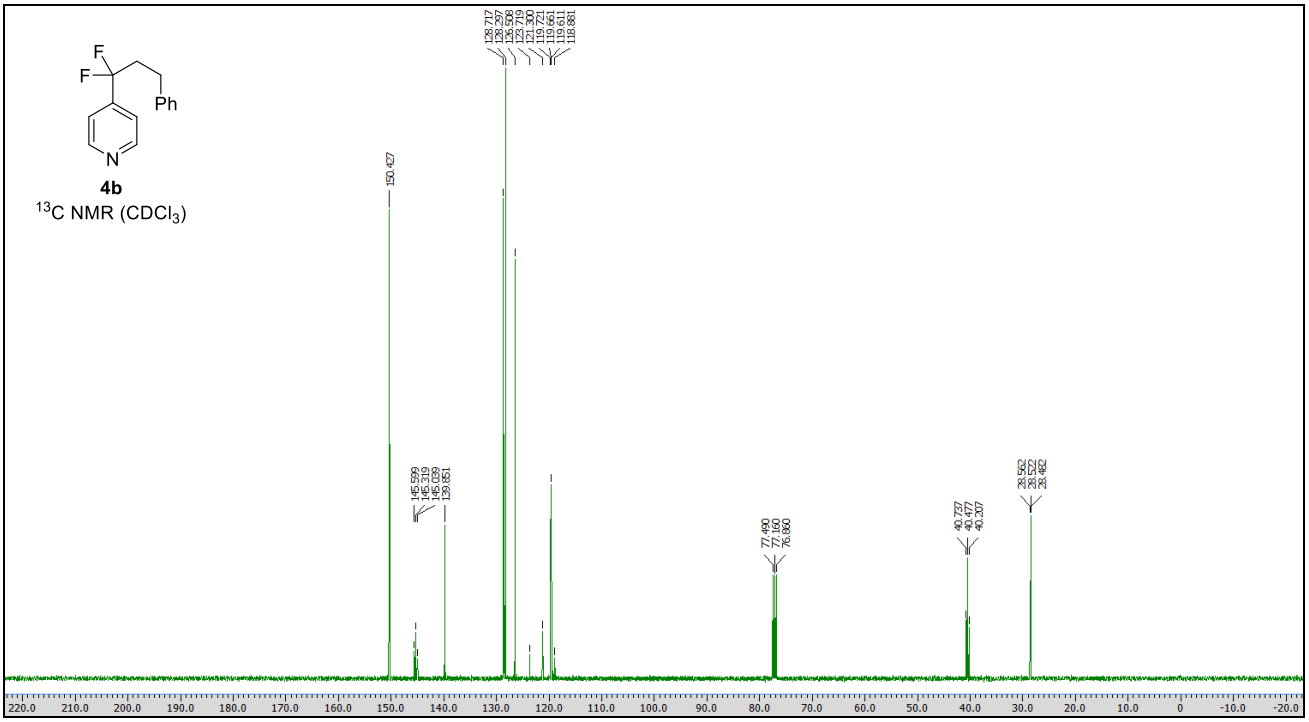
S5. NMR Spectra

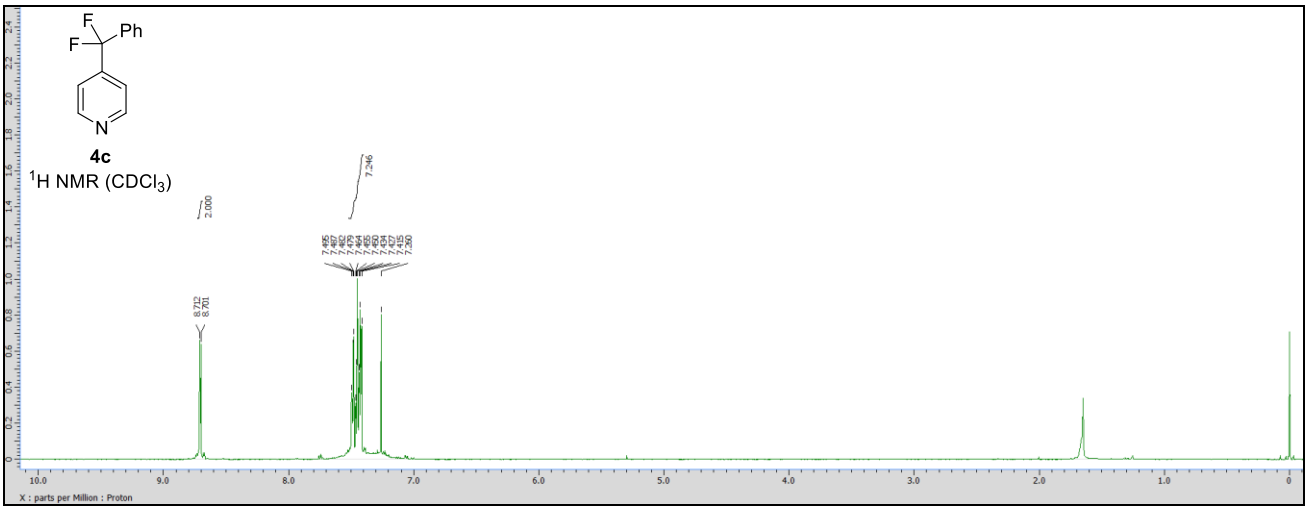


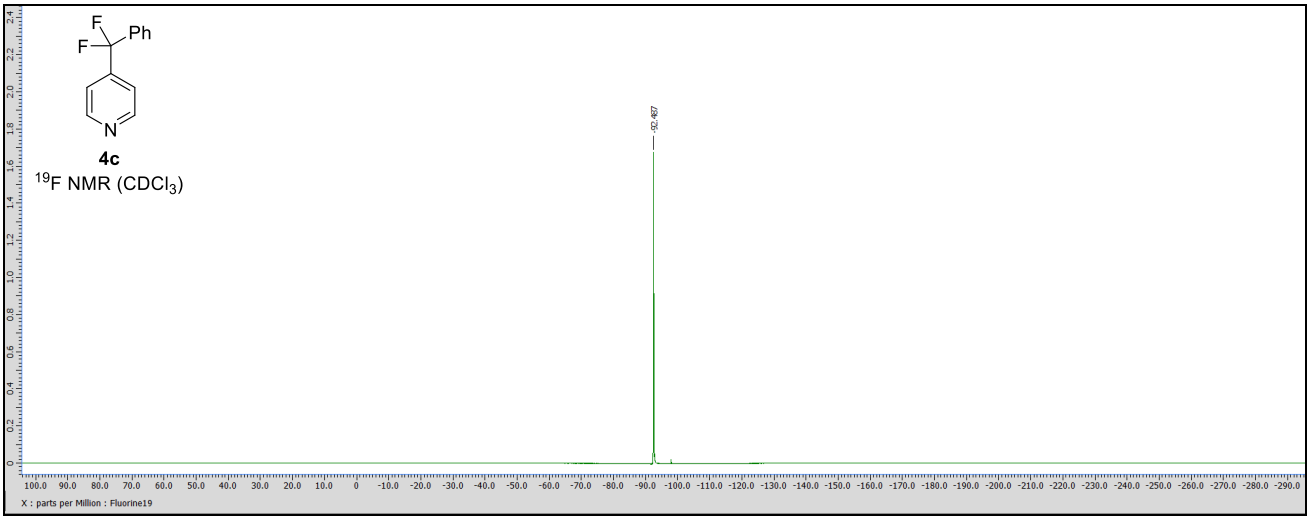


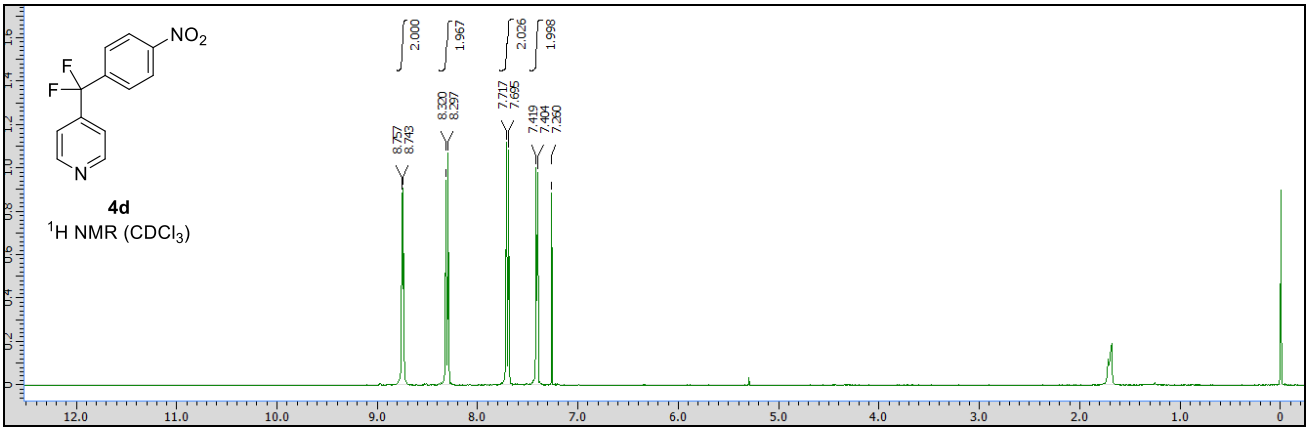

F
F
Ph
N
4b
^{1}H NMR ($CDCl_3$)
X : parts per Million : Proton

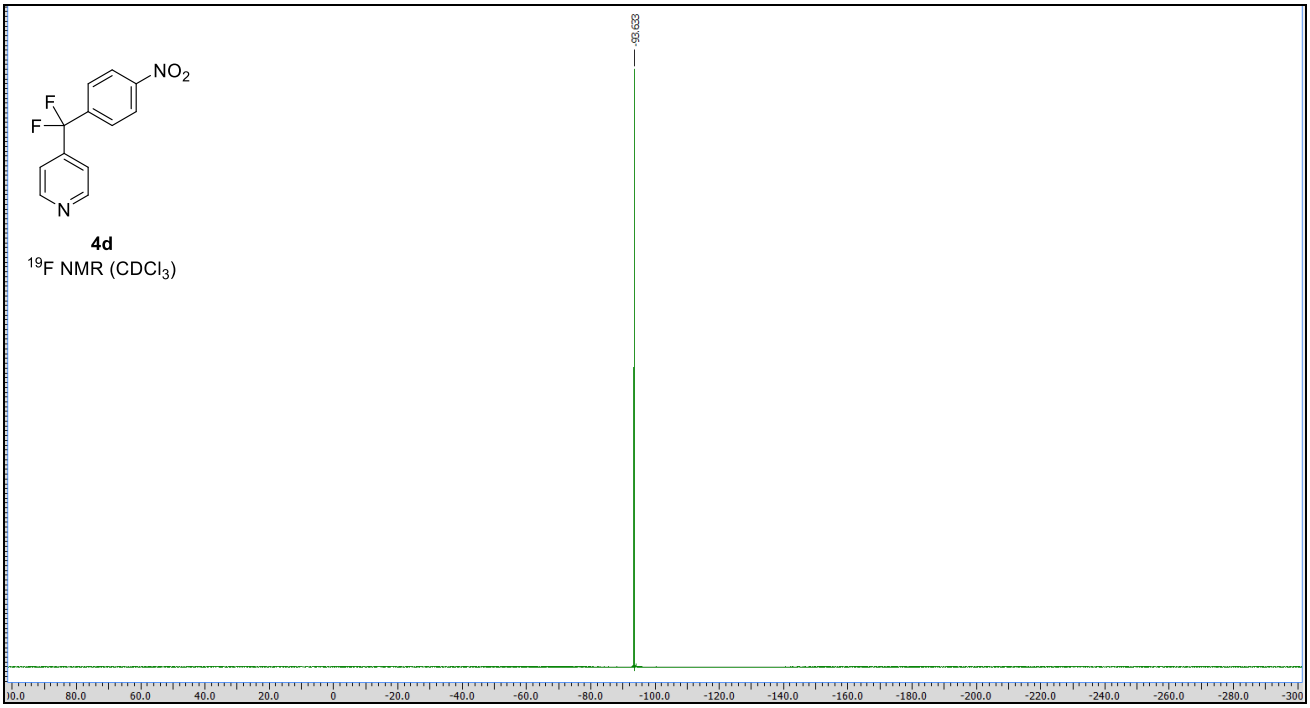

F
F
Ph
N
4b
^{19}F NMR ($CDCl_3$)
X : parts per Million : Fluorine19

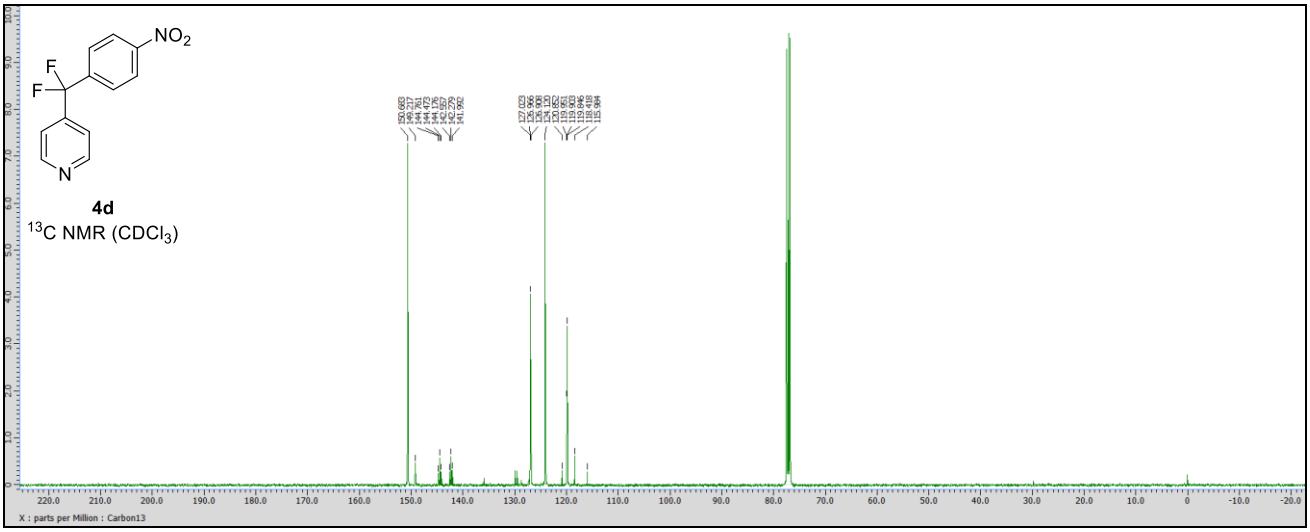

F
F
Ph
N
4b
^{13}C NMR ($CDCl_3$)

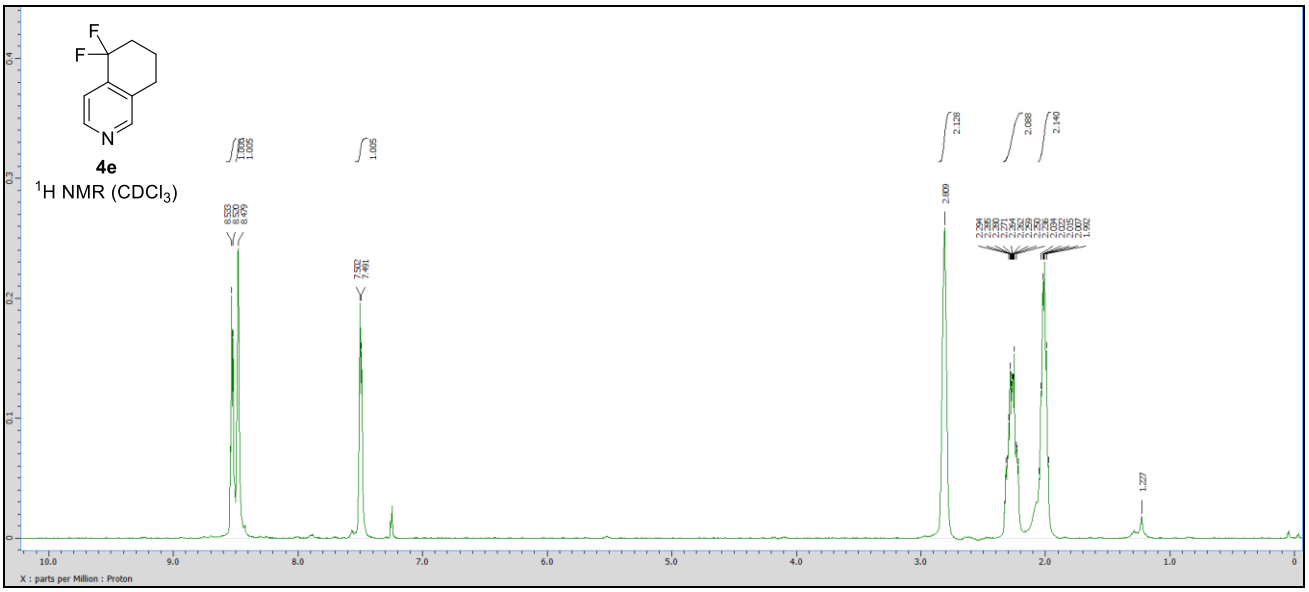

F
F
Ph
N
4c
1H NMR (CDCl3)
2.000
7.246
8.702
8.701
X : parts per Million : Proton

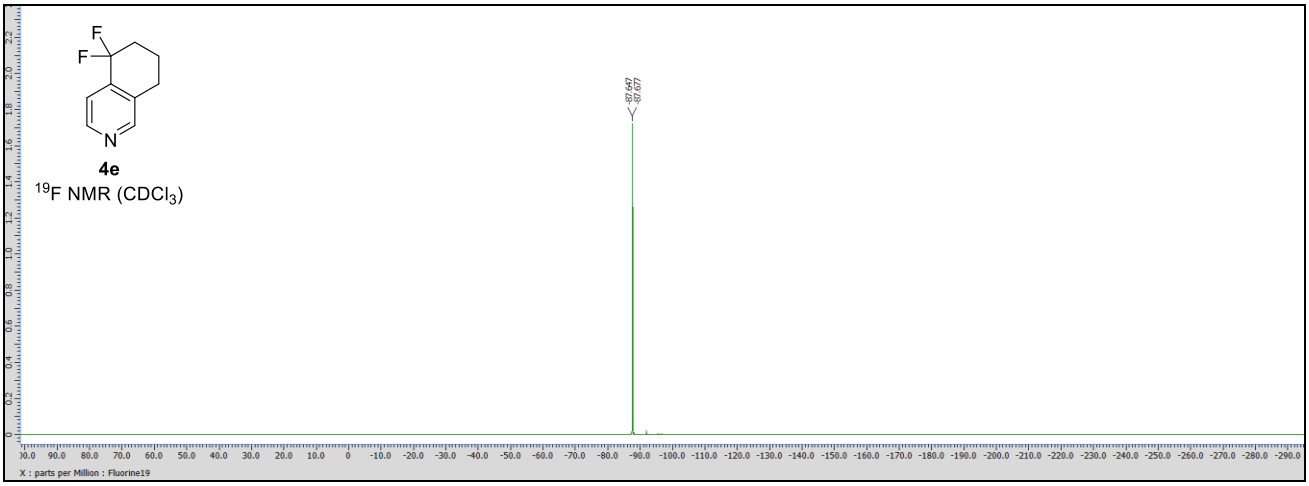

F
F
Ph
N
4c
19F NMR (CDCl3)
-92.487
X : parts per Million : Fluorine19

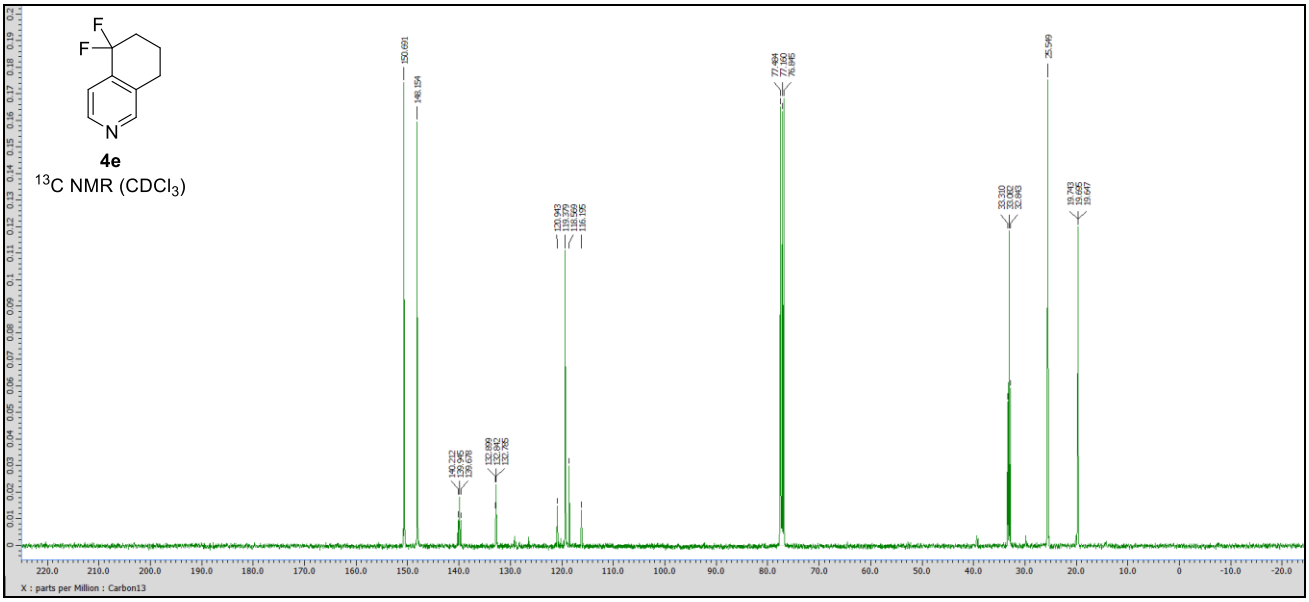

NO2
F
F
N
4d
1H NMR (CDCl3)
2.000
1.967
2.026
1.998
8.757
8.743
8.320
8.297
7.717
7.695
7.419
7.404
7.390
7.260

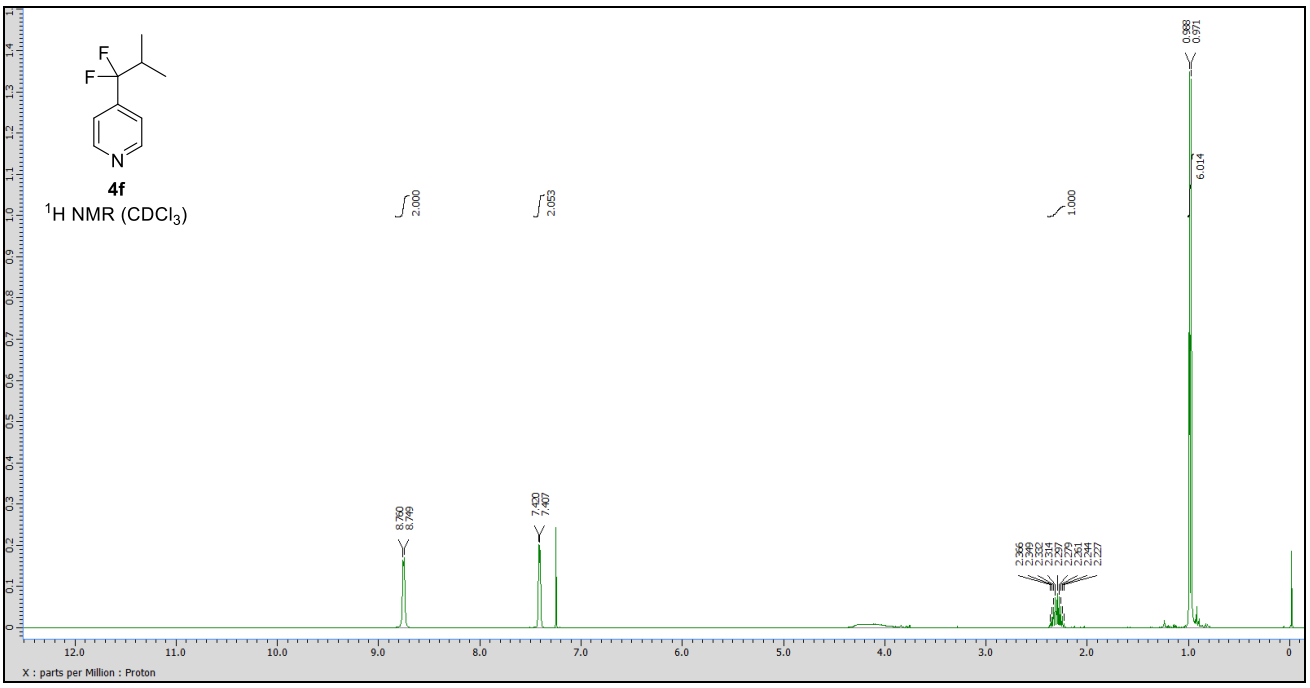

NO2
F
F
N
4d
19F NMR (CDCl3)
-93.633

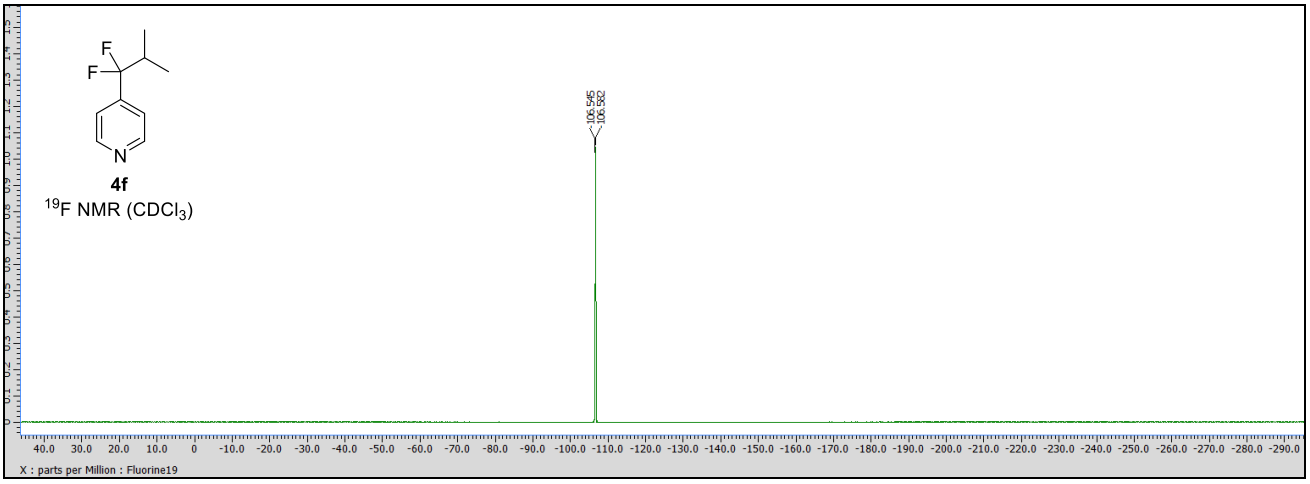

NO2
F
F
N
4d
13C NMR (CDCl3)
X : parts per Million : Carbon13

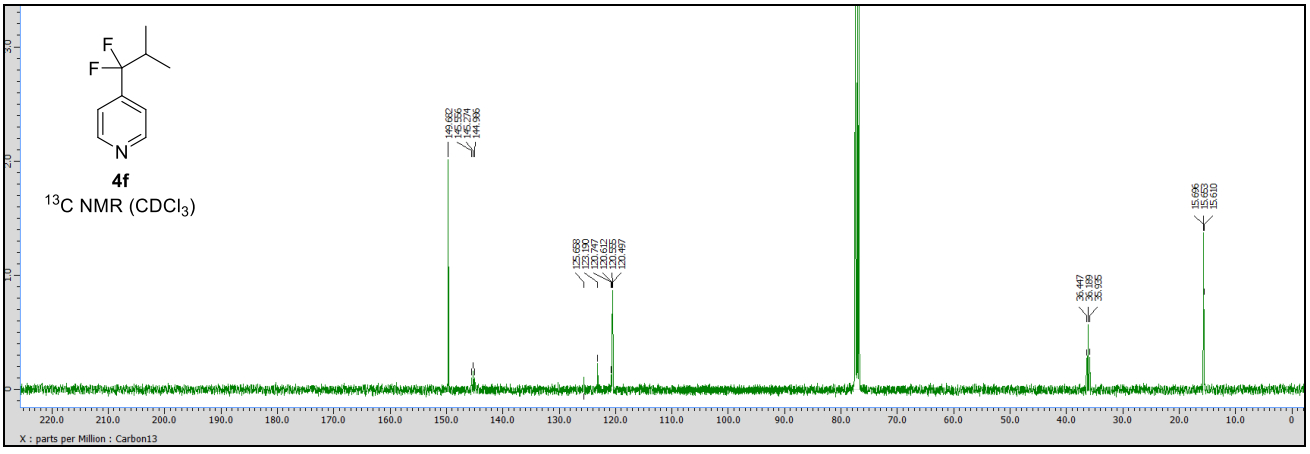

F
F
N
4e
1H NMR (CDCl3)
X : parts per Million : Proton

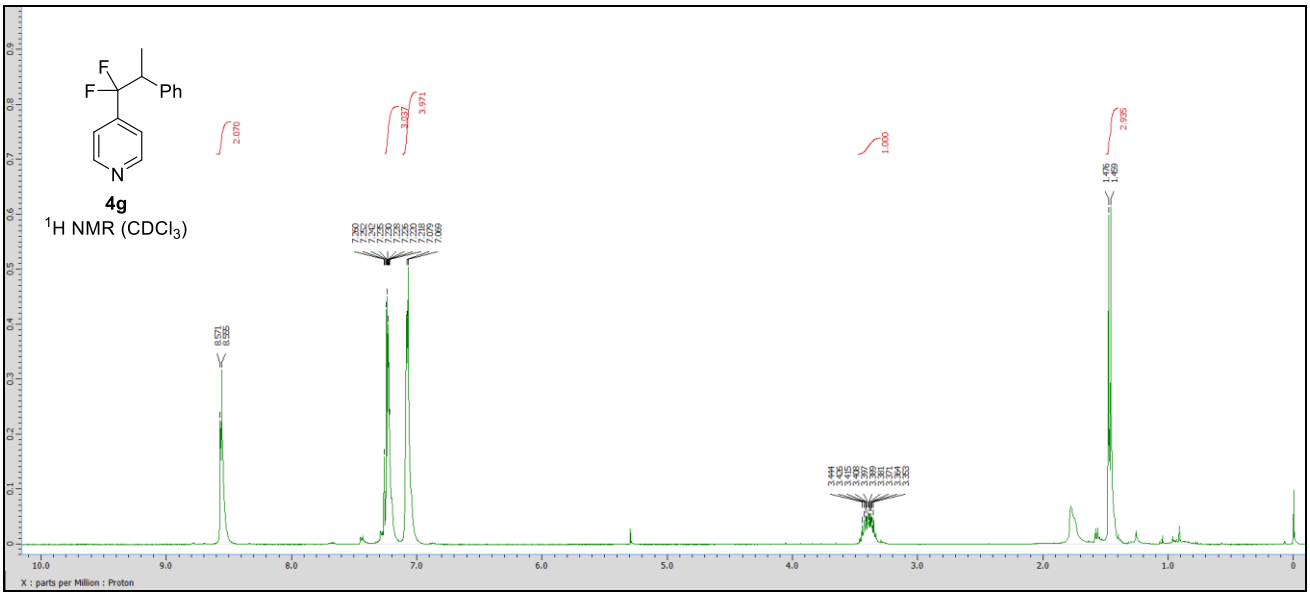

F
F
N
4e
19F NMR (CDCl3)
X : parts per Million : Fluorine19

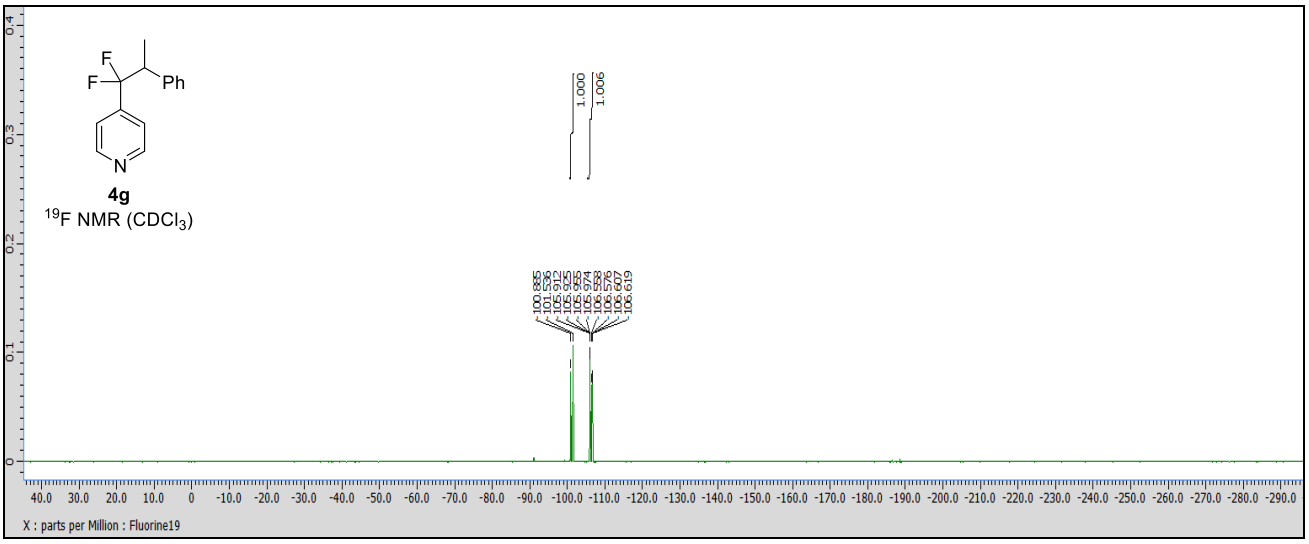

F
F
N
4e
13C NMR (CDCl3)
X : parts per Million : Carbon13

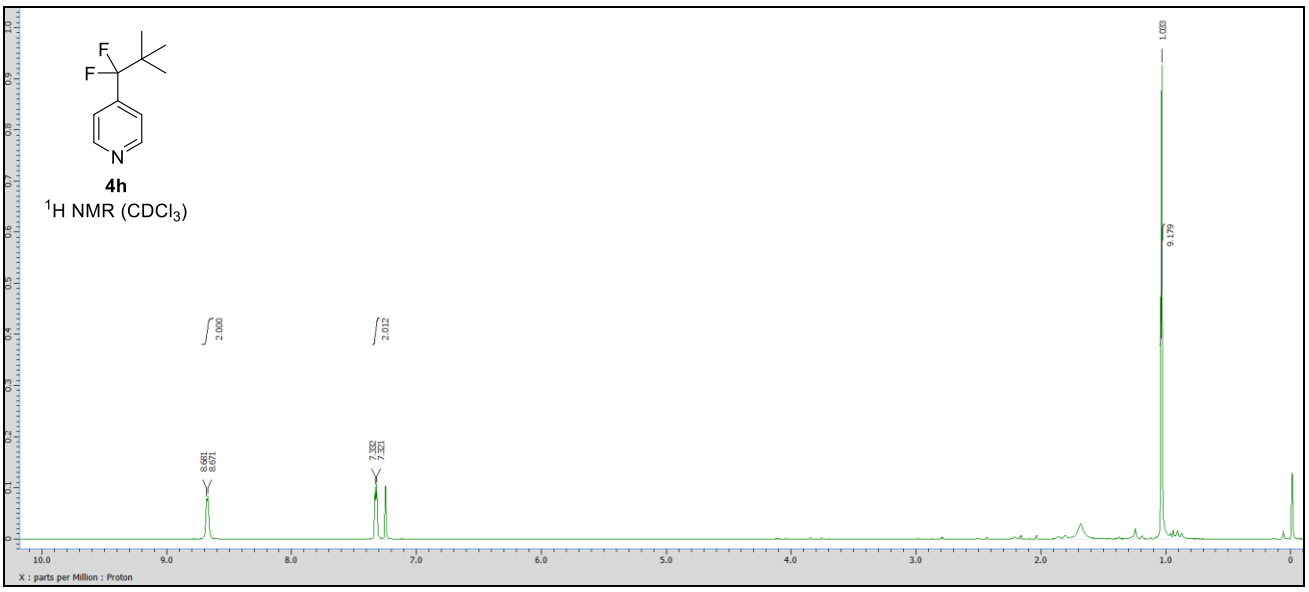

F
F
N
4f
^{1}H NMR ($CDCl_3$)
2.000
2.053
1.000
6.014
0.988
0.971
8.769
8.749
7.420
7.407
X : parts per Million : Proton

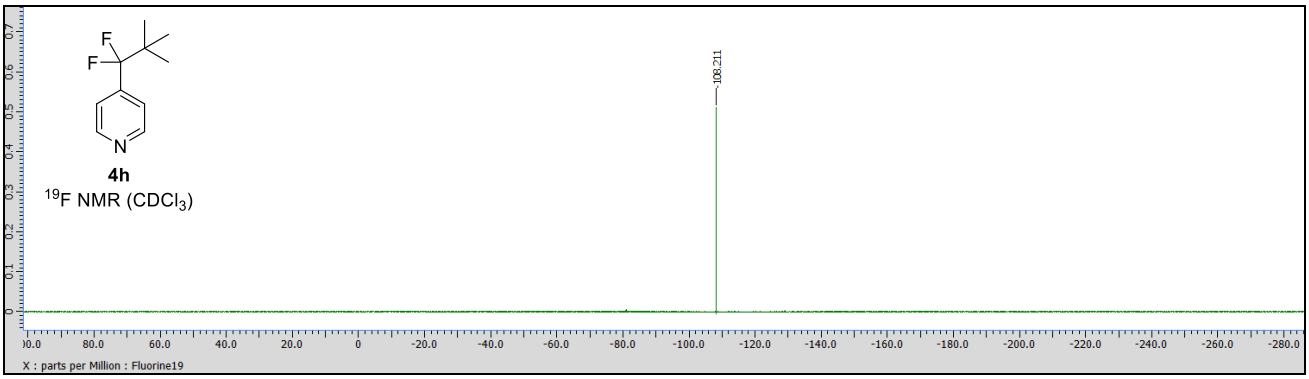

F
F
N
4f
^{19}F NMR ($CDCl_3$)
106.545
106.502
X : parts per Million : Fluorine19

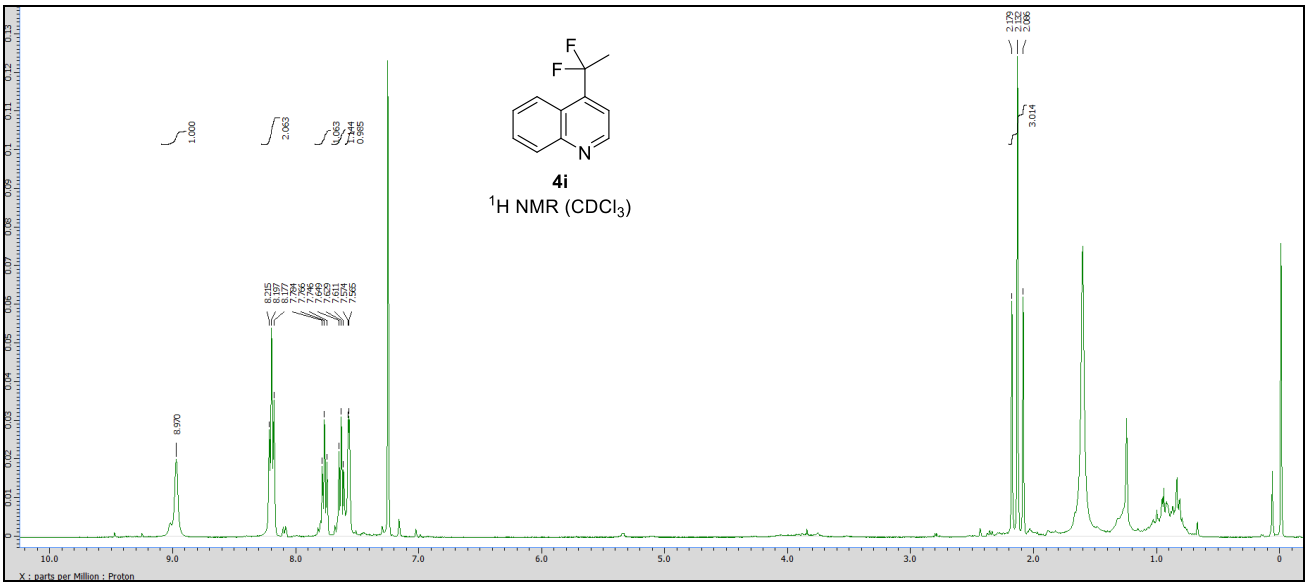

F
F
N
4f
^{13}C NMR ($CDCl_3$)
149.692
145.556
145.274
144.986
125.698
125.570
120.747
120.612
120.565
120.497
36.447
36.349
36.035
15.696
15.653
15.610
X : parts per Million : Carbon13

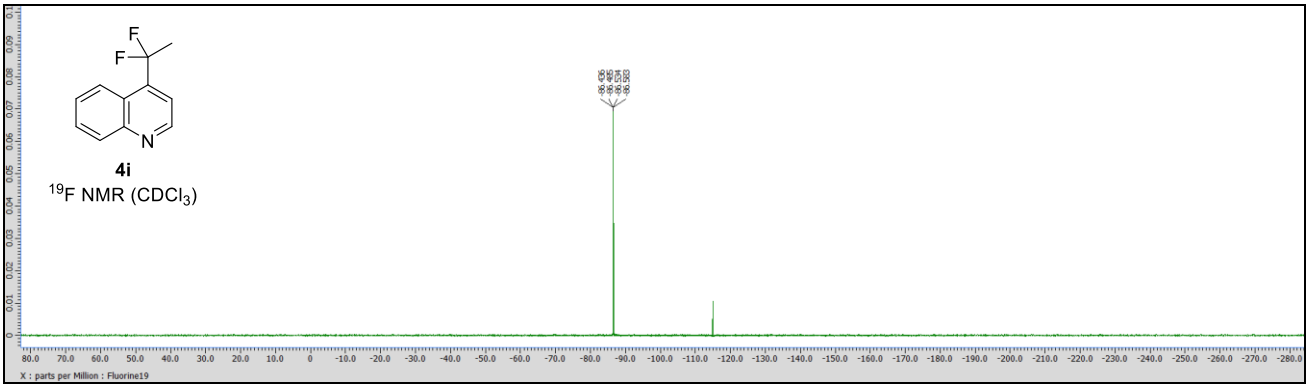

F
F
Ph
N
4g
1H NMR (CDCl3)
X : parts per Million : Proton

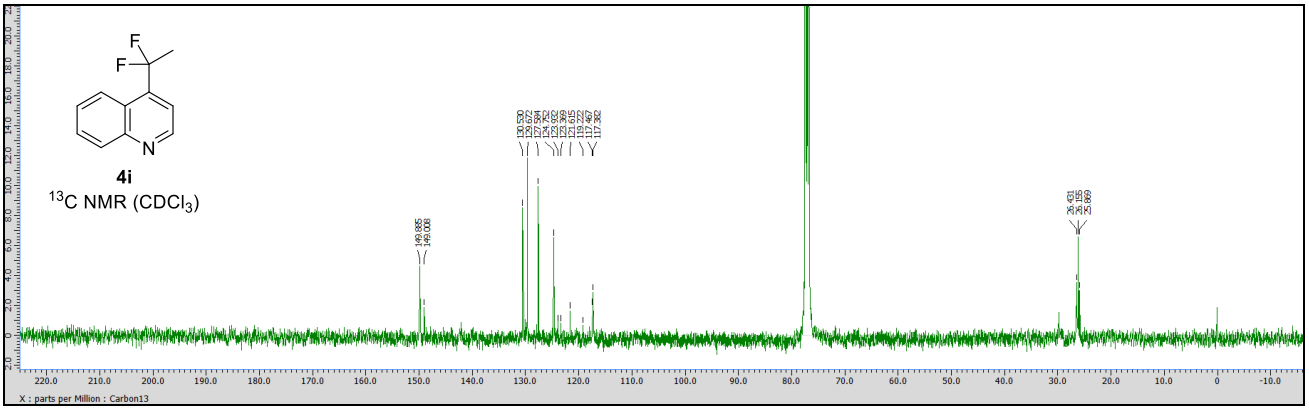

F
F
Ph
N
4g
19F NMR (CDCl3)
X : parts per Million : Fluorine19

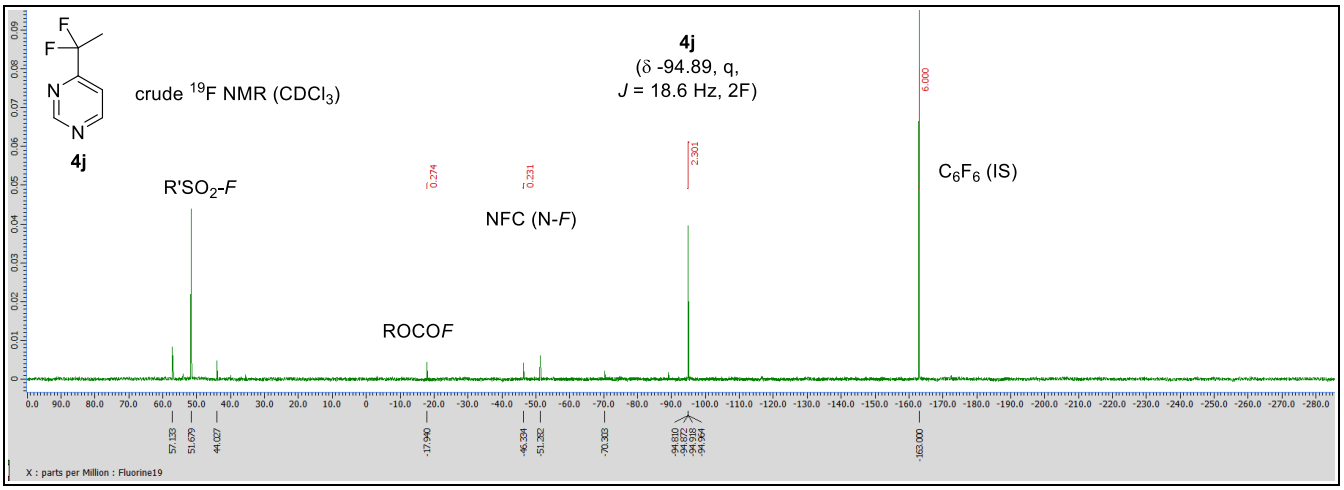

F
F
N
4h
1H NMR (CDCl3)
2.000
2.012
1.000
9.179
8.681
8.671
7.332
7.321
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
X : parts per Million : Proton

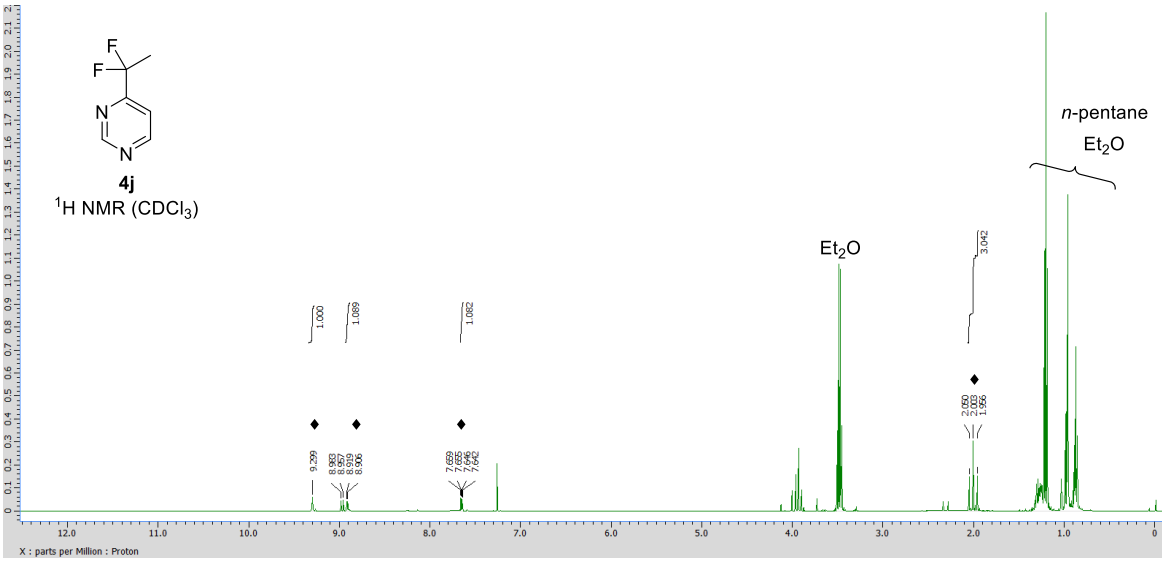

F
F
N
4h
19F NMR (CDCl3)
-108.211
80.0
60.0
40.0
20.0
0
-20.0
-40.0
-60.0
-80.0
-100.0
-120.0
-140.0
-160.0
-180.0
-200.0
-220.0
-240.0
-260.0
-280.0
X : parts per Million : Fluorine19

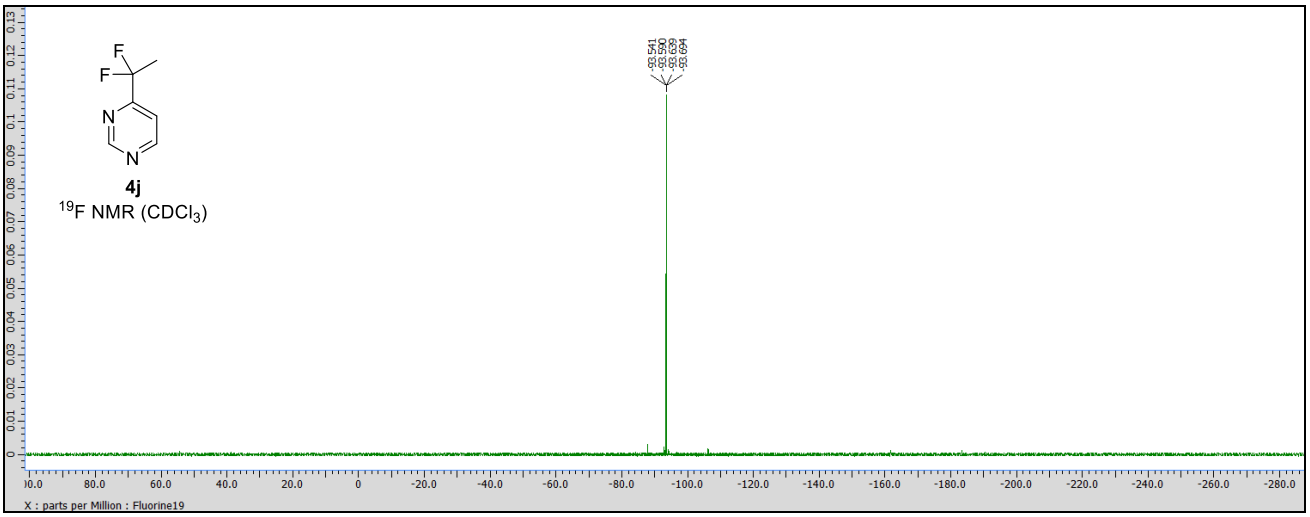

F
F
N
4i
1H NMR (CDCl3)
X : parts per Million : Proton

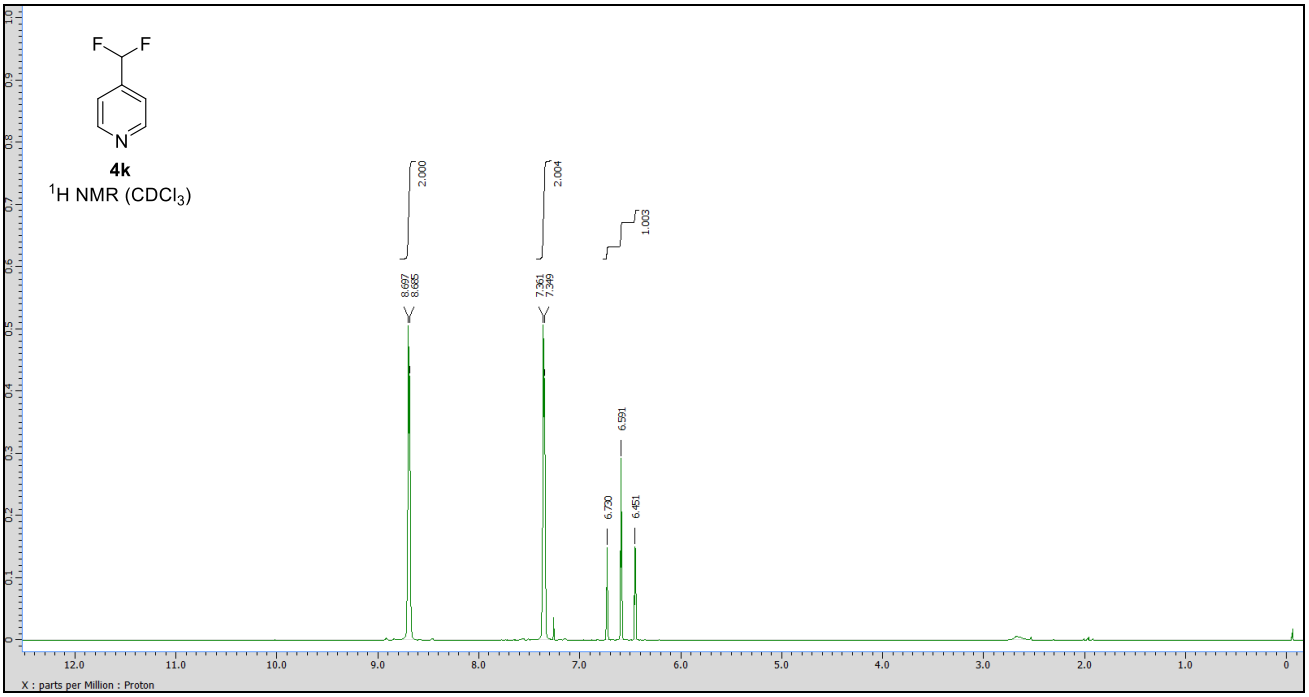

F
F
N
4i
19F NMR (CDCl3)
X : parts per Million : Fluorine19

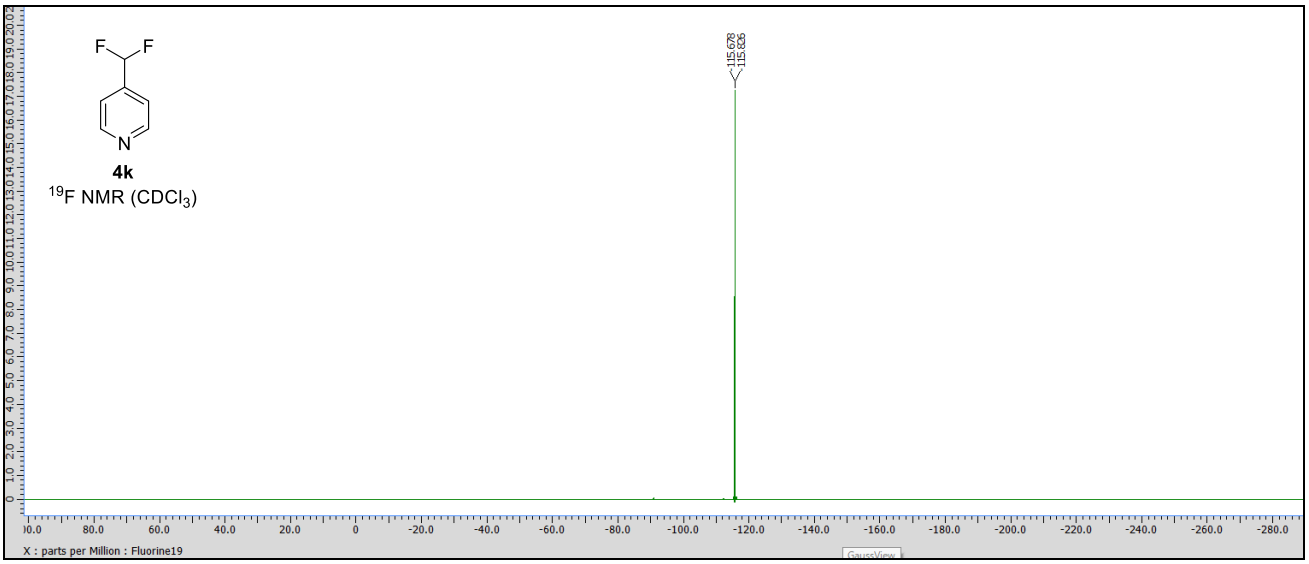

F
F
N
4i
13C NMR (CDCl3)
X : parts per Million : Carbon13

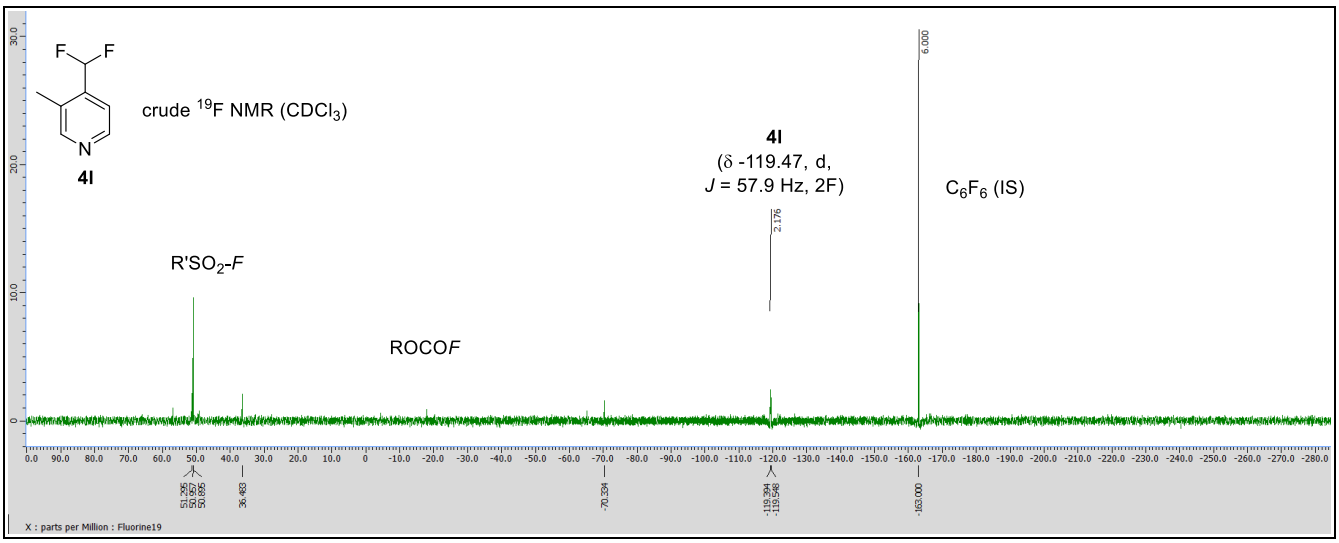

4j
crude ^{19}F NMR ($CDCl_3$)
4j
(δ -94.89, q,
J = 18.6 Hz, 2F)
R'SO_2-*F*
NFC (N-*F*)
ROCO*F*
C_6F_6 (IS)
X : parts per Million : Fluorine19

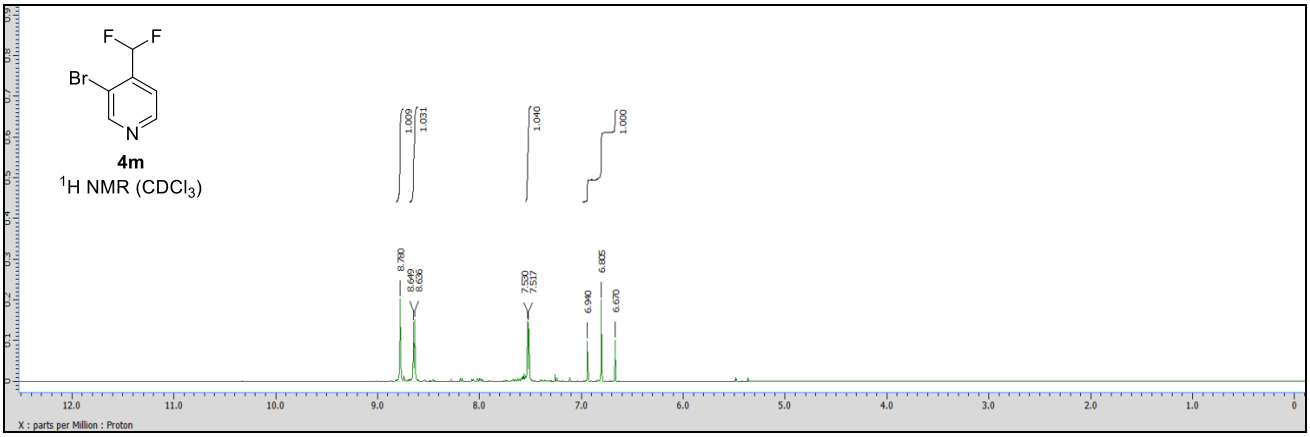

4j
^{1}H NMR ($CDCl_3$)
n-pentane
Et_2O
Et_2O
X : parts per Million : Proton

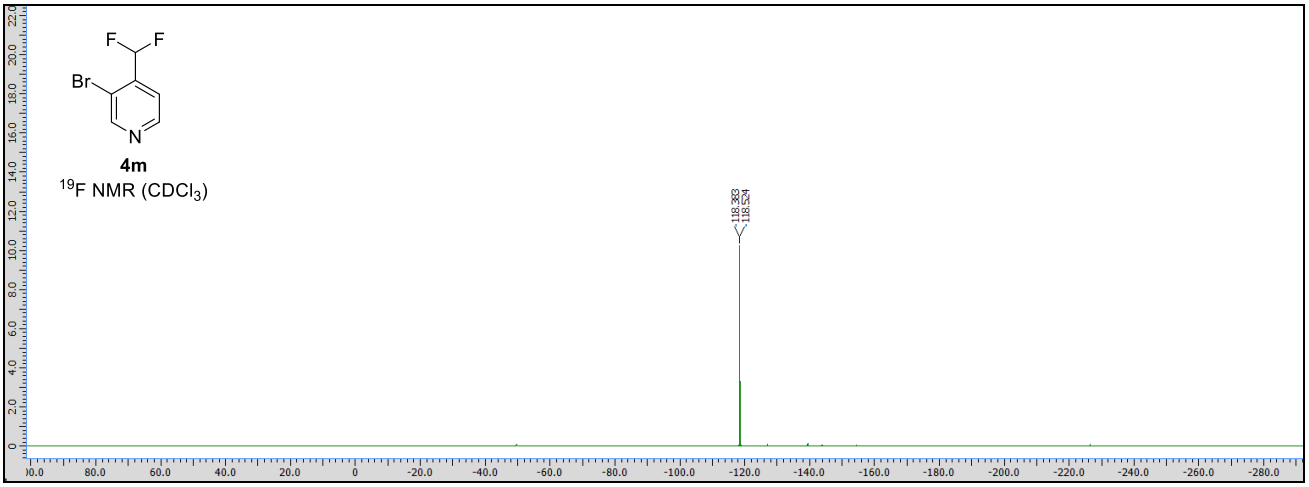

4j
^{19}F NMR ($CDCl_3$)
X : parts per Million : Fluorine19

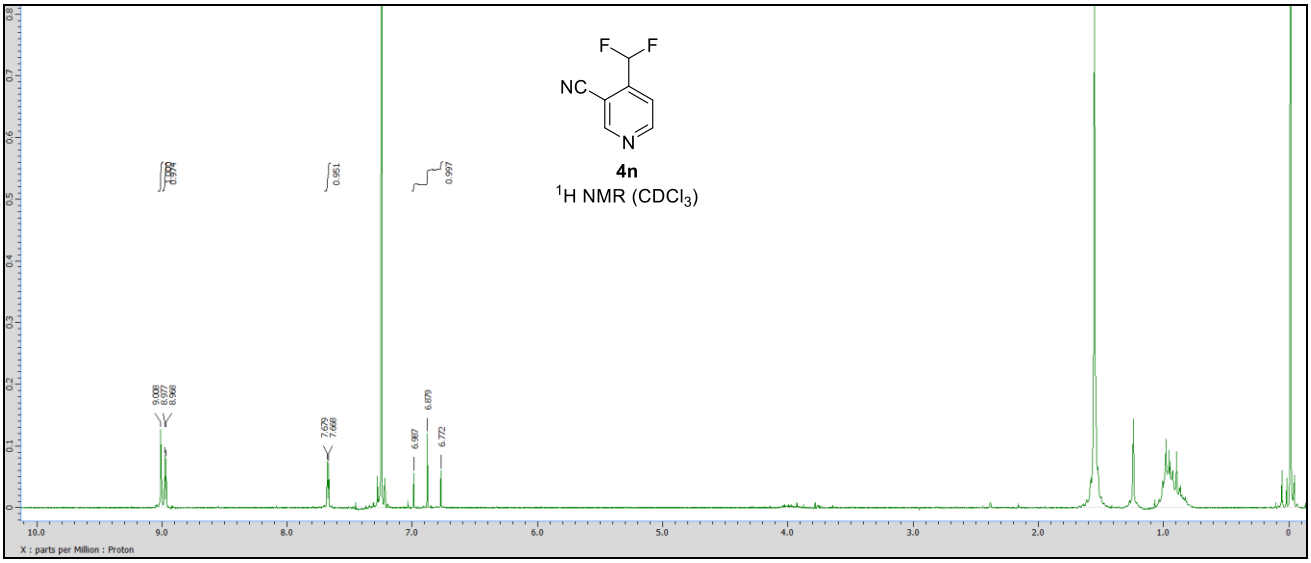

F
F
N
4k
^{1}H NMR ($CDCl_3$)
2.000
2.004
1.003
8.697
8.685
7.361
7.349
6.591
6.730
6.451
X : parts per Million : Proton

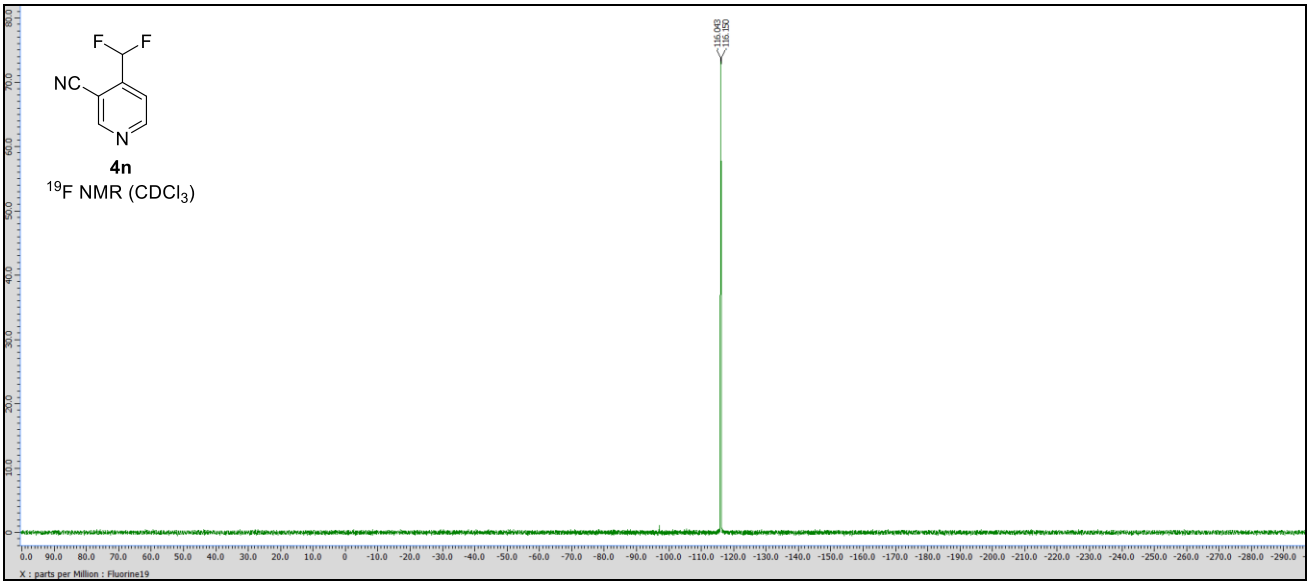

F
F
N
4k
^{19}F NMR ($CDCl_3$)
115.678
115.836
X : parts per Million : Fluorine19

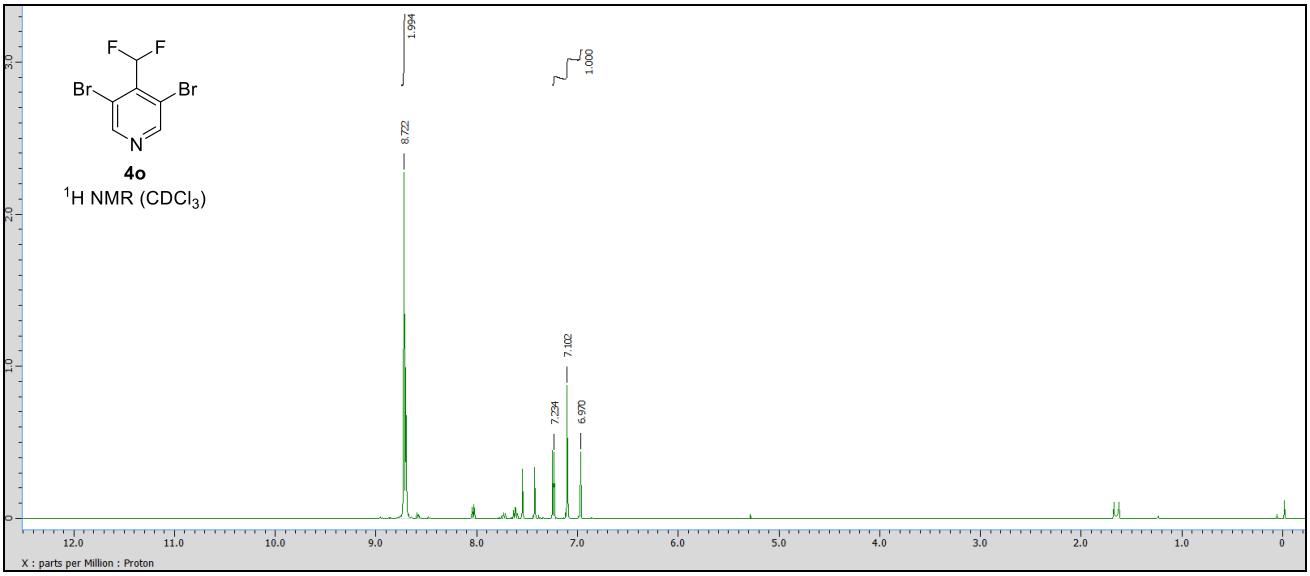

crude ^{19}F NMR ($CDCl_3$)
4l
4l
(δ -119.47, d,
J = 57.9 Hz, 2F)
C_6F_6 (IS)
R'SO_2-F
ROCOF
X : parts per Million : Fluorine19

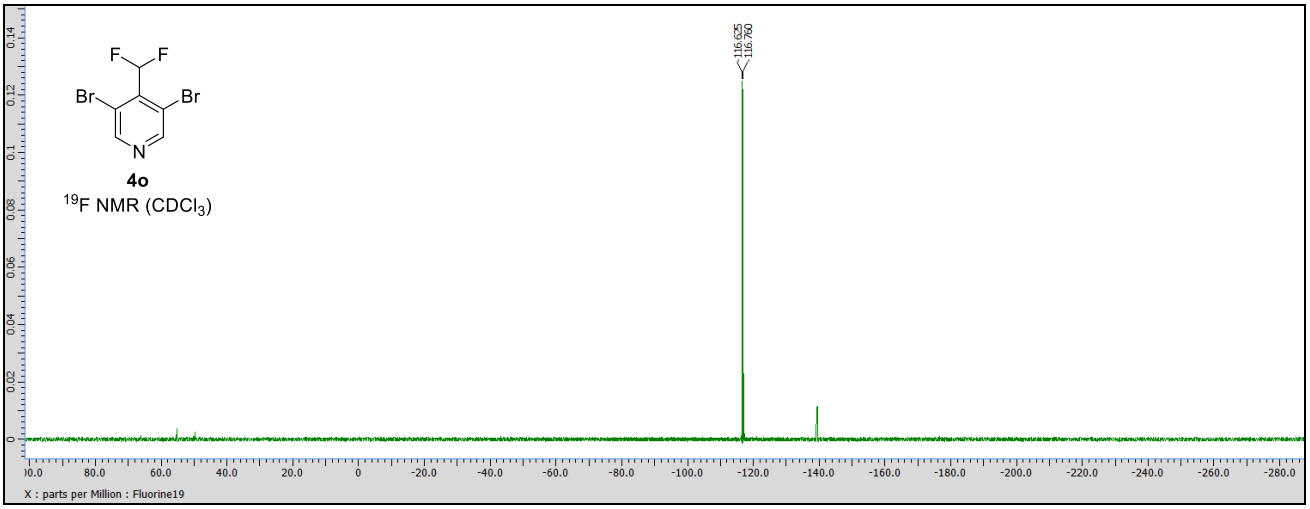

F
F
Br
N
4m
1H NMR (CDCl3)
1.009
1.031
1.040
1.000
8.790
8.649
8.636
7.530
7.517
6.940
6.835
6.670
X : parts per Million : Proton

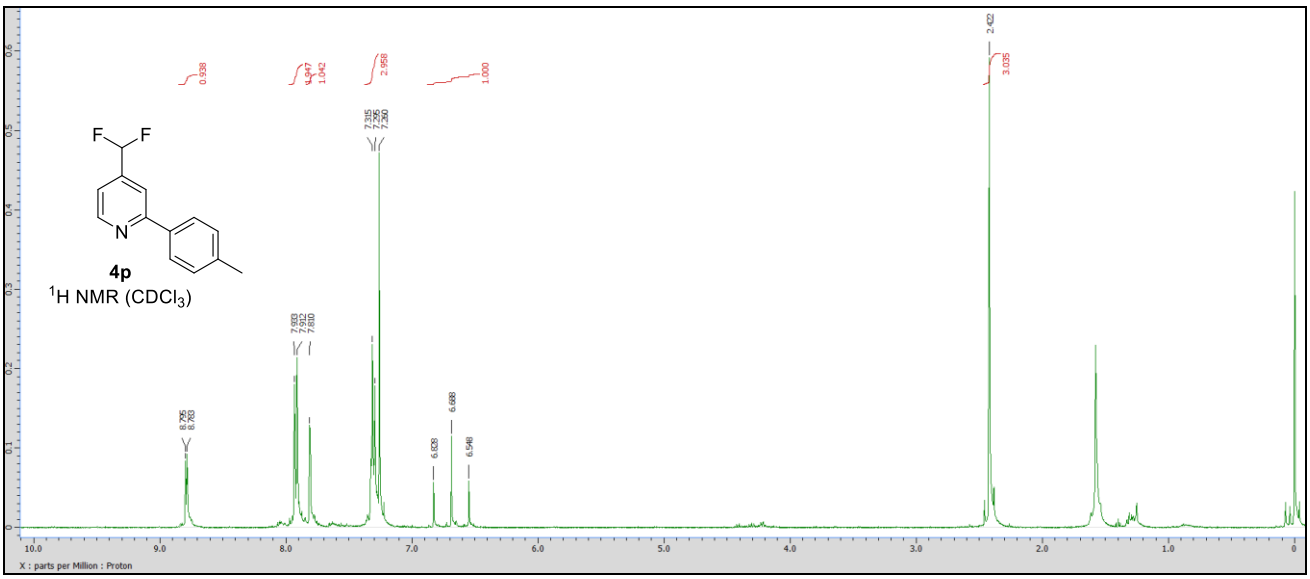

F
F
Br
N
4m
19F NMR (CDCl3)
-118.383
-118.524

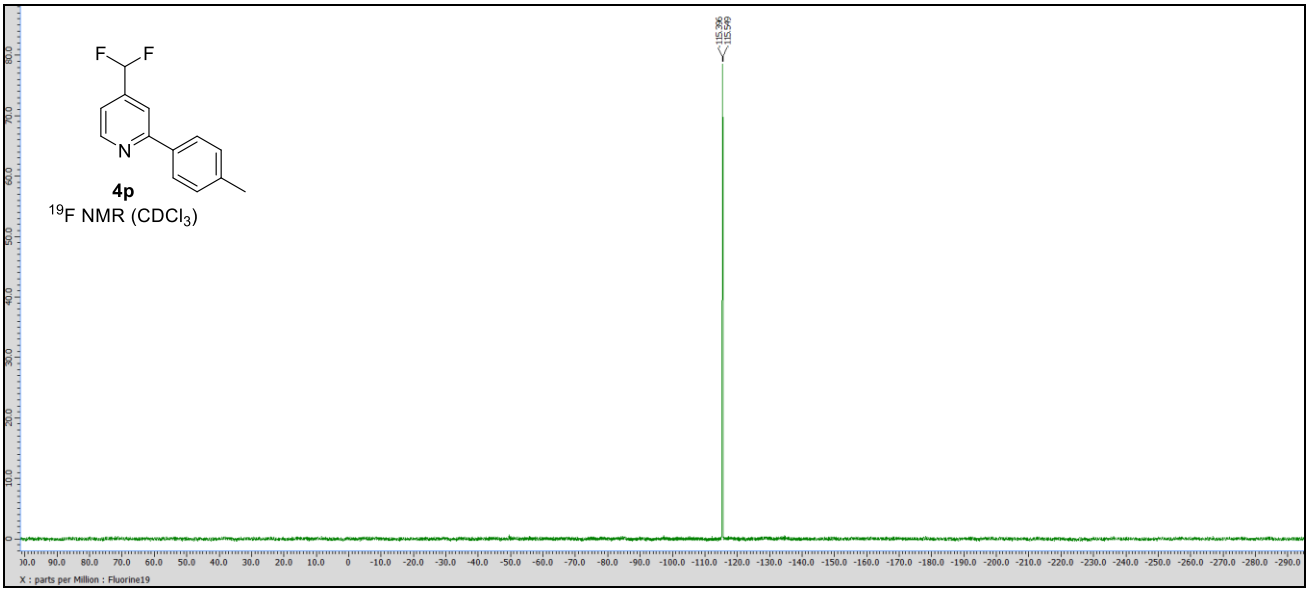

F
F
NC
N
4n
^{1}H NMR ($CDCl_3$)
X : parts per Million : Proton

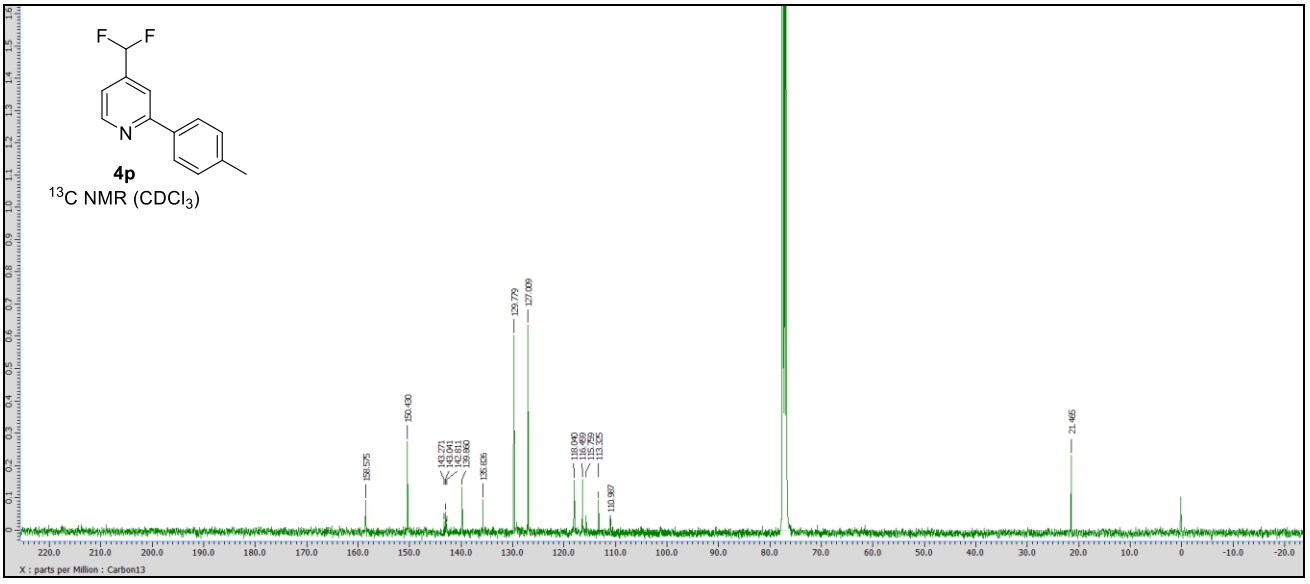

F
F
NC
N
4n
^{19}F NMR ($CDCl_3$)
X : parts per Million : Fluorine19

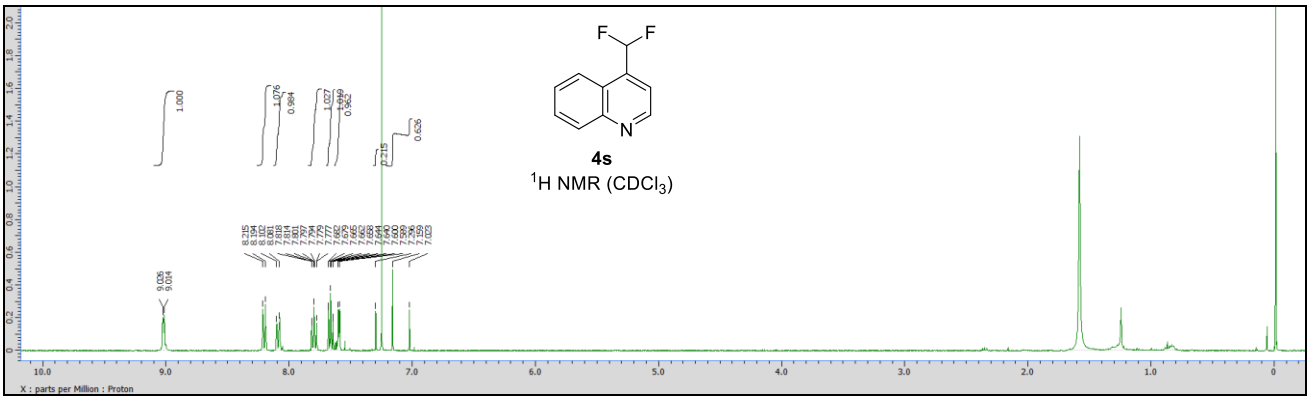

F
F
Br
Br
N
4o
1H NMR (CDCl3)
1.994
1.000
8.722
7.102
7.294
6.970
X : parts per Million : Proton

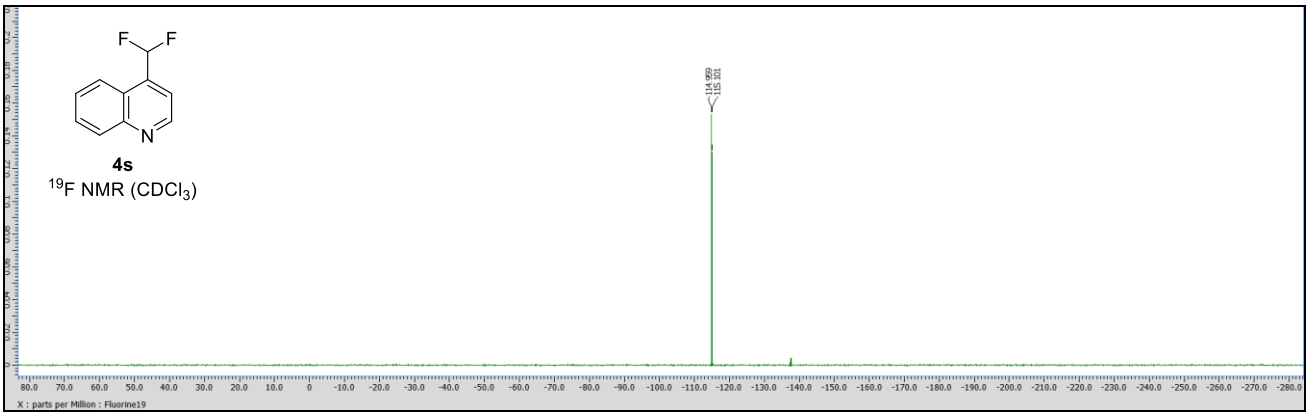

F
F
Br
Br
N
4o
19F NMR (CDCl3)
-116.625
-116.760
X : parts per Million : Fluorine19

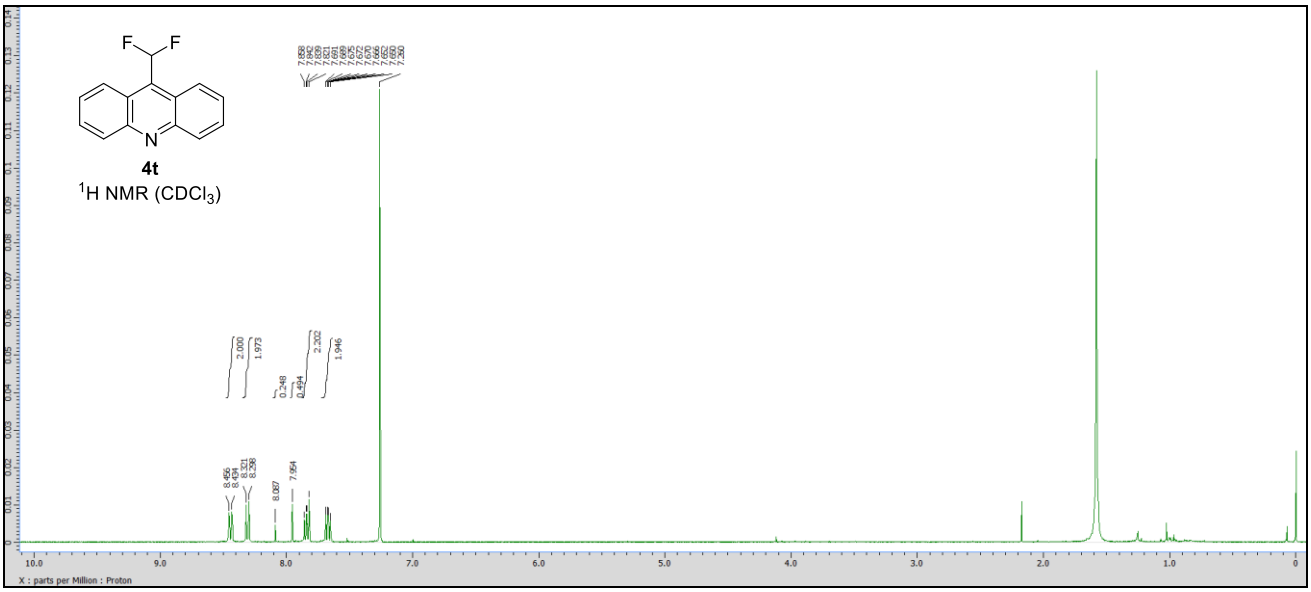

F
F
N
4p
^{1}H NMR ($CDCl_3$)
X : parts per Million : Proton

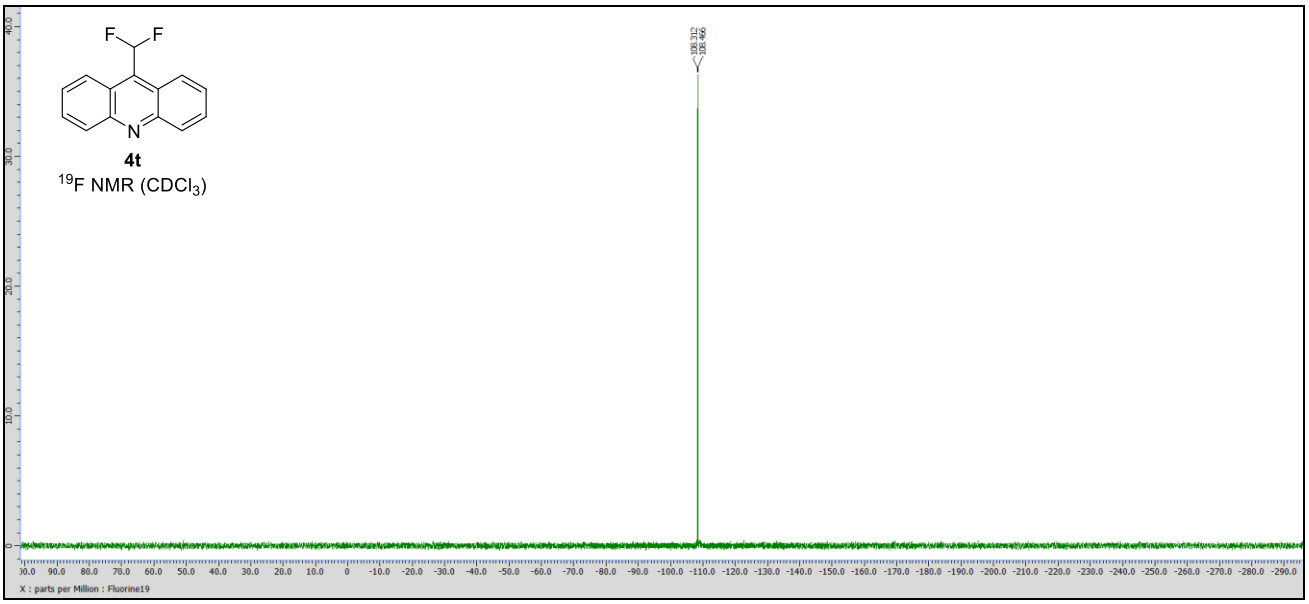

F
F
N
4p
^{19}F NMR ($CDCl_3$)
X : parts per Million : Fluorine19

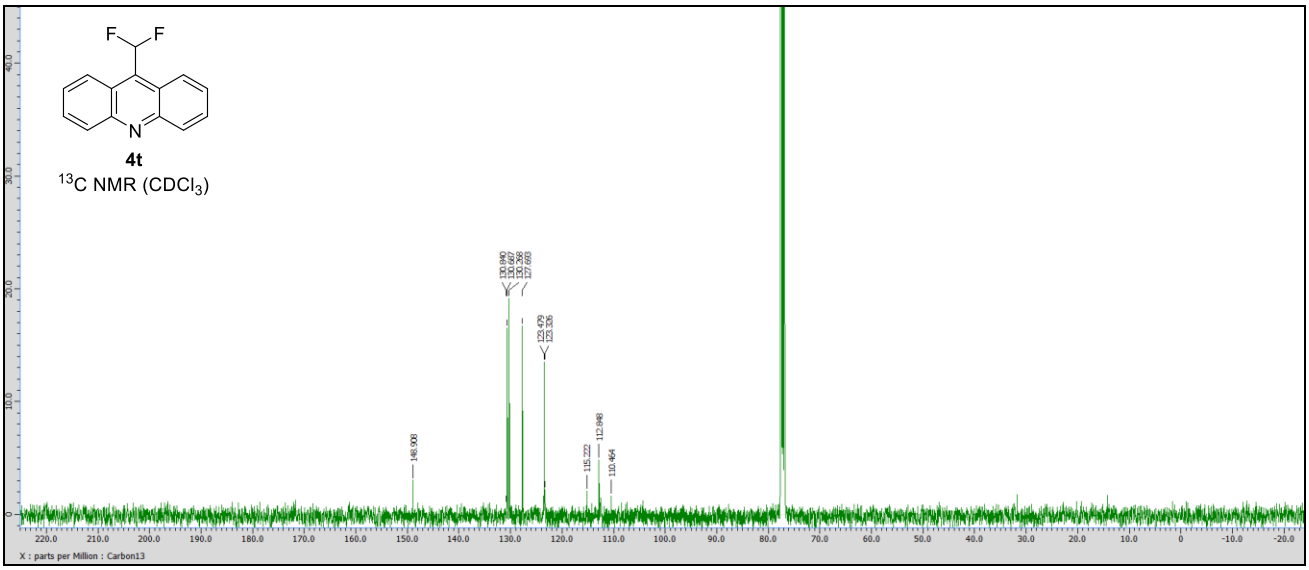

F
F
N
4p
^{13}C NMR ($CDCl_3$)
X : parts per Million : Carbon13

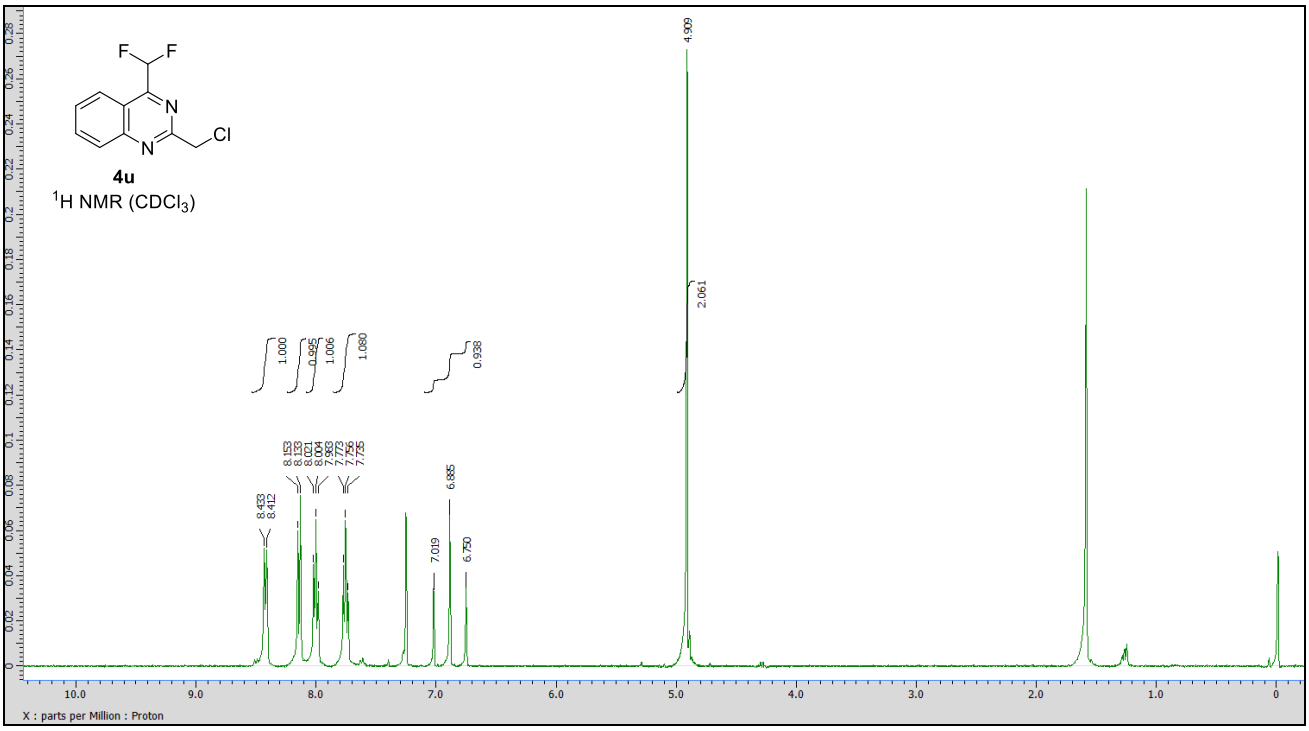

F
F
N
4s
1H NMR (CDCl3)
X : parts per Million : Proton

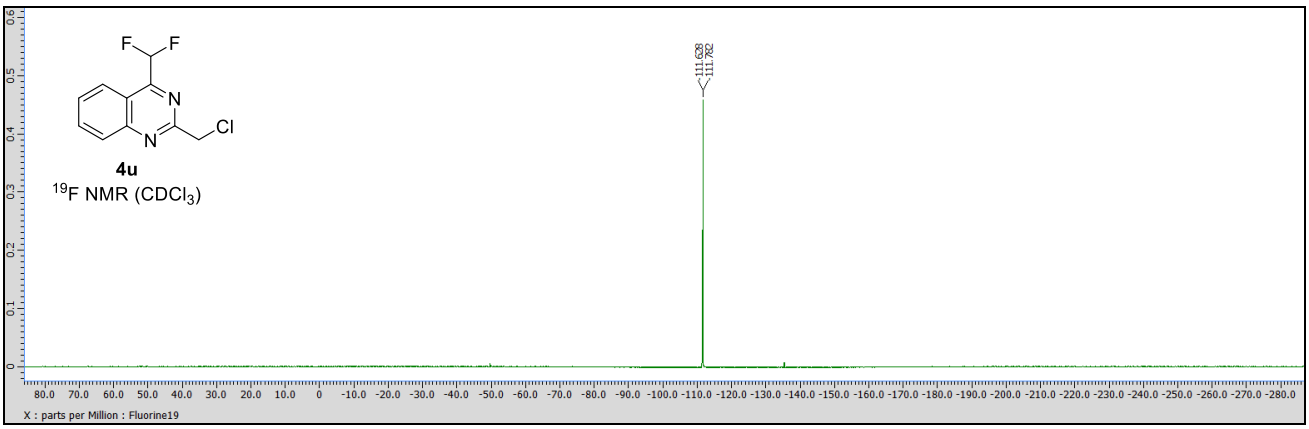

F
F
N
4s
19F NMR (CDCl3)
X : parts per Million : Fluorine19

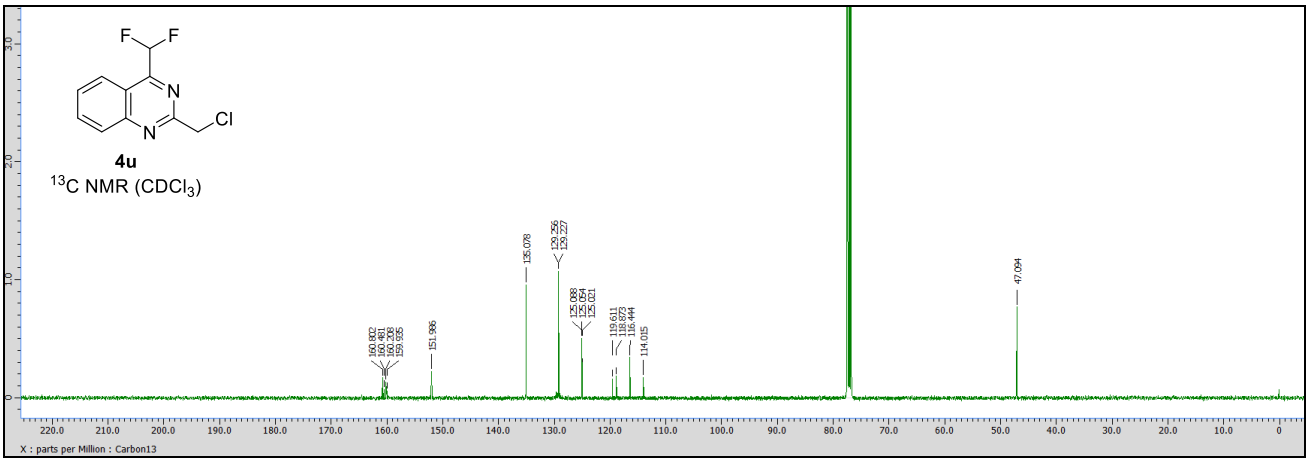

F
F
N
4t
1H NMR (CDCl3)
X : parts per Million : Proton

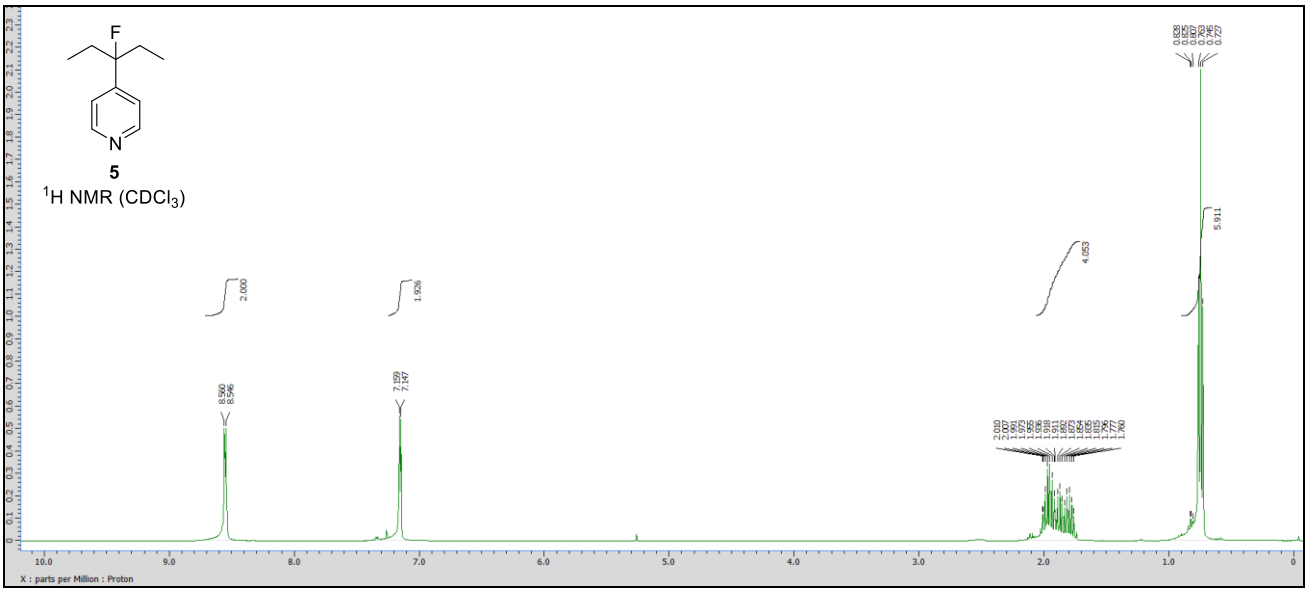

F
F
N
4t
19F NMR (CDCl3)
X : parts per Million : Fluorine19

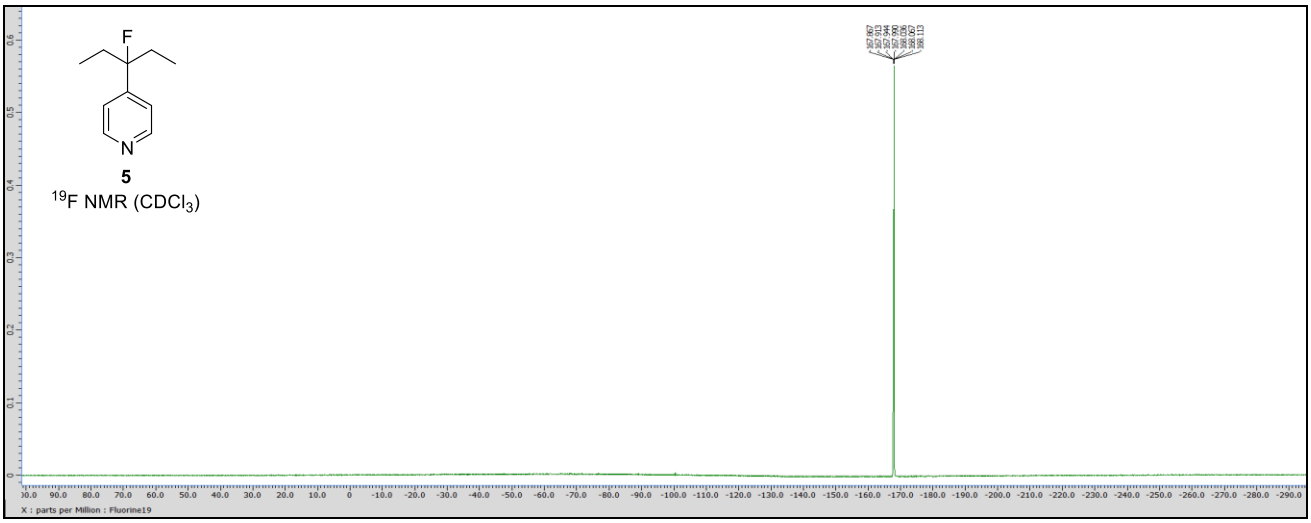

F
F
N
4t
13C NMR (CDCl3)
X : parts per Million : Carbon13

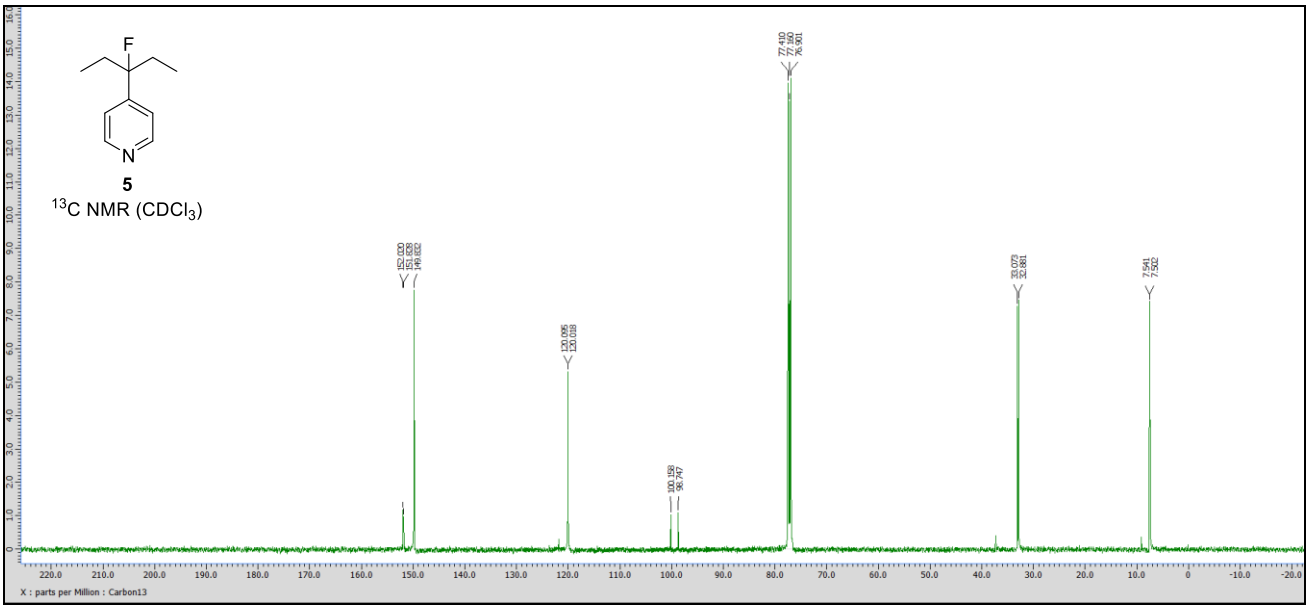

F
F
N
N
Cl
4u
^{1}H NMR ($CDCl_3$)
4.909
2.061
1.000
0.995
1.006
1.080
0.938
8.433
8.412
8.153
8.133
8.071
8.054
7.993
7.773
7.756
7.735
7.019
6.885
6.750
X : parts per Million : Proton

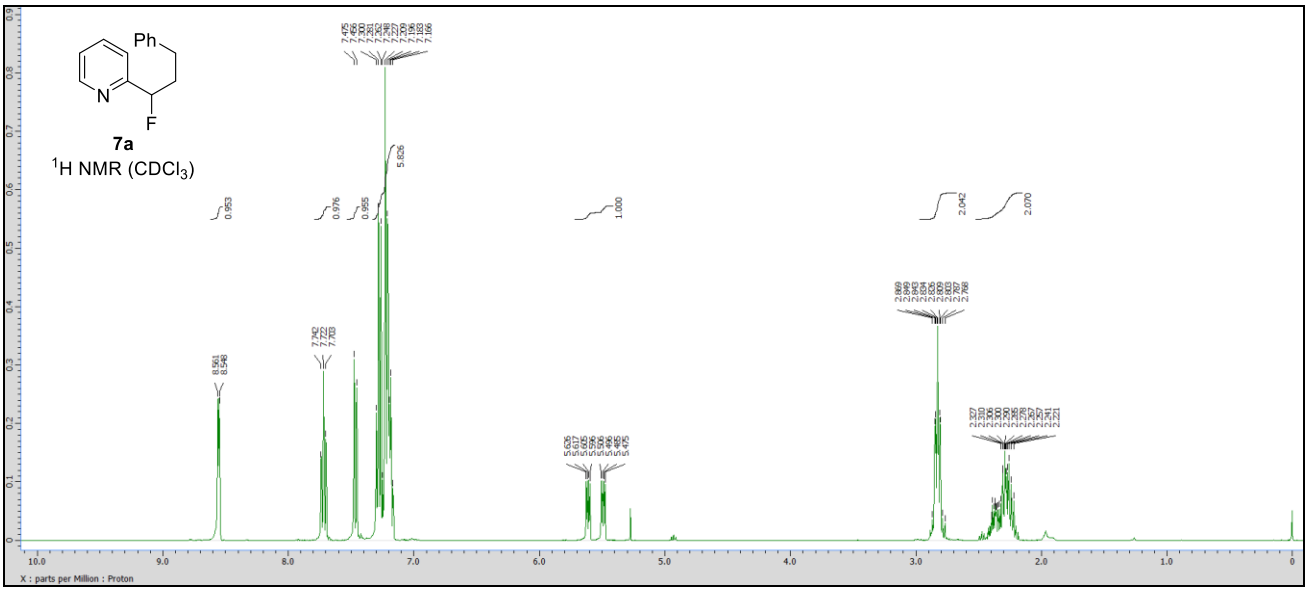

F
F
N
N
Cl
4u
^{19}F NMR ($CDCl_3$)
111.638
111.762
X : parts per Million : Fluorine19

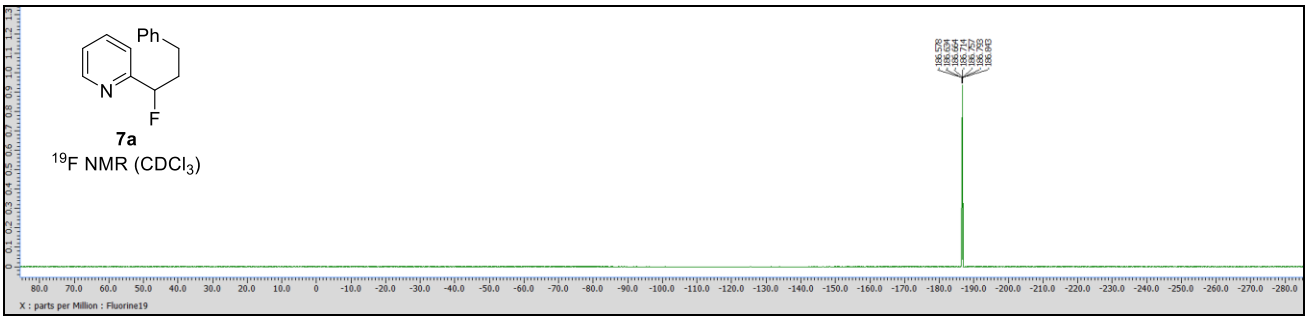

F
F
N
N
Cl
4u
^{13}C NMR ($CDCl_3$)
160.802
160.461
160.236
159.935
151.986
135.078
129.256
129.227
125.088
125.054
125.021
119.611
118.873
116.444
114.015
47.094
X : parts per Million : Carbon13

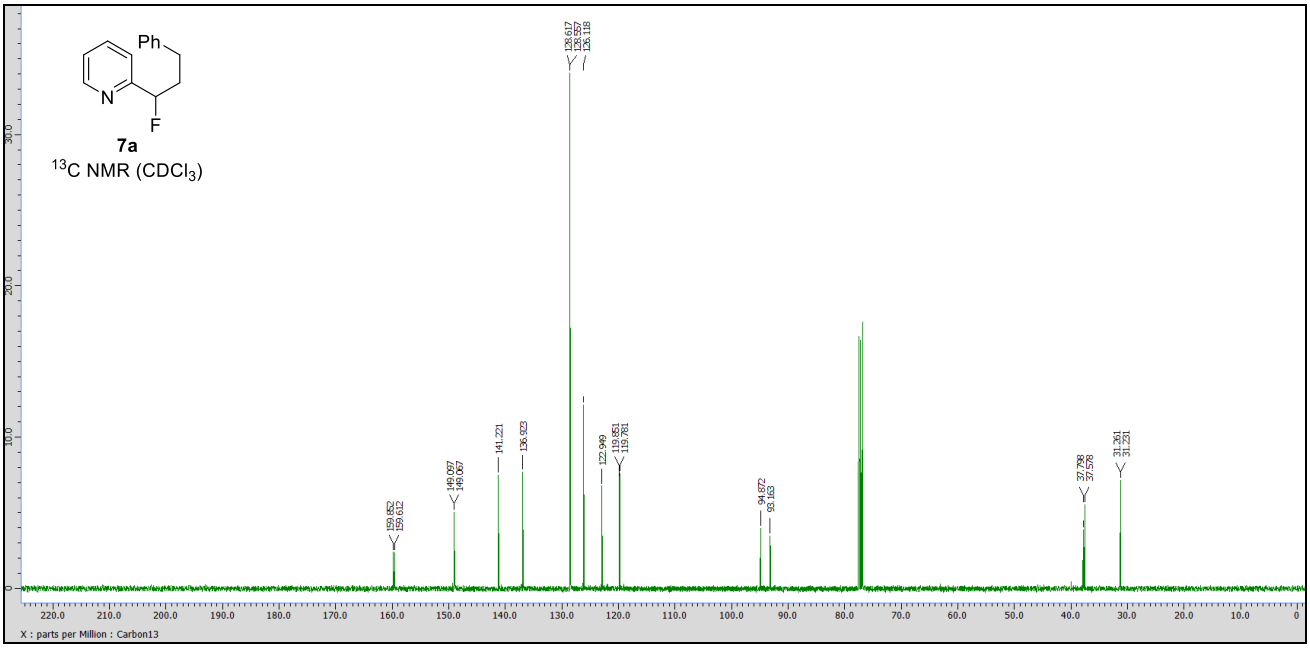

F
N
5
^{1}H NMR ($CDCl_3$)
X : parts per Million : Proton

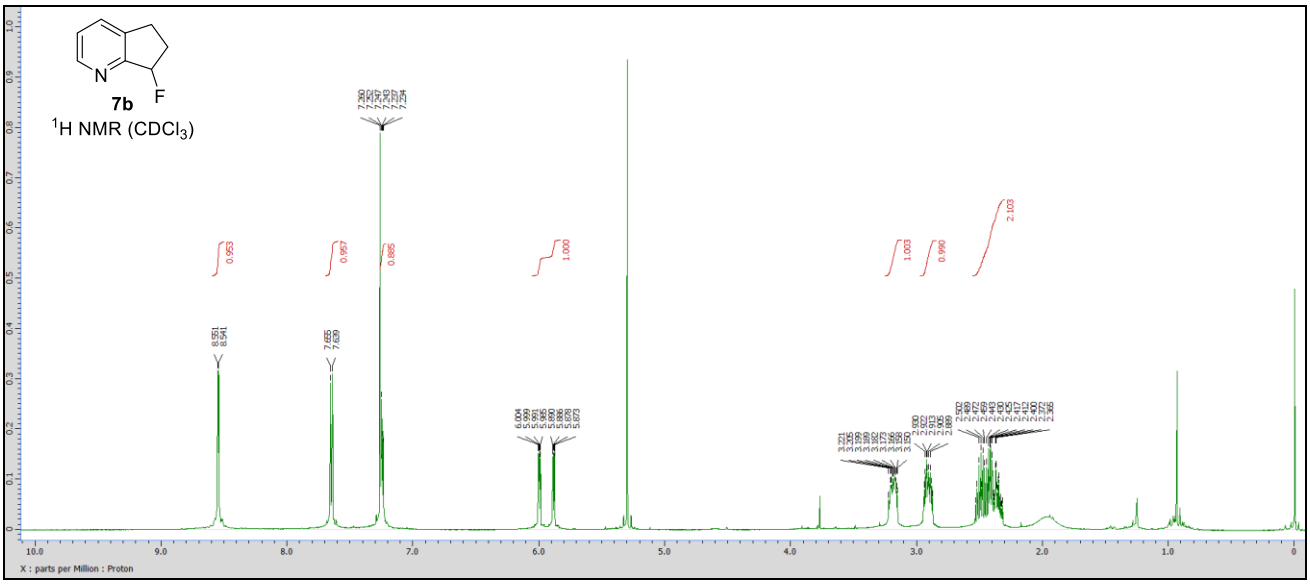

F
N
5
^{19}F NMR ($CDCl_3$)
X : parts per Million : Fluorine19

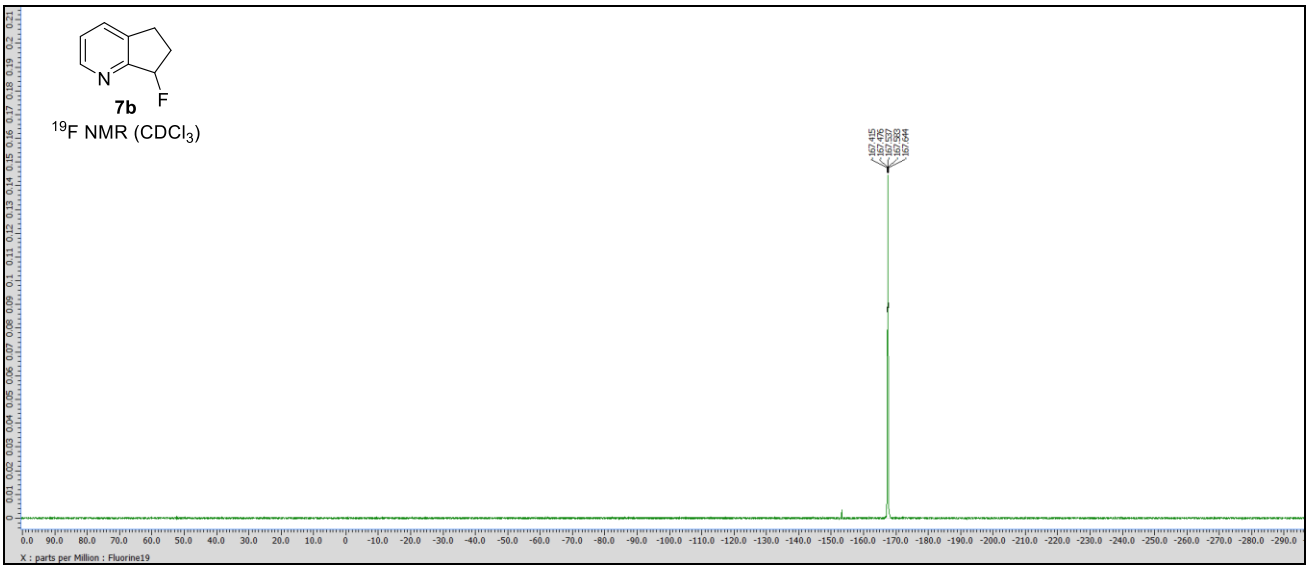

F
N
5
^{13}C NMR ($CDCl_3$)
X : parts per Million : Carbon13

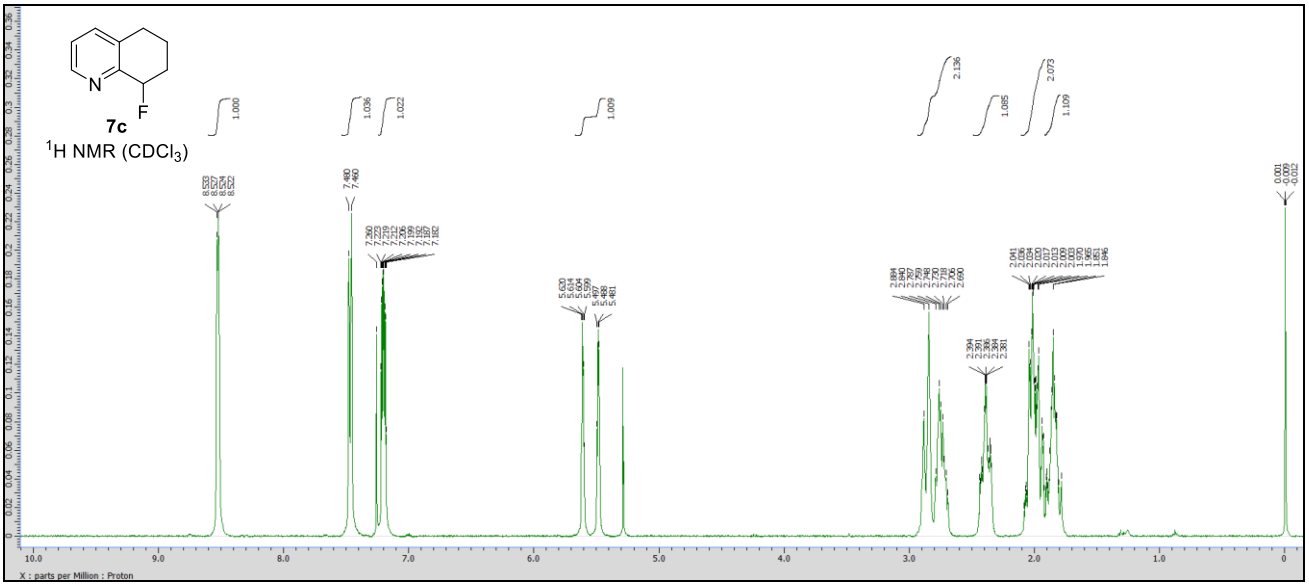

Ph
N
F
7a
1H NMR (CDCl3)
X : parts per Million : Proton

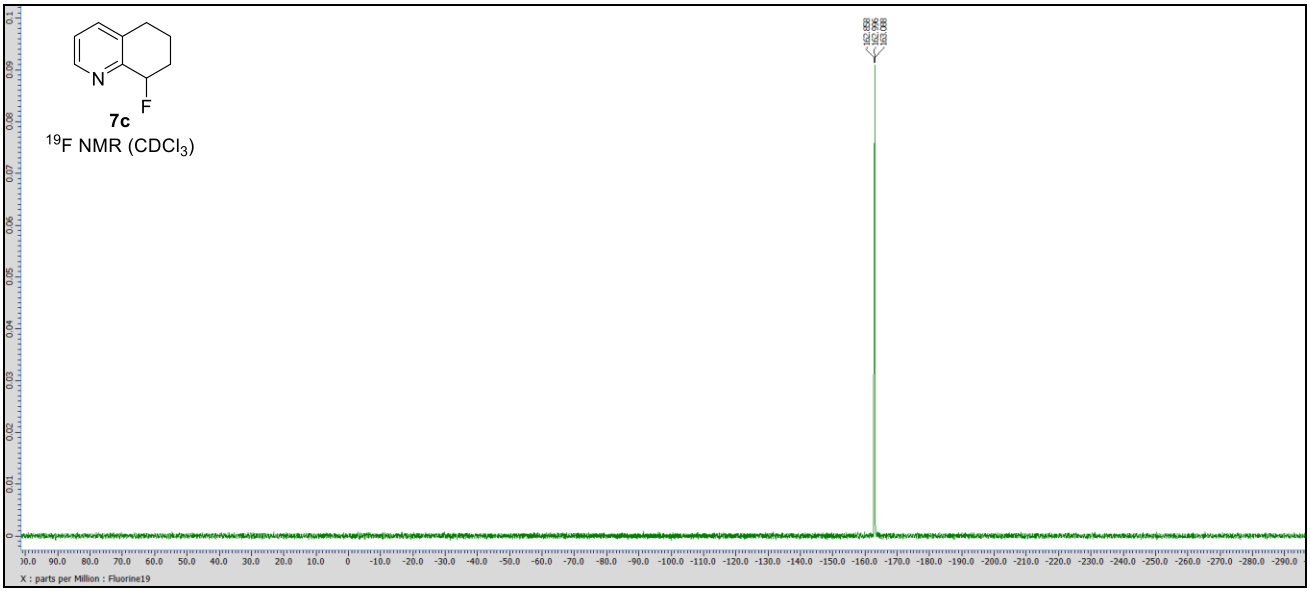

Ph
N
F
7a
19F NMR (CDCl3)
X : parts per Million : Fluorine19

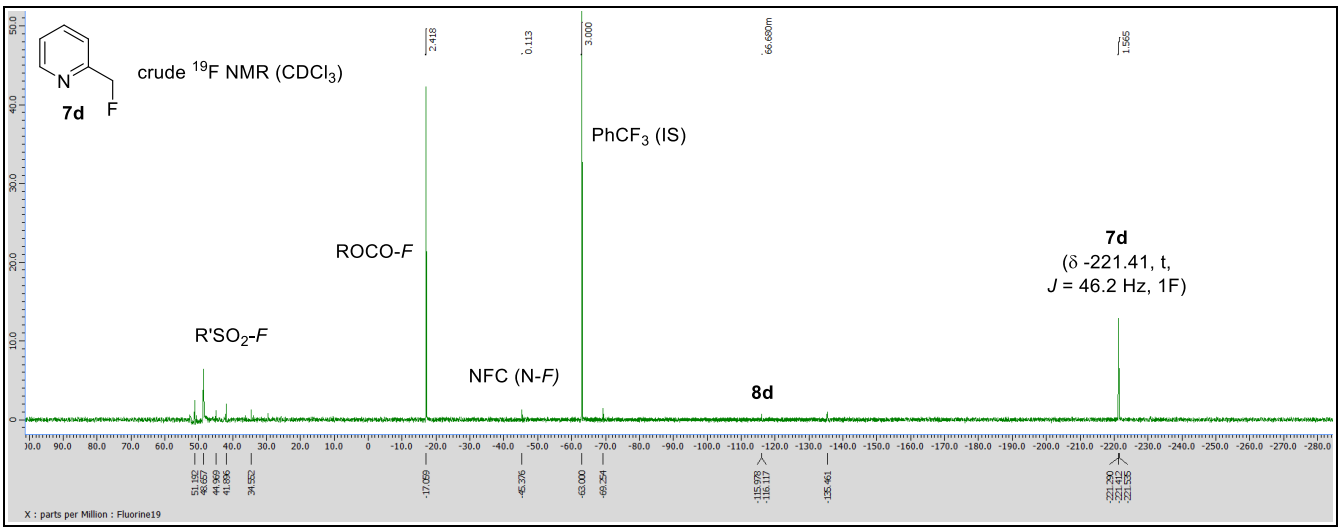

Ph
N
F
7a
13C NMR (CDCl3)
X : parts per Million : Carbon13

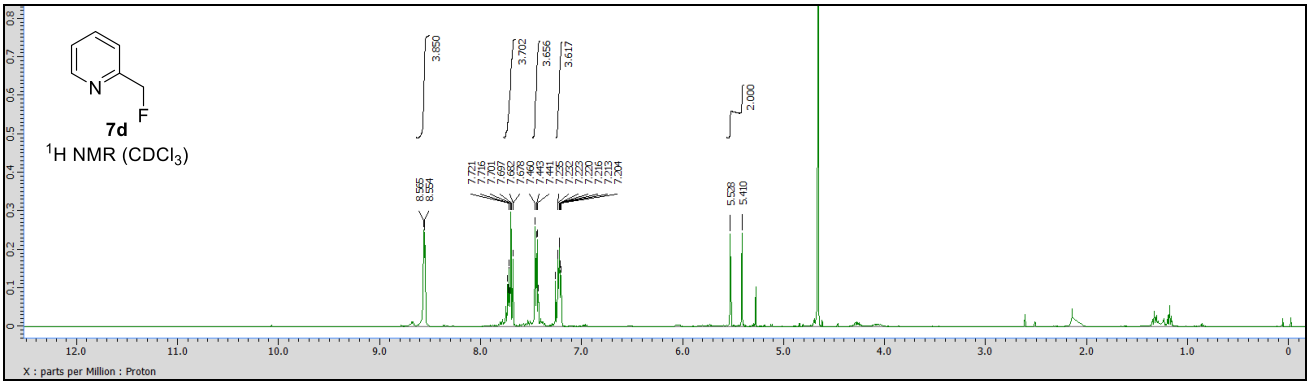

7b
^{1}H NMR ($CDCl_3$)
X : parts per Million : Proton

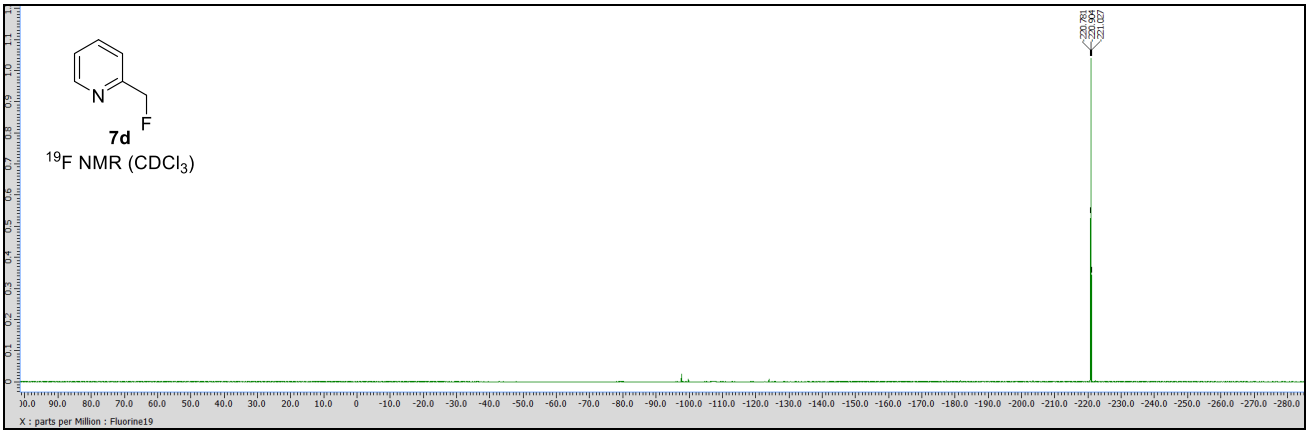

7b
^{19}F NMR ($CDCl_3$)
X : parts per Million : Fluorine19

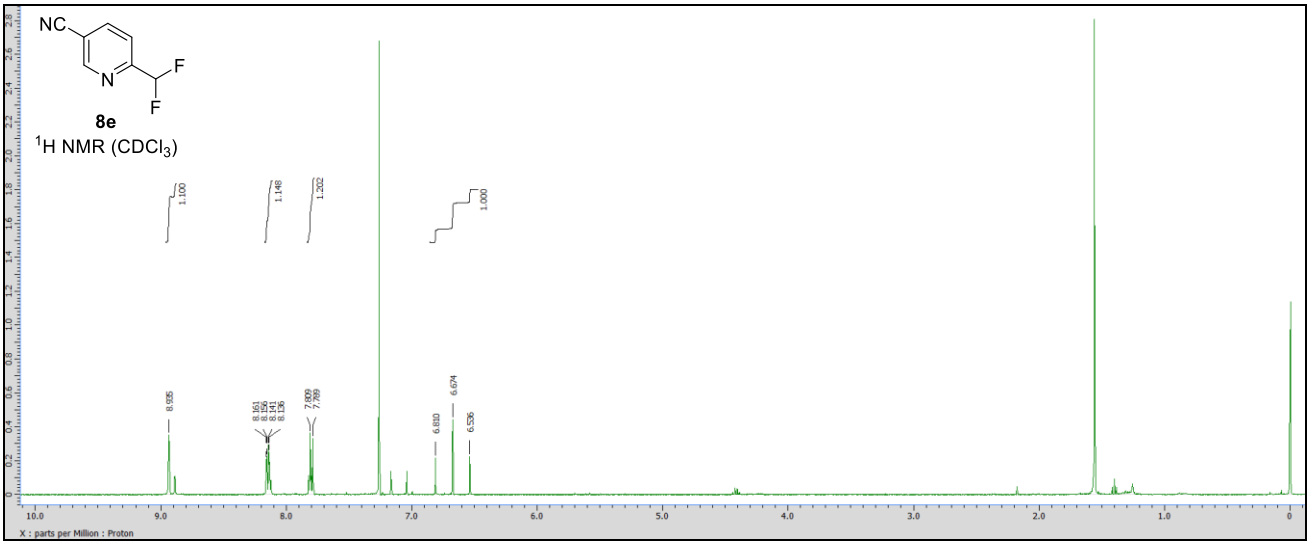

7c
1H NMR (CDCl3)
X : parts per Million : Proton

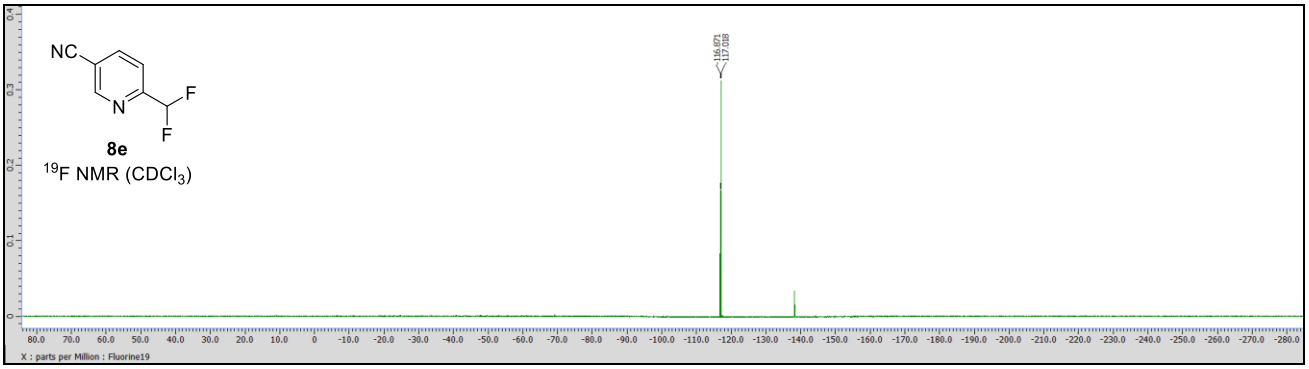

7c
19F NMR (CDCl3)
X : parts per Million : Fluorine19

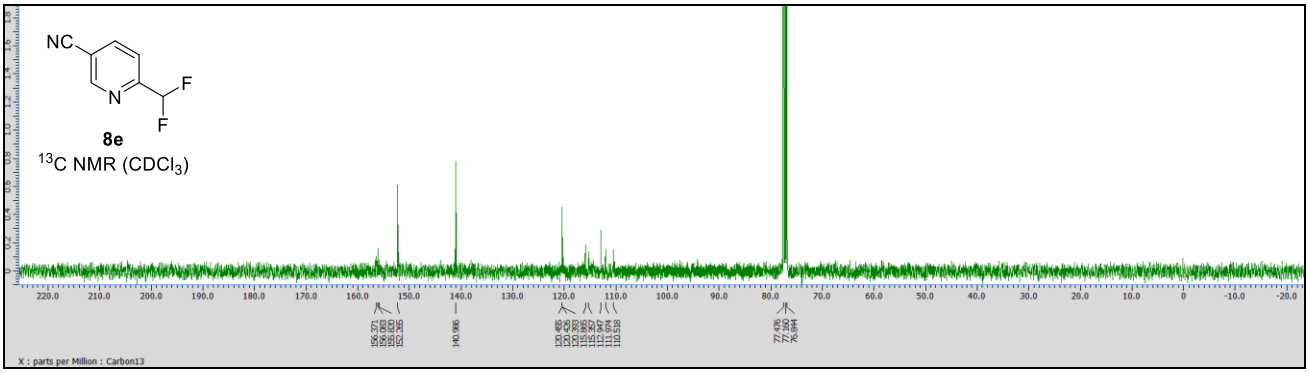

7d
crude ^{19}F NMR ($CDCl_3$)
$PhCF_3$ (IS)
ROCO-*F*
R'SO_2-*F*
NFC (N-*F*)
8d
7d
(δ -221.41, t,
J = 46.2 Hz, 1F)
X : parts per Million : Fluorine19

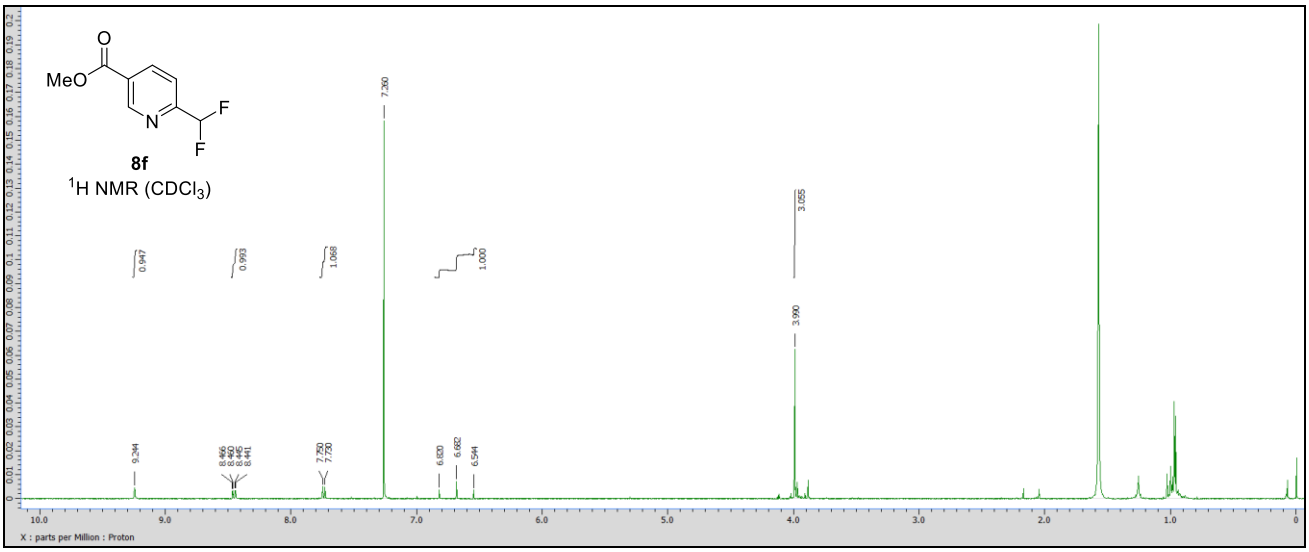

7d
^{1}H NMR ($CDCl_3$)
X : parts per Million : Proton

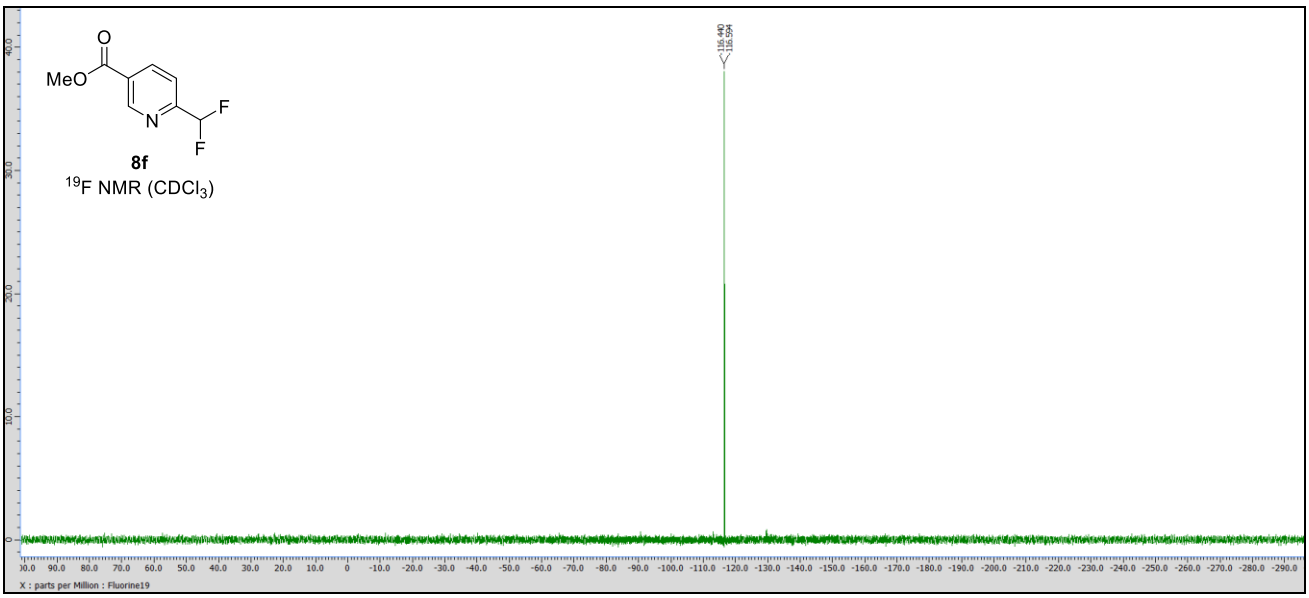

7d
^{19}F NMR ($CDCl_3$)
X : parts per Million : Fluorine19

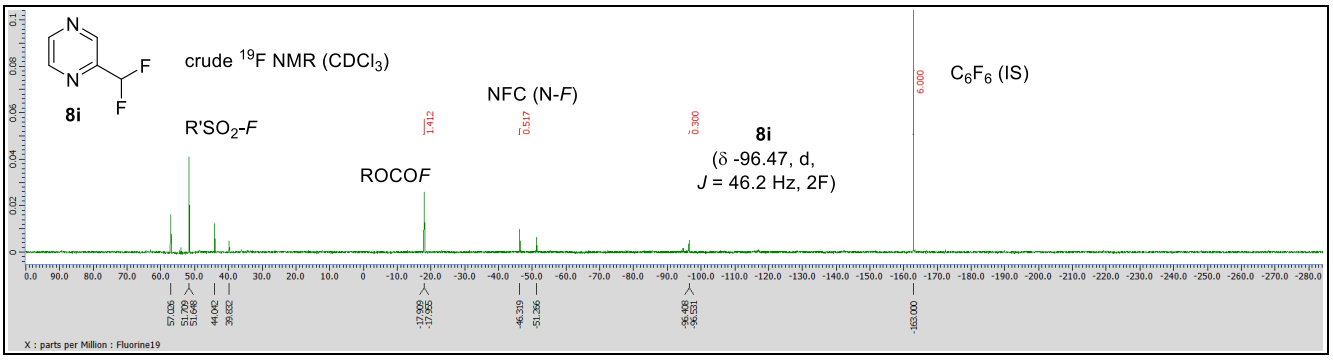

NC
F
N
F
8e
^{1}H NMR ($CDCl_3$)
X : parts per Million : Proton

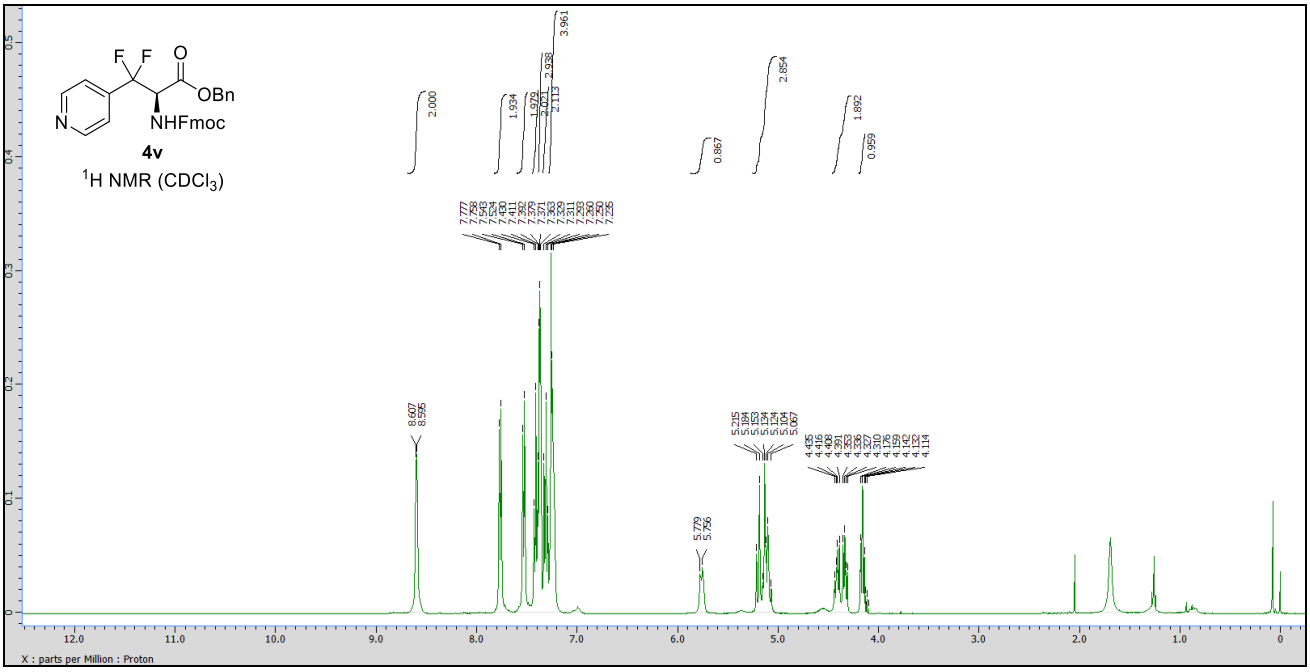

NC
F
N
F
8e
^{19}F NMR ($CDCl_3$)
X : parts per Million : Fluorine19

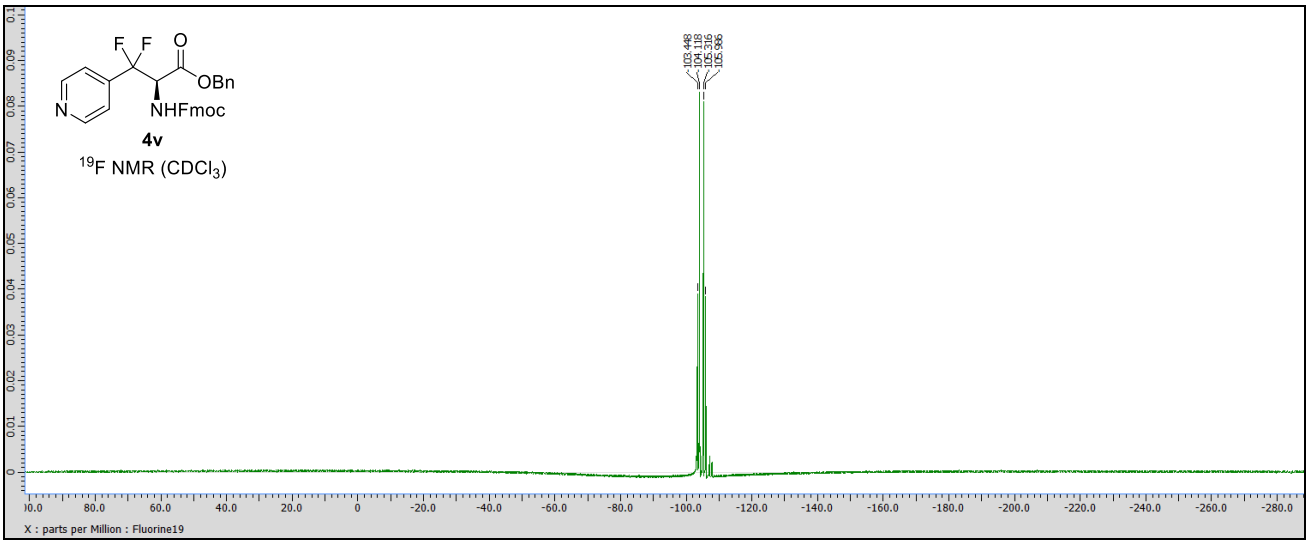

NC
F
N
F
8e
^{13}C NMR ($CDCl_3$)
X : parts per Million : Carbon13

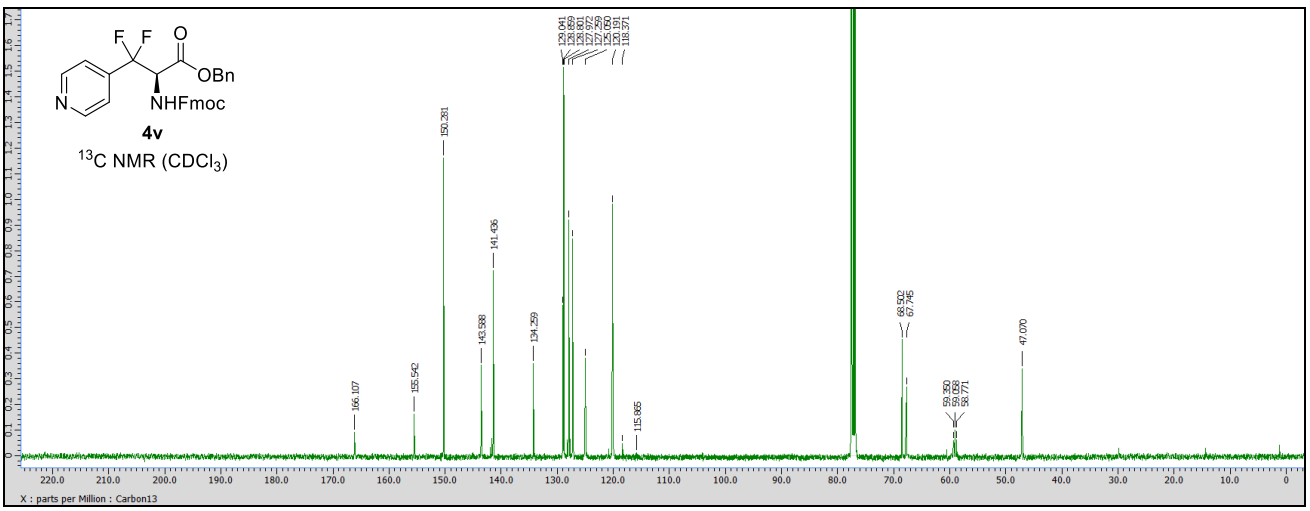

MeO
O
N
F
F
8f
^{1}H NMR ($CDCl_3$)
X : parts per Million : Proton


MeO
O
N
F
F
8f
^{19}F NMR ($CDCl_3$)
X : parts per Million : Fluorine19


crude ^{19}F NMR ($CDCl_3$)
8i
R'SO_2-*F*
ROCO*F*
NFC (N-*F*)
8i
(δ -96.47, d,
J = 46.2 Hz, 2F)
C_6F_6 (IS)
X : parts per Million : Fluorine19


F F O
OBn
N
NHFmoc
4v
^{1}H NMR ($CDCl_3$)
X : parts per Million : Proton


F F O
OBn
N
NHFmoc
4v
^{19}F NMR ($CDCl_3$)
X : parts per Million : Fluorine19


F F O
OBn
N
NHFmoc
4v
^{13}C NMR ($CDCl_3$)
X : parts per Million : Carbon13

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