Supporting Information

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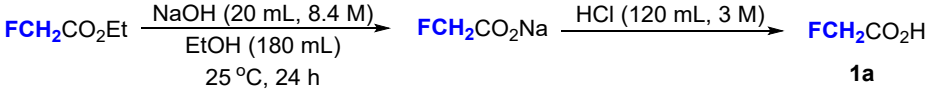
1. General Information and Materials

General information: ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on a 400 MHz NMR spectrometer. ^{1}H NMR spectroscopy chemical shifts were determined relative to internal Me_4Si (TMS) at δ 0.0 or to the signal of the residual protonated solvent $CDCl_3$ δ 7.26. ^{13}C NMR spectroscopy chemical shifts were determined relative to the signal of $CDCl_3$ δ 77.0. For the reaction mixtures, ^{19}F NMR spectroscopy chemical shifts were determined relative to $PhCF_3$ at δ –62.0. Data for ^{1}H, ^{13}C and ^{19}F NMR spectra are recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, q = quartet, br = broad, hept = heptet). FT-IR spectra were obtained with a Nicolet 5700 spectrophotometer. GC-MS data were recorded on a Finnigan 4021 instrument and GCMS-QP2010. Melting points were recorded on a SGW X-4 melting point apparatus and are uncorrected. High-resolution mass spectral (HRMS) were collected on Waters Micromass GCT Premier and Bruker MicroTof Q II 10410. All reactions were monitored by TLC or ^{19}F NMR spectroscopy.

Materials: Commercial reagents and solvents were used without further purification. 2-Fluoroacetic acid (FCH_2CO_2H, **1a**) and 2-fluoro-2-methylpropanoic acid (Me_2CFCO_2H, **1c**) were prepared with a similar procedure to the literature.[1] 2-Fluoropropanoic acid ($MeCHFCO_2H$, **1b**) was prepared with a similar procedure to the literature.[2]

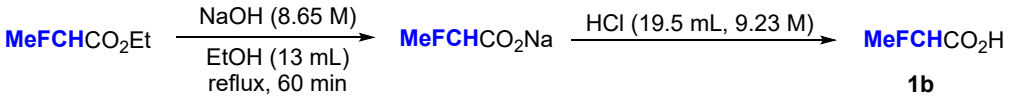
Procedure for the synthesis of FCH_2CO_2H (1a)



A solution of ethyl fluoroacetate (FCH_2CO_2Et) (13.6 mL, 141 mmol) in EtOH (180 mL) was treated with 20 mL of aqueous NaOH (8.4 M) and stirred at room temperature for 24 h. The solvent was rotary evaporated to dryness. The sodium fluoroacetate thus obtained was redissolved in 120 mL of aqueous HCl (3 M), and then the solution was saturated with solid NaCl and then extracted with Et_2O (4×25 mL). The organic extract was dried with $MgSO_4$, filtered, and the filtrate was rotary evaporated to produce 2-

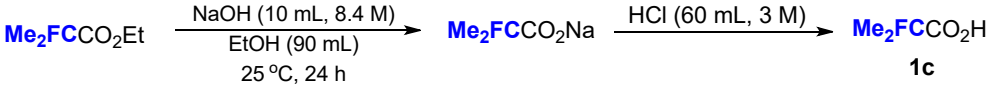
fluoroacetic acid as a clear oil. This crude product, which was still slightly wet, was redissolved in anhydrous Et_2O, dried with copious amount of $MgSO_4$ overnight, filtered, and rotary evaporated to dryness to produce FCH_2CO_2H (5.0 g, 46% yield) as a colorless liquid. ^1H NMR (400 MHz, $CDCl_3$): δ 4.91 (d, J = 46.8 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$): δ –230.5 (t, $J_{H\text{-}F}$ = 47.0 Hz, 1F). **1a** is a known compound and has been reported in the previous paper.[1]

Procedure for the synthesis of $MeCHFCO_2H$ (1b)



Sodium hydroxide (4.5 g, 112.5 mmol) was dissolved in water (13 mL) and ethyl 2-fluoropropionate (5.9 g, 49.1 mmol) was added together with ethanol (13 mL). The mixture was heated under reflux for 60 min, cooled to room temperature, and concentrated to a volume of about 10 mL under reduced pressure. Water (4.5 mL) and concentrated hydrochloric acid (9 mL) were added, and the product was extracted with diethyl ether (6×15 mL). The organic extract was dried with Na_2SO_4, diethyl ether was rotary evaporated to produce $MeCHFCO_2H$ (3.9 g, 81% yield) as a colorless oil. ^1H NMR (400 MHz, $CDCl_3$): δ 4.90 (d, J = 48.4 Hz, 1H), 1.37 (dd, J = 24.0, 6.4 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$): δ –185.3 (dq, $J_{H\text{-}F}$ = 48.9 Hz, 24.1 Hz, 1F). **1b** is a known compound and has been reported in the previous paper.[2]

Procedure for the Synthesis of Me_2CFCO_2H (1c)



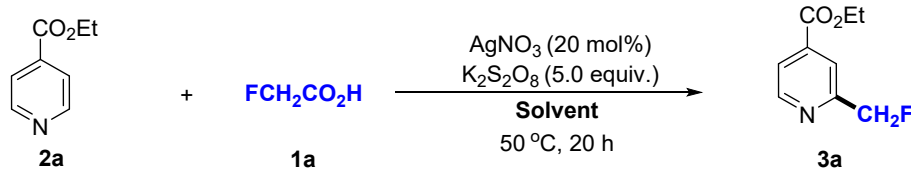
A solution of methyl 2-fluoro-2-methylpropanoate (Me_2FCCO_2Et) (6.3 mL, 70.5 mmol) in EtOH of 90 mL of anhydrous EtOH was treated with 10 mL of aqueous NaOH (8.4 M) and stirred at rt for 1 day. The solvent was rotary evaporated to dryness. The sodium fluoroacetate thus obtained was redissolved in 90 mL HCl of 3 M aqueous HCl, the solution was saturated with NaCl and then extracted four times with Et_2O (4 × 15 mL). The organic extract was dried with $MgSO_4$, filtered, and the filtrate was rotary

evaporated to produce 2-fluoro-2-methylpropanoic acid as a clear oil. This crude product，which was still slightly wet, was redissolved in anhydrous Et_2O, dried with copious amount of $MgSO_4$ overnight, filtered, and rotary evaporated to dryness to produce Me_2CFCO_2H (4.2 g, 56% yield) as a colorless oil. ^1H NMR (400 MHz, $CDCl_3$): δ 1.63 (d, J = 21.6 Hz, 6H). ^{19}F NMR (376 MHz, $CDCl_3$): δ −148.2 (hept, $J_{H\text{-}F}$ = 21.3 Hz, 1F). **1c** is a known compound and has been reported in the previous paper.[3]

2. Optimization of Monofluoroalkylation Reaction

To a 10 mL of Schlenk tube were added $AgNO_3$ (7.0 mg, 20 mol%) and $K_2S_2O_8$ (1.0-5.0 equiv.). The mixture was evacuated and backfilled with N_2 for three times, 4-picolinic acid ethyl ester (0.2 mmol, 1.0 equiv.), 2-fluoroacetic acid (2.0-3.0 equiv.) and solvent (1.5 mL) were then added. The Schlenk tube was screw capped and put into a preheated oil bath (50-100 °C). After stirring for 20 h, the reaction mixture was cooled to room temperature. Saturated solution of $NaHCO_3$ (3 mL) was added and the mixture was extracted with ethyl acetate (3×10 mL). The organic layer was washed with brine (10 mL), dried with anhydrous Na_2SO_4 and concentrated. The residue was purified by silica gel flash column chromatography to give product **3a**.

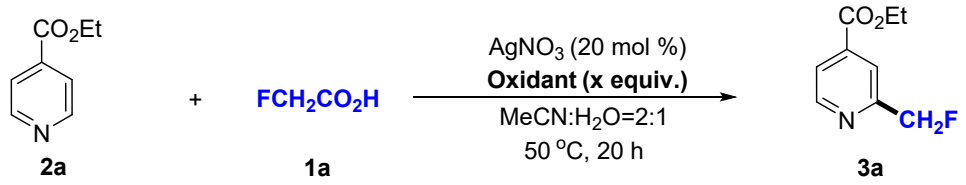
Table S1. Optimization of solvents[a]



Entry	Solvent (v:v)	Yield (%)
1	DCE/H_2O (2:1)	44
2	**MeCN/H_2O (2:1)**	**52**
3	DCM/H_2O (2:1)	35
4	DMSO/H_2O (2:1)	28
5	dioxane/H_2O (2:1)	<5
6	DMF/H_2O (2:1)	0
7	toluene/H_2O (2:1)	trace
8	THF/H_2O (2:1)	0
9	MeCN/H_2O (3:1)	48
10	MeCN/H_2O (1:1)	45

[a]Reaction conditions: **2a** (0.2 mmol, 1.0 equiv.), **1a** (0.4 mmol). Isolated yield.

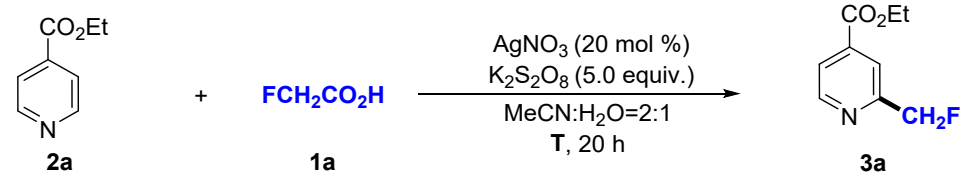
Table S2. Optimization of oxidants[a]



Entry	oxidant (x)	Yield (%)
1	$K_2S_2O_8$ (1.0)	24
2	$K_2S_2O_8$ (3.0)	33
3	**$K_2S_2O_8$ (5.0)**	**52**
4	$(NH_4)_2S_2O_8$ (5.0)	32
5	^{t}BuOOH (5.0)	0

[a]Reaction conditions: **2a** (0.2 mmol,1.0 equiv.), **1a (**0.4 mmol**)**. Isolated yield.

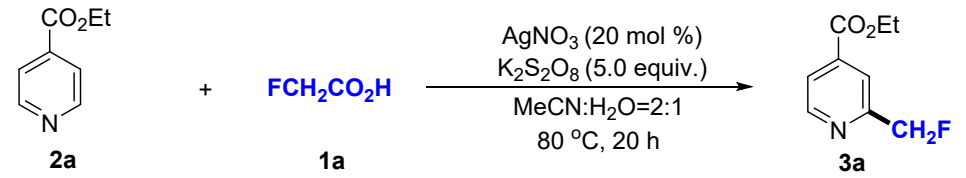
Table S3. Optimization of reaction temperature[a]



Entry	T (°C)	Yield (%)
1	50	52
2	60	57
3	70	65
4	**80**	**78**
5	90	70
6	100	56

[a]Reaction conditions: **2a** (0.2 mmol,1.0 equiv.), **1a (**0.4 mmol**)**. Isolated yield.

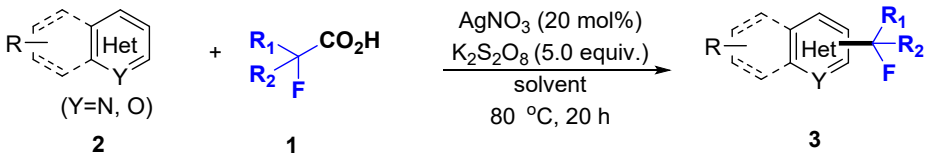
Table S4. Optimization of acid equivalent[a]



Entry	Acid Equivalent	Yield (%)
1	**2.0**	**78**
2	3.0	72

[a]Reaction conditions: **2a** (0.2 mmol,1.0 equiv.). Isolated yield.

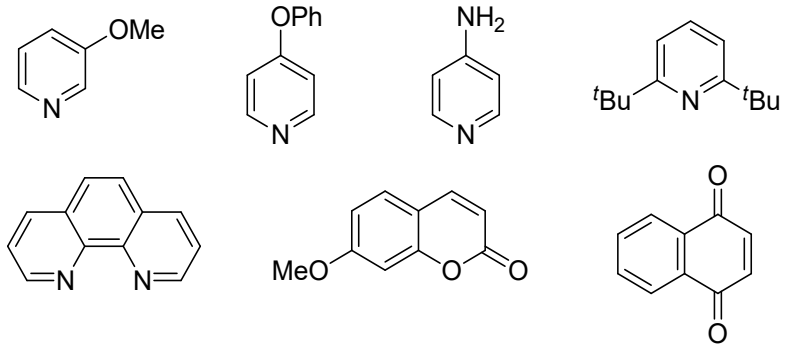
3. Substrate Scope of Monofluoroalkylation Reaction



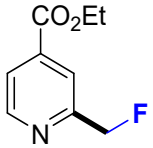
Typical experiment procedure:

To a 10 mL of Schlenk tube were added the heteroarene (0.2 mmol, 1.0 equiv.), $AgNO_3$ (20 mol%) and $K_2S_2O_8$ (5.0 equiv.). The mixture was evacuated and backfilled with N_2 for three times. Monofluoroalkyl carboxylic acids (1.5-3.0 equiv.), MeCN (1.0 mL) or DCE (1.0 mL) and water (0.5 mL) were then added. The Schlenk tube was screw capped and put into a preheated oil bath (80 °C). After stirring for 20 h, the reaction mixture was cooled to room temperature. Saturated solution of $NaHCO_3$ (3 mL) was added and the mixture was extracted with ethyl acetate (3×10 mL). The organic layer was washed with brine (10 mL), dried with anhydrous Na_2SO_4 and concentrated. The residue was purified by silica gel flash column chromatography to give product **3**.

Unsuccessful examples

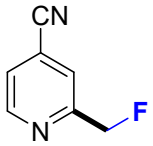


None or a trace of the desired products was detected when the above substrates proceeded the monofluoromethylation reactions.



Ethyl 2-(trifluoromethyl)isonicotinate (3a)

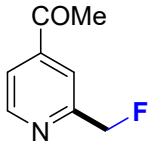
For 0.2 mmol scale, the standard procedure of method was followed to provide **3a** by column chromatography on silica gel (petroleum ether/EtOAc = 5:1, v/v) as a yellow oil (28 mg, 78%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.71 (d, J = 4.8 Hz, 1H), 8.00 (s, 1H), 7.79 (d, J = 4.8 Hz, 1H), 5.53 (d, J = 46.8 Hz, 2H), 4.41 (q, J = 7.2 Hz, 2H), 1.40 (t, J = 7.4 Hz, 3 H). ^{19}F NMR (376 MHz, $CDCl_3$): δ -222.0 (t, J_{F-H} = 47.0 Hz, 1F). GC-MS (*m*/*z*): 183. **3a** is a known compound and has been reported in the previous paper.[4]



2-(Fluoromethyl)isonicotinonitrile (3b)

For 0.2 mmol scale, the standard procedure of method was followed to provide **3b** by column chromatography on silica gel (petroleum ether/EtOAc = 10:1 to 5:1, v/v) as a white solid (16 mg, 58%). M.p.: 49.8-51.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.75 (d, J = 4.8 Hz, 1H), 7.69 (s, 1H), 7.48 (d, J = 4.4 Hz, 1H), 5.53 (d, J = 46.4 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$): δ -224.3 (t, J_{F-H} = 45.1 Hz, 1F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.4 (d, $^{2}J_{C-F}$ = 23.0 Hz), 150.1, 124.4, 121.7 (d, $^{3}J_{C-F}$ = 4.0 Hz), 121.3, 116.2, 83.3 (d, $^{1}J_{C-F}$ = 171.0 Hz). HRMS (ESI): calcd. For $C_7H_6FN_2$ $(M+H)^+$: 137.0515, found: 137.0520.

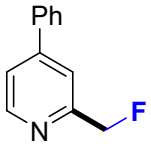
(Note: the low isolated yield of **3b** is due to its easily volatile.)



1-(2-(Fluoromethyl)pyridin-4-yl)ethan-1-one (3c)

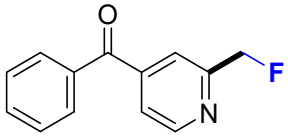
For 0.2 mmol scale, the standard procedure of method was followed to provide **3c**

by column chromatography on silica gel (petroleum ether/EtOAc = 5:1, v/v) as a yellow oil (21 mg, 70%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.76 (d, J = 4.4 Hz, 1H), 7.89 (s, 1H), 7.69 (d, J = 4.4 Hz, 1H), 5.57 (d, J = 46.8 Hz, 2H), 2.65 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$): δ -222.4 (t, J_{F-H} = 47.0 Hz, 1F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.1, 158.0 (d, $^{2}J_{C-F}$ = 22.0 Hz), 150.4, 143.7, 120.5, 118.0 (d, $^{3}J_{C-F}$ = 6.0 Hz), 84.0 (d, $^{1}J_{C-F}$ = 170.0 Hz), 26.8. HRMS (ESI): calcd. For C_8H_9FNO $(M+H)^+$: 154.0668, found: 154.0671.



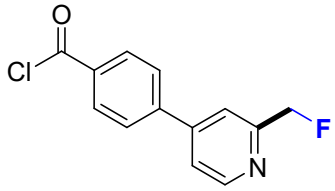
2-(Fluoromethyl)-4-phenylpyridine (3d)

For 0.2 mmol scale, the standard procedure of method was followed to provide **3d** by column chromatography on silica gel (petroleum ether/EtOAc = 10:1 to 5:1, v/v) as a yellow oil (25 mg, 68%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.62 (d, J = 5.2 Hz, 1H), 7.69-7.68 (m, 2H), 7.66 (s, 1H), 7.52-7.44 (m, 4H), 5.56 (d, J = 46.8 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$): δ -221.4 (t, J_{F-H} = 45.1 Hz, 1F). GC-MS (*m*/*z*): 187. **3d** is a known compound and has been reported in the previous paper.[5]



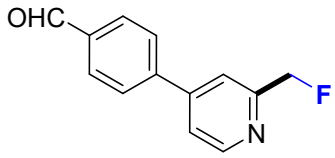
Phenyl(2-(trifluoromethyl)pyridin-4-yl)methanone (3e)

For 0.2 mmol scale, the standard procedure of method was followed to provide **3e** by column chromatography on silica gel (petroleum ether/EtOAc = 10:1 to 5:1, v/v) as a yellow oil (27 mg, 62%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.76 (d, J = 4.8 Hz, 1H), 7.82 (d, J = 24.8 Hz, 2H), 7.73 (s, 1H), 7.65 (t, J = 7.4 Hz, 1H), 7.52 (m, 3H), 5.57 (d, J = 46.8 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$): δ -222.1 (t, J_{F-H} = 45.1 Hz, 1F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 194.9, 157.3 (d, $^{2}J_{C-F}$ = 21.0 Hz), 149.8 (d, J = 2.0 Hz), 145.5, 135.7, 133.6, 130.1, 128.7, 122.2, 119.6 (d, $^{3}J_{C-F}$ = 6.0 Hz), 84.0 (d, $^{1}J_{C-F}$ = 170.0 Hz). HRMS (ESI): calcd. For $C_{13}H_{11}FNO$ $(M+H)^+$: 216.0825, found: 216.0824.



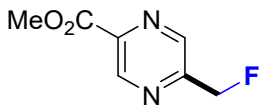
4-(2-(Fluoromethyl)pyridin-4-yl)benzoyl chloride (3f)

For 0.2 mmol scale, the standard procedure of method was followed to provide **3f** by column chromatography on silica gel (petroleum ether/EtOAc = 5:1 to 2:1, v/v) as a white solid (27 mg, 54%). M.p.: 65.9-66.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.76 (d, J = 4.4 Hz, 1H), 7.77 (d, J = 8.0 Hz, 2H), 7.70 (s, 1H), 7.50-7.48 (m, 3H), 5.57 (d, J = 46.8 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$): δ -222.4 (t, J_{F-H} = 47.0 Hz, 1F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 193.7, 157.5 (d, $^{2}J_{C-F}$ = 22.0 Hz), 149.9 (d, J = 2.0 Hz), 145.1, 140.3, 134.0, 131.5, 129.1, 122.0, 119.3 (d, $^{3}J_{C-F}$ = 6.0 Hz), 84.0 (d, $^{1}J_{C-F}$ = 170.0 Hz). HRMS (ESI): calcd. For $C_{13}H_{10}ClFNO$ $(M+H)^+$: 250.0435, found: 250.0435.



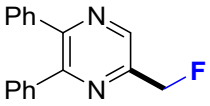
4-(2-(Fluoromethyl)pyridin-4-yl)benzaldehyde (3g)

For 0.2 mmol scale, the standard procedure of method was followed to provide **3g** by column chromatography on silica gel (petroleum ether/EtOAc = 8:1 to 4:1, v/v) as a white solid (24 mg, 53%). M.p.: 72.8-74.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.10 (s, 1H), 8.69 (d, J = 4.8 Hz, 1H), 8.03 (d, J = 7.6 Hz, 2H), 7.84 (d, J = 8.0 Hz, 2H), 7.73 (s, 1H), 7.51 (d, J = 4.4 Hz, 1H), 5.59 (d, J = 46.4 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$): δ -222.1 (t, J_{F-H} = 47.0 Hz, 1F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.6, 157.4 (d, $^{2}J_{C-F}$ = 27.0 Hz), 149.9, 148.0, 143.8, 136.6, 130.4, 127.8, 121.1, 118.3 (d, $^{3}J_{C-F}$ = 6.0 Hz), 84.3 (d, $^{1}J_{C-F}$ = 170.0 Hz). HRMS (ESI): calcd. For $C_{13}H_{11}FNO$ $(M+H)^+$: 216.0819, found: 216.0830.



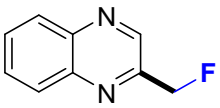
Methyl 5-(fluoromethyl)pyrazine-2-carboxylate (3h)

For 0.2 mmol scale, the standard procedure of method was followed to provide **3h** by column chromatography on silica gel (petroleum ether/EtOAc = 5:1 to 2:1, v/v) as a yellow oil (17 mg, 50%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.28 (s, 1H), 8.89 (s, 1H), 5.65 (d, J = 46.4 Hz, 2H), 4.07 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$): δ -226.3 (t, J_{F-H} = 47.0 Hz, 1F). GC-MS (*m/z*): 170. **3h** is a known compound and has been reported in the previous paper.[6]



5-(Fluoromethyl)-2,3-diphenylpyrazine (3i)

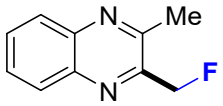
For 0.2 mmol scale, the standard procedure of method was followed to provide **3i** by column chromatography on silica gel (petroleum ether/EtOAc = 10:1 to 5:1, v/v) as a yellow oil (22 mg, 42%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.70 (s, 1H), 7.38-7.36 (m, 3H), 7.28-7.21 (m, 7H), 5.58 (d, J = 46.8 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$): δ -222.2 (t, J_{F-H} = 47.0 Hz, 1F). ^{19}F NMR (376 MHz, $CDCl_3$): δ -222.2 (t, J_{F-H} = 47.0 Hz, 1F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.3, 151.7, 148.6 (d, $^{2}J_{C-F}$ = 21.0 Hz), 139.9, 139.8, 138.2, 138.1, 129.6, 128.83, 128.76, 128.3 (d, $^{3}J_{C-F}$ = 4.0 Hz), 83.0 (d, $^{1}J_{C-F}$ = 169.0 Hz). HRMS (ESI): calcd. For $C_{17}H_{14}FN_2$ $(M+H)^+$: 265.1141, found: 265.1143.



2-(Fluoromethyl)quinoxaline (3j)

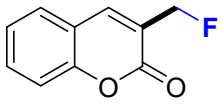
For 0.2 mmol scale, the standard procedure of method was followed to provide **3j** by column chromatography on silica gel (petroleum ether/EtOAc = 10:1 to 5:1, v/v) as a white solid (20 mg, 61%). M.p.: 50.2-51.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.02 (s, 1H), 8.13-8.11 (m, 1H), 8.05-8.03 (m, 1H), 7.78-7.76 (m, 2H), 5.70 (d, J = 46.8 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$): δ -223.0 (t, J_{F-H} = 47.0 Hz, 1F). ^{13}C NMR (100

MHz, $CDCl_3$): δ 150.9 (d, $^2J_{C\text{-}F}$ = 21.0 Hz), 143.1 (d, $^3J_{C\text{-}F}$ = 5.0 Hz), 142.3, 141.4, 130.5, 130.2, 129.4 129.1, 83.6 (d, $^1J_{C\text{-}F}$ = 169.0 Hz). HRMS (ESI): calcd. For $C_9H_8FN_2$ $(M+H)^+$: 163.0672, found: 163.0679.



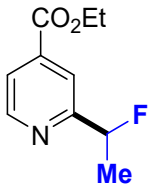
2-(Fluoromethyl)-3-methylquinoxaline (3k)

For 0.2 mmol scale, the standard procedure of method was followed to provide **3k** by column chromatography on silica gel (petroleum ether/EtOAc = 10:1 to 5:1, v/v) as a white solid (19 mg, 54%). M.p.: 75.0-76.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08-8.02 (m, 2H), 7.78-7.70 (m, 2H), 5.70 (d, J = 47.2 Hz, 2H), 2.84 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$): δ -217.5 (t, $J_{F\text{-}H}$ = 47.0 Hz, 1F). GC-MS (*m/z*): 176. **3k** is a known compound and has been reported in the previous paper.[4]



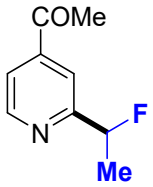
3-(Fluoromethyl)-2H-chromen-2-one (3l)

For 0.2 mmol scale, the standard procedure of method was followed to provide **3l** by column chromatography on silica gel (petroleum ether/EtOAc = 10:1 to 5:1, v/v) as a yellow oil (24 mg, 67%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 (s, 1H), 7.57-7.53 (m, 2H), 7.37-7.30 (m, 2H), 5.38 (d, J = 46.4 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$): δ -225.7 (t, $J_{F\text{-}H}$ = 47.0 Hz, 1F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.5 (d, $^3J_{C\text{-}F}$ = 6.0 Hz), 153.4, 138.9 (d, $^3J_{C\text{-}F}$ = 10.0 Hz), 131.8, 128.0, 124.7, 124.3 (d, $^2J_{C\text{-}F}$ = 19.0 Hz), 118.6, 116.7, 79.5 (d, $^1J_{C\text{-}F}$ = 170.0 Hz). HRMS (ESI): calcd. For $C_{10}H_8FO_2$ $(M+H)^+$: 179.0508, found: 179.0509.



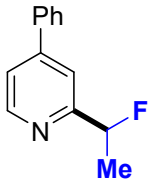
Ethyl-2-(1-fluoroethyl)isonicotinate (3m)

For 0.2 mmol scale, the standard procedure of method was followed to provide **3m** by column chromatography on silica gel (petroleum ether/EtOAc = 5:1, v/v) as a yellow oil (31 mg, 80%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.69 (d, J = 4.8 Hz, 1H), 8.00 (s, 1H), 7.78 (d, J = 4.8 Hz, 1H), 5.72 (dq, J = 47.6 Hz, 6.0 Hz, 1H), 4.41 (q, J = 6.8 Hz, 2H), 1.69 (dd, J = 25.2 Hz, 6.4 Hz, 3H), 1.40 (t, J = 7.0 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$): δ -178.0 (dq, J_{F-H} = 48.9 Hz, 26.3 Hz, 1F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.0, 161.8 (d, $^{2}J_{C-F}$ = 24.0 Hz), 149.7, 138.7, 122.1, 118.5 (d, $^{3}J_{C-F}$ = 7.0 Hz), 91.1 (d, $^{1}J_{C-F}$ = 170.0 Hz), 61.9, 21.6 (d, $^{2}J_{C-F}$ = 23.0 Hz), 14.2. HRMS (ESI): calcd. For $C_{10}H_{13}FNO_2$ $(M+H)^+$: 198.0930, found: 198.0939.



1-(2-(1-Ethyl)pyridin-4-yl)ethan-1-one hydrofluoride (3n)

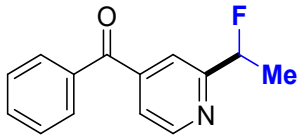
For 0.2 mmol scale, the standard procedure of method was followed to provide **3n** by column chromatography on silica gel (petroleum ether/EtOAc = 10:1 to 5:1, v/v) as a yellow oil (24 mg, 72%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.75 (d, J = 4.4 Hz, 1H), 7.91 (s, 1H), 7.68 (d, J = 4.4 Hz, 1H), 5.76 (dq, J = 48.0 Hz, 6.4 Hz, 1H), 2.67 (s, 3H), 1.72 (dd, J = 24.4 Hz, 6.4 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$): δ -178.3 (dq, J_{F-H} = 48.9 Hz, 26.3 Hz, 1F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.1, 162.1 (d, $^{2}J_{C-F}$ = 24.0 Hz), 150.0 (d, J = 2.0 Hz), 143.6, 120.2, 116.8 (d, $^{3}J_{C-F}$ = 7.0 Hz), 91.0 (d, $^{1}J_{C-F}$ = 170.0 Hz), 26.6, 21.5 (d, $^{2}J_{C-F}$ = 23.0 Hz). HRMS (ESI): calcd. For $C_9H_{11}FNO$ $(M+H)^+$: 168.0829, found: 168.0825.



2-(1-Fluoroethyl)-4-phenylpyridine (3o)

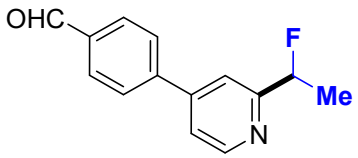
For 0.2 mmol scale, the standard procedure of method was followed to provide **3o**

by column chromatography on silica gel (petroleum ether/EtOAc = 10:1 to 5:1, v/v) as a yellow oil (32 mg, 79%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.60 (d, J = 5.2 Hz, 1H), 7.70 (s, 1H), 7.67 (d, J = 7.6 Hz, 2H), 7.51-7.43 (m, 4H), 5.75 (dq, J = 48.0 Hz, 6.4 Hz, 1H), 1.74 (dd, J = 24.4 Hz, 6.4 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$): δ -177.5 (dq, J_{F-H} = 48.9 Hz, 22.6 Hz, 1F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.2 (d, $^{2}J_{C-F}$ = 24.0 Hz), 149.3 (d, J = 2.0 Hz), 138.1, 129.12, 129.07, 127.0, 127.0, 117.0 (d, $^{3}J_{C-F}$ = 7.0 Hz), 91.4 (d, $^{1}J_{C-F}$ = 168.0 Hz), 21.7 (d, $^{2}J_{C-F}$ = 23.0 Hz). HRMS (ESI): calcd. For $C_{13}H_{13}FN$ $(M+H)^{+}$: 202.1032, found: 202.1037.



(2-(1-Fluoroethyl)pyridin-4-yl)(phenyl)methanone (3p)

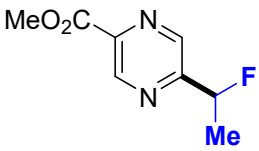
For 0.2 mmol scale, the standard procedure of method was followed to provide **3p** by column chromatography on silica gel (petroleum ether/EtOAc = 10:1 to 5:1, v/v) as a yellow oil (29 mg, 64%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.60 (d, J = 5.2 Hz, 1H), 7.70 (s, 1H), 7.67 (d, J = 7.6 Hz, 2H), 7.51-7.43 (m, 4H), 5.75 (dq, J = 48.4 Hz, 6.4 Hz, 1H), 1.74 (dd, J = 24.4 Hz, 6.4 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$): δ -178.1 (dq, J_{F-H} = 48.9 Hz, 26.3 Hz, 1F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.1, 161.6 (d, $^{2}J_{C-F}$ = 24.0 Hz), 149.5 (d, J = 2.0 Hz), 145.5, 135.7, 133.6, 130.1, 128.7, 122.0, 118.4 (d, $^{3}J_{C-F}$ = 8.0 Hz), 91.1 (d, $^{1}J_{C-F}$ = 170.0 Hz), 21.6 (d, $^{2}J_{C-F}$ = 23.0 Hz). HRMS (ESI): calcd. For $C_{14}H_{13}FNO$ $(M+H)^{+}$: 230.0981, found: 230.0986.



4-(2-(1-Fluoroethyl)pyridin-4-yl)benzaldehyde (3q)

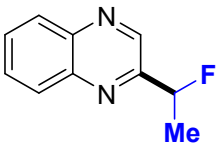
For 0.2 mmol scale, the standard procedure of method was followed to provide **3q** by column chromatography on silica gel (petroleum ether/EtOAc = 10:1 to 5:1, v/v) as an orange oil (25 mg, 55%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.10 (s, 1H), 8.66 (d, J =

4.8 Hz, 1H), 8.01 (d, J = 7.6 Hz, 2H), 7.83 (d, J = 7.6 Hz, 2H), 7.74 (s, 1H), 7.48 (d, J = 4.4 Hz, 1H), 5.77 (dq, J = 48.9 Hz, 6.4 Hz, 1H), 1.75 (dd, J = 24.4 Hz, 6.4 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$): δ -178.1 (dq, J_{F-H} = 48.0 Hz, 22.6 Hz, 1F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.6, 161.7 (d, $^2J_{C-F}$ = 23.0 Hz), 149.6 (d, J = 2.0 Hz), 148.0, 143.9, 136.5, 130.4, 127.8, 120.8, 117.2 (d, $^3J_{C-F}$ = 8.0 Hz), 91.3 (d, $^1J_{C-F}$ = 169.0 Hz), 21.7 (d, $^2J_{C-F}$ = 23.0 Hz). HRMS (ESI): calcd. For $C_{14}H_{13}FNO$ $(M+H)^+$: 230.0984, found: 230.0981.



Methyl-5-(1-fluoroethyl)pyrazine-2-carboxylate (3r)

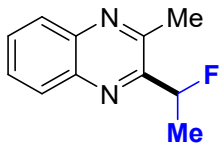
For 0.2 mmol scale, the standard procedure of method was followed to provide **3r** by column chromatography on silica gel (petroleum ether/EtOAc = 5:1, v/v) as a yellow oil (28 mg, 75%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.22 (s, 1H), 8.87 (s, 1H), 5.80 (dq, J = 47.6 Hz, 6.4 Hz, 1H), 4.04 (s, 3H), 1.73 (dd, J = 24.4 Hz, 6.4 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$): δ -182.3 (dq, J_{F-H} = 48.9 Hz, 26.3 Hz, 1F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.2, 158.9 (d, $^2J_{C-F}$ = 24.0 Hz), 144.9 (d, J = 2.0 Hz), 142.3, 140.9 (d, $^3J_{C-F}$ = 8.0 Hz), 89.9 (d, $^1J_{C-F}$ = 170.0 Hz), 53.2, 20.1 (d, $^2J_{C-F}$ = 23.0 Hz). HRMS (ESI): calcd. For $C_8H_{10}FN_2O_2$ $(M+H)^+$: 185.0726, found: 185.0729.



2-(Fluoroethyl)quinoxaline (3s)

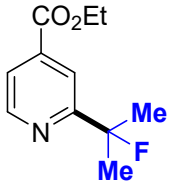
For 0.2 mmol scale, the standard procedure of method was followed to provide **3s** by column chromatography on silica gel (petroleum ether/EtOAc = 10:1 to 5:1, v/v) as a yellow oil (25 mg, 70%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.07 (s, 1H), 8.14-8.06 (m, 2H), 7.80-7.78 (m, 2H), 5.92 (dq, J = 48.0 Hz, 6.8 Hz, 1H), 1.83 (dd, J = 24.4 Hz, 6.4 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$): δ -179.6 (dq, J_{F-H} = 48.9 Hz, 26.3 Hz, 1F). ^{13}C

NMR (100 MHz, $CDCl_3$): δ 154.9 (d, $^2J_{C\text{-}F}$ = 24.0 Hz), 142.4 (d, $^3J_{C\text{-}F}$ = 7.0 Hz), 142.2, 141.3 (d, J = 2.0 Hz), 130.4, 130.0, 129.3, 129.2, 90.8 (d, $^1J_{C\text{-}F}$ = 168.0 Hz), 21.3 (d, $^2J_{C\text{-}F}$ = 23.0 Hz). HRMS (ESI): calcd. For $C_{10}H_{10}FN_2$ $(M+H)^+$: 177.0831, found: 177.0828.



2-(1-Fluoroethyl)-3-methylquinoxaline (3t)

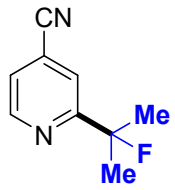
For 0.2 mmol scale, the standard procedure of method was followed to provide **3t** by column chromatography on silica gel (petroleum ether/EtOAc = 10:1 to 5:1, v/v) as a yellow oil (24 mg, 62%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 (d, J = 7.6 Hz, 1H), 8.00 (d, J = 8.0 Hz, 1H), 7.75-7.68 (m, 2H), 6.01 (dq, J = 47.6 Hz, 6.4 Hz, 1H), 2.85 (s, 3H), 1.86 (dd, J = 24.0 Hz, 6.4 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$): δ -173.8 (dq, $J_{F\text{-}H}$ = 48.9 Hz, 24.1 Hz, 1F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.6, 152.1 (d, $^2J_{C\text{-}F}$ = 19.0 Hz), 141.7 (d, J = 1.0 Hz), 140.2, 130.2, 129.2 (d, $^3J_{C\text{-}F}$ = 5.0 Hz), 128.3, 89.6 (d, $^1J_{C\text{-}F}$ = 167.0 Hz), 22.4 (d, J = 4.0 Hz), 18.9 (d, $^2J_{C\text{-}F}$ = 23.0 Hz). HRMS (ESI): calcd. For $C_{11}H_{12}FN_2$ $(M+H)^+$: 191.0988, found: 191.0985.



Ethyl 2-(2-fluoropropan-2-yl)isonicotinate (3u)

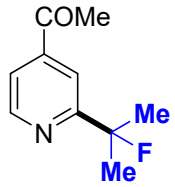
For 0.2 mmol scale, the standard procedure of method was followed to provide **3u** by column chromatography on silica gel (petroleum ether/EtOAc = 5:1, v/v) as a yellow oil (35 mg, 83%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.70 (d, J = 4.8 Hz, 1H), 8.12 (s, 1H), 7.77 (d, J = 4.8 Hz, 1H), 4.44 (q, J = 7.2 Hz, 2H), 1.74 (d, J = 22.0 Hz, 6H), 1.43 (t, J = 7.0 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$): δ -144.1 (hept, $J_{H\text{-}F}$ = 22.6 Hz, 1F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.1 (d, $^2J_{C\text{-}F}$ = 27.0 Hz), 165.0, 149.3 (d, J = 2.0 Hz), 138.4 (d, J = 2.0 Hz), 121.4, 117.4 (d, $^3J_{C\text{-}F}$ = 10.0 Hz), 96.6 (d, $^1J_{C\text{-}F}$ = 169.0 Hz), 61.7,

27.7 (d, $^{2}J_{C\text{-}F}$ = 24.0 Hz), 14.1. HRMS (ESI): calcd. For $C_{11}H_{15}FNO_2$ $(M+H)^+$: 212.1089, found: 212.1087.



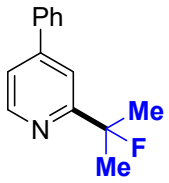
2-(2-Fluoropropan-2-yl)isonicotinonitrile (3v)

For 0.2 mmol scale, the standard procedure of method was followed to provide **3v** by column chromatography on silica gel (petroleum ether/EtOAc = 10:1 to 5:1, v/v) as a yellow oil (21 mg, 65%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.71 (d, J = 4.4 Hz, 1H), 7.79 (s, 1H), 7.42 (d, J = 4.8 Hz, 1H), 1.70 (d, J = 22.0 Hz, 6H). ^{19}F NMR (376 MHz, $CDCl_3$): δ -145.0 (hept, $J_{H\text{-}F}$ = 21.9 Hz, 1F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.8 (d, $^{2}J_{C\text{-}F}$ = 28.0 Hz), 149.6 (d, J = 2.0 Hz), 123.7, 121.1 (d, J = 2.0 Hz), 120.1 (d, $^{3}J_{C\text{-}F}$ = 11.0 Hz), 116.5, 96.6 (d, $^{1}J_{C\text{-}F}$ = 171.0 Hz), 27.6 (d, $^{2}J_{C\text{-}F}$ = 23.0 Hz). HRMS (ESI): calcd. For $C_9H_{10}FN_2$ $(M+H)^+$: 165.0833, found: 165.0828.



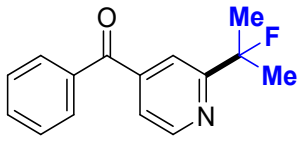
1-(2-(2-Fluoropropan-2-yl)pyridin-4-yl)ethan-1-one (3w)

For 0.2 mmol scale, the standard procedure of method was followed to provide **3w** by column chromatography on silica gel (petroleum ether/EtOAc = 10:1 to 5:1, v/v) as a yellow oil (26 mg, 73%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.72 (d, J = 4.8 Hz, 1H), 7.98 (s, 1H), 7.64 (d, J = 4.8 Hz, 1H), 2.65 (s, 3H), 1.73 (d, J = 22.0 Hz, 6H). ^{19}F NMR (376 MHz, $CDCl_3$): δ -144.2 (hept, $J_{H\text{-}F}$ = 21.9 Hz, 1F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.5, 165.7 (d, $^{2}J_{C\text{-}F}$ = 27.0 Hz), 149.8 (d, J = 2.0 Hz), 143.7, 119.7, 116.5 (d, $^{3}J_{C\text{-}F}$ = 11.0 Hz), 96.9 (d, $^{1}J_{C\text{-}F}$ = 169.0 Hz), 27.9 (d, $^{2}J_{C\text{-}F}$ = 24.0 Hz), 26.8. HRMS (ESI): calcd. For $C_{10}H_{13}FNO$ $(M+H)^+$: 182.0988, found: 182.0981.



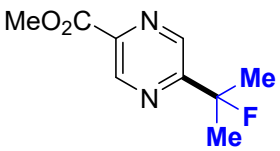
2-(2-Fluoropropan-2-yl)-4-phenylpyridine (3x)

For 0.2 mmol scale, the standard procedure of method was followed to provide **3x** by column chromatography on silica gel (petroleum ether/EtOAc = 10:1 to 5:1, v/v) as a yellow oil (35 mg, 81%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.59 (d, J = 4.4 Hz, 1H), 7.81 (s, 1H), 7.67 (d, J = 7.2 Hz, 2H), 7.50-7.41 (m, 4H), 1.77 (d, J = 22.4 Hz, 6H). ^{19}F NMR (376 MHz, $CDCl_3$): δ -143.7 (hept, $J_{H\text{-}F}$ = 21.9 Hz, 1F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.6 (d, $^{2}J_{C\text{-}F}$ = 26.0 Hz), 149.2, 149.1 (d, J = 2.0 Hz), 138.3, 129.0 (d, J = 2.0 Hz), 127.1, 120.2, 116.0 (d, $^{3}J_{C\text{-}F}$ = 11.0 Hz), 97.0 (d, $^{1}J_{C\text{-}F}$ = 168.0 Hz), 28.0 (d, $^{2}J_{C\text{-}F}$ = 24.0 Hz). HRMS (ESI): calcd. For $C_{14}H_{15}FN$ $(M+H)^+$: 216.1193, found: 216.1189.



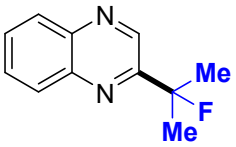
(2-(2-Fluoropropan-2-yl)pyridin-4-yl)(phenyl)methanone (3y)

For 0.2 mmol scale, the standard procedure of method was followed to provide **3y** by column chromatography on silica gel (petroleum ether/EtOAc = 15:1 to 8:1, v/v) as a yellow oil (32 mg, 66%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.60 (d, J = 4.8 Hz, 1H), 7.72 (d, J = 5.6 Hz, 2H), 7.69 (s, 1H), 7.51 (t, J = 7.4 Hz, 1H), 7.40-7.35 (m, 3H), 1.63 (d, J = 22.4 Hz, 6H). ^{19}F NMR (376 MHz, $CDCl_3$): δ -144.0 (hept, $J_{H\text{-}F}$ = 21.9 Hz, 1F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.1, 164.8 (d, $^{2}J_{C\text{-}F}$ = 27.0 Hz), 149.1 (d, J = 2.0 Hz), 145.3 (d, J = 2.0 Hz), 135.7, 133.4, 130.0, 128.5, 121.4, 117.3 (d, $^{3}J_{C\text{-}F}$ = 10.0 Hz), 96.7 (d, $^{1}J_{C\text{-}F}$ = 169.0 Hz), 27.7 (d, $^{2}J_{C\text{-}F}$ = 24.0 Hz). HRMS (ESI): calcd. For $C_{15}H_{15}FNO$ $(M+H)^+$: 244.1136, found: 244.1138.



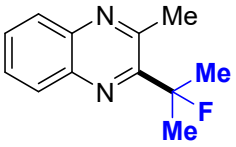
Methyl 5-(2-fluoropropan-2-yl)pyrazine-2-carboxylate (3z)

For 0.2 mmol scale, the standard procedure of method was followed to provide **3z** by column chromatography on silica gel (petroleum ether/EtOAc = 10:1 to 5:1, v/v) as a white solid (33 mg, 83%). M.p.: 71.6-72.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.18 (s, 1H), 8.93 (s, 1H), 4.01 (s, 3H), 1.71 (d, J = 22.0 Hz, 6H). ^{19}F NMR (376 MHz, $CDCl_3$): δ -147.5 (hept, $J_{H\text{-}F}$ = 21.9 Hz, 1F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.3, 162.2 (d, $^{2}J_{C\text{-}F}$ = 27.0 Hz), 144.6 (d, J = 2.0 Hz), 141.8, 140.1 (d, $^{3}J_{C\text{-}F}$ = 11.0 Hz), 96.2 (d, $^{1}J_{C\text{-}F}$ = 169.0 Hz), 53.0, 27.5 (d, $^{2}J_{C\text{-}F}$ = 24.0 Hz). HRMS (ESI): calcd. For $C_9H_{12}FN_2O_2$ $(M+H)^+$: 199.0884, found: 199.0883.



2-(2-Fluoropropan-2-yl)quinoxaline (3aa)

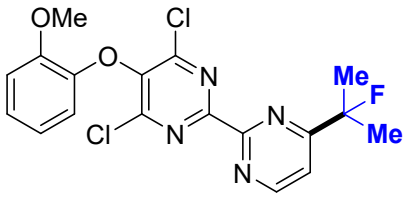
For 0.2 mmol scale, the standard procedure of method was followed to provide **3aa** by column chromatography on silica gel (petroleum ether/EtOAc = 15:1 to 8:1, v/v) as an orange oil (32 mg, 84%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.16 (s, 1H), 8.13-8.11 (m, 1H), 8.06-8.04 (m, 1H), 7.77-7.75 (m, 2H), 1.85 (d, J = 22.4 Hz, 6H). ^{19}F NMR (376 MHz, $CDCl_3$): δ -145.2 (hept, $J_{H\text{-}F}$ = 21.9 Hz, 1F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.2 (d, $^{2}J_{C\text{-}F}$ = 27.0 Hz), 141.86, 141.82, 141.76, 141.1 (d, J = 1.0 Hz), 130.1, 129.7, 129.2 (d, $^{3}J_{C\text{-}F}$ = 5.0 Hz), 96.8 (d, $^{1}J_{C\text{-}F}$ = 167.0 Hz), 27.7 (d, $^{2}J_{C\text{-}F}$ = 23.0 Hz). HRMS (ESI): calcd. For $C_{11}H_{12}FN_2$ $(M+H)^+$: 191.0989, found: 191.0985.



2-(2-Fluoropropan-2-yl)-3-methylquinoxaline (3ab)

For 0.2 mmol scale, the standard procedure of method was followed to provide **3ab**

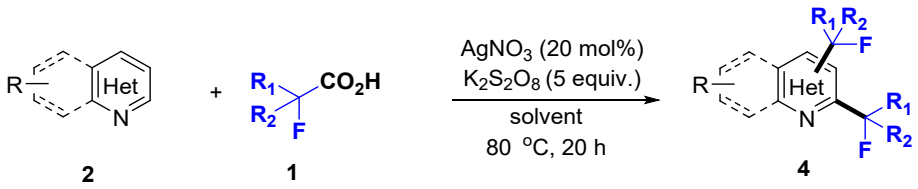
by column chromatography on silica gel (petroleum ether/EtOAc = 10:1 to 5:1, v/v) as a semi solid (28 mg, 69%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (d, J = 8.4 Hz, 2H), 7.73-7.66 (m, 2H), 2.93 (d, J = 5.6 Hz, 3H), 1.88 (d, J = 22.0 Hz, 6H). ^{19}F NMR (376 MHz, $CDCl_3$): δ -142.4 (hq, J_{H-F} = 21.9 Hz, 5.6 Hz, 1F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.1 (d, $^{2}J_{C-F}$ = 27.0 Hz), 152.2 (d, J = 2.0 Hz), 141.0, 139.5 (d, J = 3.0 Hz), 129.8, 129.0 (d, $^{3}J_{C-F}$ = 4.0 Hz), 128.1, 98.0 (d, $^{1}J_{C-F}$ = 165.0 Hz), 27.3 (d, $^{2}J_{C-F}$ = 24.0 Hz), 24.7 (d, J = 11.0 Hz). HRMS (ESI): calcd. For $C_{12}H_{14}FN_2$ $(M+H)^+$: 205.1143, found: 205.1141.



4,6-Dichloro-4'-(2-fluoropropan-2-yl)-5-(2-methoxyphenoxy)-2,2'-bipyrimidine (3ac)

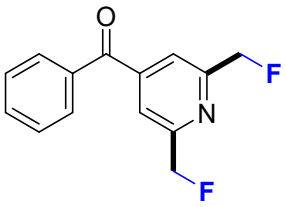
For 0.2 mmol scale, the standard procedure of method was followed to provide **3ac** by column chromatography on silica gel (petroleum ether: EtOAc = 5:1 to 2:1, v/v) as a white solid (51 mg, 62%). M.p.: 117.6-119.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.00 (d, J = 4.8 Hz, 1H), 7.68 (d, J = 4.8 Hz, 1H), 7.11 (t, J = 7.6 Hz, 1H), 7.00 (d, J = 8.8 Hz, 1H), 6.88 (t, J = 7.8 Hz, 1H), 6.72 (d, J = 8.0 Hz, 1H), 3.87 (s, 3H), 1.79 (d, J = 22.0 Hz, 6H). ^{19}F NMR (376 MHz, $CDCl_3$): δ -146.2 (hept, J_{H-F} = 21.9 Hz, 1F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.8 (d, $^{2}J_{C-F}$ = 29.0 Hz), 159.9 (d, J = 3.0 Hz), 158.7 (d, J = 2.0 Hz), 157.1, 155.4, 149.1, 144.6, 124.8, 120.9, 116.3, 115.9 (d, $^{3}J_{C-F}$ = 10.0 Hz), 112.9, 96.3 (d, $^{1}J_{C-F}$ = 170.0 Hz), 56.2, 27.3 (d, $^{2}J_{C-F}$ = 23.0 Hz). HRMS (ESI): calcd. For $C_{18}H_{16}Cl_2FN_4O_2$: 409.0639, found: 409.0634.

4. Substrate Scope of Bis-monofluoroalkylation Reaction



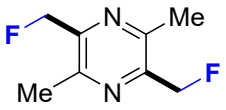
Typical experiment procedure：

To a 10 mL of Schlenk tube were added the heteroarene (0.2 mmol, 1.0 equiv.), $AgNO_3$ (20 mol%) and $K_2S_2O_8$ (5.0 equiv.). The mixture was evacuated and backfilled with N_2 for three times. Monofluoroalkyl carboxylic acids (2.0-5.0 equiv.), CH_3CN (1.0 mL) or DCE (1.0 mL) and water (0.5 mL) were then added. The Schlenk tube was screw capped and put into a preheated oil bath (80 °C). After stirring for 20 h, the reaction mixture was cooled to room temperature. Saturated solution of $NaHCO_3$ (3 mL) was added and the mixture was extracted with ethyl acetate (3×10 mL). The organic layer was washed with brine (10 mL), dried with anhydrous Na_2SO_4 and concentrated. The residue was purified with silica gel chromatography (petroleum ether) to give product **4**.



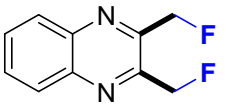
(2,6-Bis(trifluoromethyl)pyridin-4-yl)0(phenyl)methanone (4a)

For 0.2 mmol scale, the standard procedure of method was followed to provide **4a** by column chromatography on silica gel (petroleum ether/EtOAc = 10:1 to 5:1, v/v) as a yellow oil (33 mg, 68%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83 (d, J = 7.6 Hz, 2H), 7.69-7.65 (m, 3H), 7.53 (t, J = 7.4 Hz, 2H), 5.55 (d, J = 46.4 Hz, 4H). ^{19}F NMR (376 MHz, $CDCl_3$): δ -222.2 (t, J_{F-H} = 47.0 Hz, 2F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 194.8, 157.0 (dd, J_{C-F} = 22.0 Hz, 2.0 Hz), 146.6, 135.6, 133.8, 130.1, 128.8, 119.0 (d, J_{C-F} = 6.0 Hz), 83.8 (d, J_{C-F} = 170.0 Hz). HRMS (ESI): calcd. For $C_{14}H_{12}F_2NO$ $(M+H)^+$: 248.0887, found: 248.0887.



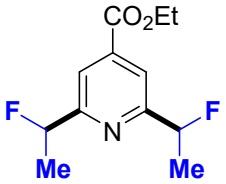
2,5-Bis(fluoromethyl)-3,6-dimethylpyrazine (4b)

For 0.2 mmol scale, the standard procedure of method was followed to provide **4b** by column chromatography on silica gel (petroleum ether/EtOAc = 10:1 to 5:1, v/v) as a yellow oil (28 mg, 80%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.52 (d, J = 48.4 Hz, 4H), 2.63 (s, 6H). ^{19}F NMR (376 MHz, $CDCl_3$): δ -216.4 (t, $J_{F\text{-}H}$ = 47.0 Hz, 2F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.0, 147.8 (d, $J_{C\text{-}F}$ = 20.0 Hz), 83.5 (d, $J_{C\text{-}F}$ = 167.0 Hz), 20.4. HRMS (ESI): calcd. For $C_8H_{11}F_2N_2$ $(M+H)^+$: 173.0893, found: 173.0890.



2,3-Bis(fluoromethyl)quinoxaline (4c)

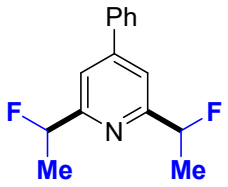
For 0.2 mmol scale, the standard procedure of method was followed to provide **4c** by column chromatography on silica gel (petroleum ether/EtOAc = 10:1 to 5:1, v/v) as a yellow oil (26 mg, 67%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.14 (m, 2H), 7.84 (m, 2H), 5.82 (d, J = 46.8 Hz, 4H). ^{19}F NMR (376 MHz, $CDCl_3$): δ -218.6 (t, $J_{F\text{-}H}$ = 47.0 Hz, 2F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.2 (d, $J_{C\text{-}F}$ = 19.0 Hz), 141.3, 131.0 129.3, 83.6 (d, $J_{C\text{-}F}$ = 168.0 Hz). HRMS (ESI): calcd. For $C_{10}H_9F_2N_2$ $(M+H)^+$: 195.0739, found: 195.0734.



Ethyl 2,6-bis(1-fluoroethyl)isonicotinate (4d)

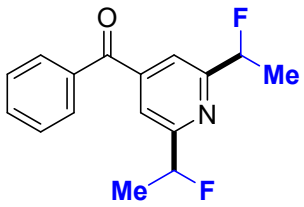
For 0.2 mmol scale, the standard procedure of method was followed to provide **4d** by column chromatography on silica gel (petroleum ether/EtOAc = 5:1, v/v) as a yellow oil (40 mg, 85%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (s, 2H), 5.69 (dq, J = 48.0 Hz, 6.4 Hz, 2H), 4.42 (q, J = 7.2 Hz, 2H), 1.67 (dd, J = 24.4 Hz, 6.4 Hz, 6H), 1.42 (t, J =

7.0 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$): δ -177.9 (dq, J_{F-H} = 45.1 Hz, 22.6 Hz, 1F), -178.1 (dq, J_{F-H} = 48.9 Hz, 24.4 Hz, 1F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.9, 161.2 (dt, J_{C-F} = 24.0 Hz, 2.0 Hz), 139.6, 117.7 (t, J_{C-F} = 6.5 Hz), 91.0 (dd, J_{C-F} = 169.0 Hz, 6.0 Hz), 61.9, 21.5 (dd, J_{C-F} = 23.0 Hz, 7.0 Hz), 14.2. HRMS (ESI): calcd. For $C_{12}H_{16}F_2NO_2$ $(M+H)^+$: 244.1152, found: 244.1149.



2,6-Bis-1-fluoroethyl)-4-phenylpyridine (4e)

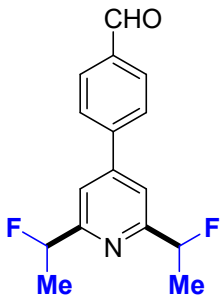
For 0.2 mmol scale, the standard procedure of method was followed to provide **4e** by column chromatography on silica gel (petroleum ether/EtOAc = 10:1 to 5:1, v/v) as a yellow oil (37 mg, 76%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (d, J = 6.8 Hz, 2H), 7.63 (s, 2H), 7.52-7.44 (m, 3H), 5.71 (dq, 48.0 Hz, 6.1 Hz, 2H), 1.72 (dd, J = 24.8 Hz, 6.4 Hz, 6H). ^{19}F NMR (376 MHz, $CDCl_3$): δ -177.3 (dq, J_{F-H} = 45.1 Hz, 24.1 Hz, 1F), -177.8 (dq, J_{F-H} = 48.9 Hz, 24.1 Hz, 1F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.6 (d, J_{C-F} = 23.0 Hz), 150.3, 138.2, 129.2, 129.1, 127.1, 116.1 (dd, J_{C-F} = 11.0 Hz, 7.0 Hz), 91.5 (dd, J_{C-F} = 168.5 Hz, 7.5 Hz), 21.8 (dd, J_{C-F} = 22.5 Hz, 7.5 Hz). HRMS (ESI): calcd. For $C_{15}H_{16}F_2N$ $(M+H)^+$: 248.1256, found: 248.1251.



(2,6-Bis(-1-fluoroethyl)pyridin-4-yl)(phenyl)methanone (4f)

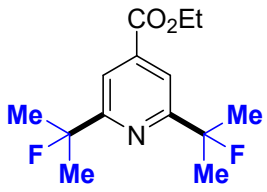
For 0.2 mmol scale, the standard procedure of method was followed to provide **4f** by column chromatography on silica gel (petroleum ether/EtOAc = 10:1 to 5:1, v/v) as a yellow oil (38 mg, 70%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (d, J = 7.6 Hz, 2H), 7.58 (s, 2H), 7.54 (t, J = 7.4 Hz, 1H), 7.42 (t, J = 8.6 Hz, 2H), 5.63 (dq, J = 48.0 Hz, 6.4 Hz, 2H), 1.61 (dd, J = 24.4 Hz, 6.4 Hz, 6H). ^{19}F NMR (376 MHz, $CDCl_3$): δ -177.9

(dq, J_{F-H} = 48.9 Hz, 24.8 Hz, 1F), -178.2 (dq, J_{F-H} = 45.1 Hz, 24.1 Hz, 1F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 194.9 (d, J = 7.0 Hz), 160.9 (d, J_{C-F} = 25.0 Hz), 146.5, 135.7, 133.5, 130.0, 128.6, 117.5 (dd, J_{C-F} = 10.0 Hz, 7.0 Hz), 91.0 (dd, J_{C-F} = 169.0 Hz, 3.5 Hz), 21.4 (dd, J_{C-F} = 23.0 Hz, 5.0 Hz). HRMS (ESI): calcd. For $C_{16}H_{16}F_2NO$ $(M+H)^+$: 276.1207, found: 276.1200.



4-(2,6-Bis(1-fluoroethyl)pyridin-4-yl)benzaldehyde (4g)

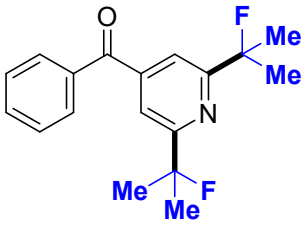
For 0.2 mmol scale, the standard procedure of method was followed to provide **4g** by column chromatography on silica gel (petroleum ether/EtOAc = 10:1 to 5:1, v/v) as a colorless oil (36 mg, 65%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.10 (s, 1H), 8.01 (d, J = 7.6 Hz, 2H), 7.85 (d, J = 7.6 Hz, 2H), 7.65 (s, 2H), 5.73 (dq, J = 48.0 Hz, 5.6 Hz, 2H), 1.72 (dd, J = 24.8 Hz, 6.4 Hz, 6H). ^{19}F NMR (376 MHz, $CDCl_3$): δ -177.9 (dq, J_{F-H} = 48.9 Hz, 24.1 Hz, 1F), -178.4 (dq, J_{F-H} = 48.9 Hz, 24.1 Hz, 1F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.7, 161.0 (d, J_{C-F} = 23.0 Hz), 148.9, 144.0, 136.5, 130.4, 127.9, 116.2 (dd, J_{C-F} = 9.5 Hz, 7.5 Hz), 91.3 (dd, J_{C-F} = 169.0 H, 7.0 Hz), 21.7 (dd, J_{C-F} = 23.5 Hz, 7.5 Hz). HRMS (ESI): calcd. For $C_{16}H_{16}F_2NO$ $(M+H)^+$: 276.1201, found: 276.1200.



Ethyl 2,6-bis(2-fluoropropan-2-yl)isonicotinate (4h)

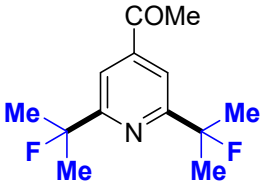
For 0.2 mmol scale, the standard procedure of method was followed to provide **4h** by column chromatography on silica gel (petroleum ether/EtOAc = 5:1, v/v) as a yellow

oil (48 mg, 89%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00 (s, 2H), 4.42 (q, J = 7.2 Hz, 2H), 1.69 (d, J = 22.0 Hz, 12H), 1.41 (t, J = 7.2 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$): δ -144.5 (hept, J_{H-F} = 21.9 Hz, 2F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.3, 164.1 (dd, J_{C-F} = 28.0 Hz, 2.0 Hz), 139.4, 116.1 (d, J_{C-F} = 10.0 Hz), 96.8 (d, J_{C-F} = 169.0 Hz), 61.8, 27.7 (d, J_{C-F} = 24.0 Hz), 14.2. HRMS (ESI): calcd. For $C_{14}H_{20}F_2NO_2$ $(M+H)^+$: 272.1465, found: 272.1462.



(2,6-Bis(1-fluoroethyl)pyridin-4-yl)(phenyl)methanone (4i)

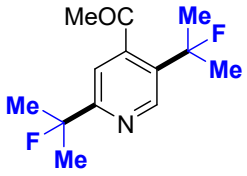
For 0.2 mmol scale, the standard procedure of method was followed to provide **4i** by column chromatography on silica gel (petroleum ether/EtOAc = 10:1 to 5:1, v/v) as a yellow oil (46 mg, 76%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 (d, J = 7.2 Hz, 2H), 7.31 (s, 2H), 7.64 (t, J = 7.4 Hz, 1H), 7.51 (t, J = 7.6 Hz, 2H), 1.73 (d, J = 22.4 Hz, 12H). ^{19}F NMR (376 MHz, $CDCl_3$): δ -144.5 (hept, J_{H-F} = 21.9 Hz, 2F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.5, 163.8 (dd, J_{C-F} = 27.0 Hz, 2.0 Hz), 146.4, 135.9, 133.5, 130.1, 128.6, 115.9 (d, J_{C-F} = 10.0 Hz), 96.9 (d, J_{C-F} = 169.0 Hz), 27.8 (d, J_{C-F} = 24.0 Hz). HRMS (ESI): calcd. For $C_{18}H_{20}F_2NO$ $(M+H)^+$: 304.1518, found: 304.1513.



1-(2,6-Bis(1-fluoroethyl)pyridin-4-yl)ethan-1-one (4j-C6)

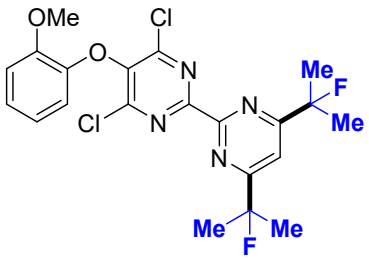
For 0.2 mmol scale, the standard procedure of method was followed to provide **4j-C6** by column chromatography on silica gel (petroleum ether/EtOAc = 10:1 to 5:1, v/v) as a yellow oil (33 mg, 69%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (s, 1H), 2.65 (s, 1H), 1.70 (d, J = 22.0 Hz, 12H). ^{19}F NMR (376 MHz, $CDCl_3$): δ -144.6 (hept, J_{H-F} = 22.6

Hz, 2F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.7, 164.6 (dd, J_{C-F} = 27.0 Hz, 2.0 Hz), 144.7, 114.4 (d, J_{C-F} = 10.0 Hz), 96.9 (d, J_{C-F} = 169.0 Hz), 27.8 (d, J_{C-F} = 24.0 Hz), 26.9. HRMS (ESI): calcd. For $C_{13}H_{18}F_2NO$ $(M+H)^+$: 242.1356, found: 242.1356.



1-(2,5-Bis(1-fluoroethyl)pyridin-4-yl)ethan-1-one (4j-C5)

For 0.2 mmol scale, the standard procedure of method was followed to provide **4j-C5** by column chromatography on silica gel (petroleum ether/EtOAc = 10:1 to 5:1, v/v) as a yellow oil (10 mg, 21%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.44 (s, 1H), 7.33 (s, 1H), 2.53 (s, 3H), 1.74 (t, J = 47.2 Hz, 12H). ^{19}F NMR (376 MHz, $CDCl_3$): δ -130.3 (hept, J_{H-F} = 22.6 Hz, 1F), -144.3 (hept, J_{H-F} = 21.9 Hz, 1F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 203.9, 163.6 (d, J_{C-F} = 26.0 Hz), 147.8 (dd, J_{C-F} = 2.0 Hz, 4.0 Hz), 145.8 (dd, J_{C-F} = 7.0 Hz, 2.0 Hz), 134.9 (d, J_{C-F} = 22.0 Hz), 113.7 (d, J_{C-F} = 10.0 Hz), 96.8 (d, J_{C-F} = 169.0 Hz), 96.0 (d, J_{C-F} = 168.0 Hz), 31.2 (d, J = 6.2 Hz), 29.4 (d, J_{C-F} = 25.0 Hz), 27.7 (d, J_{C-F} = 24.0 Hz). HRMS (ESI): calcd. For $C_{13}H_{18}F_2NO$ $(M+H)^+$: 242.1361, found: 242.1356.



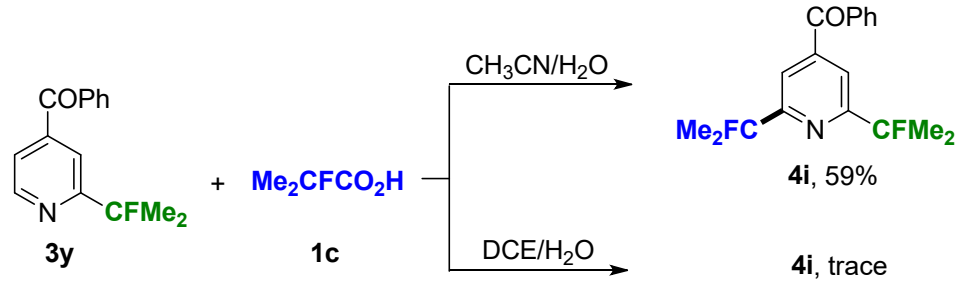
4,6-Dichloro-4',6'-bis(2-fluoropropan-2-yl)-5-(2-methoxyphenoxy)-2,2'-bipyrimidine (4k)

For 0.2 mmol scale, the standard procedure of method was followed to provide **4k** by column chromatography on silica gel (petroleum ether: EtOAc = 10:1 to 5:1, v/v) as a white solid (52 mg, 56%). M.p.: 101.3-103.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92 (s, 1H), 7.12 (t, J = 7.6 Hz, 1H), 7.02 (d, J = 8.0 Hz, 1H), 6.88 (t, J = 7.6 Hz, 1H), 6.71

(d, J = 8.0 Hz, 1H), 3.91 (s, 3H), 1.79 (d, J = 22.4 Hz, 12H). ^{19}F NMR (376 MHz, $CDCl_3$): δ -146.0 (hept, $J_{H\text{-}F}$ = 22.6 Hz, 2F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 174.4 (dd, $J_{C\text{-}F}$ = 28.0 Hz, 2.0 Hz), 159.9 (t, J = 2.5 Hz), 157.8, 155.4, 149.2, 144.7, 144.3, 124.8, 120.8 116.0, 113.0, 110.0 (t, $J_{C\text{-}F}$ = 10.0 Hz), 96.4 (d, $J_{C\text{-}F}$ = 171.0 Hz), 56.2, 27.4 (d, $J_{C\text{-}F}$ = 23.0 Hz). HRMS (ESI): calcd. For $C_{21}H_{21}Cl_2F_2N_4O_2$: 469.1016, found: 469.1010.

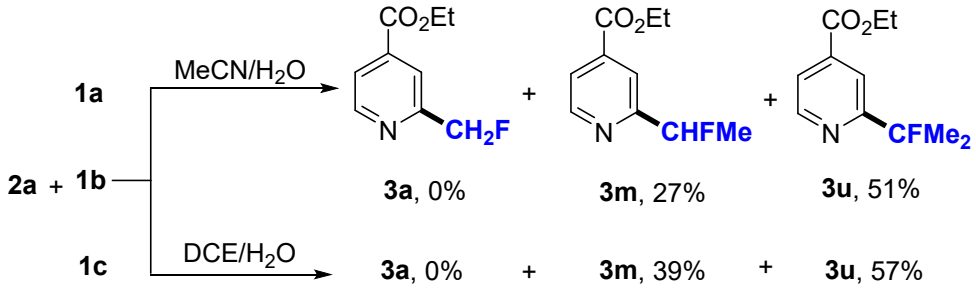
5. Control Experiments and Competition Experiments

5.1 Control Experiments of Bis-fluoroalkylation



Procedure: To a 10 mL of Schlenk tube were added $AgNO_3$ (7.0 mg, 20 mol%) and $K_2S_2O_8$ (270.3 mg, 5.0 equiv.). The mixture was evacuated and backfilled with N_2 for three times, **3y** (48.6 mg, 0.2 mmol, 1.0 equiv.), **1c** (106 mg, 5.0 equiv.), solvent (1.0 mL) and H_2O (0.5 ml) were then added. The Schlenk tube was screw capped and put into a preheated oil bath (80 °C). After stirring for 20 h, the reaction mixture was cooled to room temperature. Using a mixture of MeCN and H_2O (2:1) as a solvent, the reaction afforded the product **4i** in 59% yield, while the yield of product **4i** was trace using a mixture of DCE and H_2O (2:1) as a solvent

5.2 Competition Experiments



Procedure: To a 10 mL of Schlenk tube were added $AgNO_3$ (7.0 mg, 20 mol%) and $K_2S_2O_8$ (270.3 mg, 5.0 equiv.). The mixture was evacuated and backfilled with N_2 for three times. **2a** (30.2 mg, 0.2 mmol, 1.0 equiv.), **1a** (31.2 mg, 2.0 equiv.), **1b** (39.2 mg, 2.0 equiv.), **1c** (42.4 mg, 2.0 equiv.), MeCN or DCE (1.0 mL) and H_2O (0.5 ml) were then added. The Schlenk tube was screw capped and put into a preheated oil bath (80 °C). After stirring for 20 h, the reaction mixture was cooled to room temperature.

The product yields were determined by ^{19}F NMR spectroscopy using $PhCF_3$ as an internal standard.

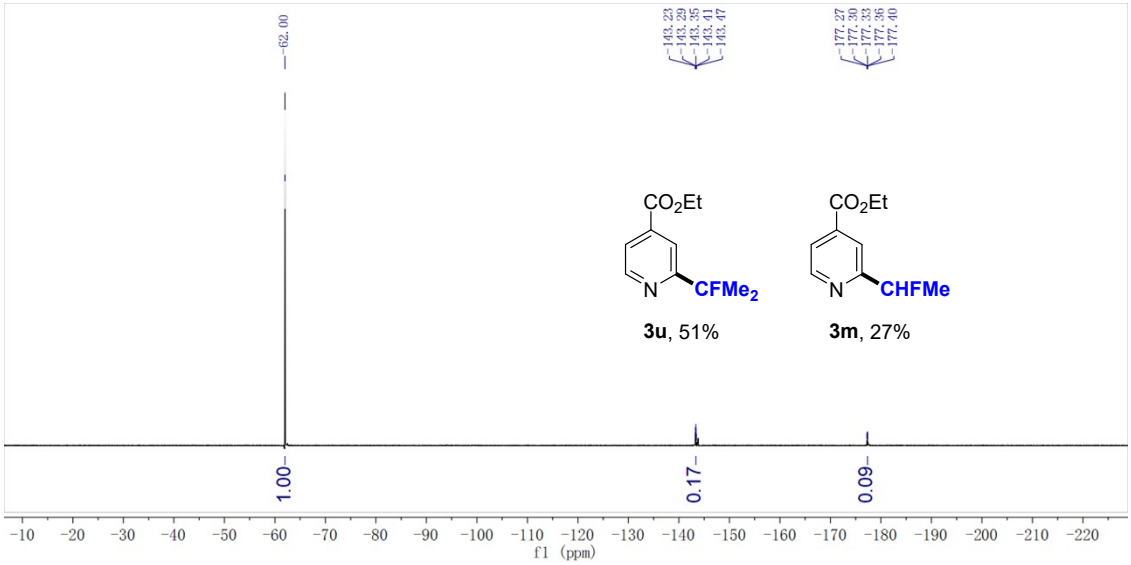


Figure S1. ^{19}F NMR analysis of competition experiment of **1** and **2a** using $MeCN/H_2O$ as solvent

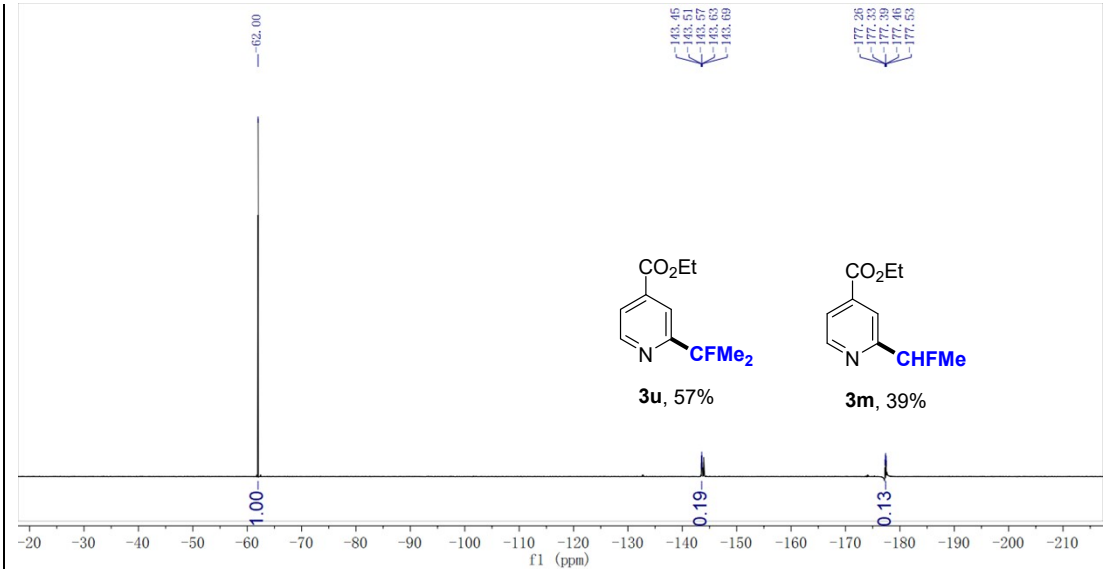
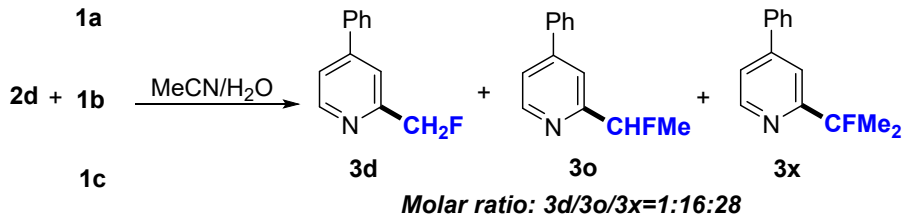


Figure S2. ^{19}F NMR analysis of competition experiment of **1** and **2a** using DCE/H_2O as solvent



Procedure: To a 10 mL of Schlenk tube were added **2d** (31.0 mg, 0.2 mmol, 1.0 equiv.), $AgNO_3$ (7.0 mg, 20 mol%) and $K_2S_2O_8$ (270.3 mg, 5.0 equiv.). The mixture was evacuated and backfilled with N_2 for three times. **1a** (15.6 mg, 1.0 equiv.), **1b** (19.6 mg, 1.0 equiv.), **1c** (21.2 mg, 1.0 equiv.), MeCN (1.0 mL) and H_2O (0.5 ml) were then added. The Schlenk tube was screw capped and put into a preheated oil bath (80 °C). After stirring for 20 h, the reaction mixture was cooled to room temperature. The molar ratio of corresponding products was determined by ^{19}F NMR using $PhCF_3$ as internal standard.

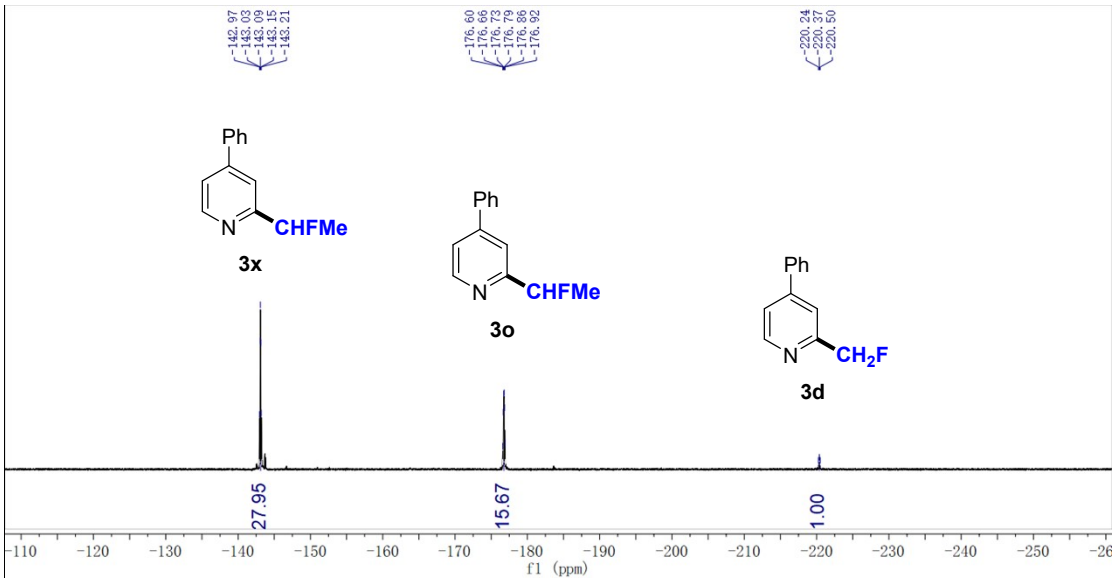
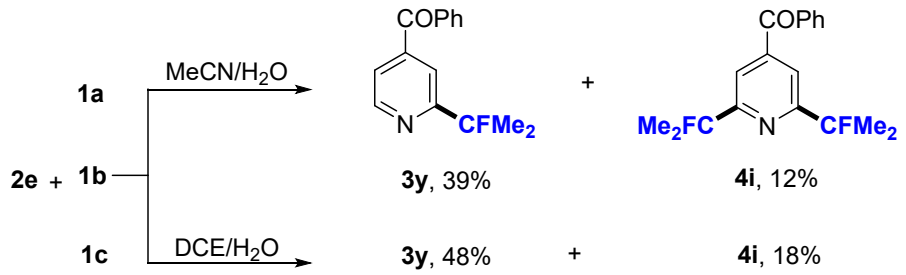


Figure S3. ^{19}F NMR analysis of competition experiment of **1** and **2d** using $MeCN/H_2O$ as solvent



Procedure: To a 10 mL of Schlenk tube were added **2e** (37.0 mg, 0.2 mmol, 1.0 equiv.), $AgNO_3$ (7.0 mg, 20 mol%) and $K_2S_2O_8$ (270.3 mg, 5.0 equiv.). The mixture was evacuated and backfilled with N_2 for three times. **1a** (78.0 mg, 5.0 equiv.), **1b** (98.1 mg, 5.0 equiv.), **1c** (106.1 mg, 5.0 equiv.), MeCN or DCE (1.0 mL) and H_2O (0.5 ml) were then added. The Schlenk tube was screw capped and put into a preheated oil bath (80 °C). After stirring for 20 h, the reaction mixture was cooled to room temperature. The product yields were determined by ^{19}F NMR spectroscopy using $PhCF_3$ as an internal standard.

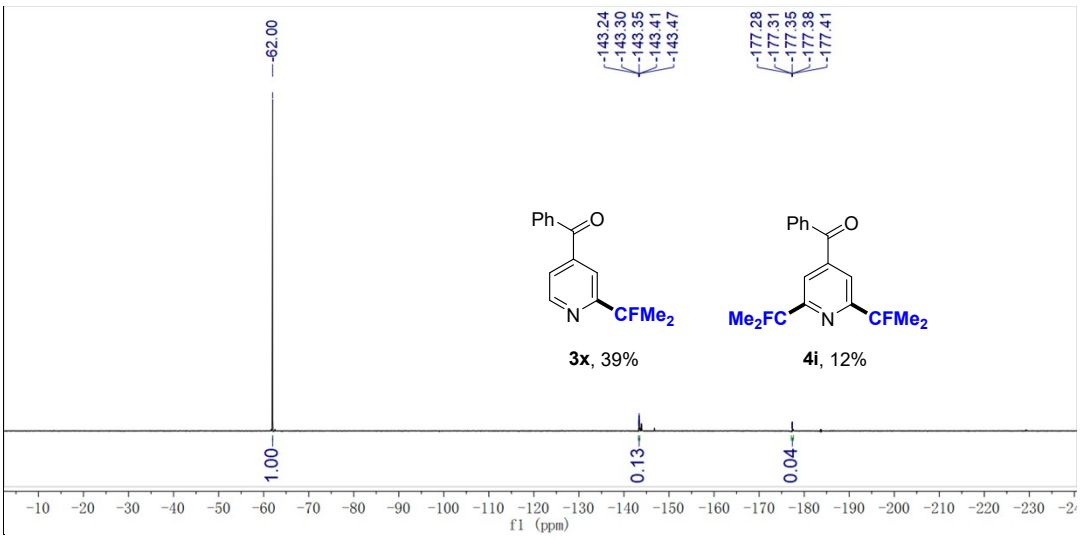


Figure S4. ^{19}F NMR analysis of competition experiment of **1** and **2e** using $MeCN/H_2O$ as solvent

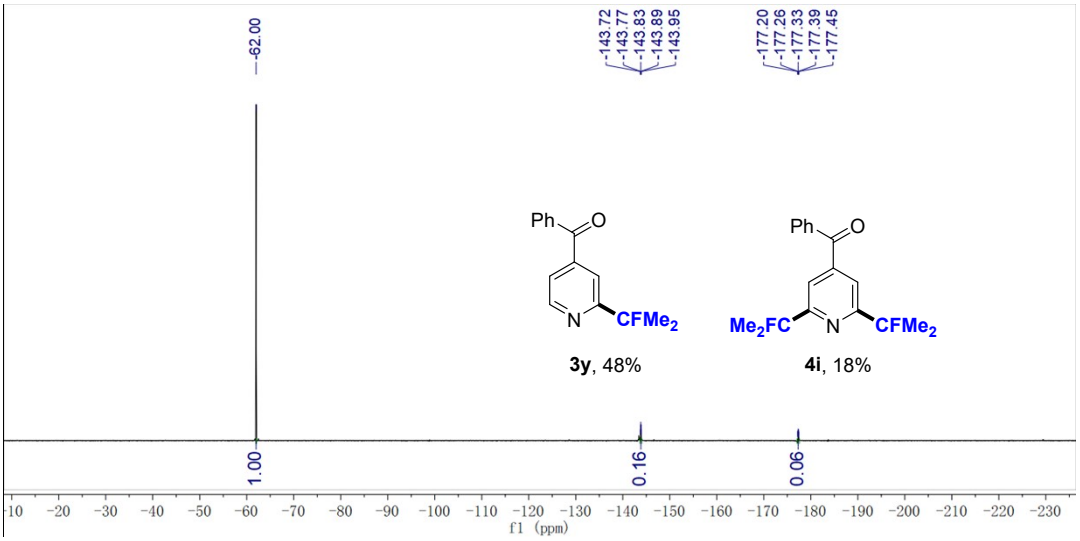
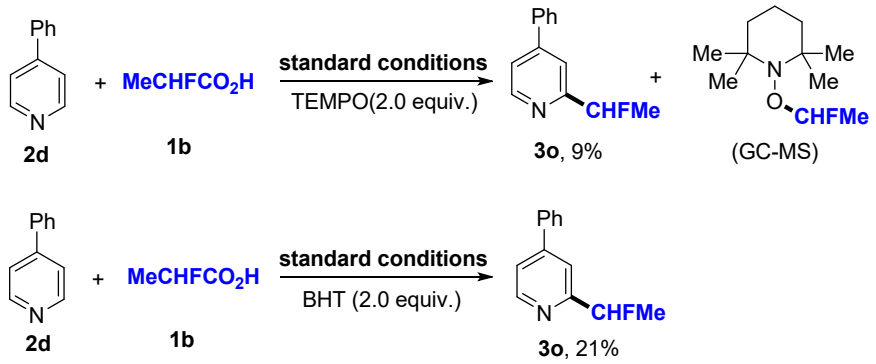
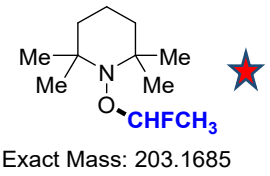


Figure S5. ^{19}F NMR analysis of competition experiment of **1** and **2e** using DCE/H_2O as solvent

6. Radical Inhibition Experiments and Plausible Reaction Mechanism



Procedure: To a 10 mL of Schlenk tube were added 4-pyridylpyridine **2d** (31.0 mg, 0.2 mmol, 1.0 equiv.), $AgNO_3$ (7.0 mg, 20 mol %), $K_2S_2O_8$ (270.3 mg, 5.0 equiv.) and TEMPO (62.5 mg, 2.0 equiv.) or BHT (88.1 mg, 2.0 equiv.). The mixture was evacuated and backfilled with N_2 for three times. 2-Difluoropropionic acid (39.0 mg, 2.0 equiv.), MeCN (1.0 mL) and H_2O (0.5 ml) were then added. The Schlenk tube was screw capped and put into a preheated oil bath (80 °C). After stirring for 20 h, the reaction mixture was cooled to room temperature. The yield was determined by ^{19}F NMR spectroscopy using $PhCF_3$ as an internal standard. The adduct of TEMPO and monofluoroethyl radical detected by GC-MS was in agreement with the reported in the literature.[7]



Exact Mass: 203.1685

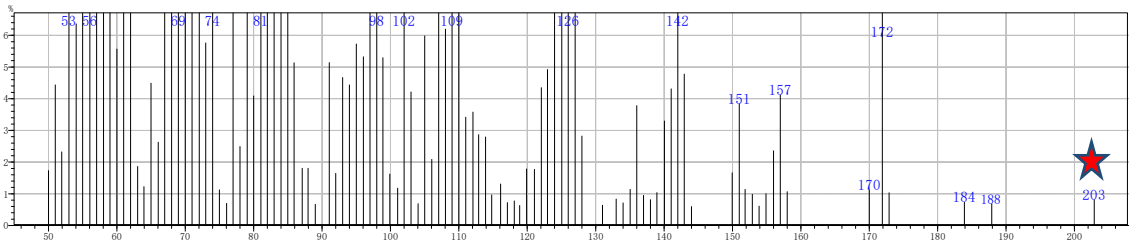


Figure S6. GC-MS analysis of adding TEMPO to standard reaction conditions

Based on these results, the reaction mechanism was proposed as shown in Figure S7. Initially, the oxidative decarboxylation of α-fluorocarboxylic acids afforded monofluoroalkyl radical in the presence of silver catalyst and $K_2S_2O_8$. Subsequently, monofluoroalkyl radical reacts the protonated heteroaromatic ring (I) to generate a cyclohexadienyl-type radical cation (II). After that, the intermediate (II) is oxidated and deprotonated to give the cationic intermediate (III), followed by deprotonation to give the monofluoralkylated product.

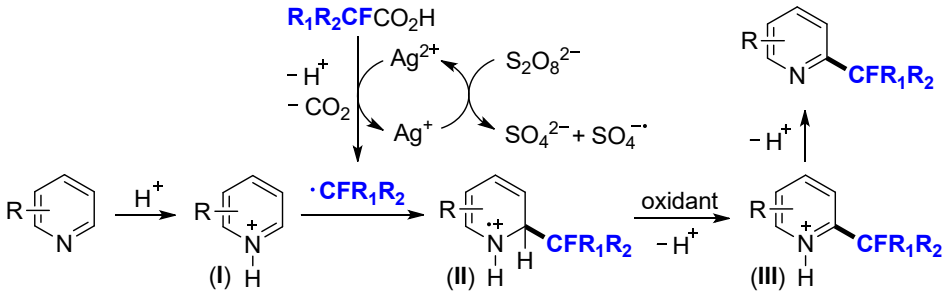


Figure S7. Plausible reaction mechanism.

7. References

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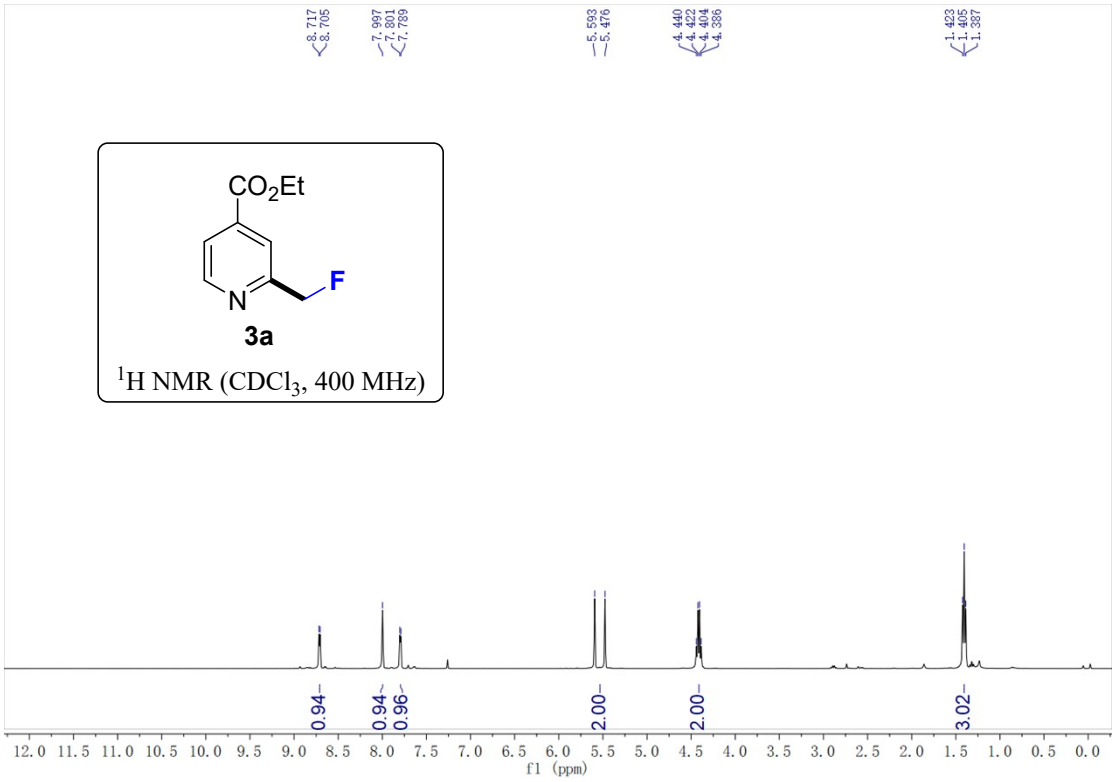
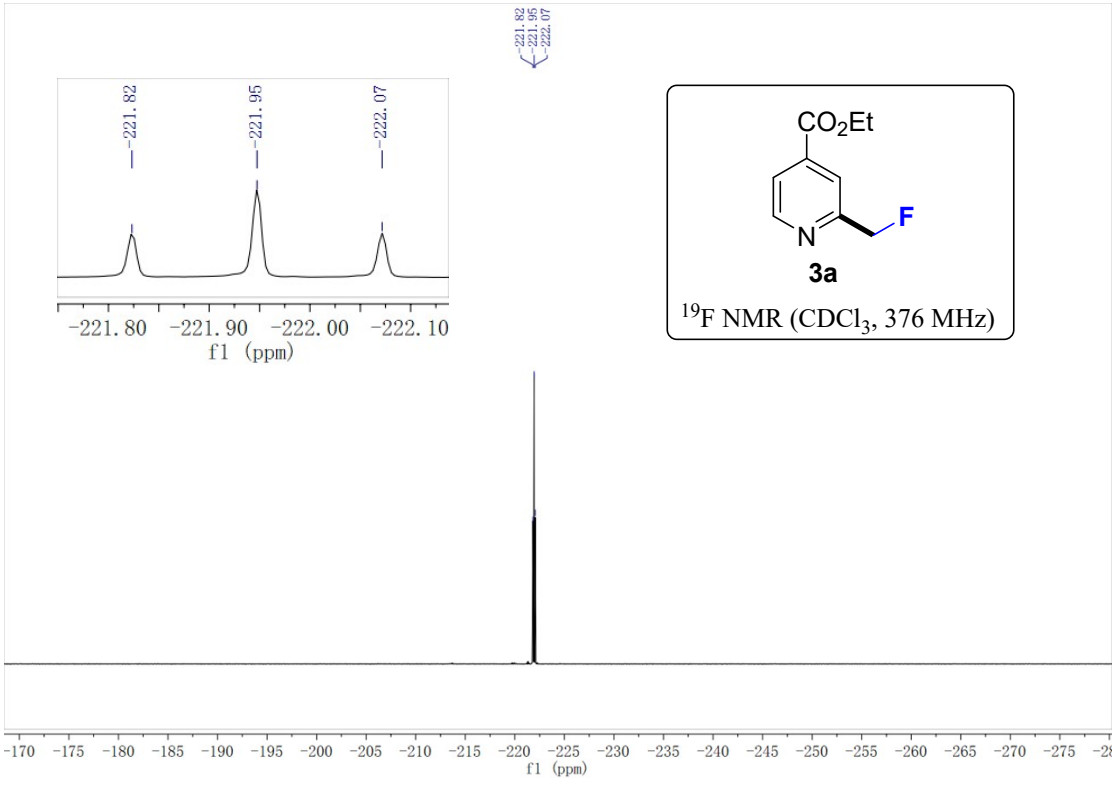
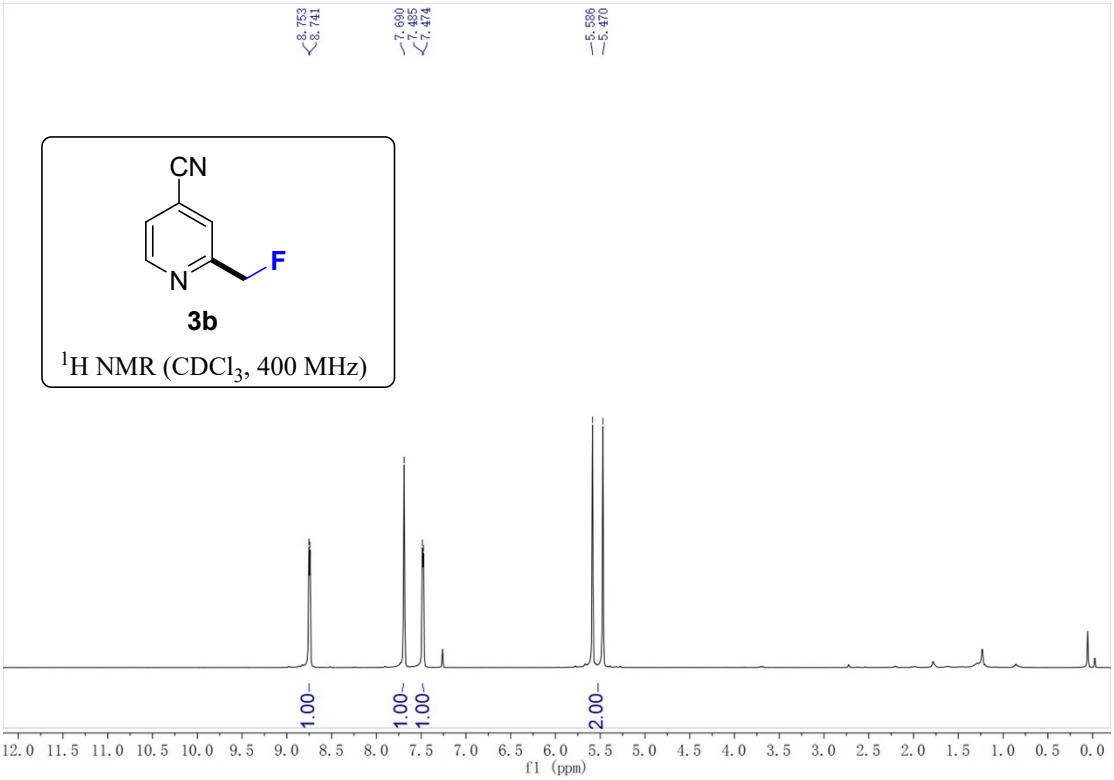
8. ^{1}H, ^{19}F and ^{13}C NMR Spectra of Isolated Products



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5.470
CN
F
N
3b
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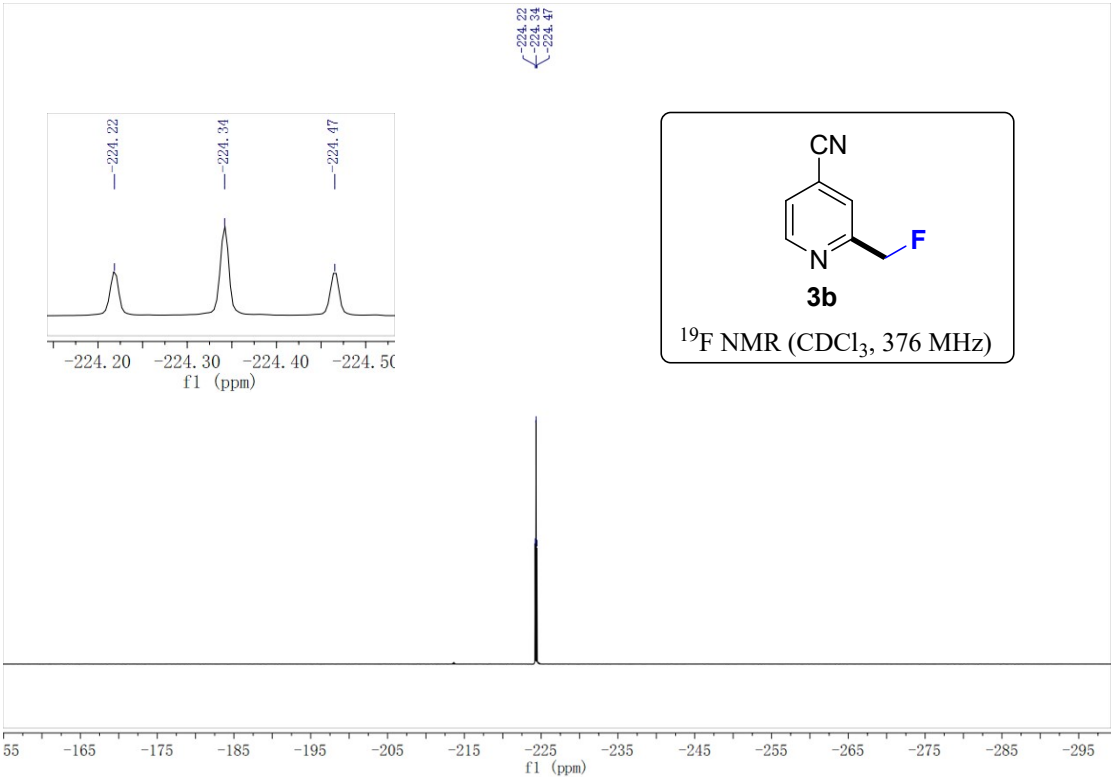
1.00
1.00
1.00
2.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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F
N
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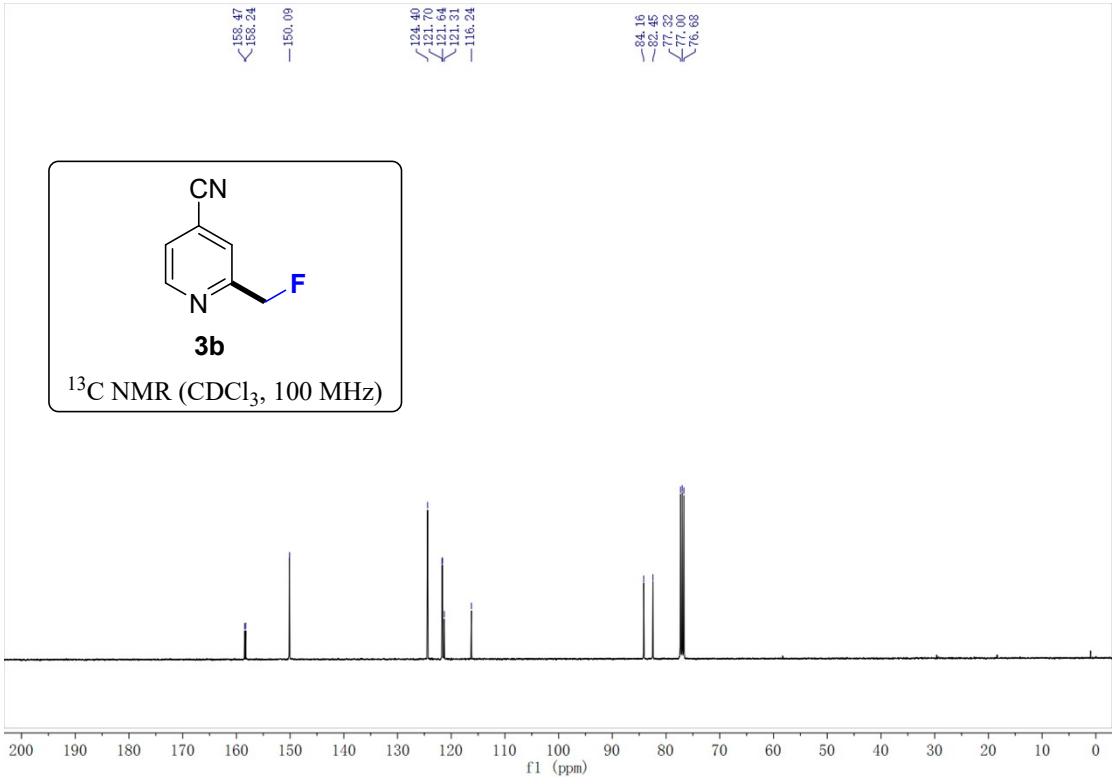
f1 (ppm)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3b
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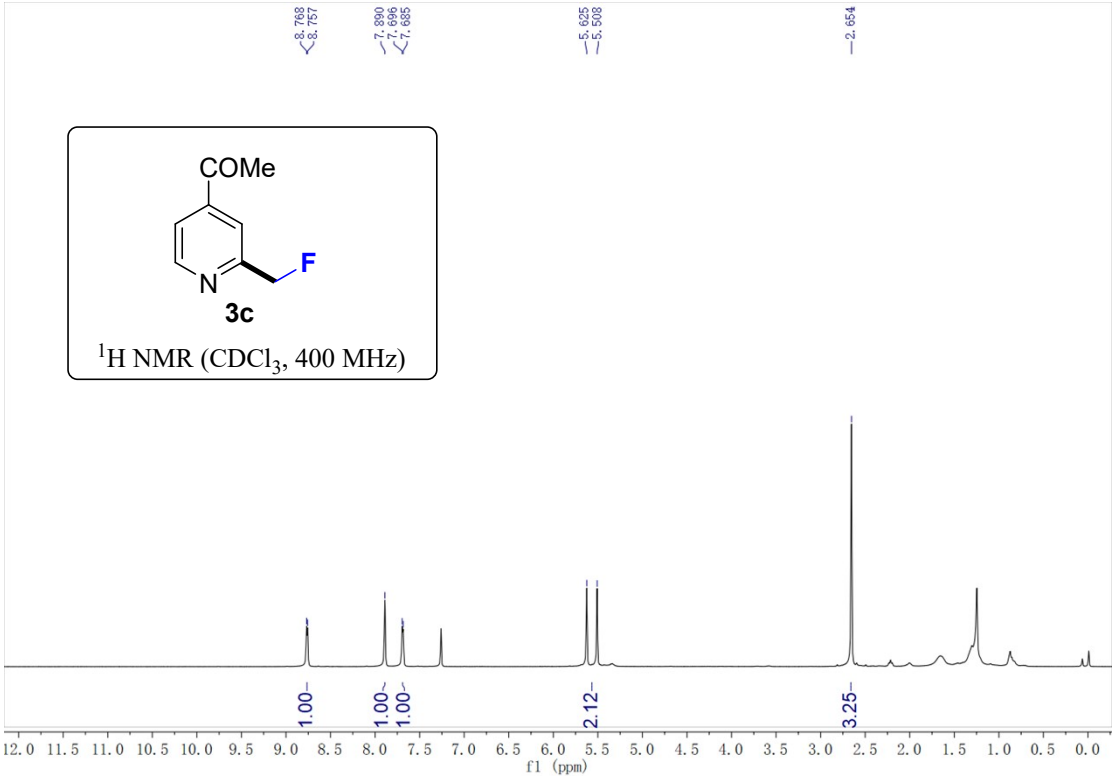
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F
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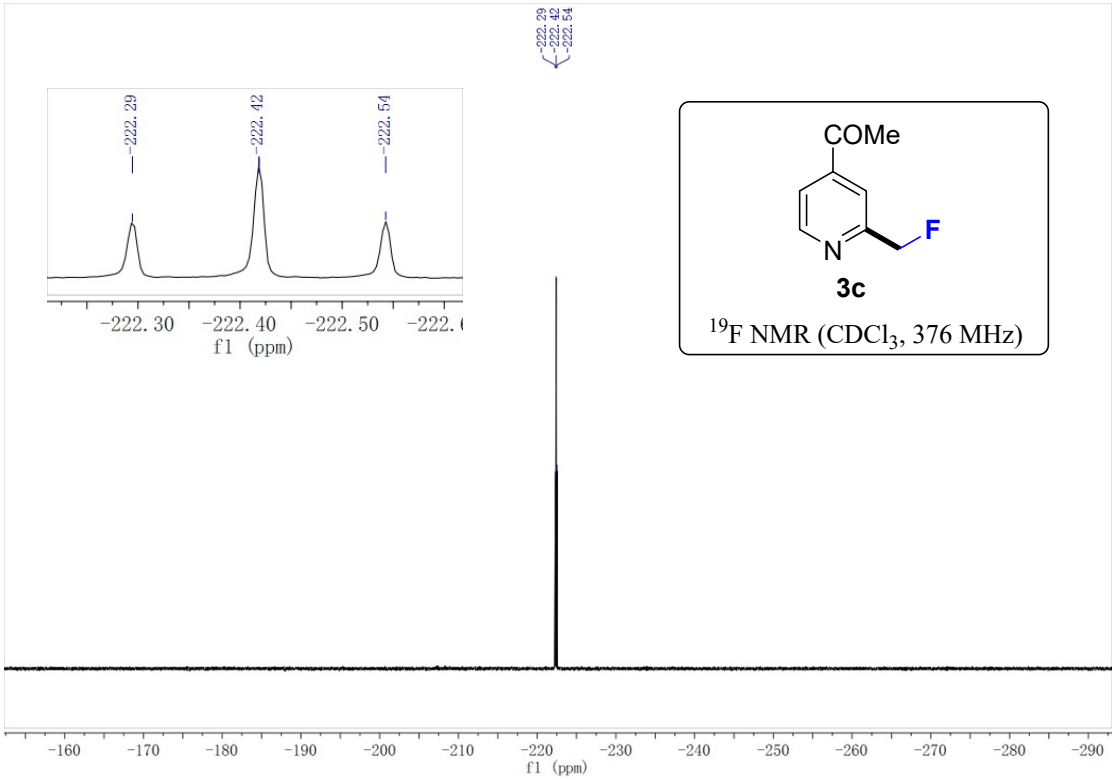
1.00
1.00
1.00
2.12
3.25
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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f1 (ppm)
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F
N
3c
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-210
-220
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-240
-250
-260
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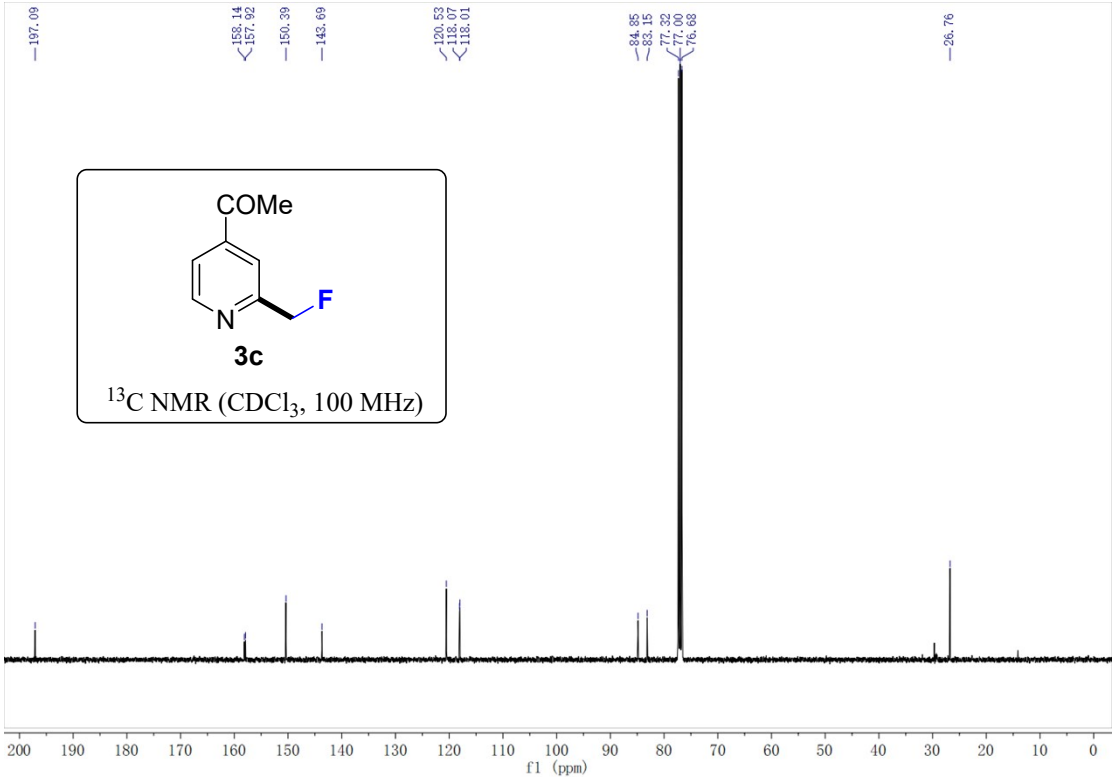
f1 (ppm)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26.76
COMe
F
N
3c
13C NMR (CDCl3, 100 MHz)
200
190
180
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130
120
110
100
90
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70
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50
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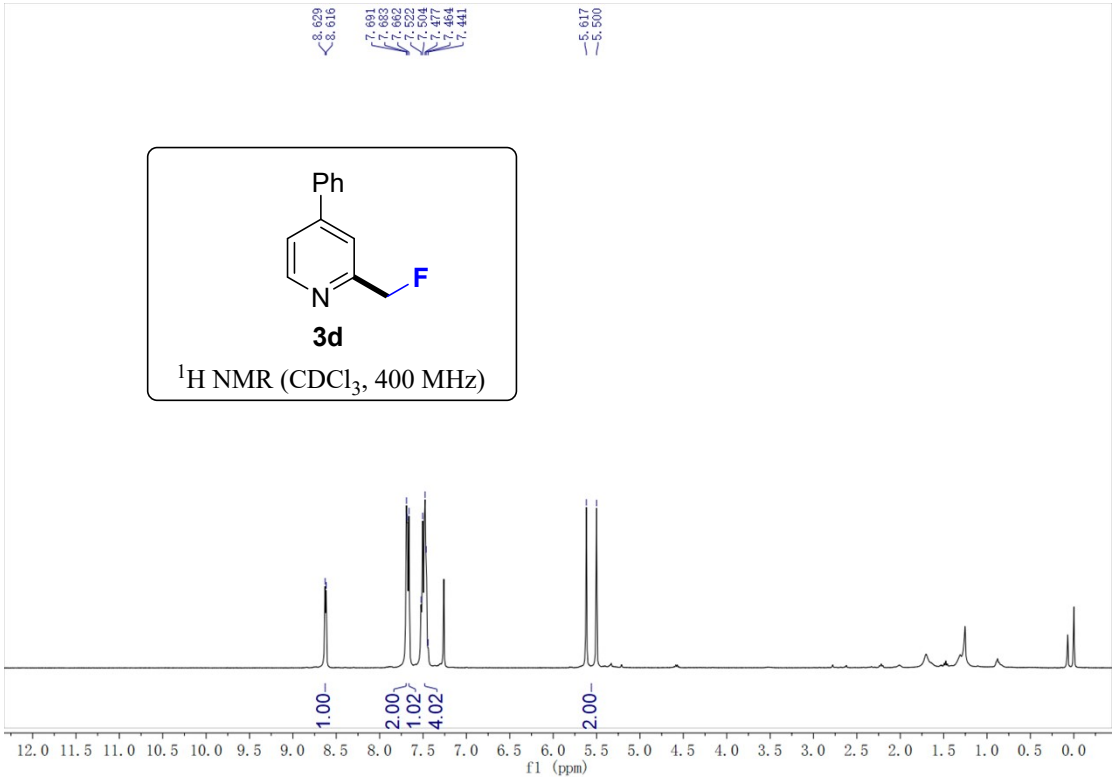
f1 (ppm)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5.500
Ph
N
F
3d
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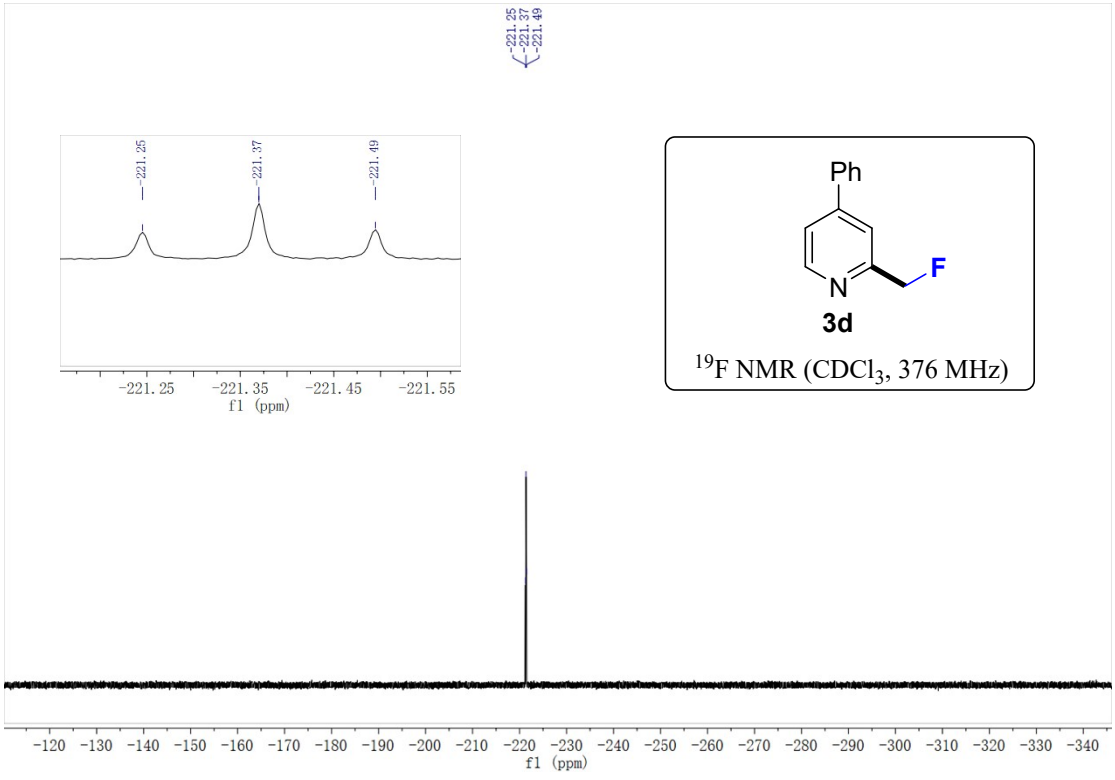
1.00
2.00
1.02
4.02
2.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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f1 (ppm)
Ph
N
F
3d
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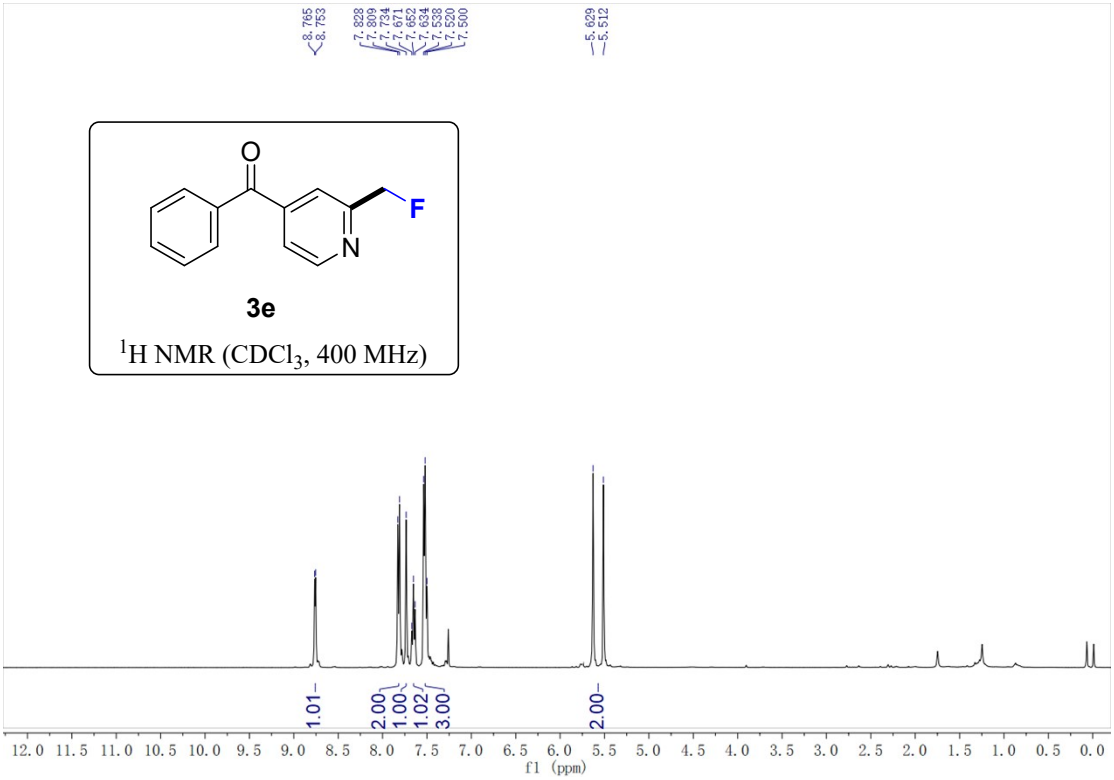
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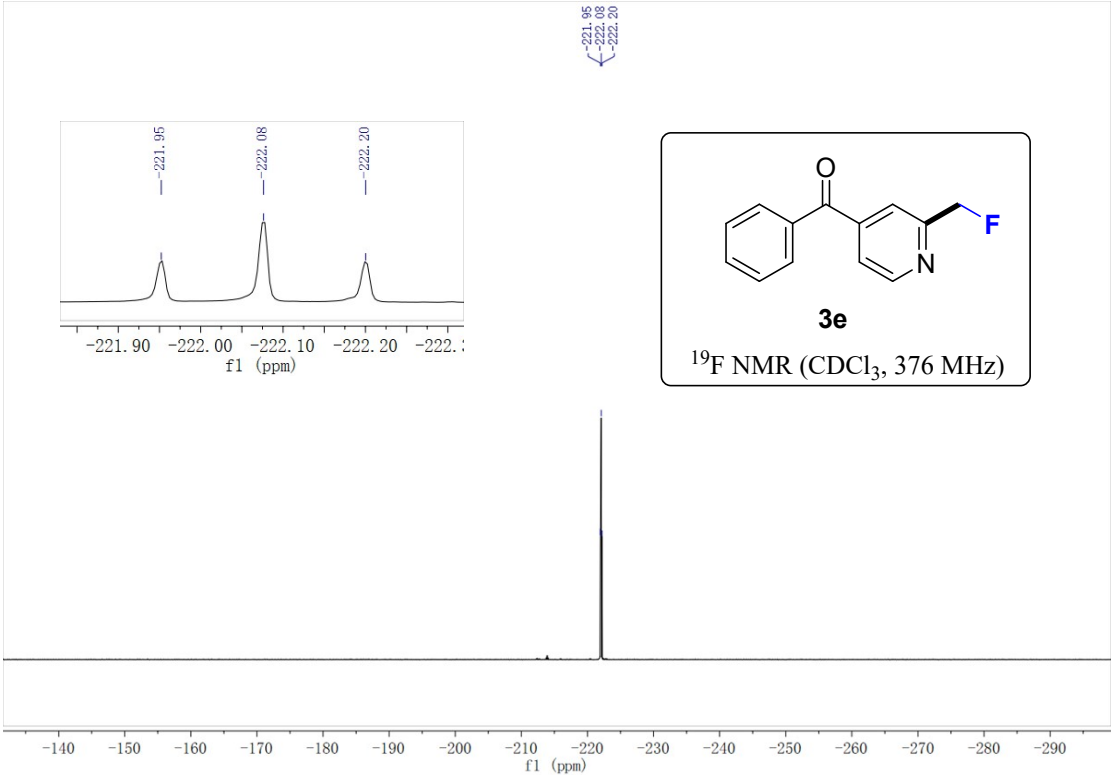
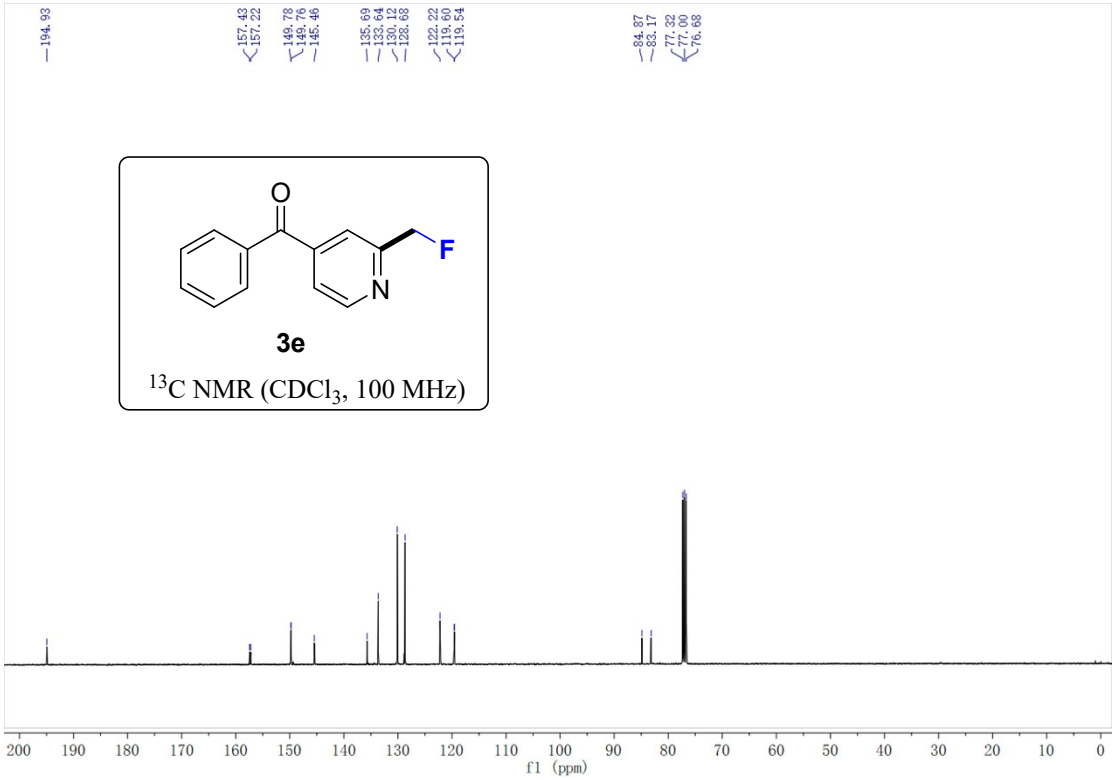
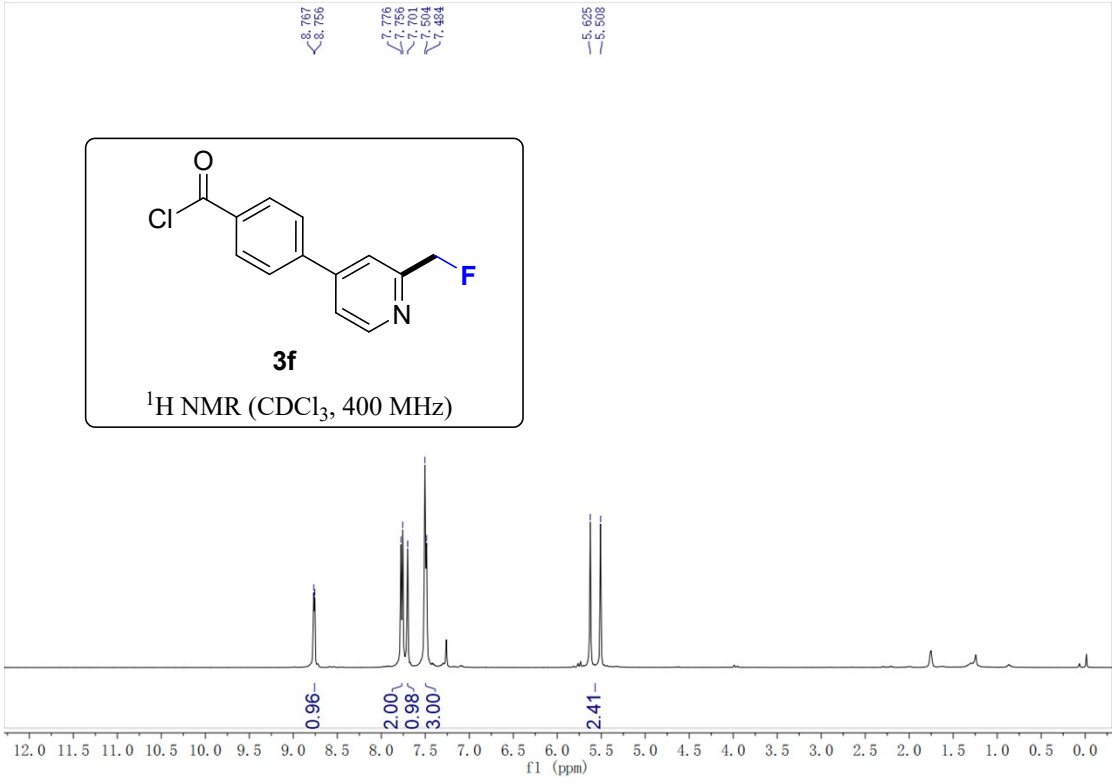
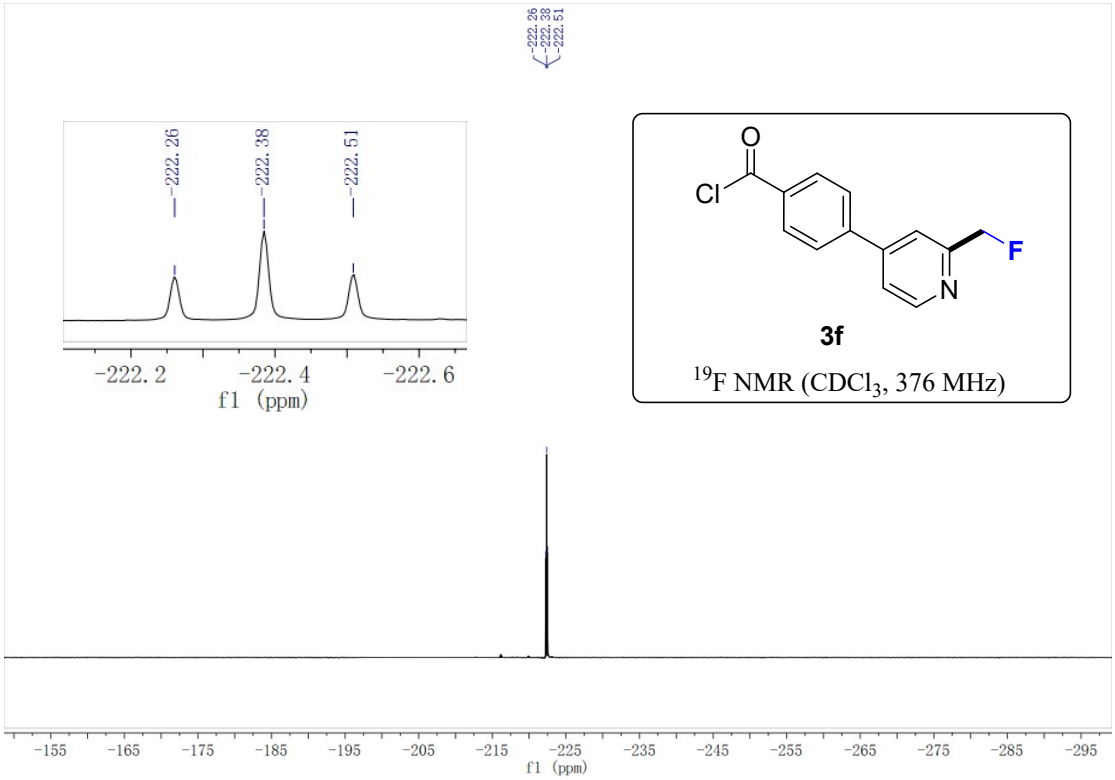
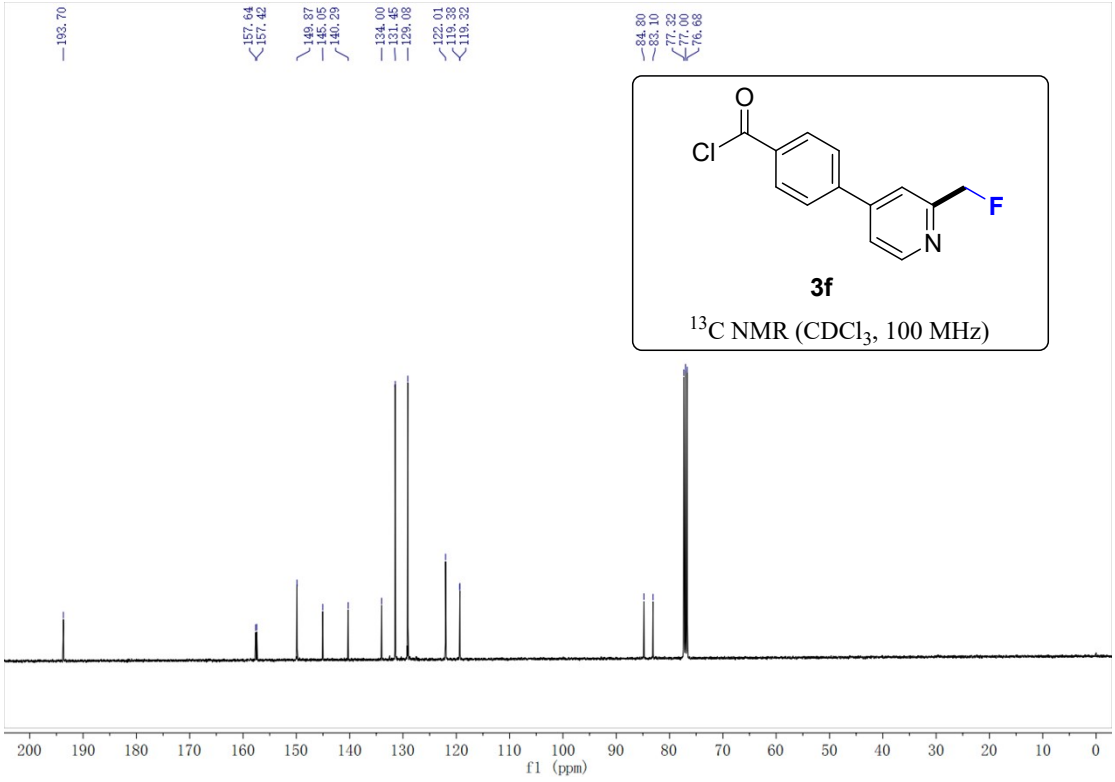
7.734
7.671
7.652
7.634
7.538
7.520
7.500
5.629
5.512
O
F
N
3e
1H NMR (CDCl3, 400 MHz)
1.01
2.00
1.00
1.02
3.00
2.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

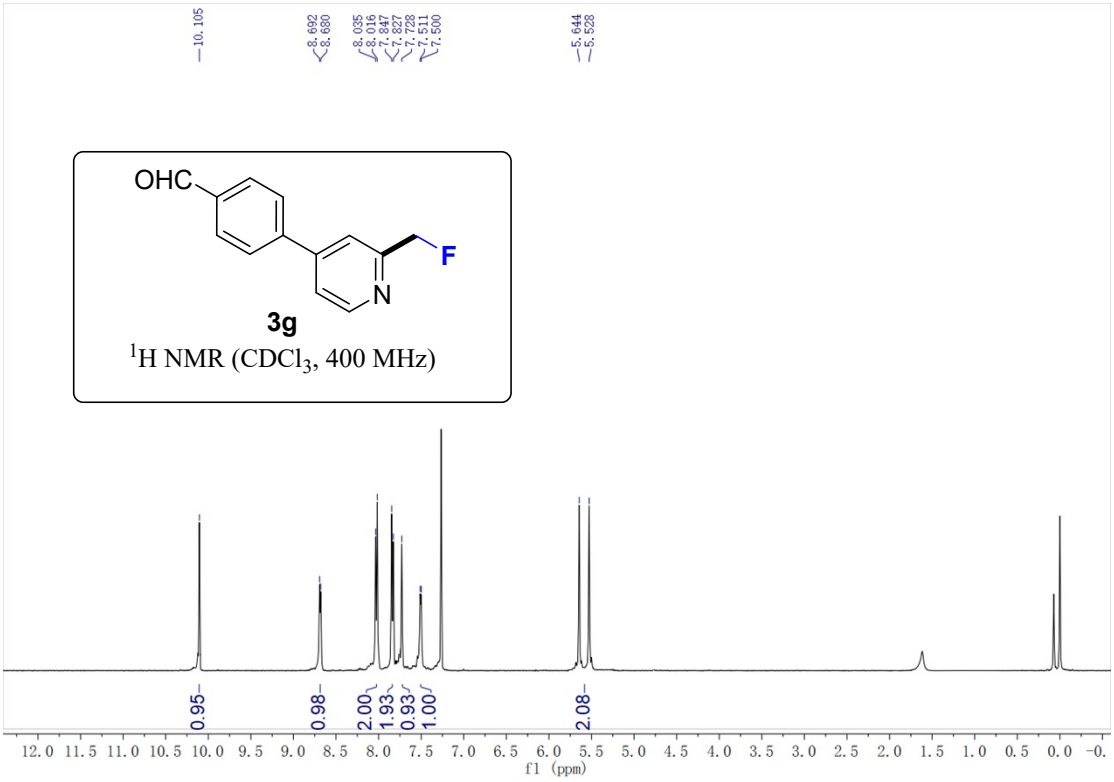

221.95
222.08
222.20
221.95
222.08
222.20
−221.90 −222.00 −222.10 −222.20
f1 (ppm)
O
F
N
3e
19F NMR (CDCl3, 376 MHz)
−140 −150 −160 −170 −180 −190 −200 −210 −220 −230 −240 −250 −260 −270 −280 −290
f1 (ppm)

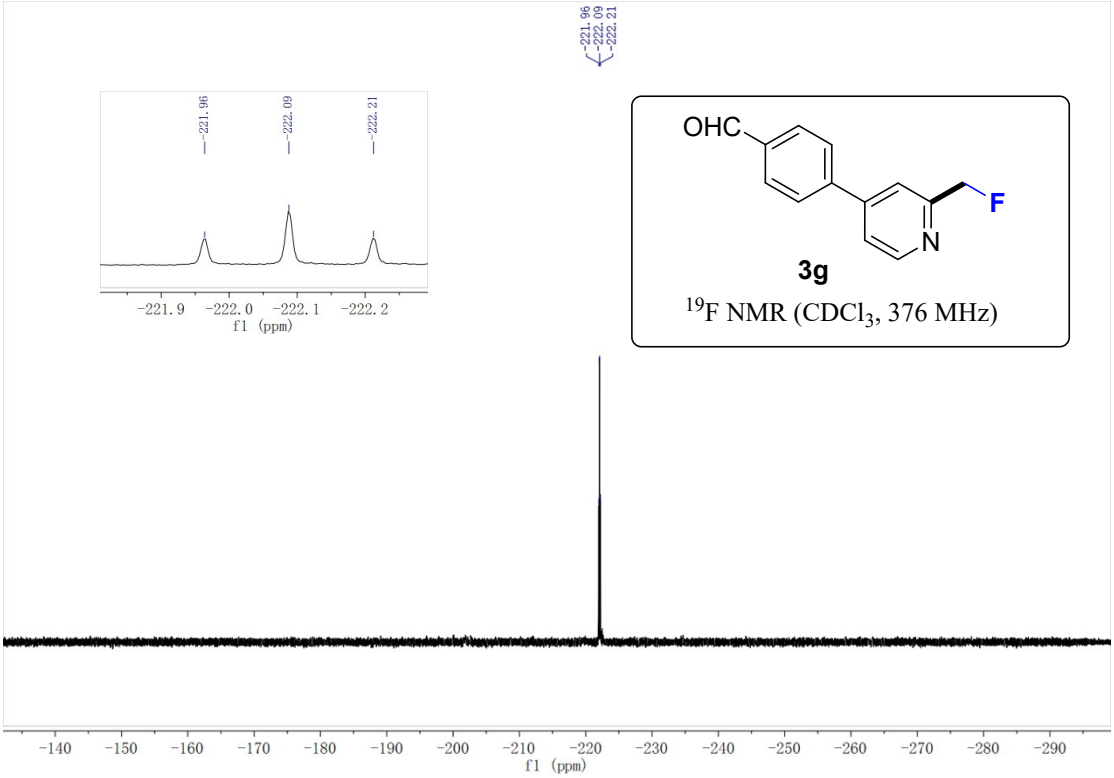

194.93
157.43
157.22
149.78
149.76
145.46
135.69
133.64
130.12
128.68
122.22
119.60
119.54
84.87
83.17
77.32
77.00
76.68
O
F
N
3e
13C NMR (CDCl3, 100 MHz)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

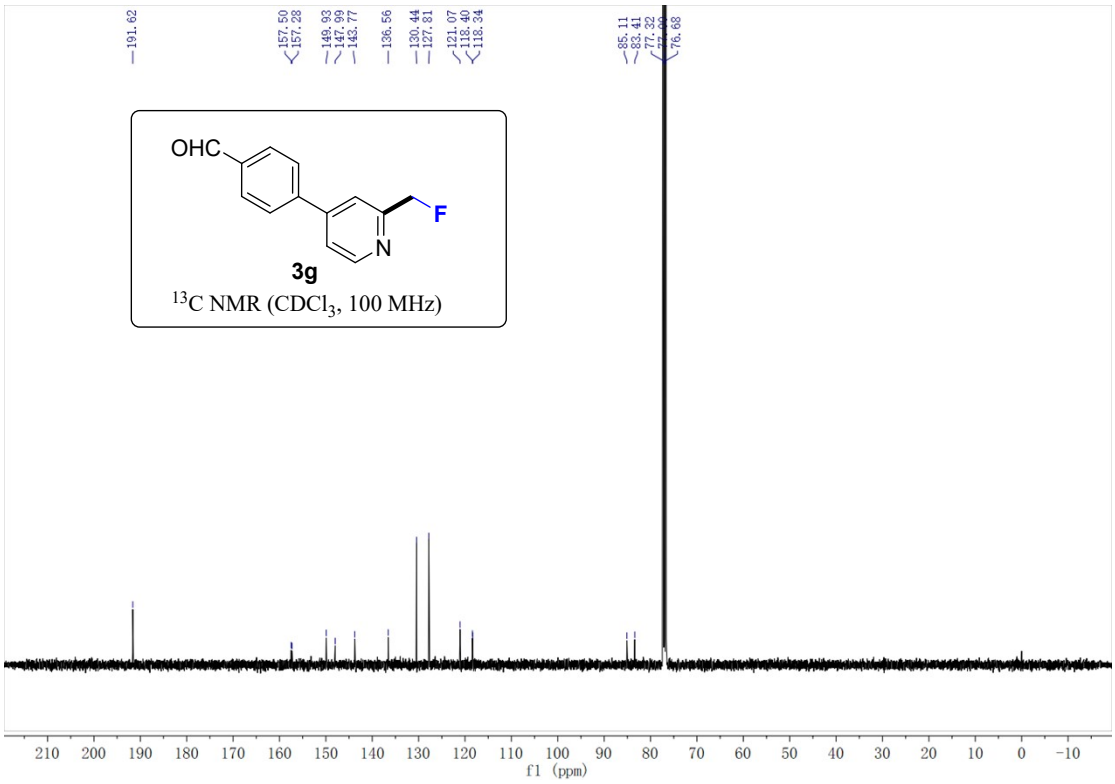

8.767
8.756
7.776
7.756
7.701
7.504
7.484
5.625
5.508
O
Cl
F
N
3f
1H NMR (CDCl3, 400 MHz)
0.96
2.00
0.98
3.00
2.41
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

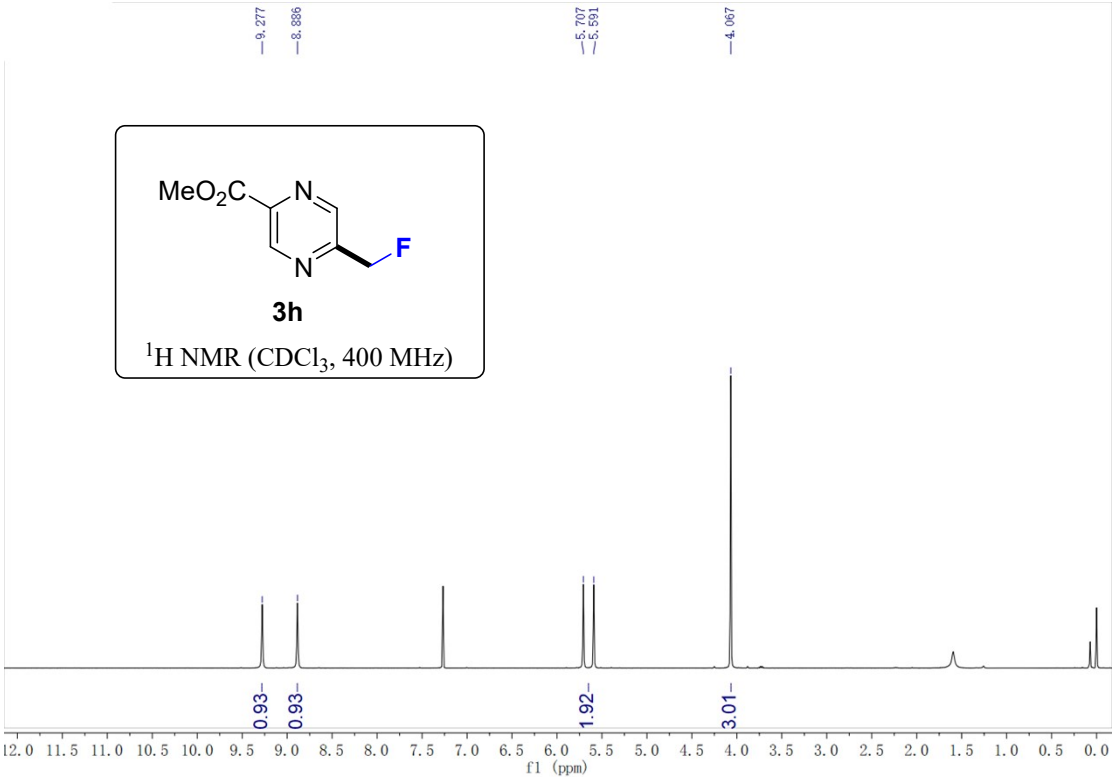

-222.26
-222.38
-222.51
-222.26
-222.38
-222.51
-222.2
-222.4
-222.6
f1 (ppm)
O
Cl
F
N
3f
19F NMR (CDCl3, 376 MHz)
-155
-165
-175
-185
-195
-205
-215
-225
-235
-245
-255
-265
-275
-285
-295
f1 (ppm)

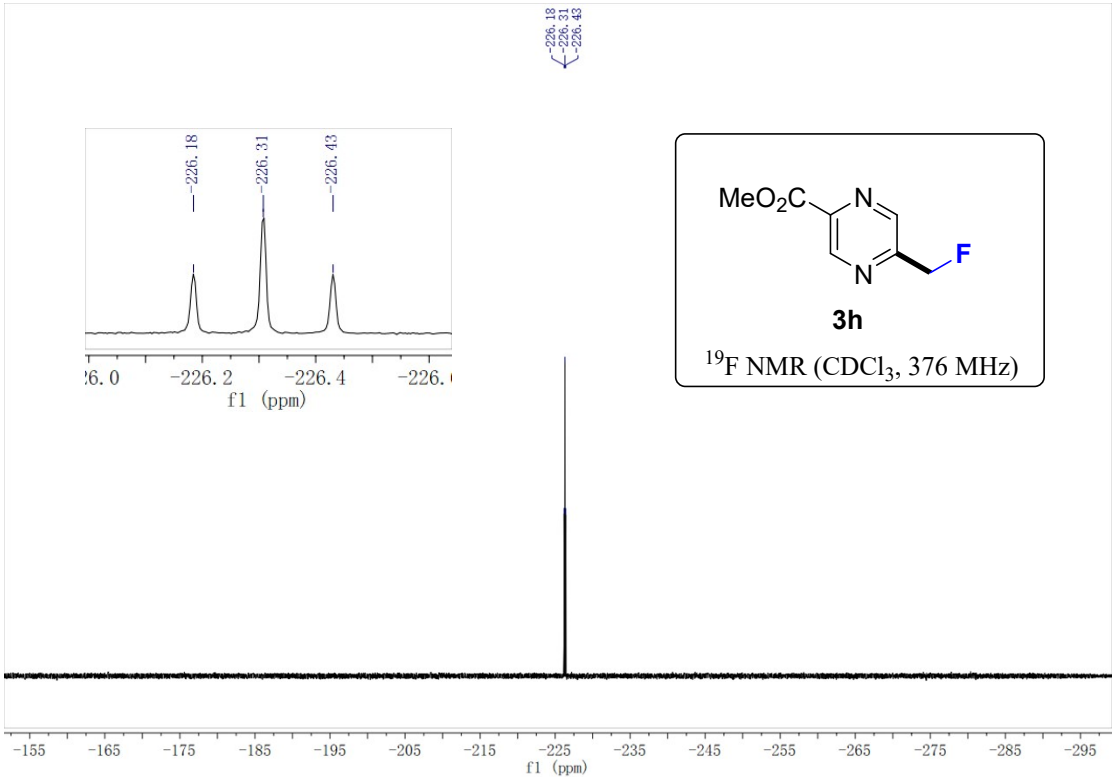

193.70
157.64
157.42
149.87
145.05
140.29
134.00
131.45
129.08
122.01
119.38
119.32
84.80
83.10
77.32
77.00
76.68
O
Cl
F
N
3f
13C NMR (CDCl3, 100 MHz)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

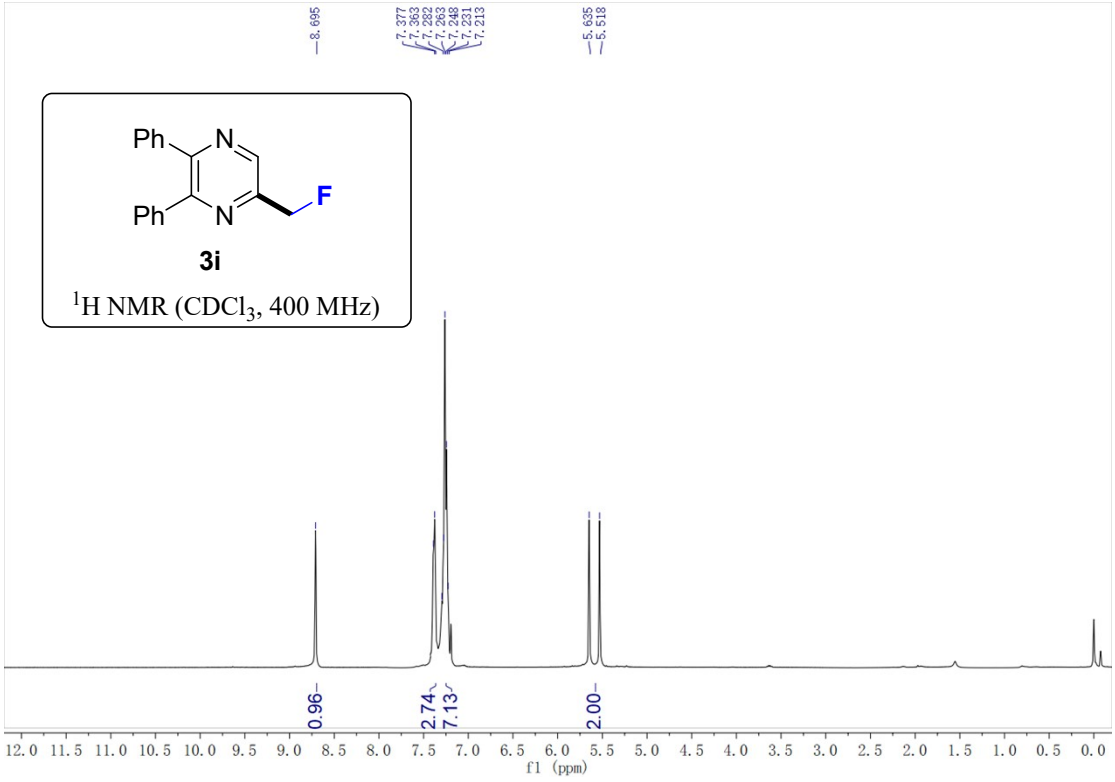

10.105
8.692
8.680
8.035
8.016
7.847
7.827
7.728
7.511
7.500
5.644
5.528
OHC
F
N
3g
^{1}H NMR ($CDCl_3$, 400 MHz)
0.95
0.98
2.00
1.93
0.93
1.00
2.08
f1 (ppm)

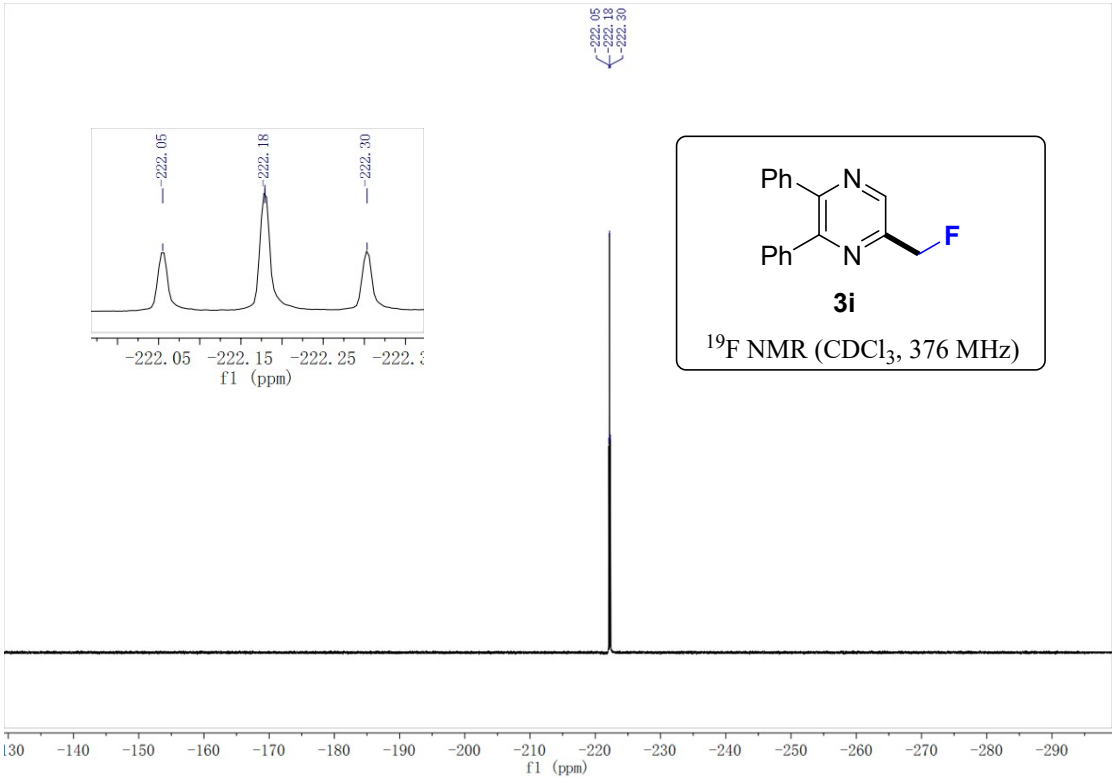

221.96
222.09
222.21
OHC
F
N
3g
^{19}F NMR ($CDCl_3$, 376 MHz)
f1 (ppm)

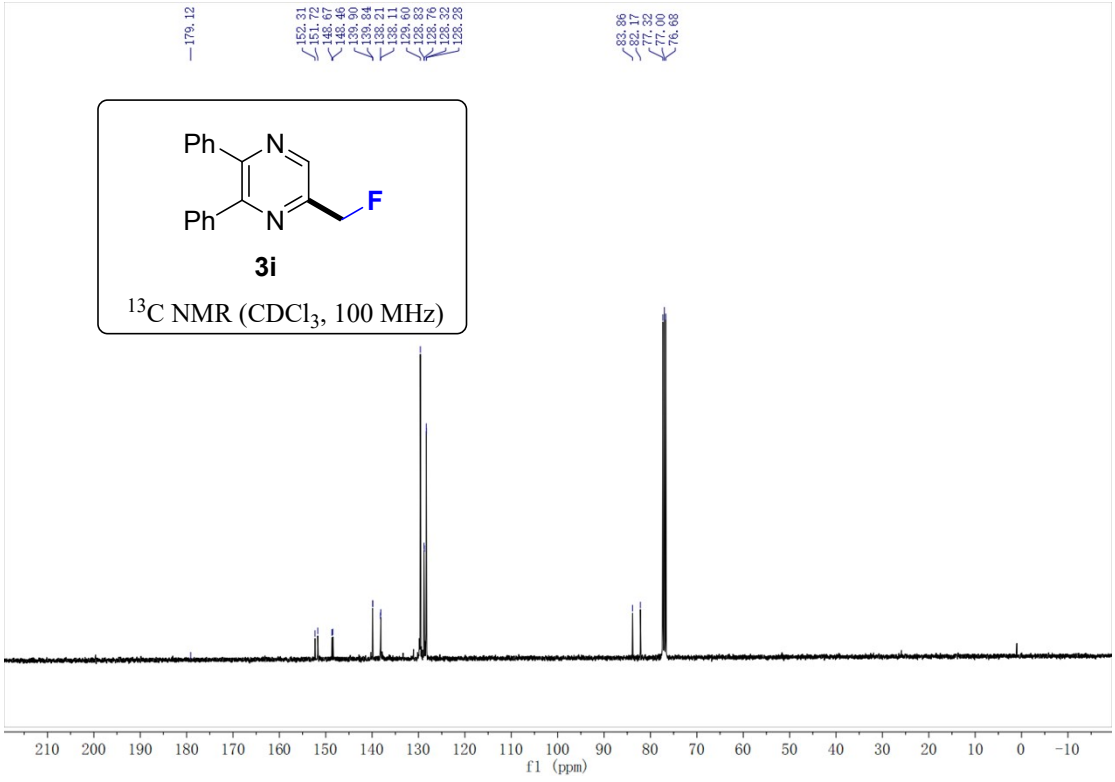

191.62
157.50
157.28
149.93
147.99
143.77
136.56
130.44
127.81
121.07
118.40
118.34
85.11
83.41
77.32
76.68
OHC
F
N
3g
13C NMR (CDCl3, 100 MHz)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

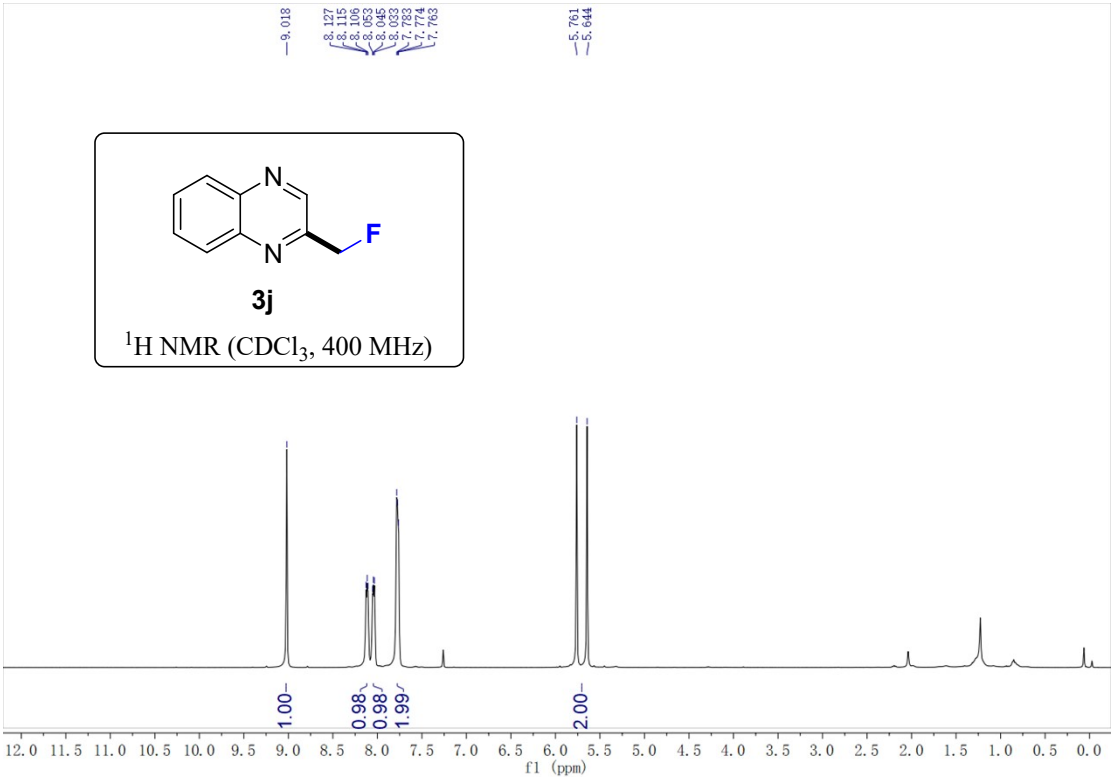

9.277
8.886
5.707
5.591
4.067
MeO2C
N
N
F
3h
1H NMR (CDCl3, 400 MHz)
0.93
0.93
1.92
3.01
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

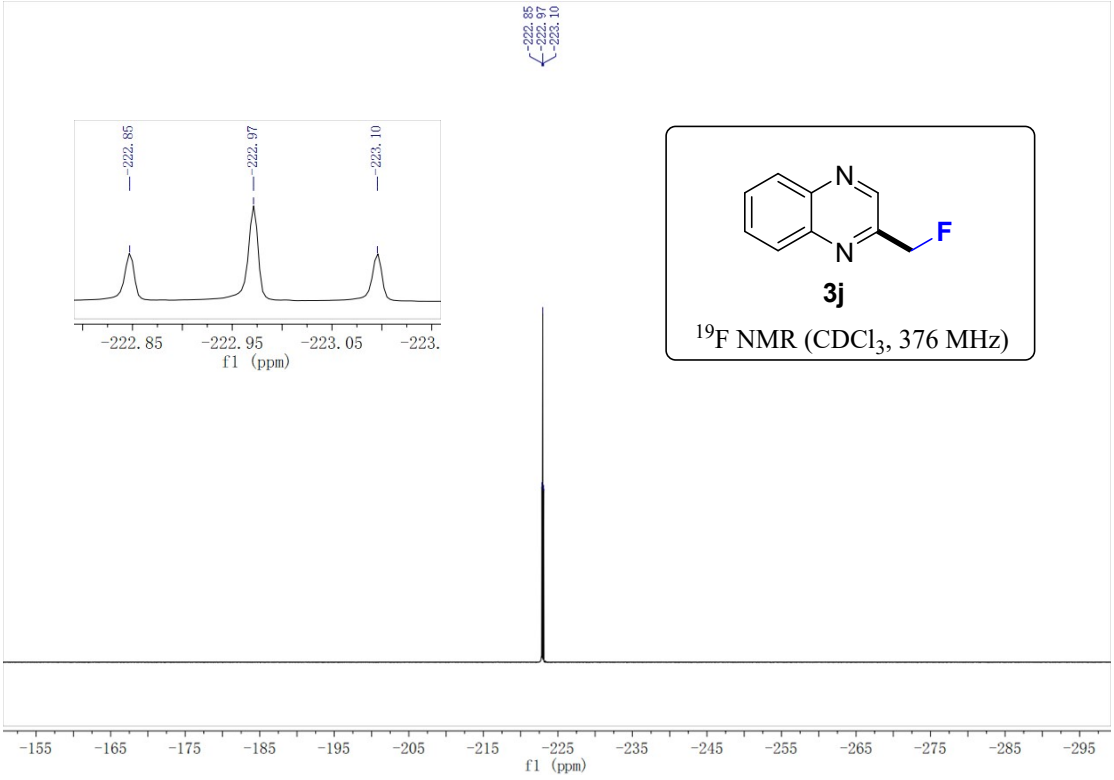

-226.18
-226.31
-226.43
MeO2C
N
N
F
3h
19F NMR (CDCl3, 376 MHz)
f1 (ppm)

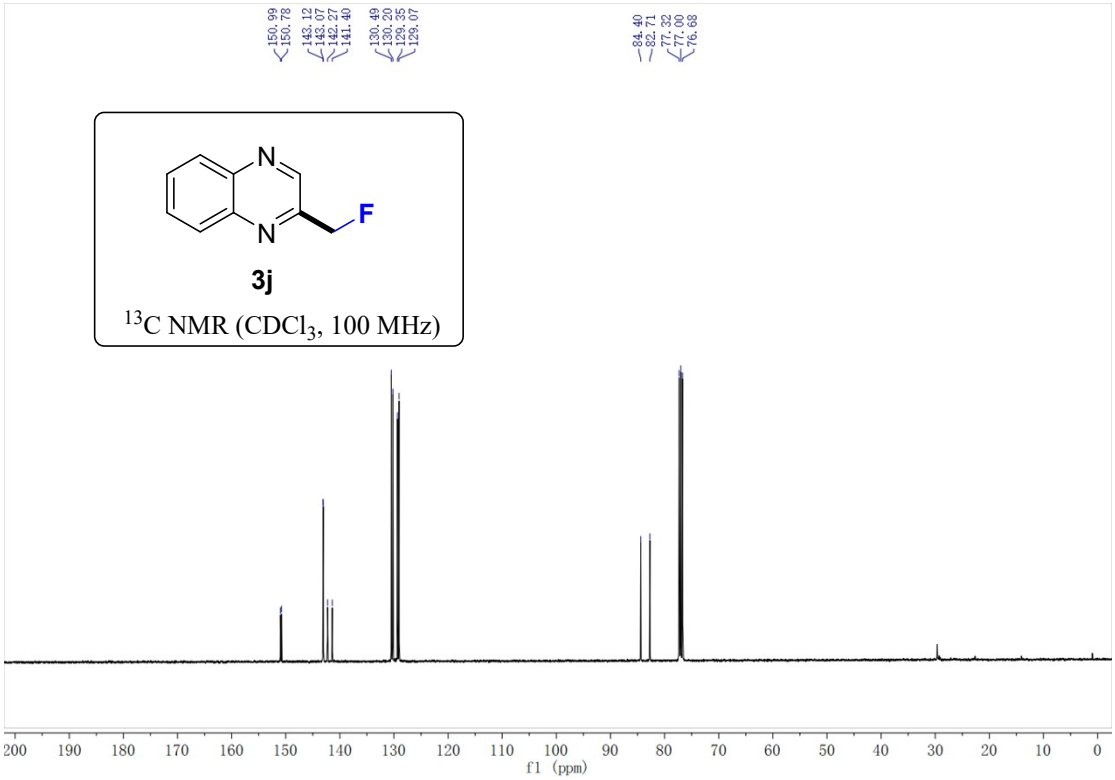

8.695
7.377
7.363
7.282
7.263
7.248
7.231
7.213
5.635
5.518
Ph
N
Ph
N
F
3i
1H NMR (CDCl3, 400 MHz)
0.96
2.74
7.13
2.00
f1 (ppm)

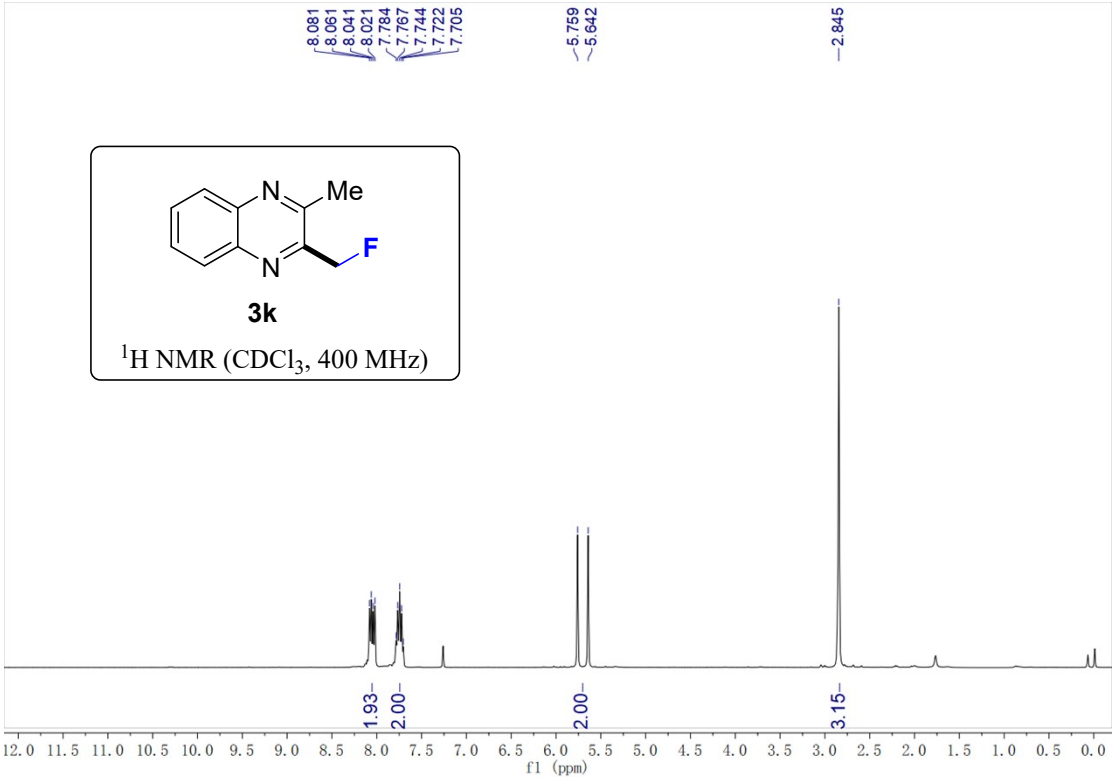

-222.05
-222.18
-222.30
-222.05
-222.18
-222.30
-222.05 -222.15 -222.25
f1 (ppm)
Ph
N
Ph
N
F
3i
19F NMR (CDCl3, 376 MHz)
-130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240 -250 -260 -270 -280 -290
f1 (ppm)

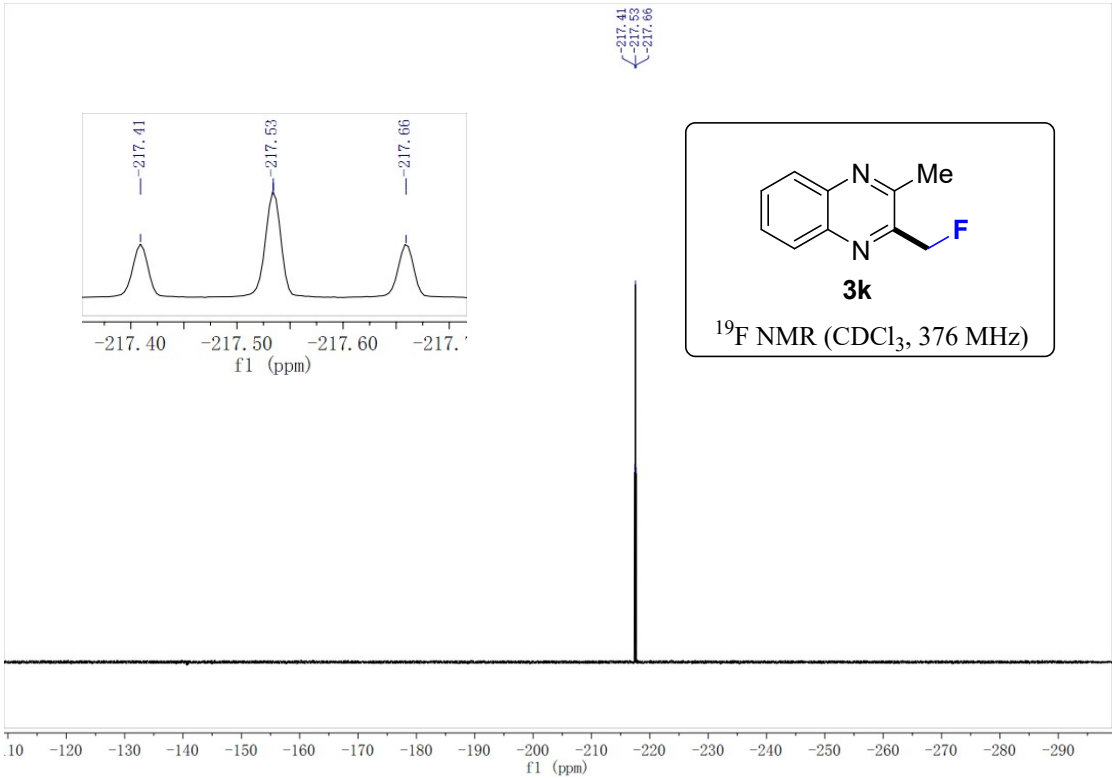

179.12
152.31
151.72
148.67
148.46
139.90
139.84
138.21
138.11
129.60
128.83
128.76
128.32
128.28
83.86
82.17
77.32
77.00
76.68
Ph
N
Ph
N
F
3i
13C NMR (CDCl3, 100 MHz)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

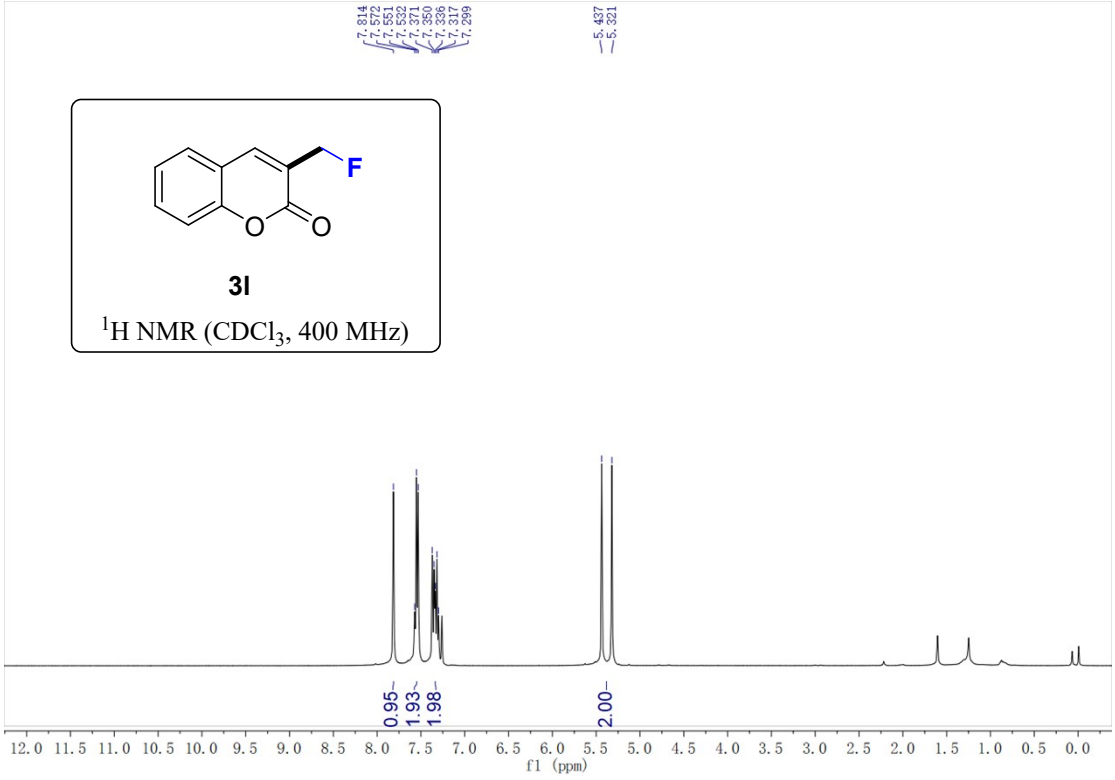

9.018
8.127
8.115
8.106
8.053
8.045
8.033
7.793
7.774
7.763
5.761
5.644
N
N
F
3j
1H NMR (CDCl3, 400 MHz)
1.00
0.98
0.98
1.99
2.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

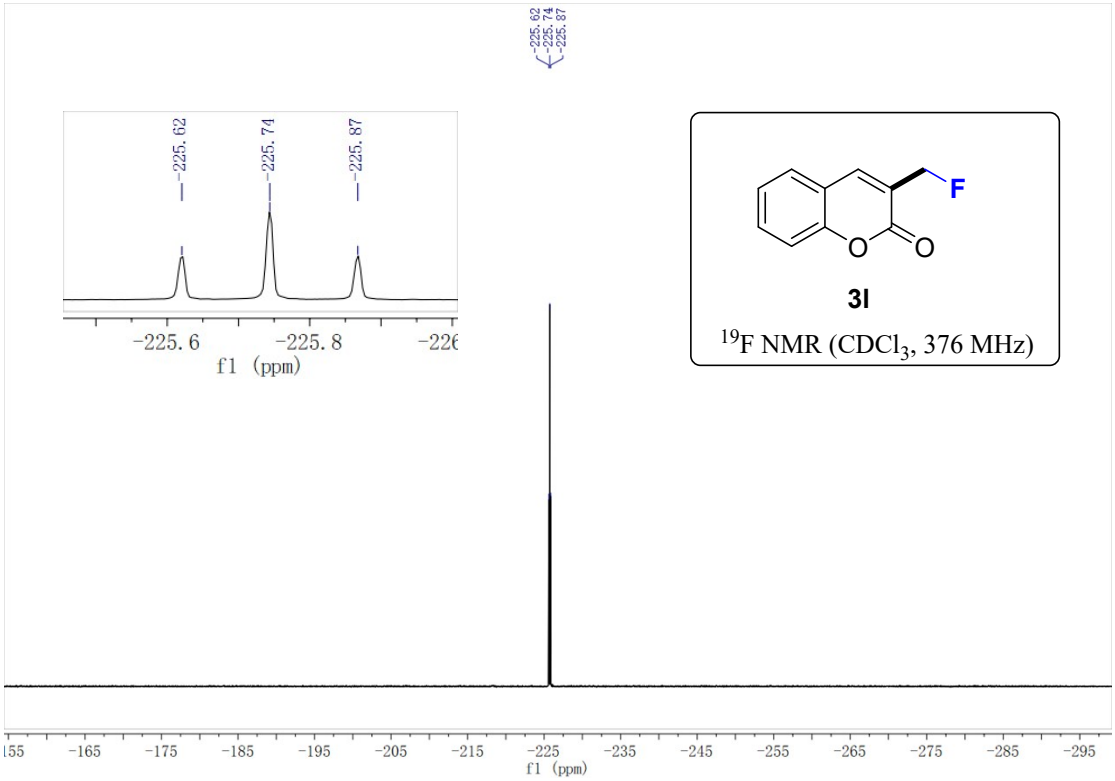

222.85
222.97
223.10
222.85
222.97
223.10
222.85
222.95
223.05
223.
f1 (ppm)
N
N
F
3j
19F NMR (CDCl3, 376 MHz)
-155 -165 -175 -185 -195 -205 -215 -225 -235 -245 -255 -265 -275 -285 -295
f1 (ppm)

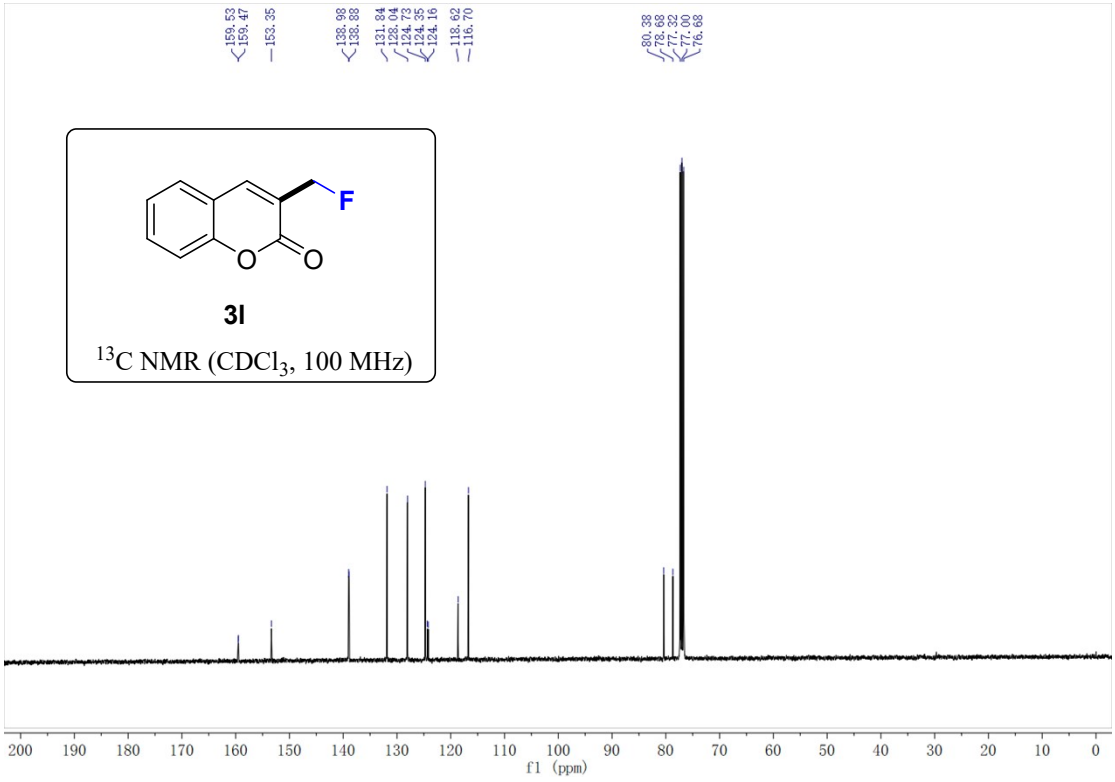

150.99
150.78
143.12
143.07
142.27
141.40
130.49
130.20
129.35
129.07
84.40
82.71
77.32
77.00
76.68
N
N
F
3j
^{13}C NMR (CDCl$_3$, 100 MHz)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

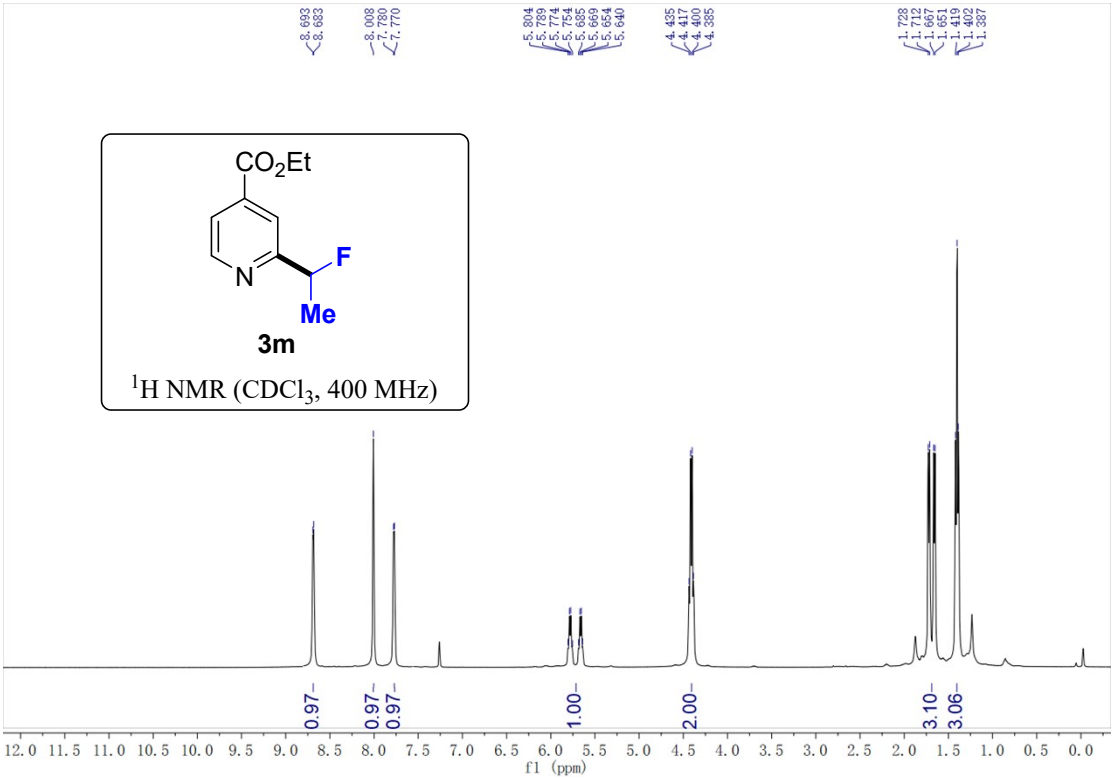

8.081
8.061
8.041
8.021
7.784
7.767
7.744
7.722
7.705
5.759
5.642
2.845
N
Me
N
F
3k
^{1}H NMR (CDCl$_3$, 400 MHz)
1.93
2.00
2.00
3.15
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

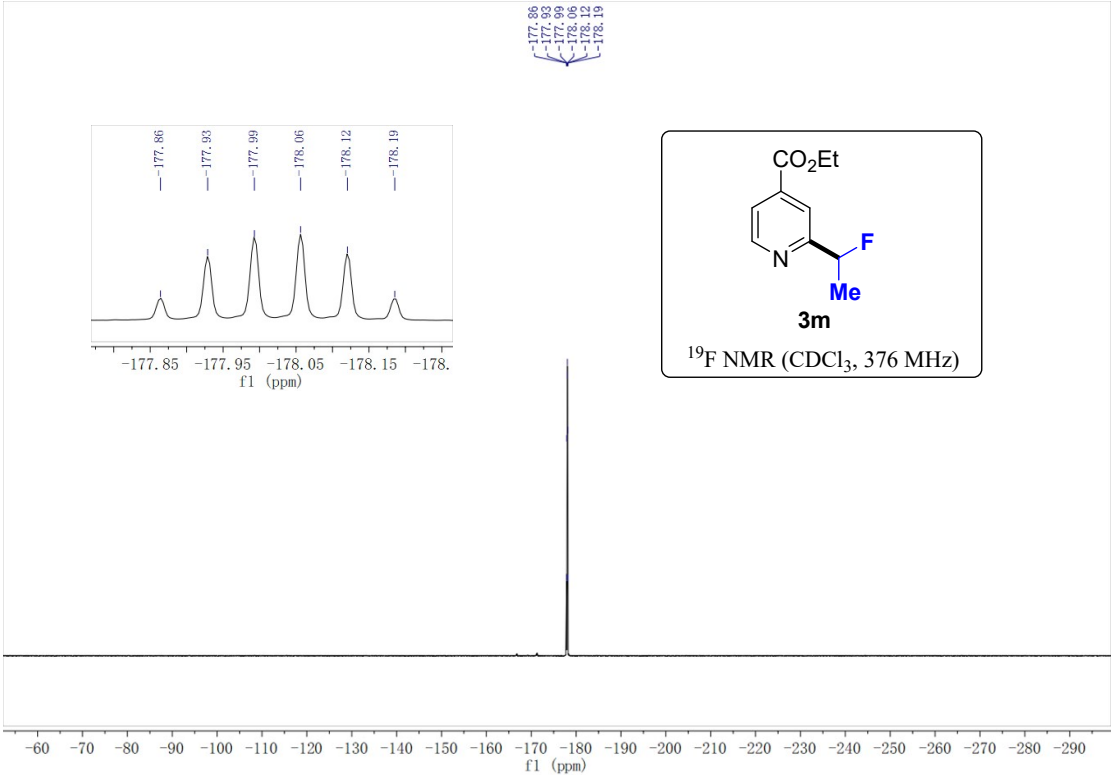

-217.41
-217.53
-217.66
-217.40
-217.50
-217.60
f1 (ppm)
N
Me
F
N
3k
^{19}F NMR ($CDCl_3$, 376 MHz)
f1 (ppm)

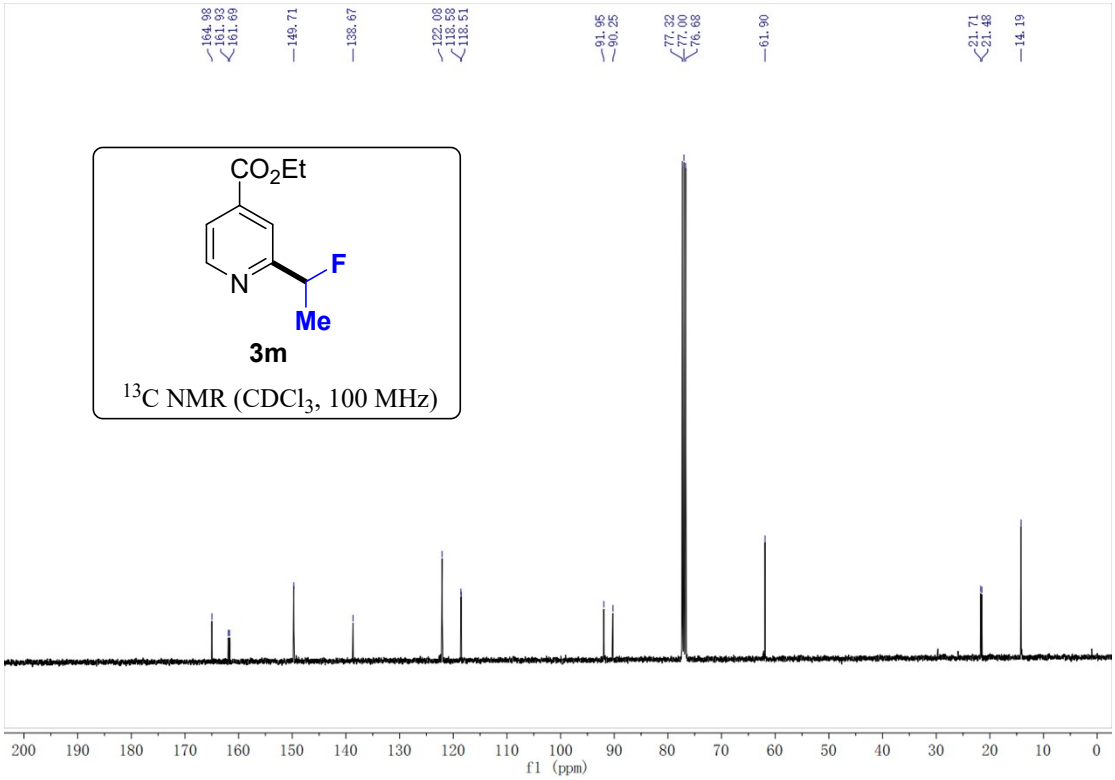

7.814
7.572
7.551
7.532
7.371
7.350
7.336
7.317
7.299
5.437
5.321
F
O
O
3l
^{1}H NMR ($CDCl_3$, 400 MHz)
0.95
1.93
1.98
2.00
f1 (ppm)

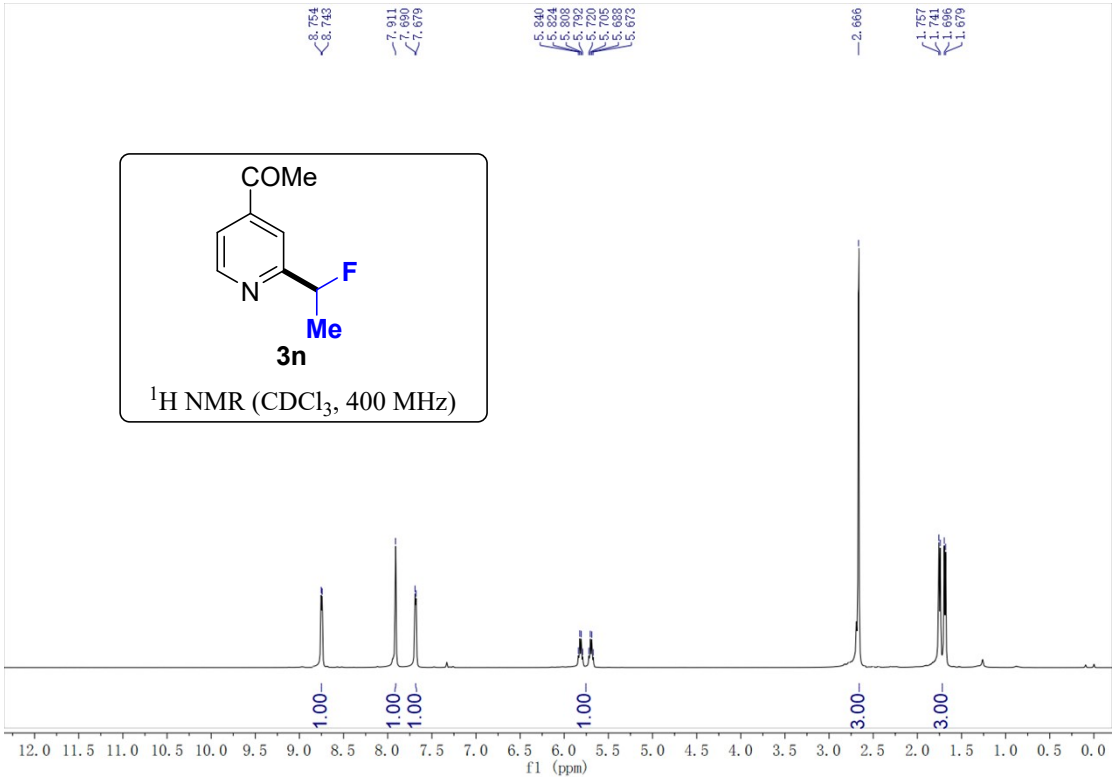

-225.62
-225.74
-225.87
-225.6
-225.8
f1 (ppm)
F
O
O
3l
19F NMR (CDCl3, 376 MHz)
f1 (ppm)

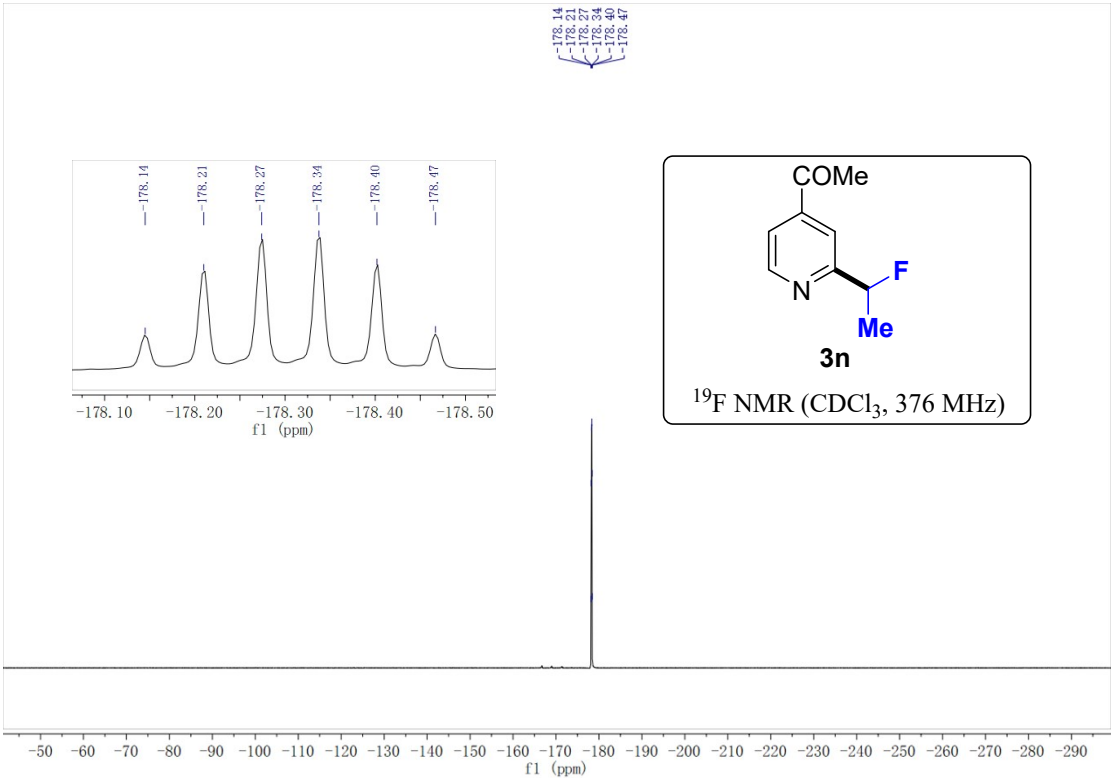

159.53
159.47
153.35
138.98
138.88
131.84
131.04
124.73
124.35
124.16
118.62
116.70
80.38
78.88
78.32
77.00
76.68
F
O
O
3l
13C NMR (CDCl3, 100 MHz)
f1 (ppm)

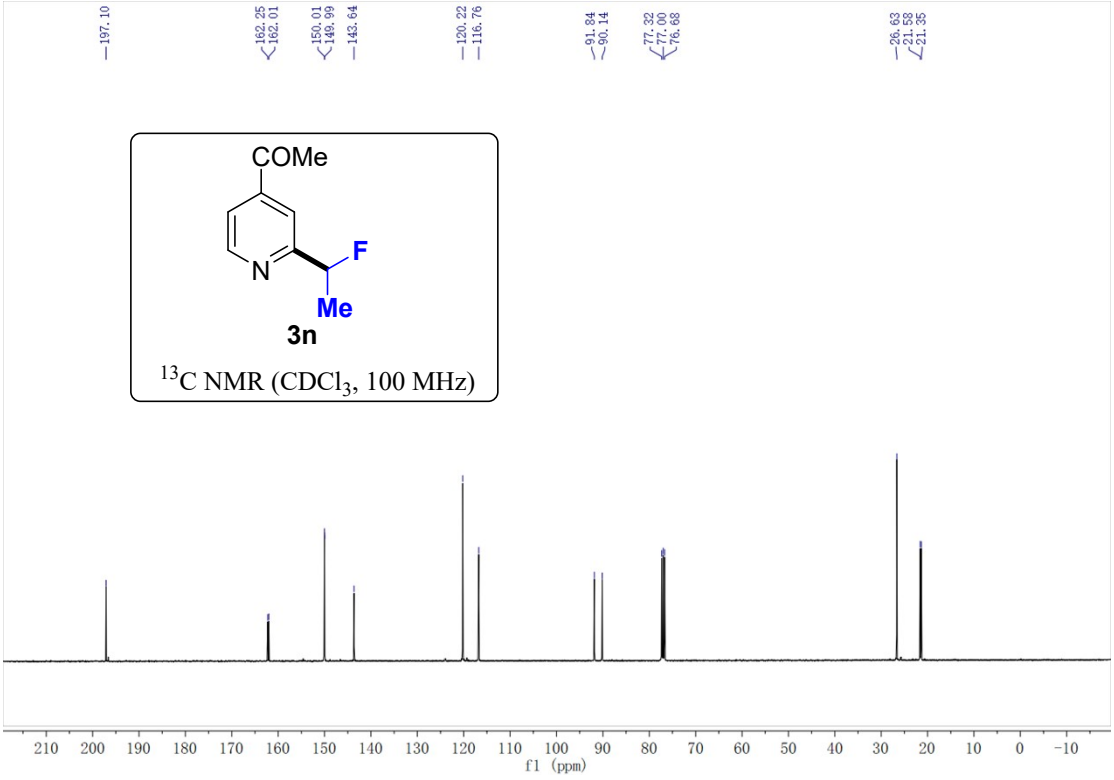

8.693
8.683
8.008
7.780
7.770
5.804
5.789
5.774
5.754
5.685
5.669
5.654
5.640
4.435
4.417
4.400
4.385
1.728
1.712
1.667
1.651
1.419
1.402
1.387
CO2Et
N
F
Me
3m
1H NMR (CDCl3, 400 MHz)
0.97
0.97
0.97
1.00
2.00
3.10
3.06
f1 (ppm)

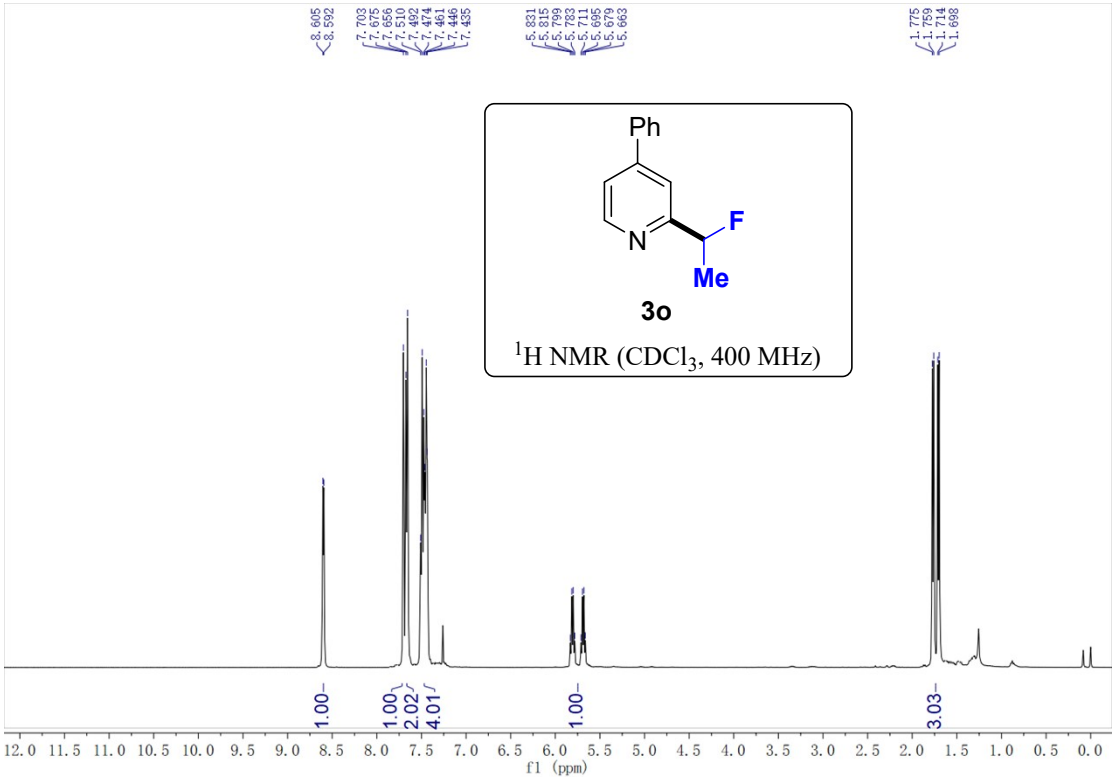

177.86
177.93
177.99
178.06
178.12
178.19
CO2Et
N
F
Me
3m
19F NMR (CDCl3, 376 MHz)
f1 (ppm)

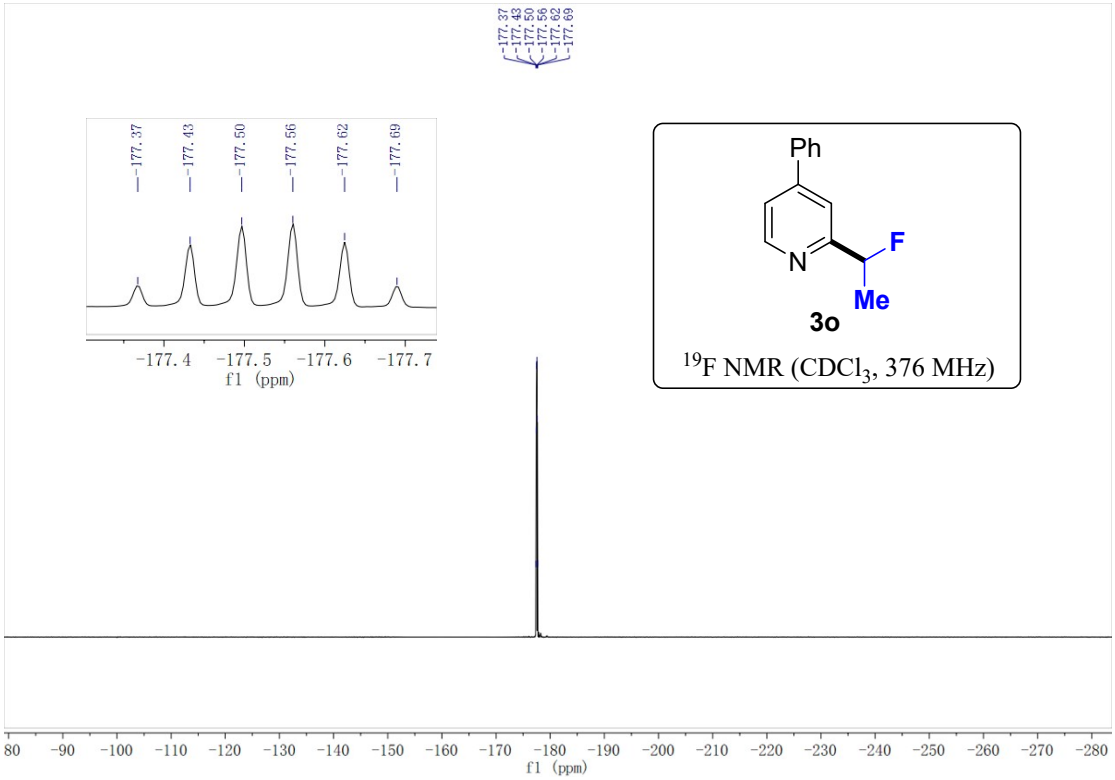

164.98
161.93
161.69
149.71
138.67
122.08
118.58
118.51
91.95
90.25
77.32
77.00
76.68
61.90
21.71
21.48
14.19
CO2Et
F
N
Me
3m
13C NMR (CDCl3, 100 MHz)
f1 (ppm)

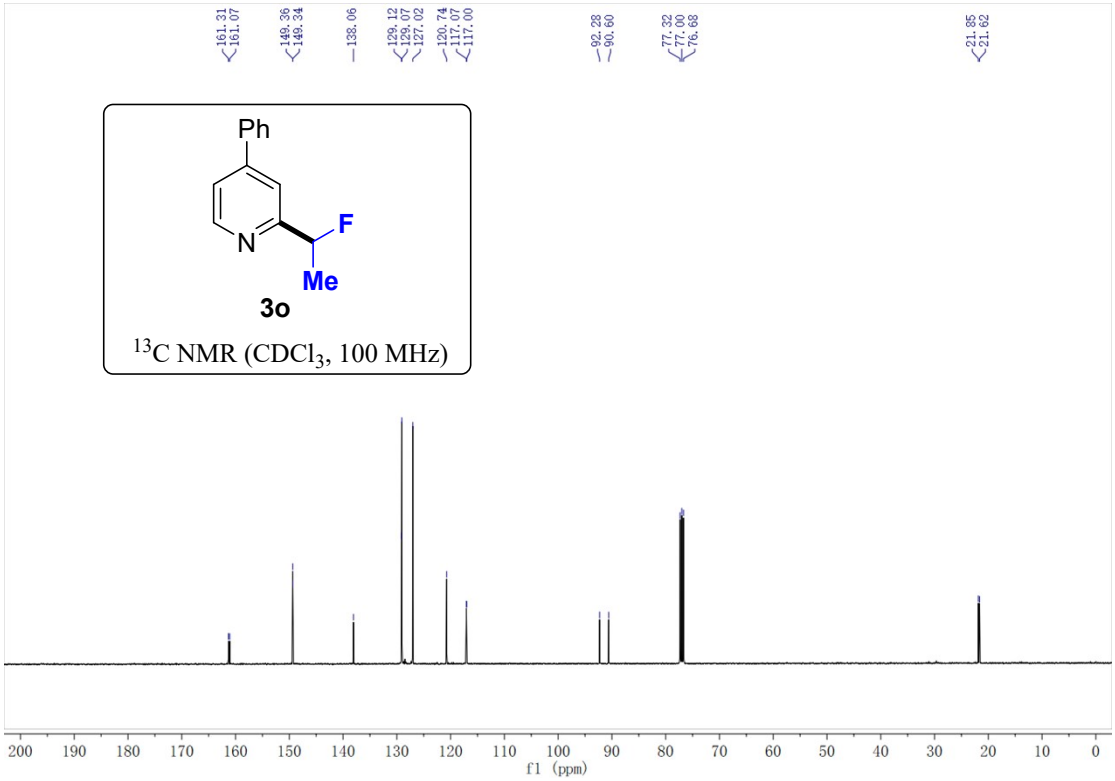

8.754
8.743
7.911
7.690
7.679
5.840
5.824
5.808
5.792
5.720
5.705
5.688
5.673
2.666
1.757
1.741
1.696
1.679
COMe
F
N
Me
3n
1H NMR (CDCl3, 400 MHz)
1.00
1.00
1.00
1.00
3.00
3.00
f1 (ppm)

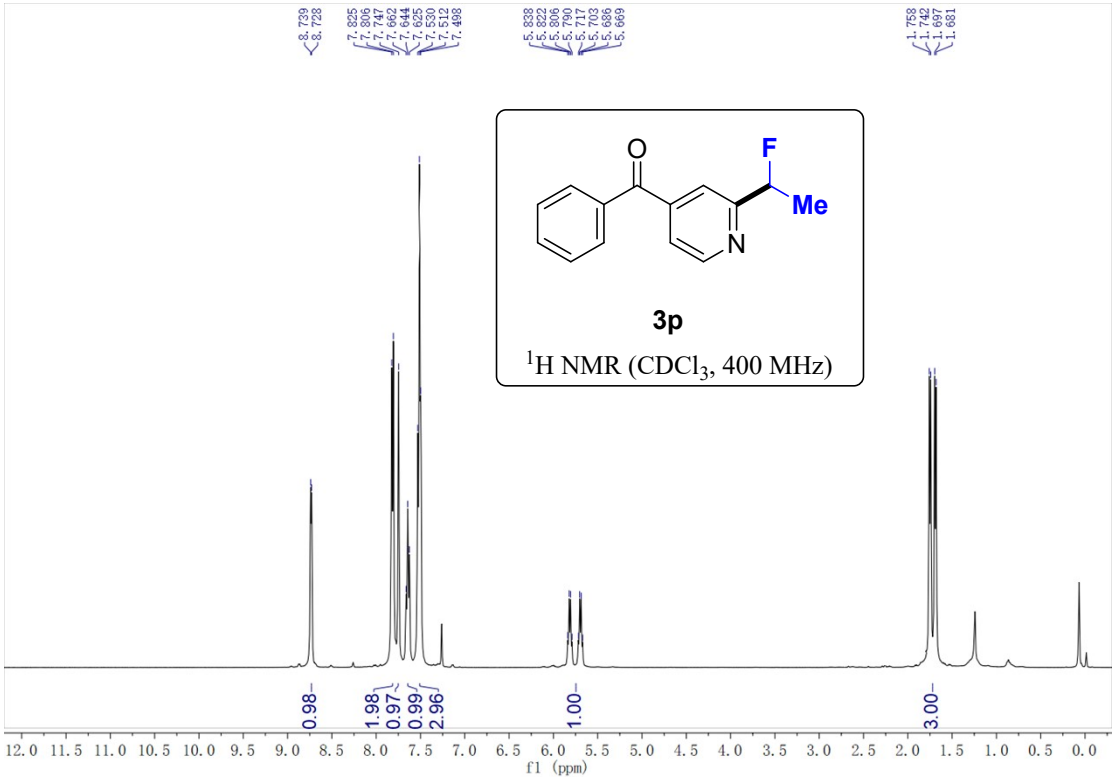

-178.14
-178.21
-178.27
-178.34
-178.40
-178.47
-178.10
-178.20
-178.30
-178.40
-178.50
f1 (ppm)
COMe
F
N
Me
3n
^{19}F NMR (CDCl$_3$, 376 MHz)
-50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240 -250 -260 -270 -280 -290
f1 (ppm)

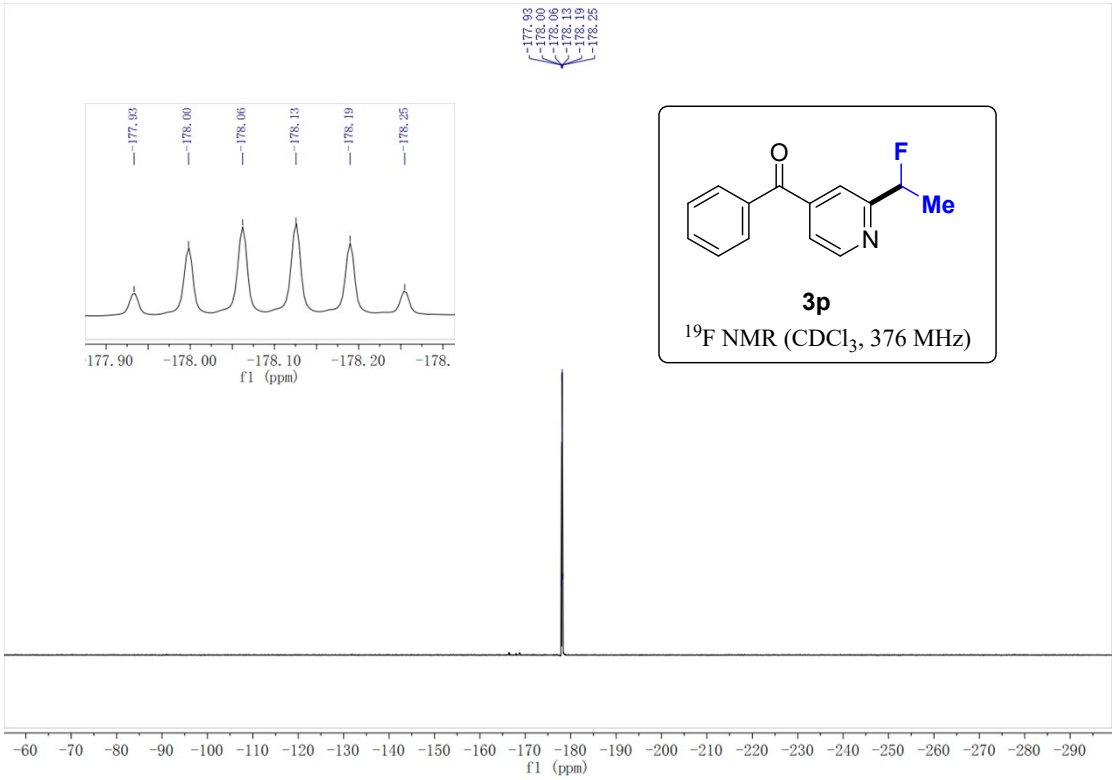

197.10
162.25
162.01
150.01
149.99
143.64
120.22
116.76
91.84
90.14
77.32
77.00
76.68
26.63
21.58
21.35
COMe
F
N
Me
3n
^{13}C NMR (CDCl$_3$, 100 MHz)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

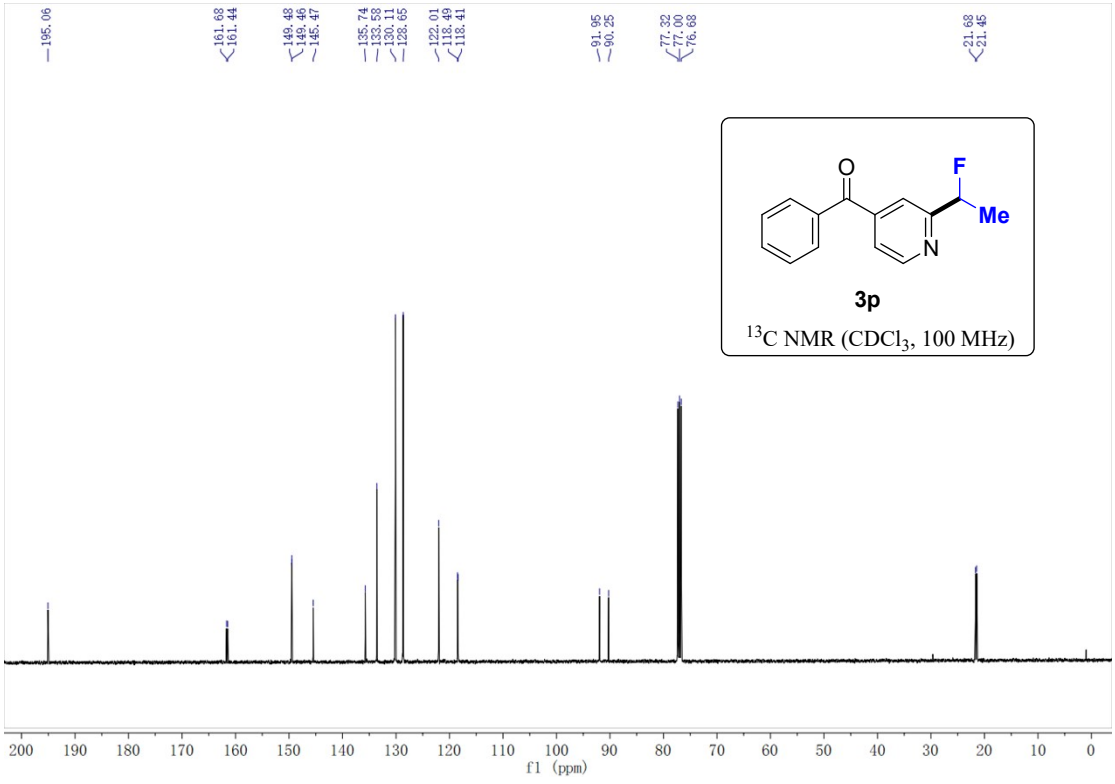

Ph
N
F
Me
3o
^{1}H NMR ($CDCl_3$, 400 MHz)
f1 (ppm)

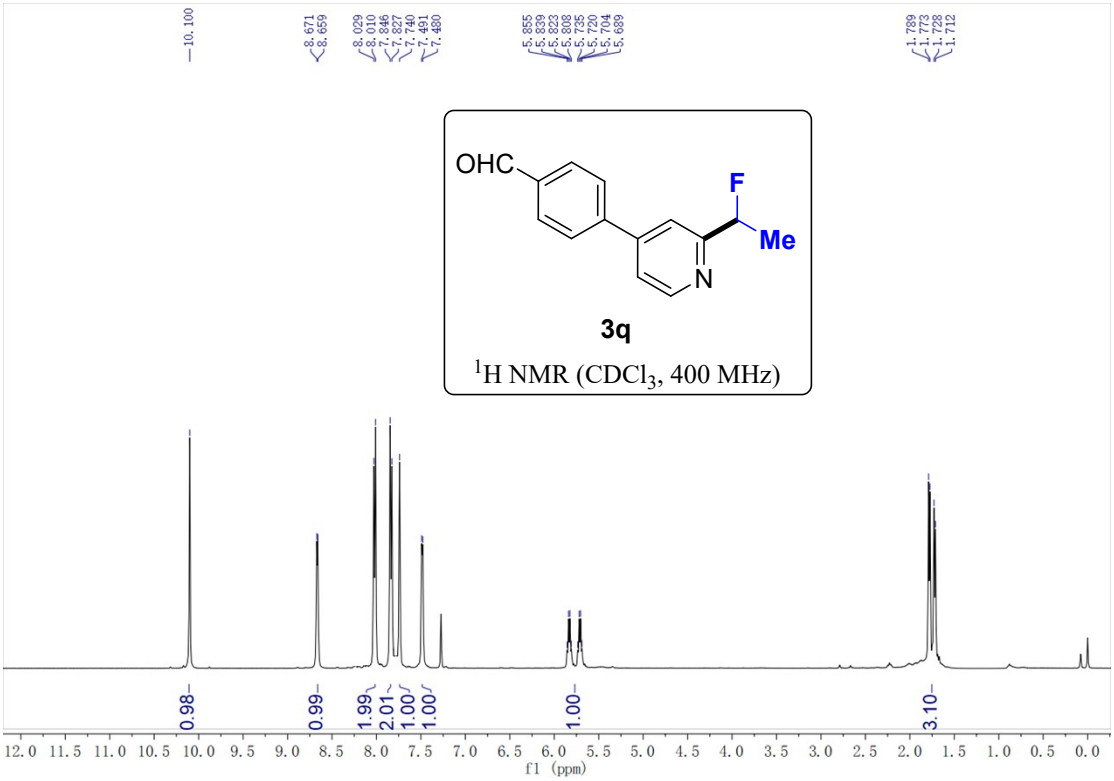

Ph
N
F
Me
3o
^{19}F NMR ($CDCl_3$, 376 MHz)
f1 (ppm)

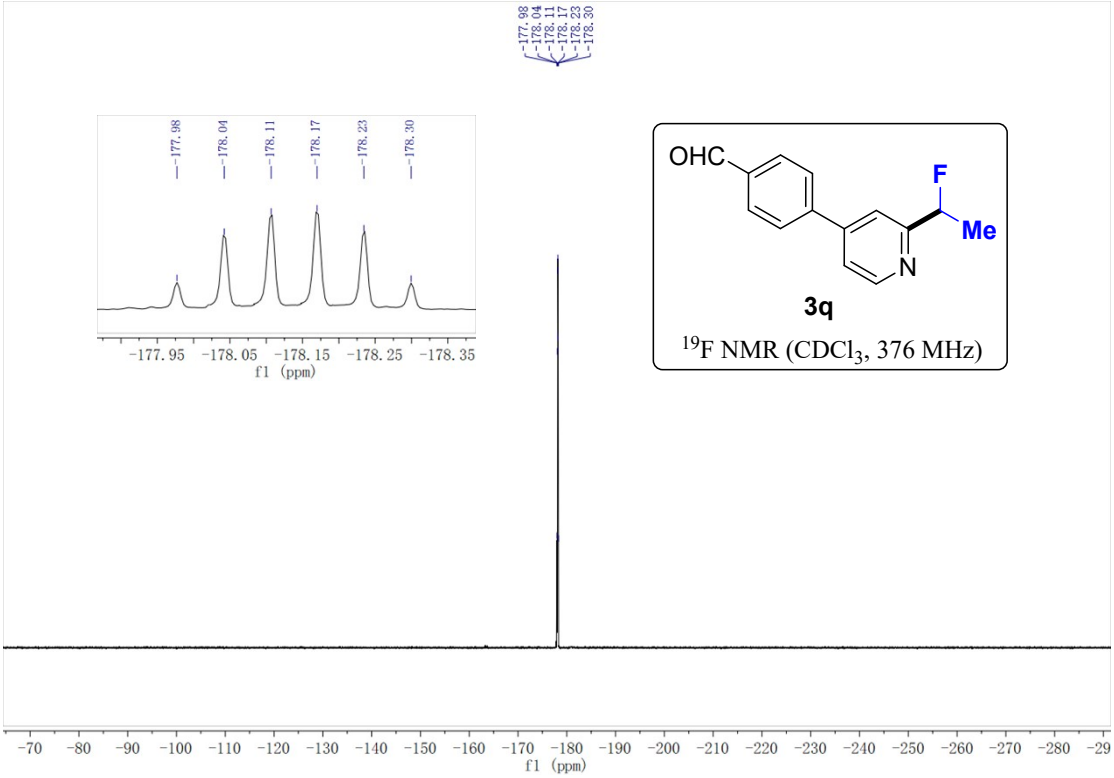

161.31
161.07
149.36
149.34
138.06
129.12
129.07
127.02
120.74
117.07
117.00
92.28
90.60
77.32
77.00
76.68
21.85
21.62
Ph
N
F
Me
3o
13C NMR (CDCl3, 100 MHz)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

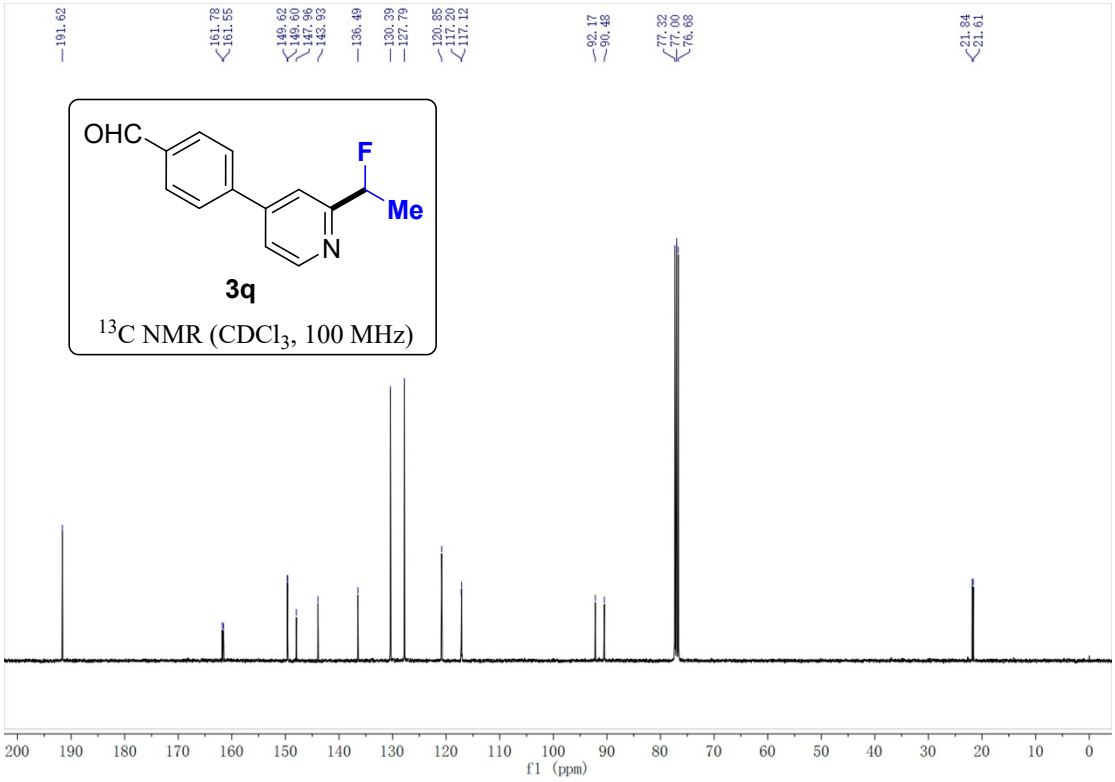

8.739
8.728
7.825
7.806
7.747
7.662
7.644
7.625
7.530
7.512
7.498
5.838
5.822
5.806
5.790
5.717
5.703
5.686
5.669
1.758
1.742
1.697
1.681
O
F
Me
N
3p
1H NMR (CDCl3, 400 MHz)
0.98
1.98
0.97
0.99
2.96
1.00
3.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

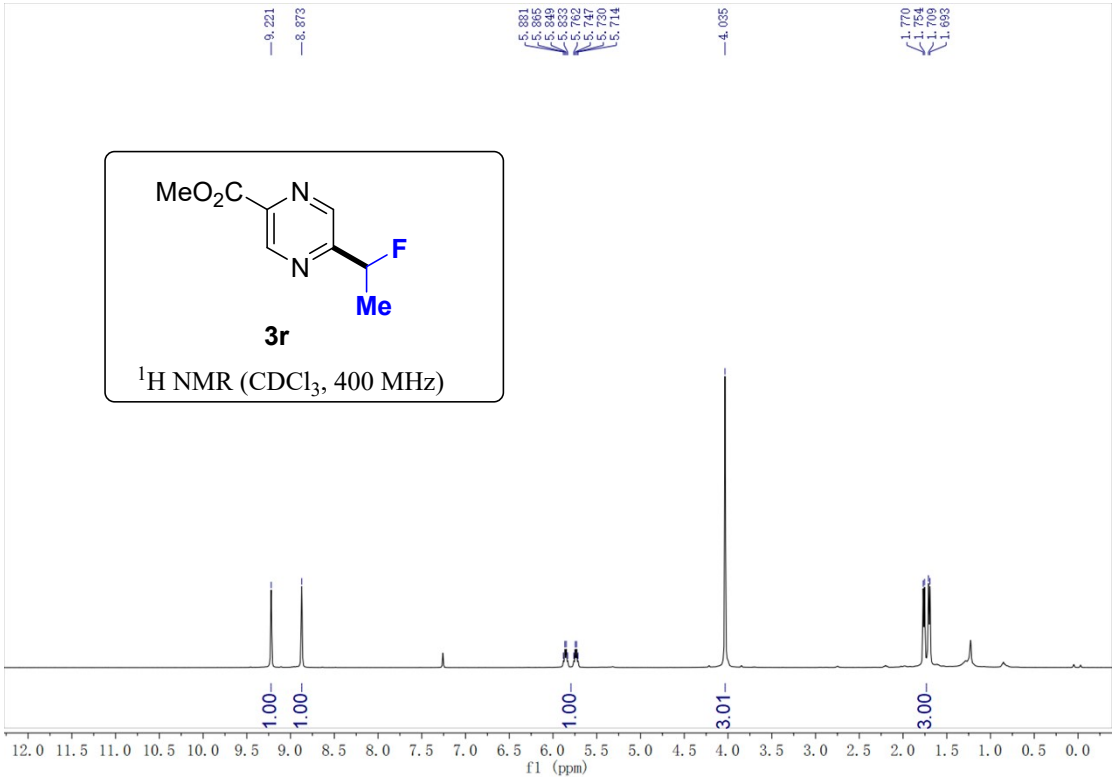

-177.93
-178.00
-178.06
-178.13
-178.19
-178.25
f1 (ppm)
O
F
Me
N
3p
19F NMR (CDCl3, 376 MHz)

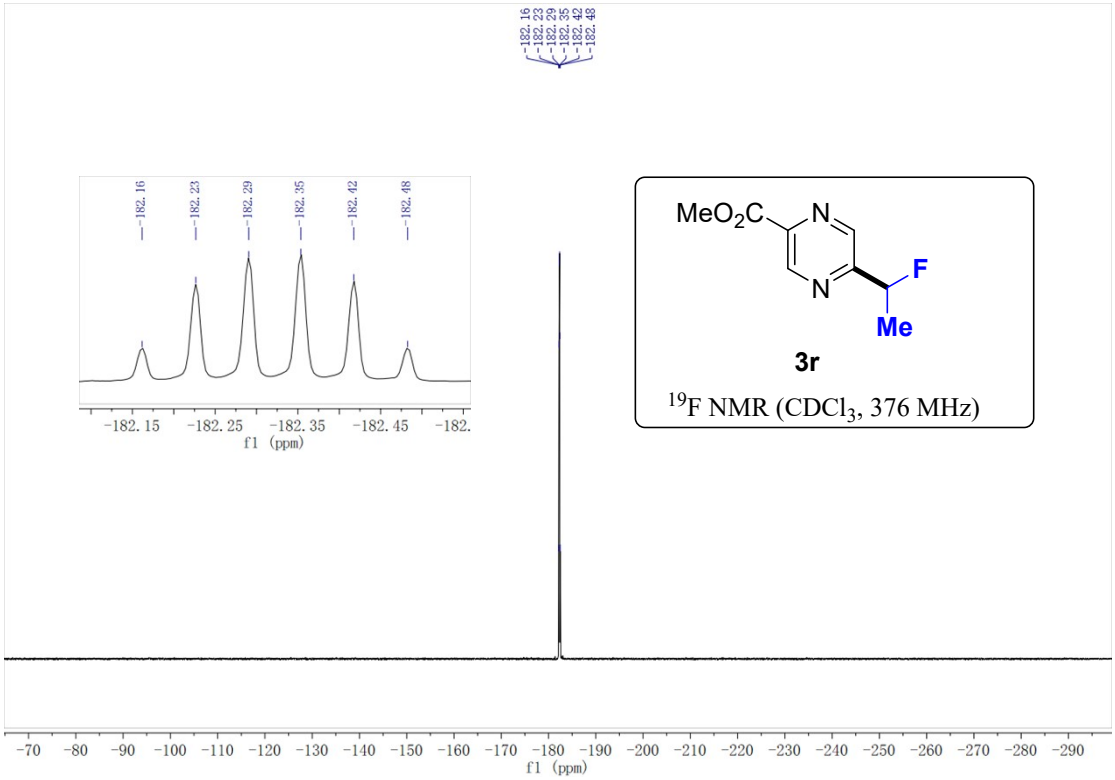

195.06
161.68
161.44
149.48
149.46
145.47
135.74
133.58
130.11
128.65
122.01
118.49
118.41
91.96
90.25
77.32
77.00
76.68
21.68
21.45
O
F
Me
N
3p
13C NMR (CDCl3, 100 MHz)
f1 (ppm)

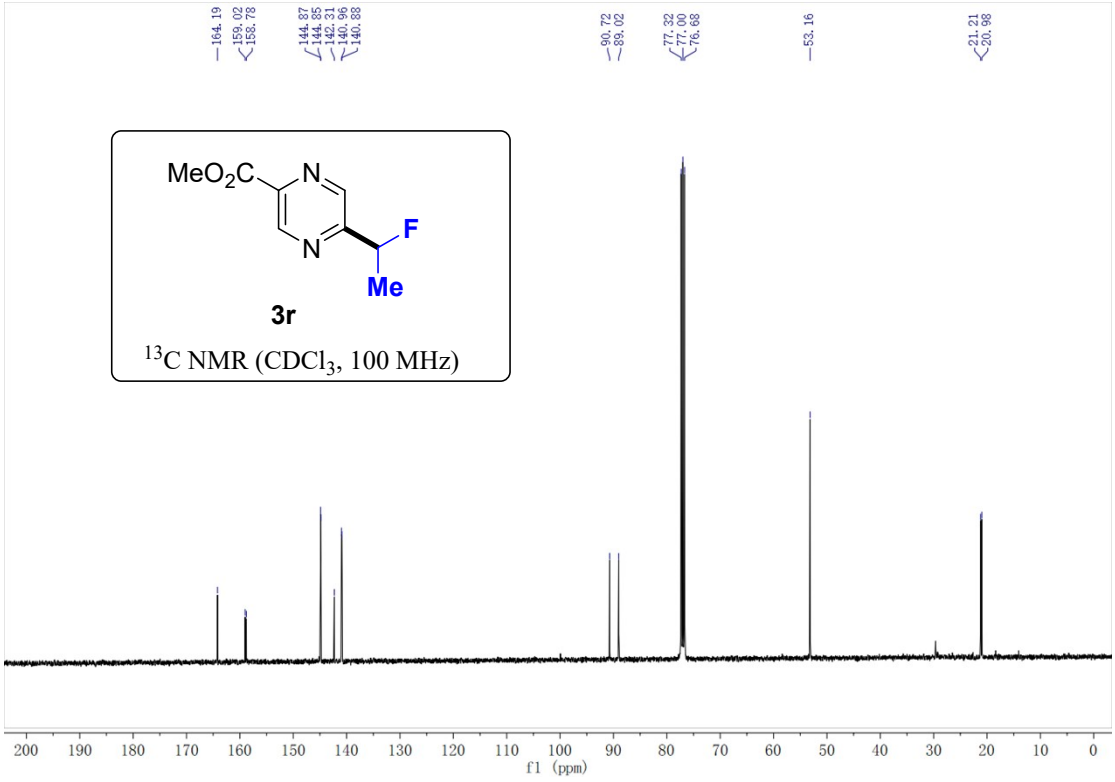

OHC
F
Me
N
3q
1H NMR (CDCl3, 400 MHz)
f1 (ppm)

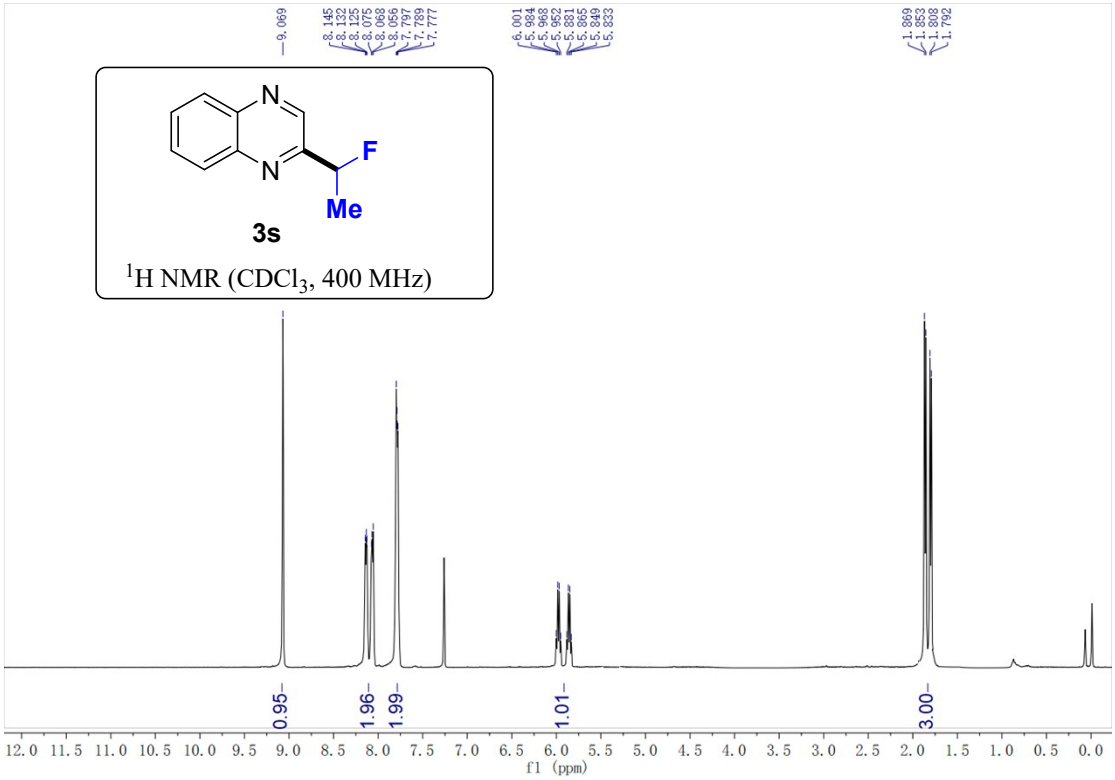

OHC
F
Me
N
3q
19F NMR (CDCl3, 376 MHz)
f1 (ppm)

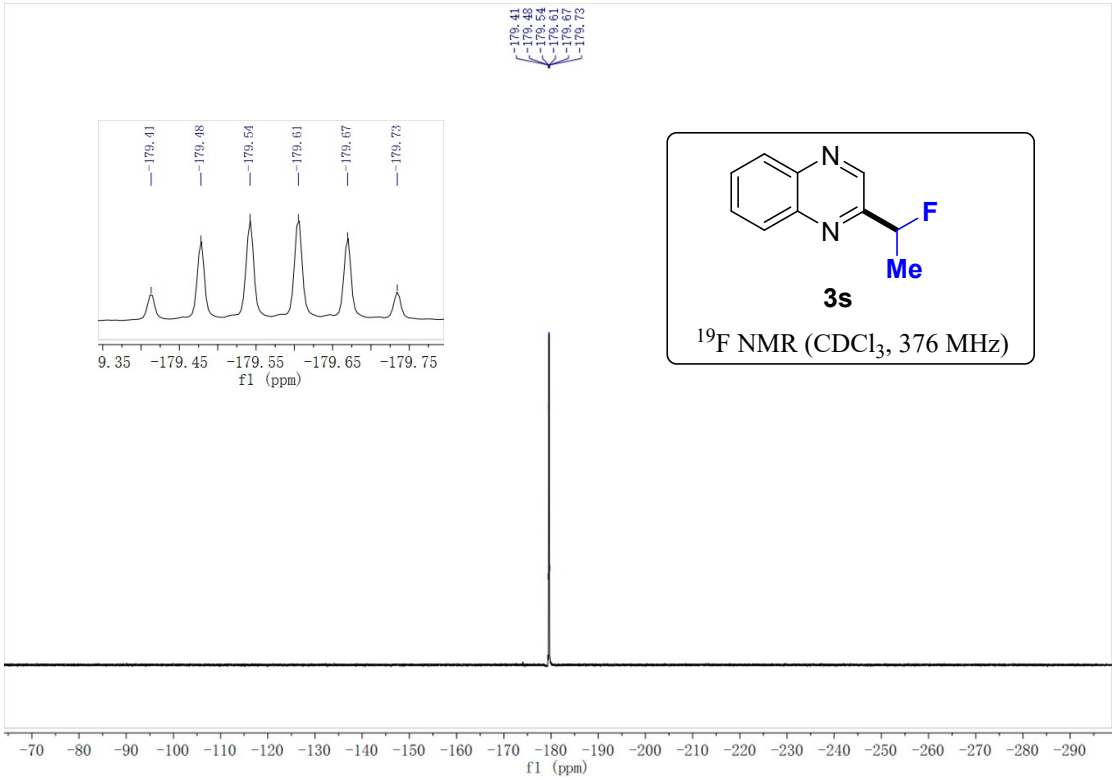

191.62
161.78
161.55
149.62
149.60
147.96
143.93
136.49
130.39
127.79
120.85
117.20
117.12
92.17
90.48
77.32
77.00
76.68
21.84
21.61
OHC
F
Me
N
3q
^{13}C NMR ($CDCl_3$, 100 MHz)
f1 (ppm)

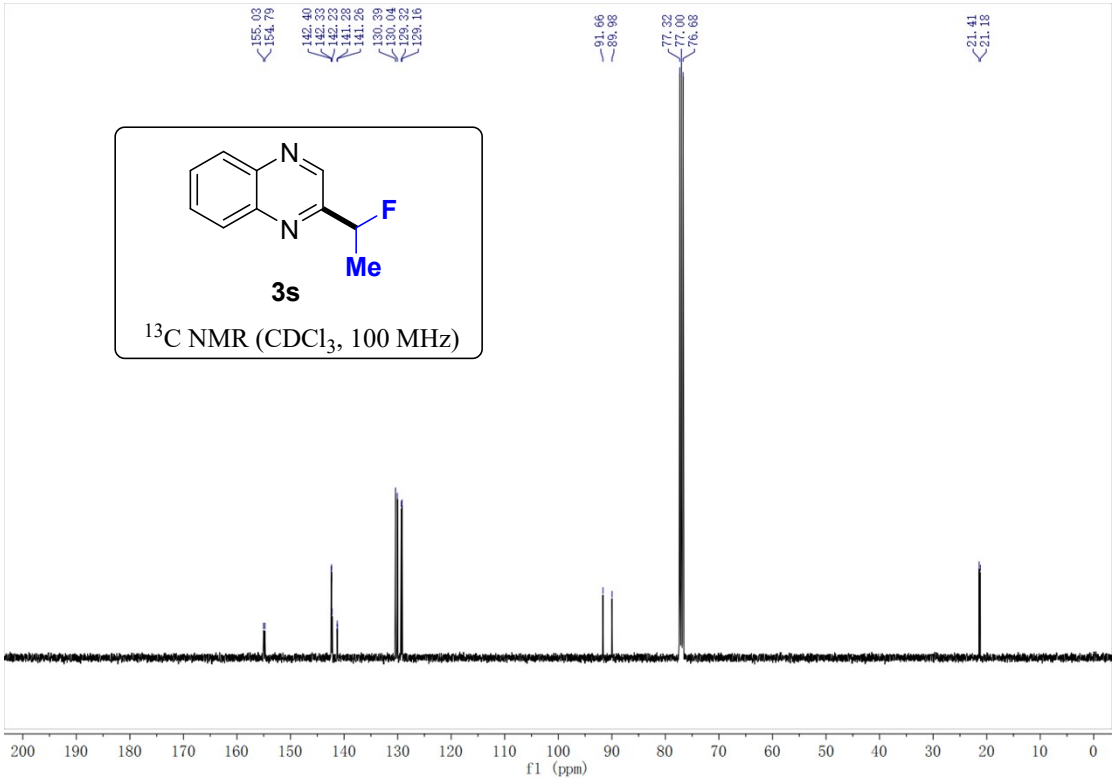

9.221
8.873
5.881
5.865
5.849
5.833
5.762
5.747
5.730
5.714
4.035
1.770
1.754
1.709
1.693
MeO_2C
N
N
F
Me
3r
^{1}H NMR ($CDCl_3$, 400 MHz)
1.00
1.00
1.00
3.01
3.00
f1 (ppm)

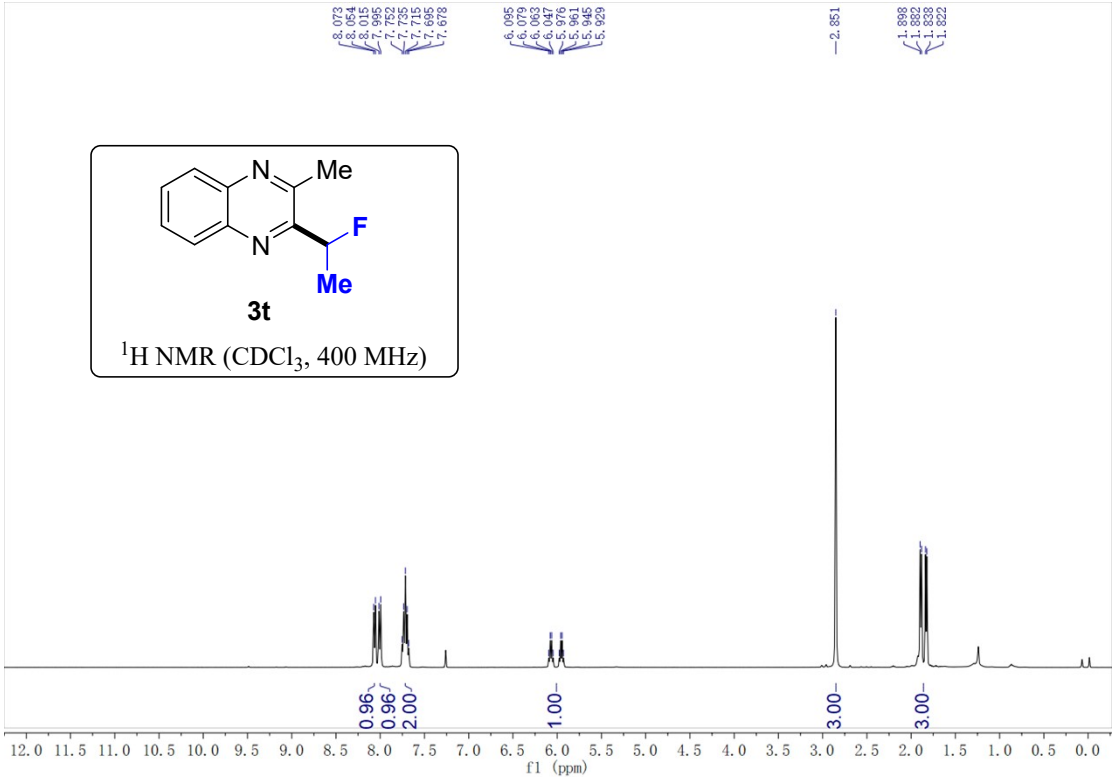

−182.16
−182.23
−182.29
−182.35
−182.42
−182.48
−182.15
−182.25
−182.35
−182.45
−182.
f1 (ppm)
MeO2C
N
N
F
Me
3r
19F NMR (CDCl3, 376 MHz)
−70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210 −220 −230 −240 −250 −260 −270 −280 −290
f1 (ppm)

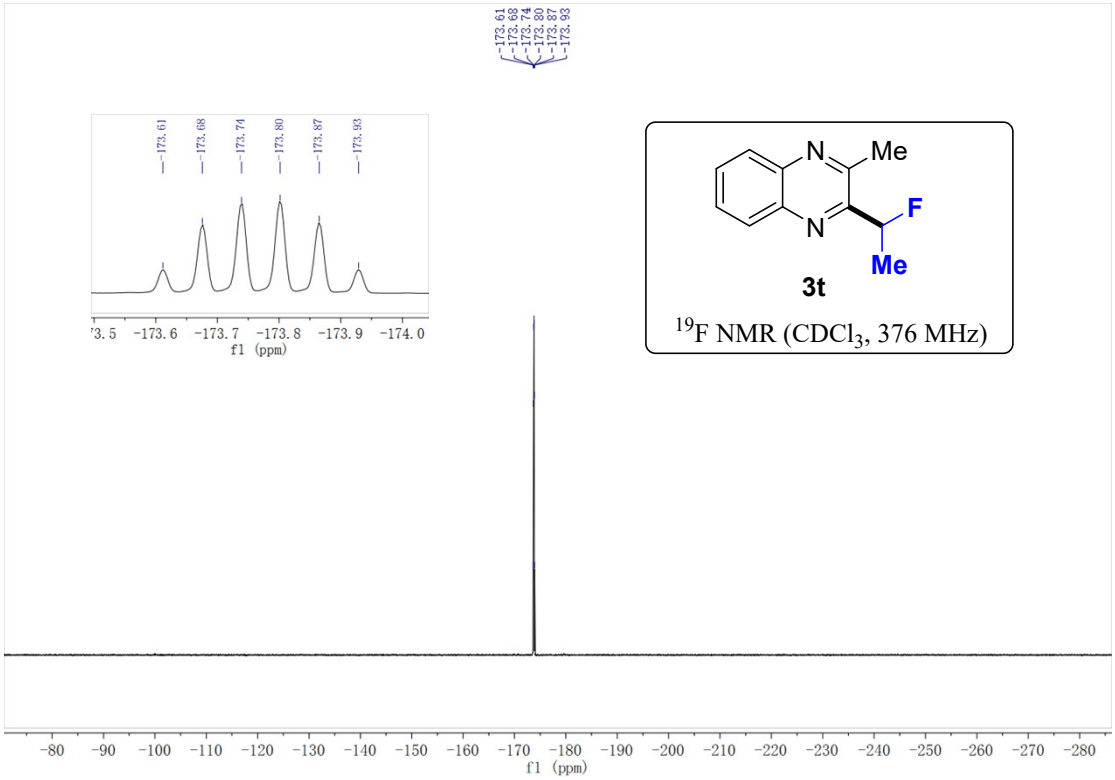

164.19
159.02
158.78
144.87
144.85
142.31
140.96
140.88
90.72
89.02
77.32
77.00
76.68
53.16
21.21
20.98
MeO2C
N
N
F
Me
3r
13C NMR (CDCl3, 100 MHz)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

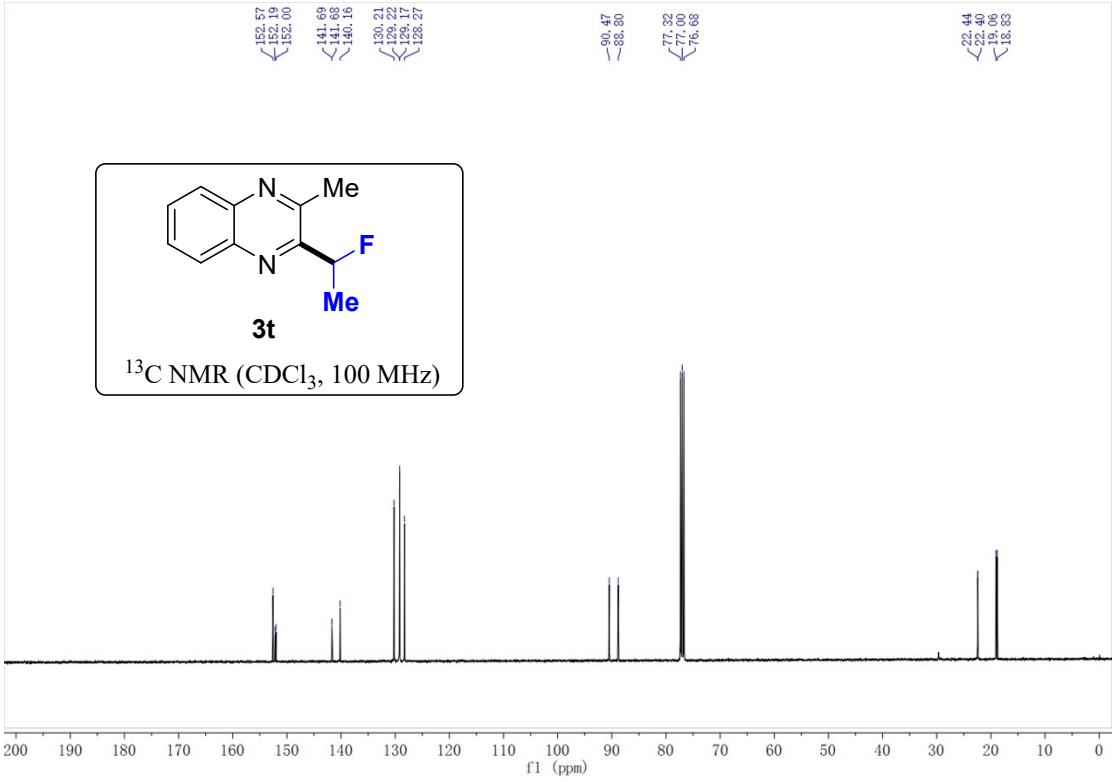

9.069
8.145
8.132
8.125
8.075
8.068
8.065
7.797
7.789
7.777
6.001
5.984
5.968
5.952
5.881
5.865
5.849
5.833
1.869
1.853
1.808
1.792
N
N
F
Me
3s
^{1}H NMR ($CDCl_3$, 400 MHz)
0.95
1.96
1.99
1.01
3.00
f1 (ppm)

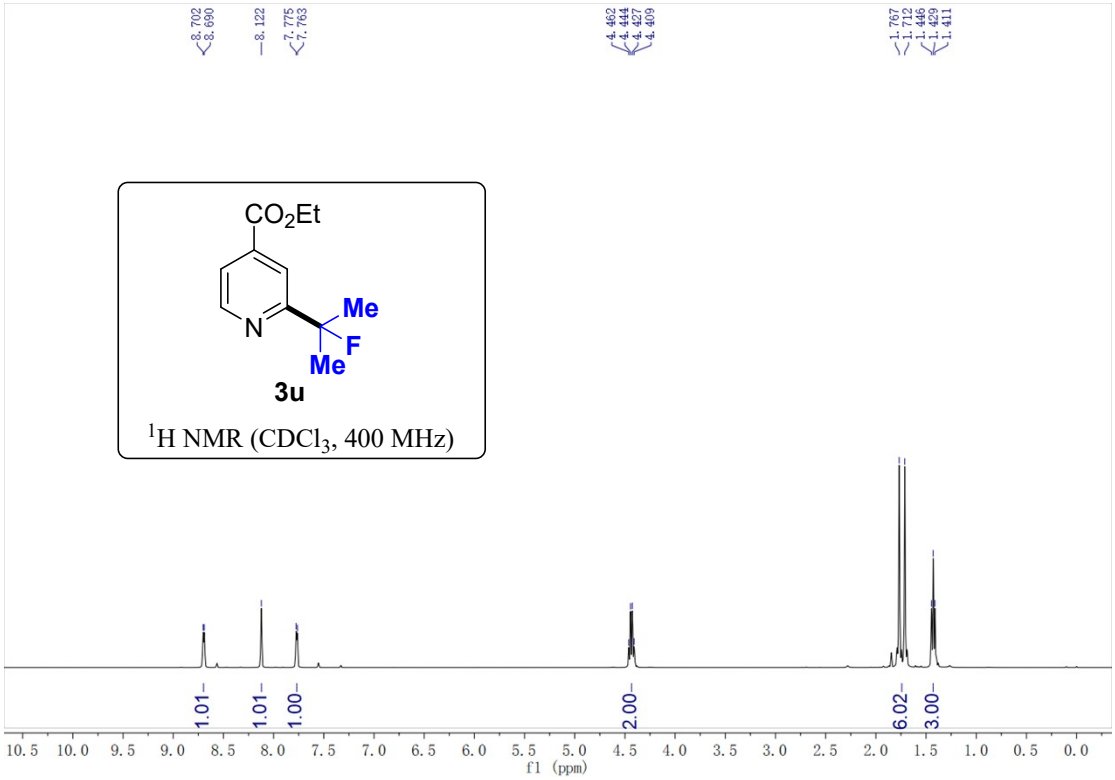

-179.41
-179.48
-179.54
-179.61
-179.67
-179.73
f1 (ppm)
N
N
F
Me
3s
^{19}F NMR ($CDCl_3$, 376 MHz)
f1 (ppm)

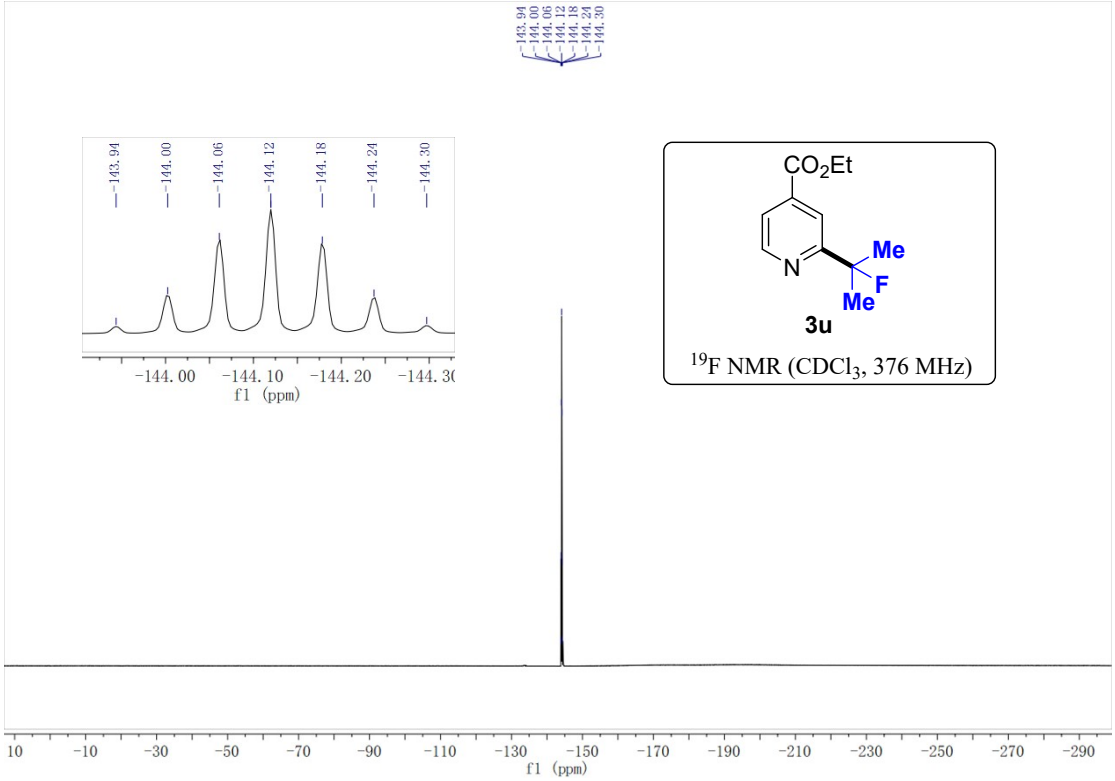

155.03
154.79
142.40
142.33
142.23
141.28
141.26
130.39
130.04
129.32
129.16
91.66
89.98
77.32
77.00
76.68
21.41
21.18
N
N
F
Me
3s
^{13}C NMR (CDCl$_3$, 100 MHz)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

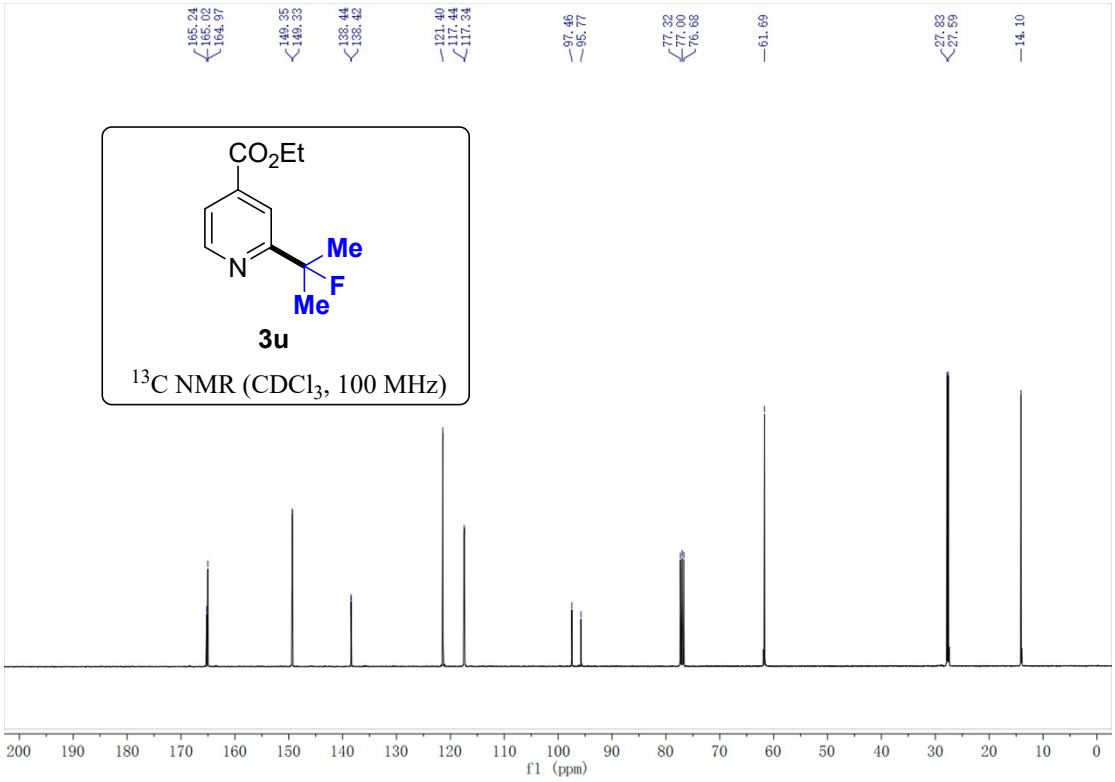

8.073
8.054
8.015
7.995
7.752
7.735
7.715
7.695
7.678
6.095
6.079
6.063
6.047
6.026
5.961
5.945
5.929
2.851
1.898
1.882
1.838
1.822
N
Me
N
F
Me
3t
^{1}H NMR (CDCl$_3$, 400 MHz)
0.96
0.96
2.00
1.00
3.00
3.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

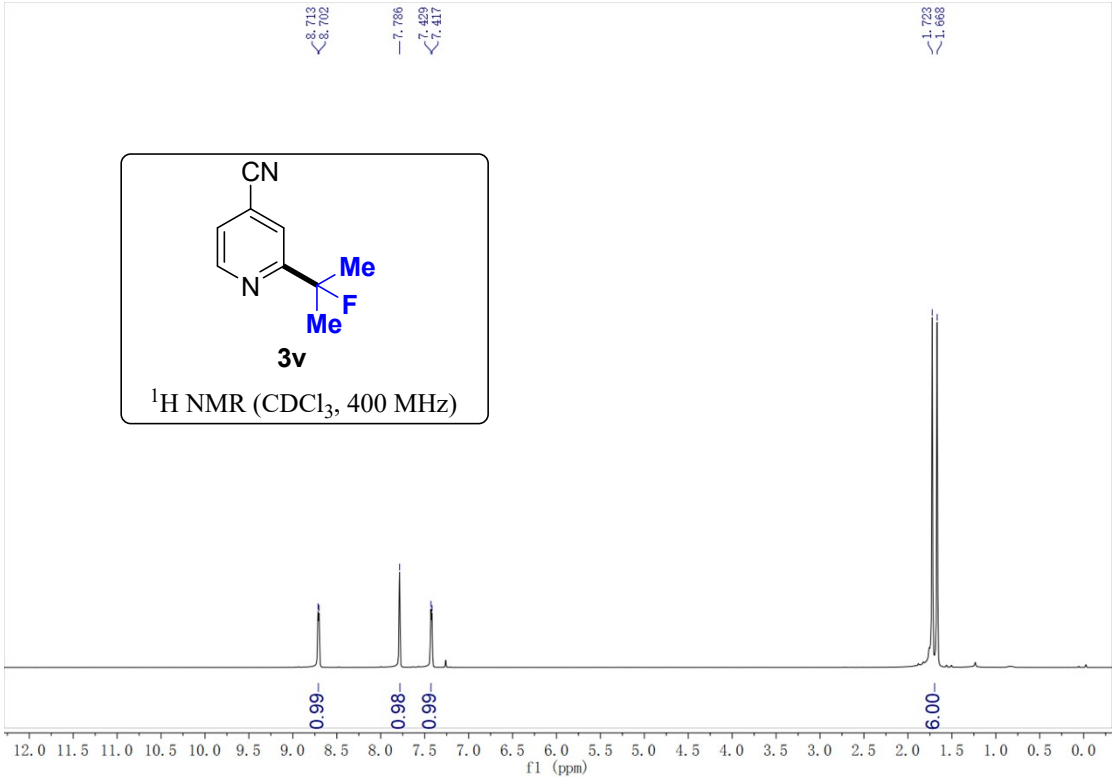

-173.61
-173.68
-173.74
-173.80
-173.87
-173.93
N
Me
F
N
Me
3t
^{19}F NMR ($CDCl_3$, 376 MHz)
f1 (ppm)

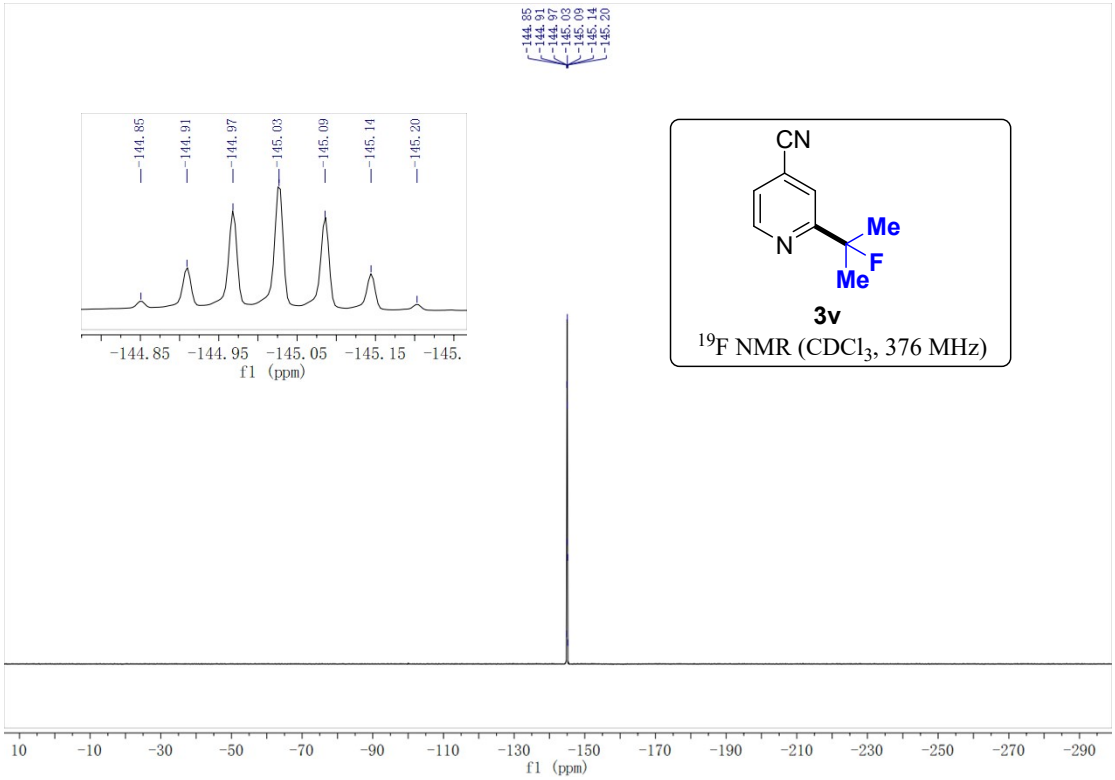

152.57
152.19
152.00
141.69
141.68
140.16
130.21
129.22
129.17
128.27
90.47
88.80
77.32
77.00
76.68
22.44
22.40
19.06
18.83
N
Me
F
N
Me
3t
^{13}C NMR ($CDCl_3$, 100 MHz)
f1 (ppm)

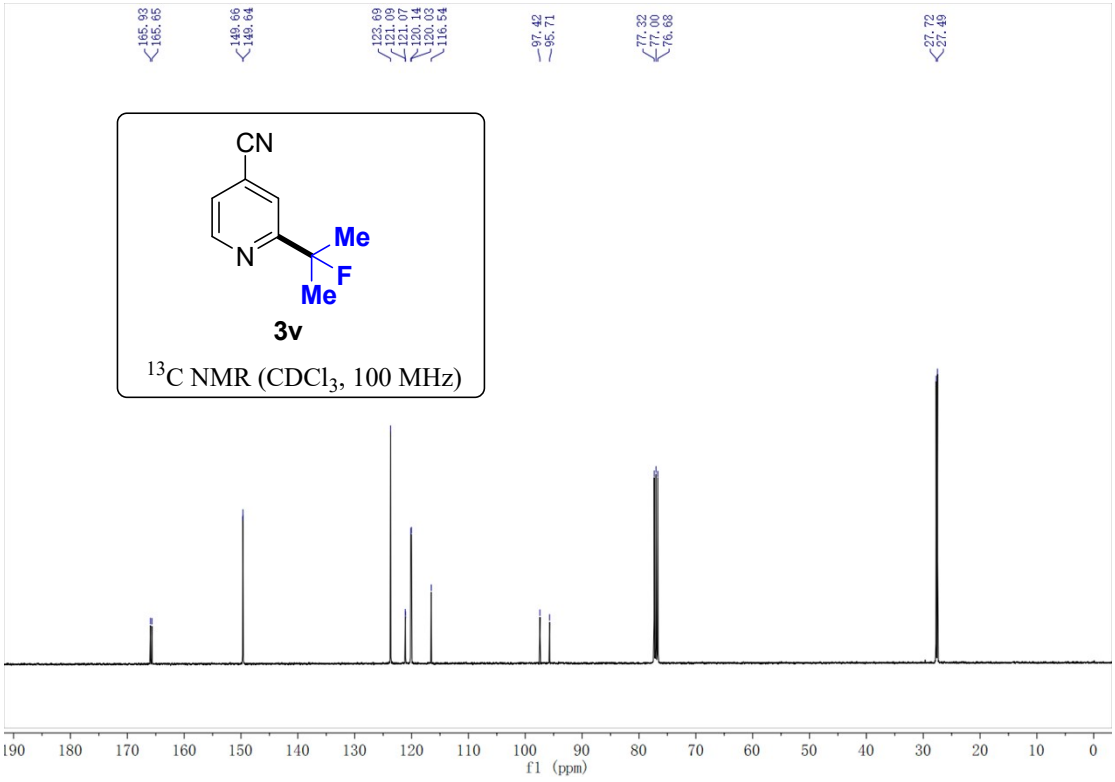

8.702
8.690
8.122
7.775
7.763
4.462
4.444
4.427
4.409
1.767
1.712
1.446
1.429
1.411
CO2Et
N
Me
F
Me
3u
1H NMR (CDCl3, 400 MHz)
1.01
1.01
1.00
2.00
6.02
3.00
f1 (ppm)

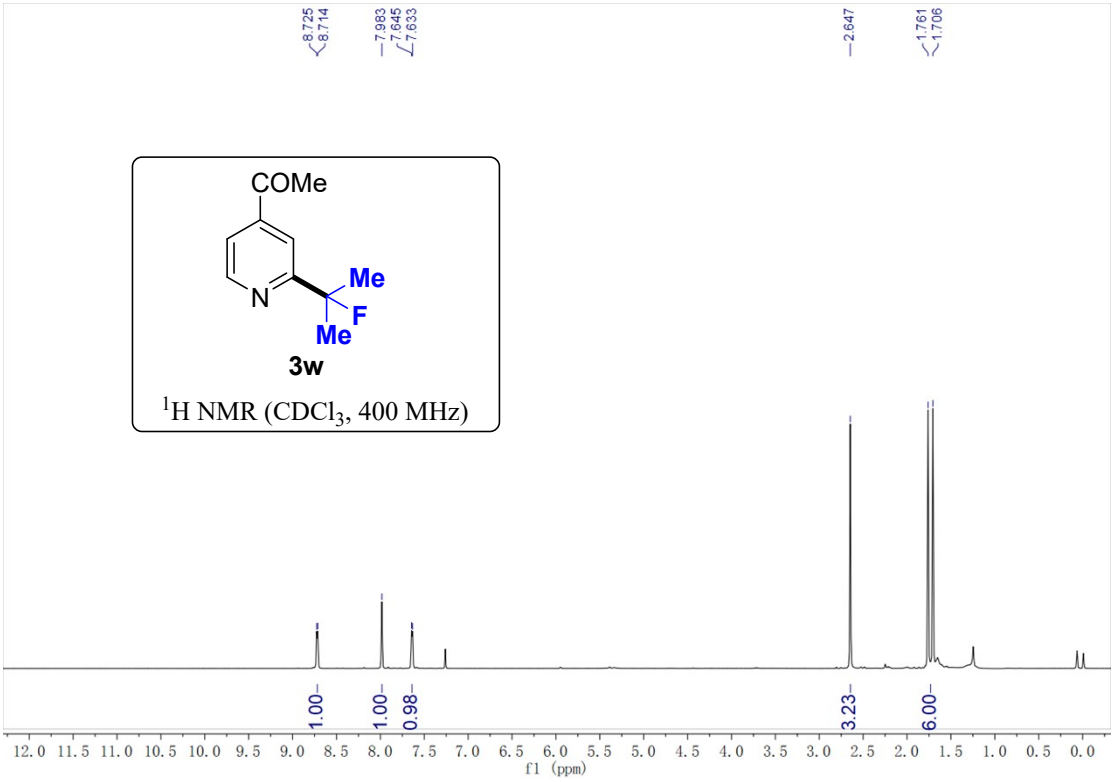

143.94
144.00
144.06
144.12
144.18
144.24
144.30
f1 (ppm)
CO2Et
N
Me
F
Me
3u
19F NMR (CDCl3, 376 MHz)
f1 (ppm)

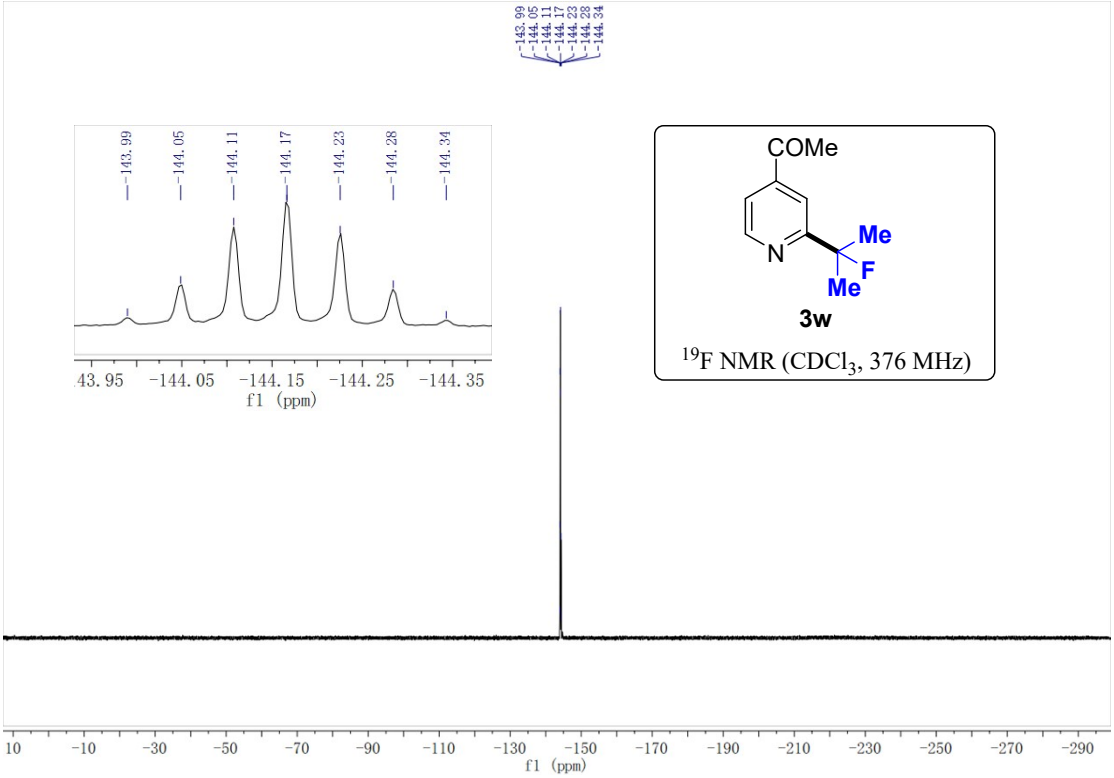

165.24
165.02
164.97
149.35
149.33
138.44
138.42
121.40
117.44
117.34
97.46
95.77
77.32
77.00
76.68
61.69
27.83
27.59
14.10
CO2Et
N
Me
F
Me
3u
13C NMR (CDCl3, 100 MHz)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

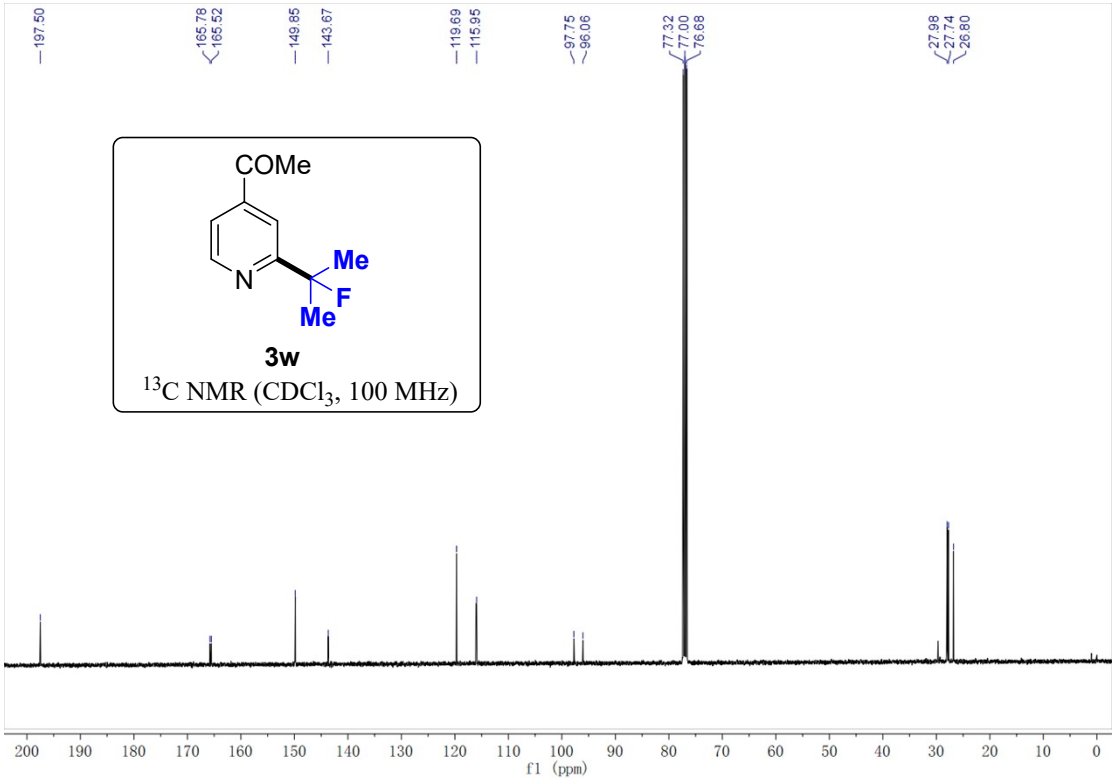

8.713
8.702
7.786
7.429
7.417
1.723
1.668
CN
N
Me
F
Me
3v
1H NMR (CDCl3, 400 MHz)
0.99
0.98
0.99
6.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

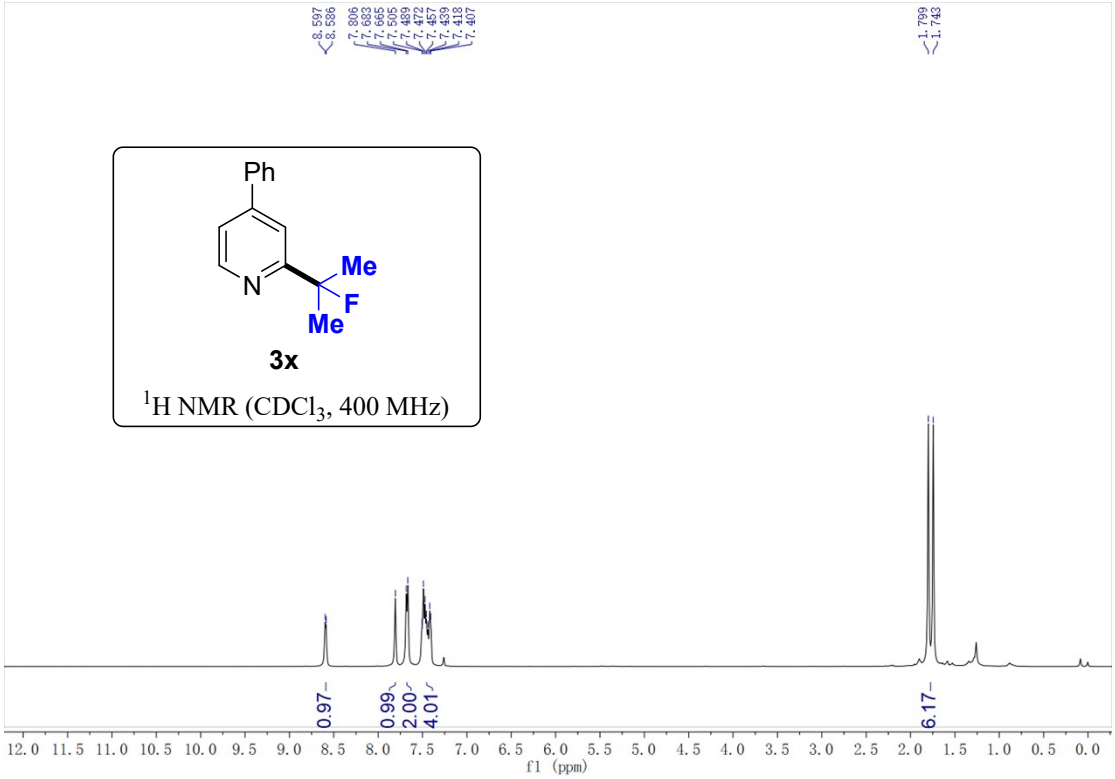

-144.85
-144.91
-144.97
-145.03
-145.09
-145.14
-145.20
-144.85 -144.95 -145.05 -145.15 -145.
f1 (ppm)
CN
N
Me
F
Me
3v
^{19}F NMR ($CDCl_3$, 376 MHz)
10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230 -250 -270 -290
f1 (ppm)

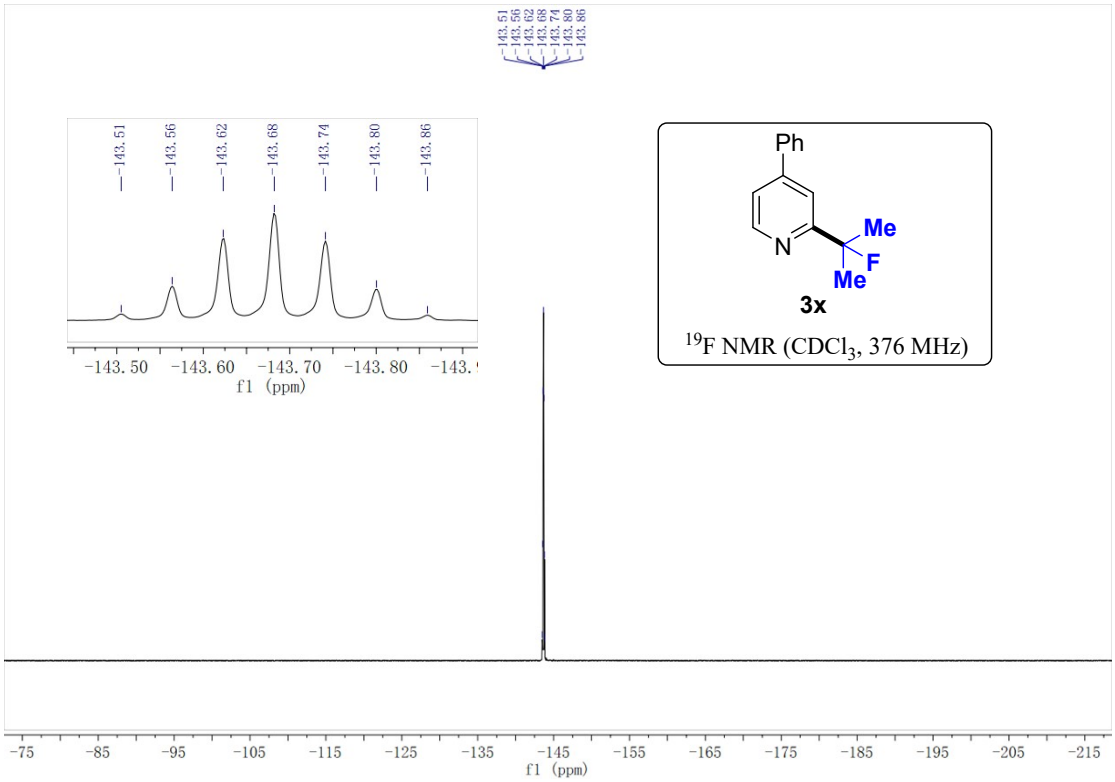

165.93
165.65
149.66
149.64
123.69
121.09
121.07
120.14
120.03
116.54
97.42
95.71
77.32
77.00
76.68
27.72
27.49
CN
N
Me
F
Me
3v
^{13}C NMR ($CDCl_3$, 100 MHz)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

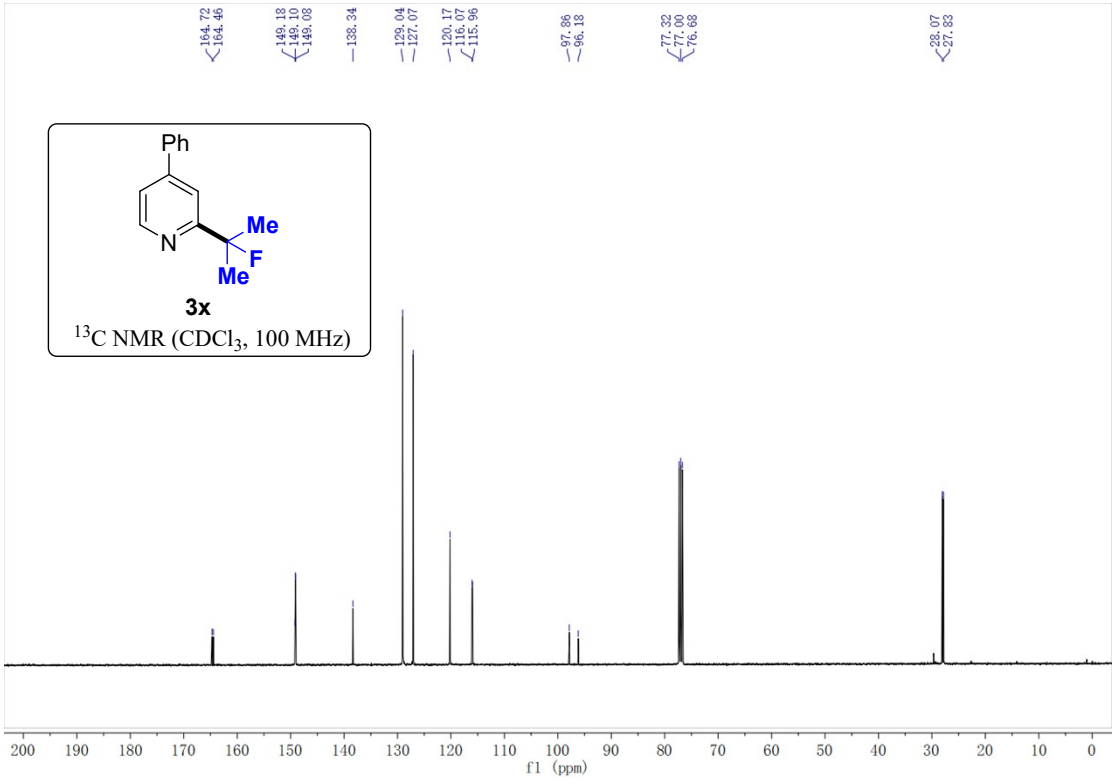

8.725
8.714
7.983
7.645
7.633
2.647
1.761
1.706
COMe
Me
F
Me
3w
^{1}H NMR ($CDCl_3$, 400 MHz)
1.00
1.00
0.98
3.23
6.00
f1 (ppm)

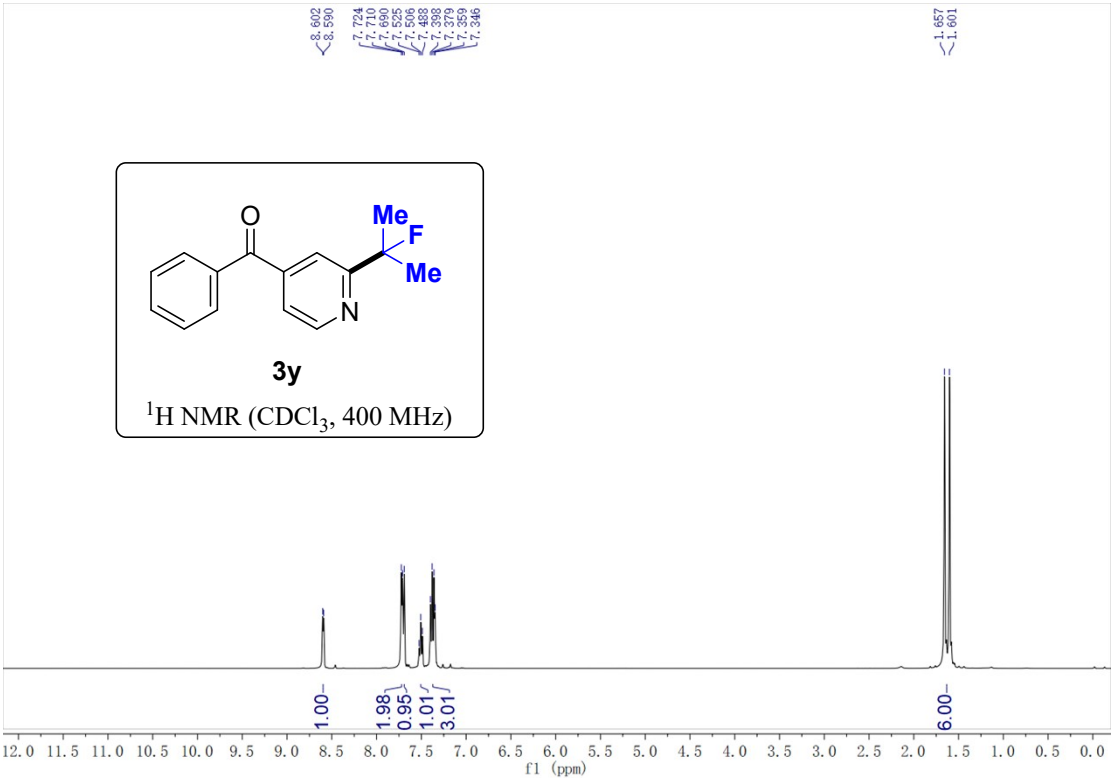

-143.99
-144.05
-144.11
-144.17
-144.23
-144.28
-144.34
f1 (ppm)
COMe
Me
F
Me
3w
^{19}F NMR ($CDCl_3$, 376 MHz)
f1 (ppm)

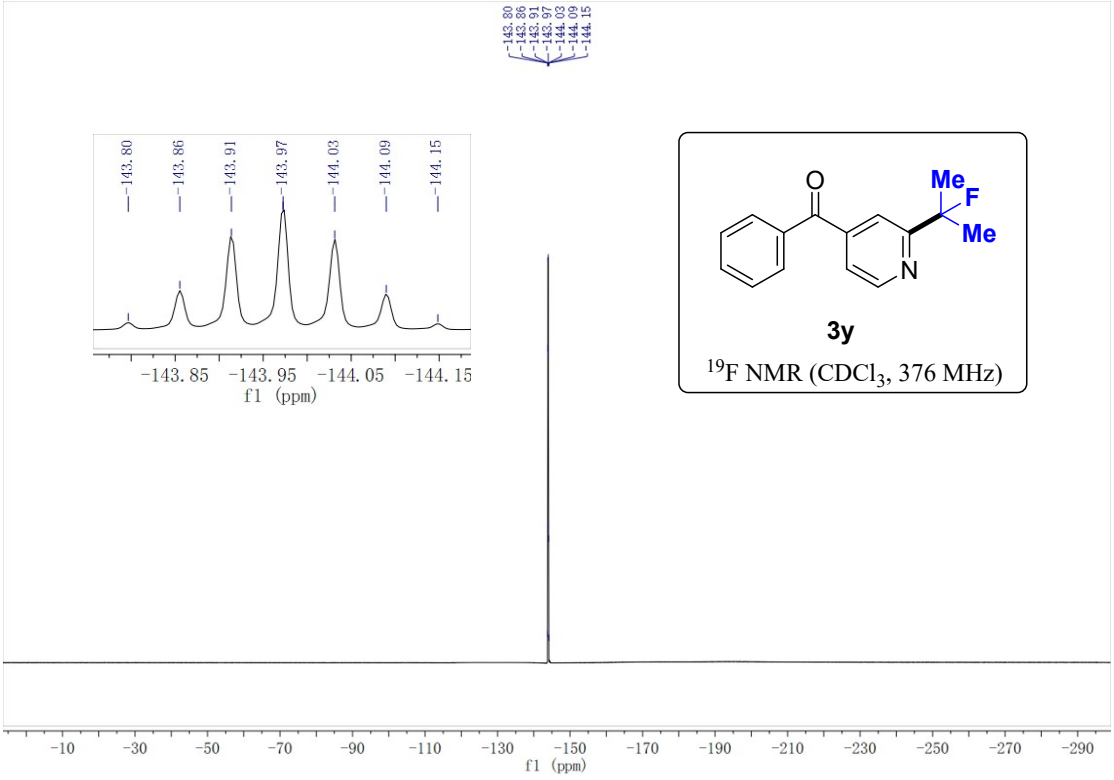

197.50
165.78
165.52
149.85
143.67
119.69
115.95
97.75
96.06
77.32
77.00
76.68
27.98
27.74
26.80
COMe
N
Me
F
Me
3w
13C NMR (CDCl3, 100 MHz)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

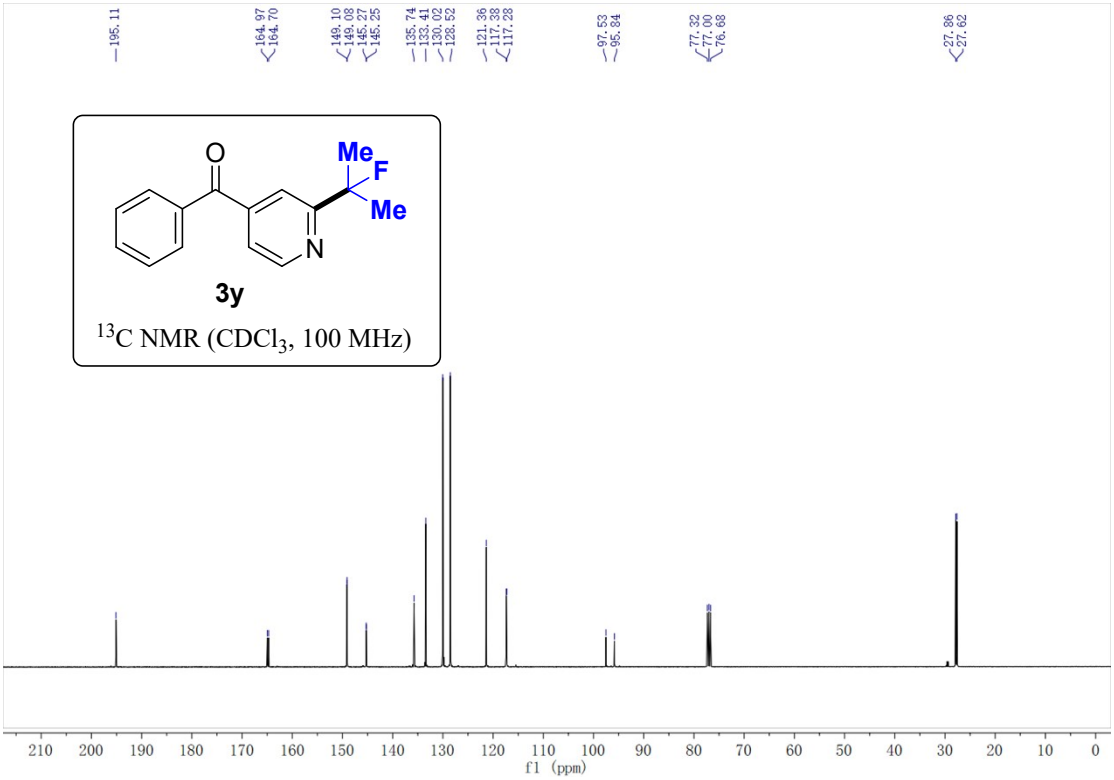

8.597
8.586
7.806
7.683
7.665
7.505
7.489
7.472
7.457
7.439
7.418
7.407
1.799
1.743
Ph
N
Me
F
Me
3x
1H NMR (CDCl3, 400 MHz)
0.97
0.99
2.00
4.01
6.17
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

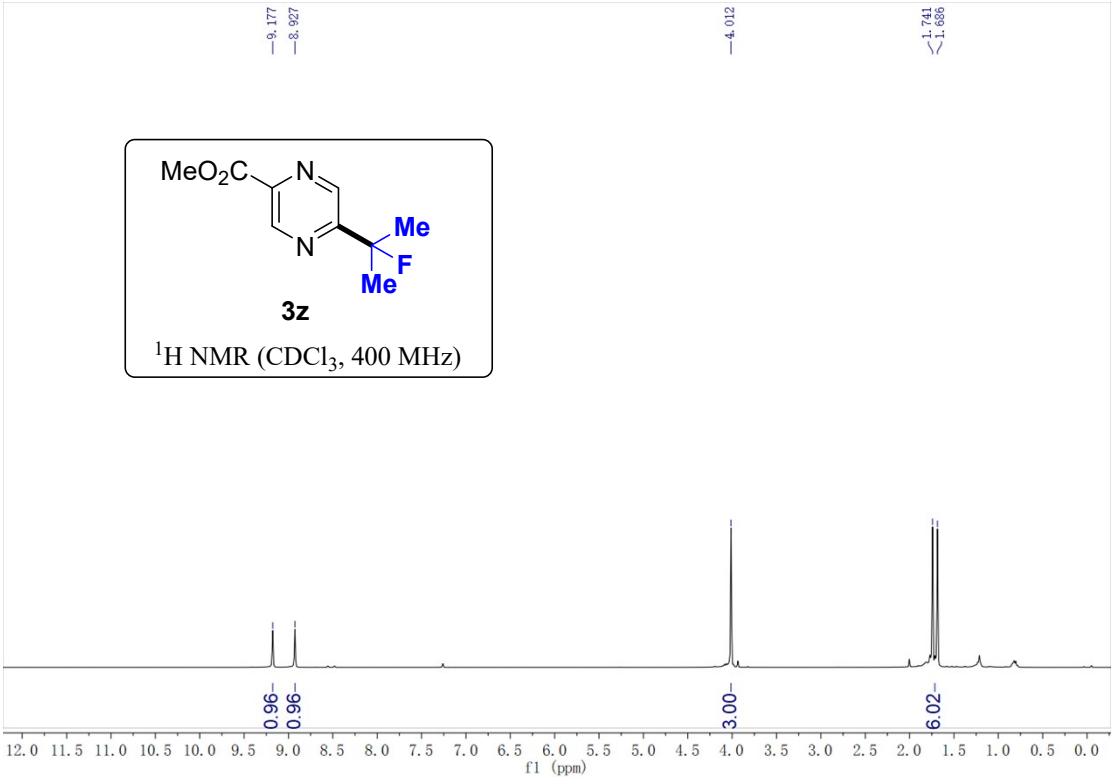

Ph
N
Me
F
Me
3x
^{19}F NMR ($CDCl_3$, 376 MHz)
f1 (ppm)

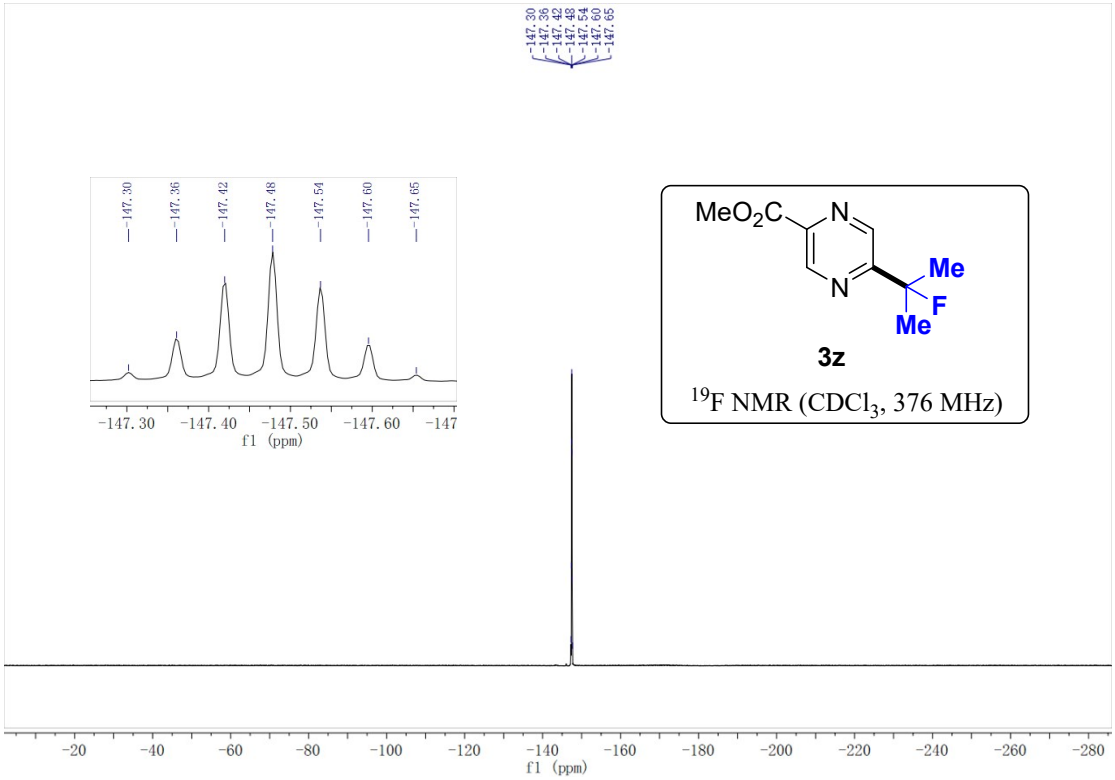

Ph
N
Me
F
Me
3x
^{13}C NMR ($CDCl_3$, 100 MHz)
f1 (ppm)

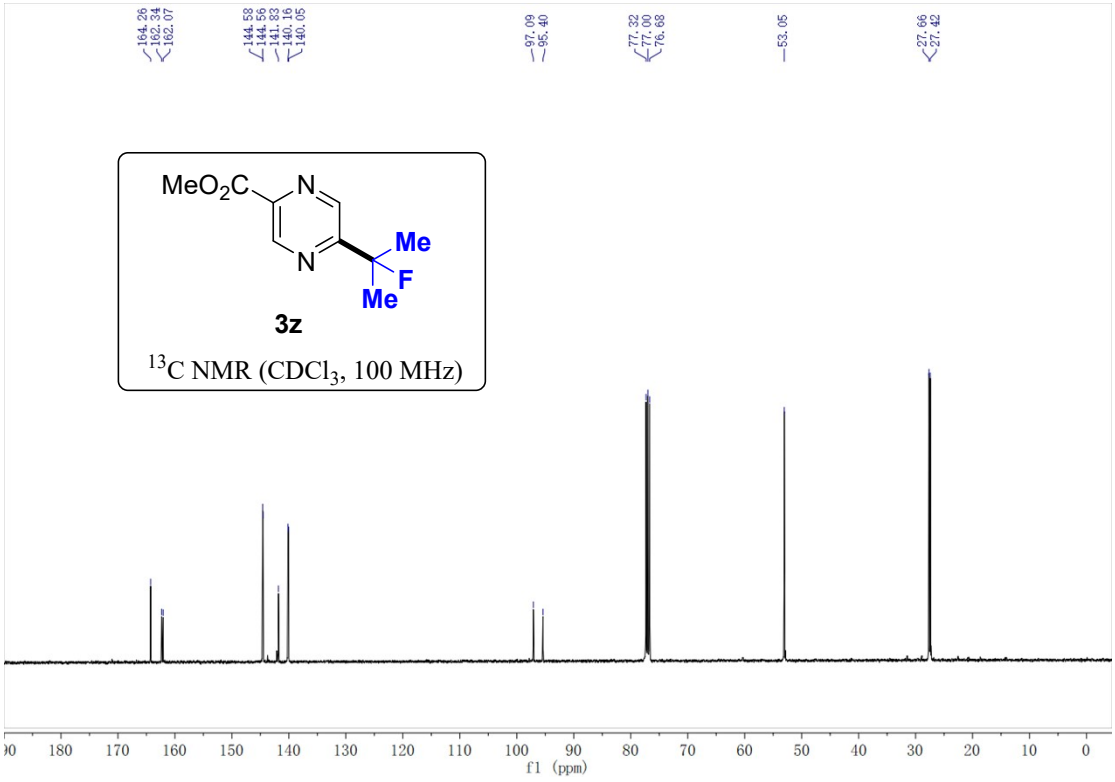

8.602
8.590
7.724
7.710
7.690
7.525
7.506
7.488
7.398
7.379
7.359
7.346
1.657
1.601
O
Me
F
Me
N
3y
1H NMR (CDCl3, 400 MHz)
1.00
1.98
0.95
1.01
3.01
6.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

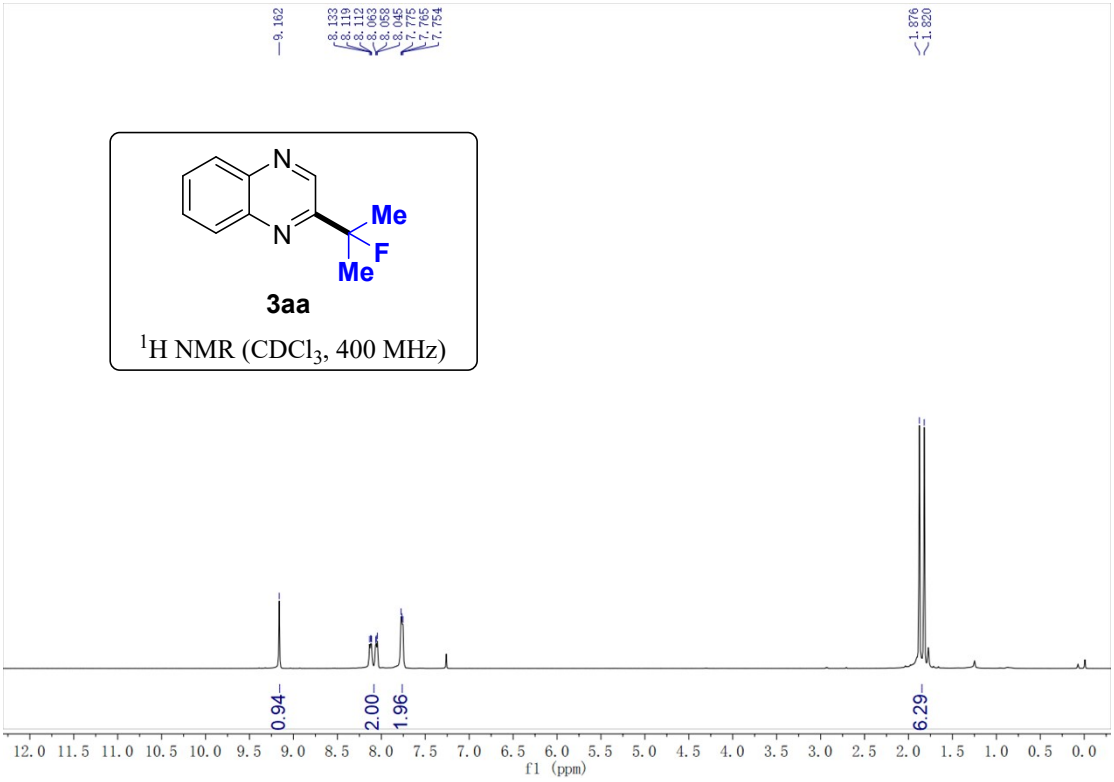

-143.80
-143.86
-143.91
-143.97
-144.03
-144.09
-144.15
-143.85 -143.95 -144.05 -144.15
f1 (ppm)
O
Me
F
Me
N
3y
19F NMR (CDCl3, 376 MHz)
-10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230 -250 -270 -290
f1 (ppm)

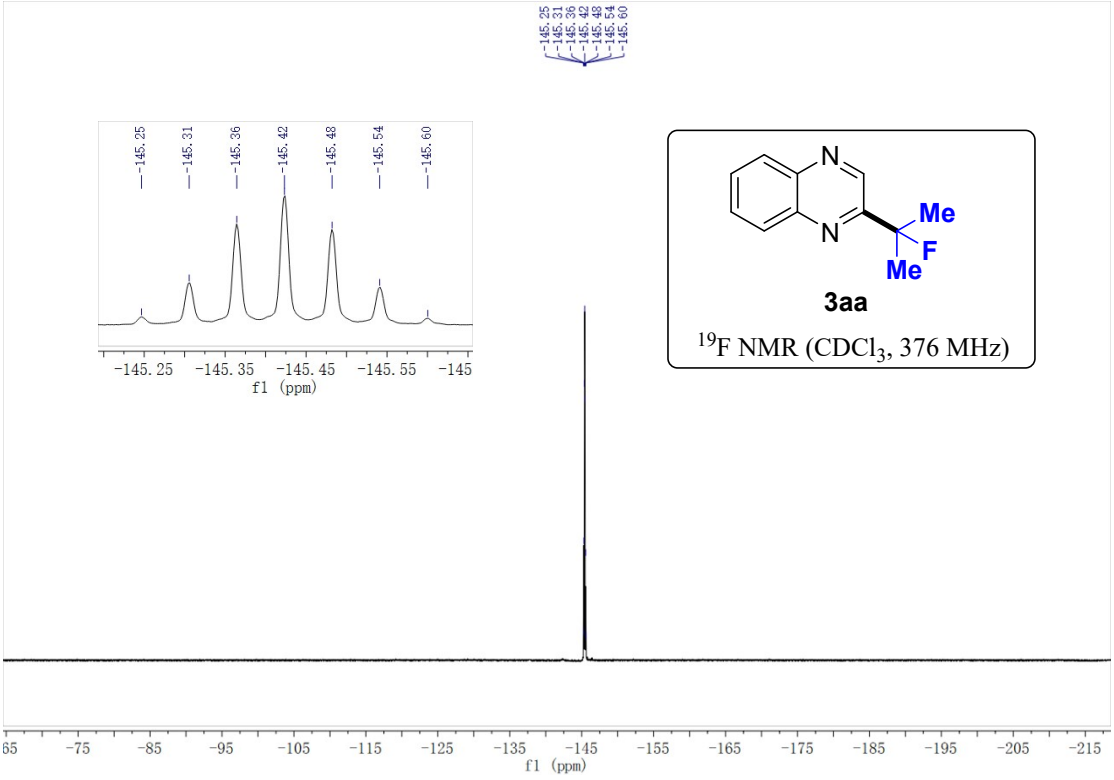

195.11
164.97
164.70
149.10
149.08
145.27
145.25
135.74
133.41
130.02
128.52
121.36
117.38
117.28
97.53
95.84
77.32
77.00
76.68
27.86
27.62
O
Me
F
Me
N
3y
13C NMR (CDCl3, 100 MHz)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

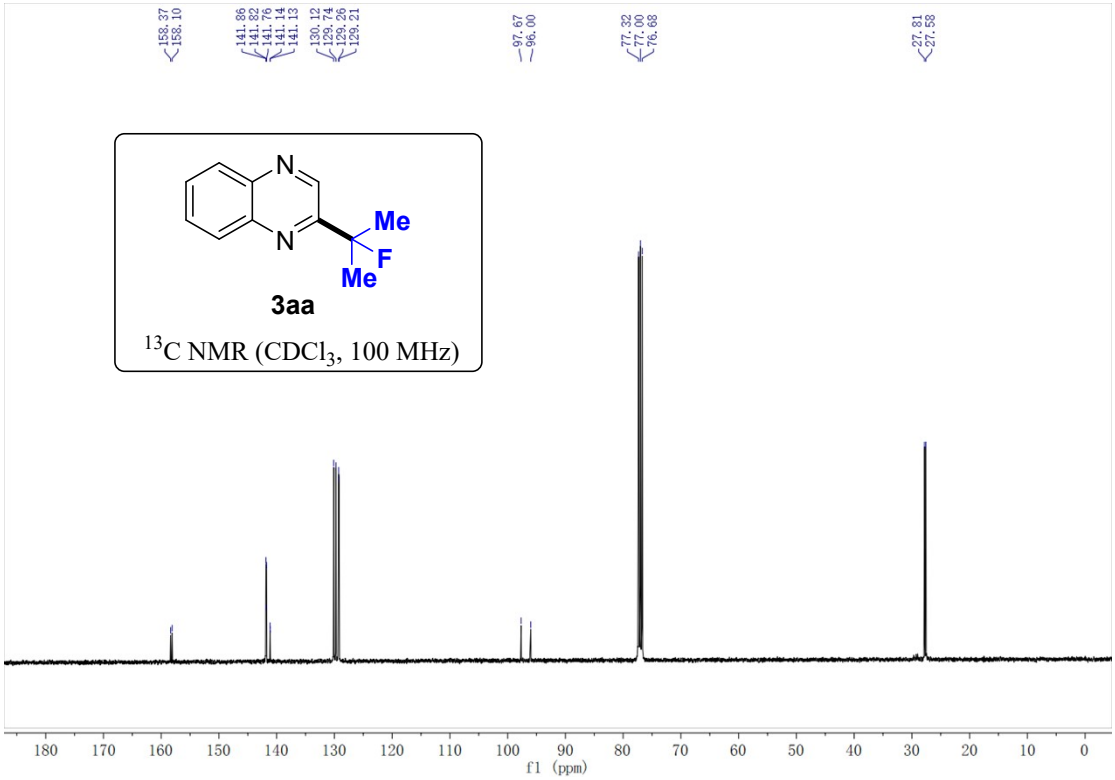

9.177
8.927
4.012
1.741
1.686
MeO2C
N
N
Me
F
Me
3z
1H NMR (CDCl3, 400 MHz)
0.96
0.96
3.00
6.02
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

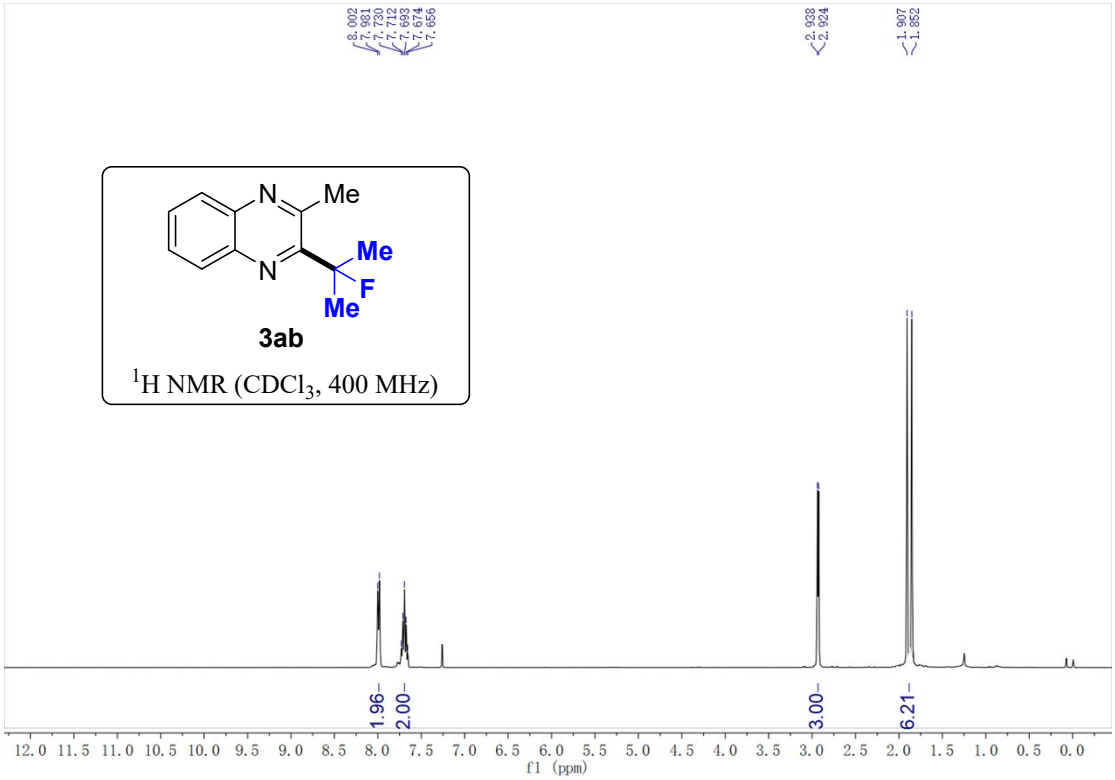

MeO2C
N
N
Me
F
Me
3z
19F NMR (CDCl3, 376 MHz)
f1 (ppm)

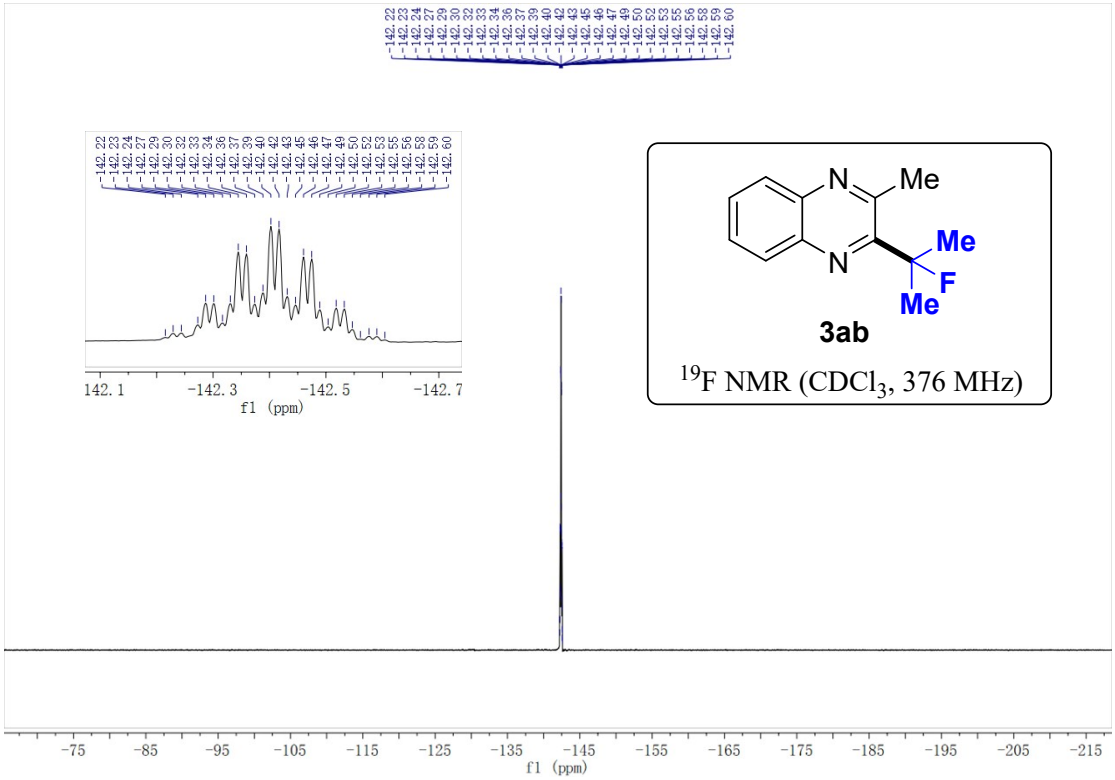

MeO2C
N
N
Me
F
Me
3z
13C NMR (CDCl3, 100 MHz)
f1 (ppm)

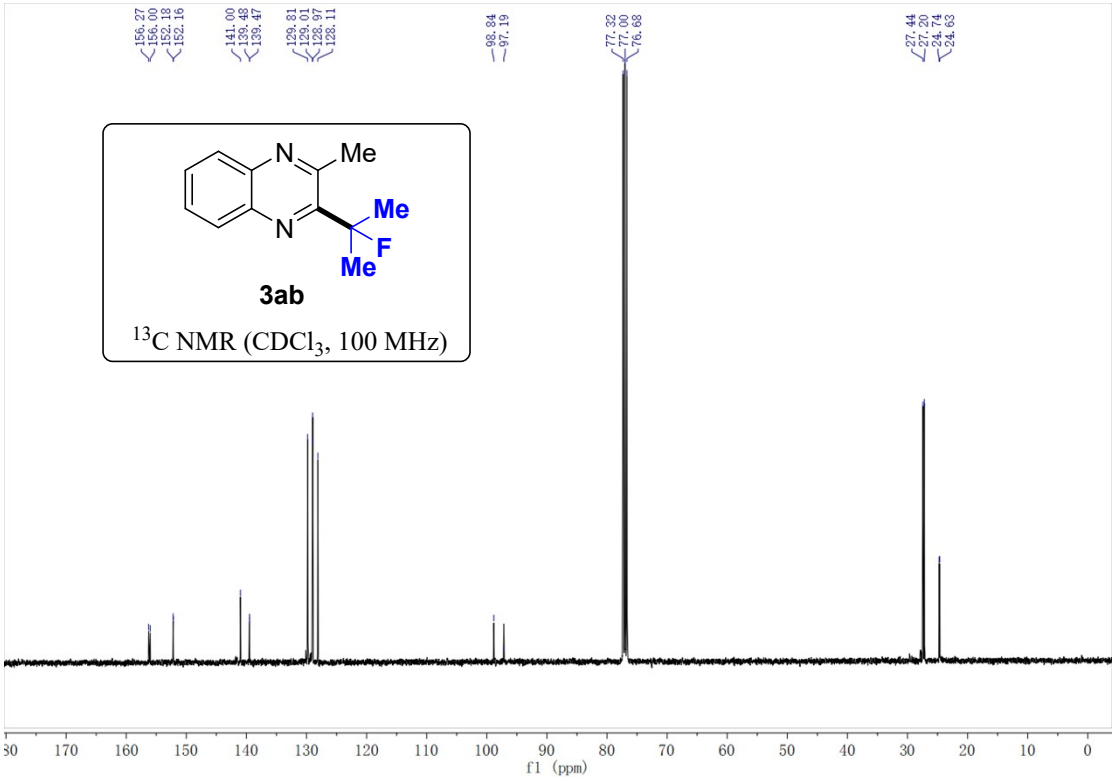

9.162
8.133
8.119
8.112
8.063
8.058
8.045
7.775
7.765
7.754
1.876
1.820
N
N
Me
F
Me
3aa
^{1}H NMR (CDCl$_3$, 400 MHz)
0.94
2.00
1.96
6.29
f1 (ppm)

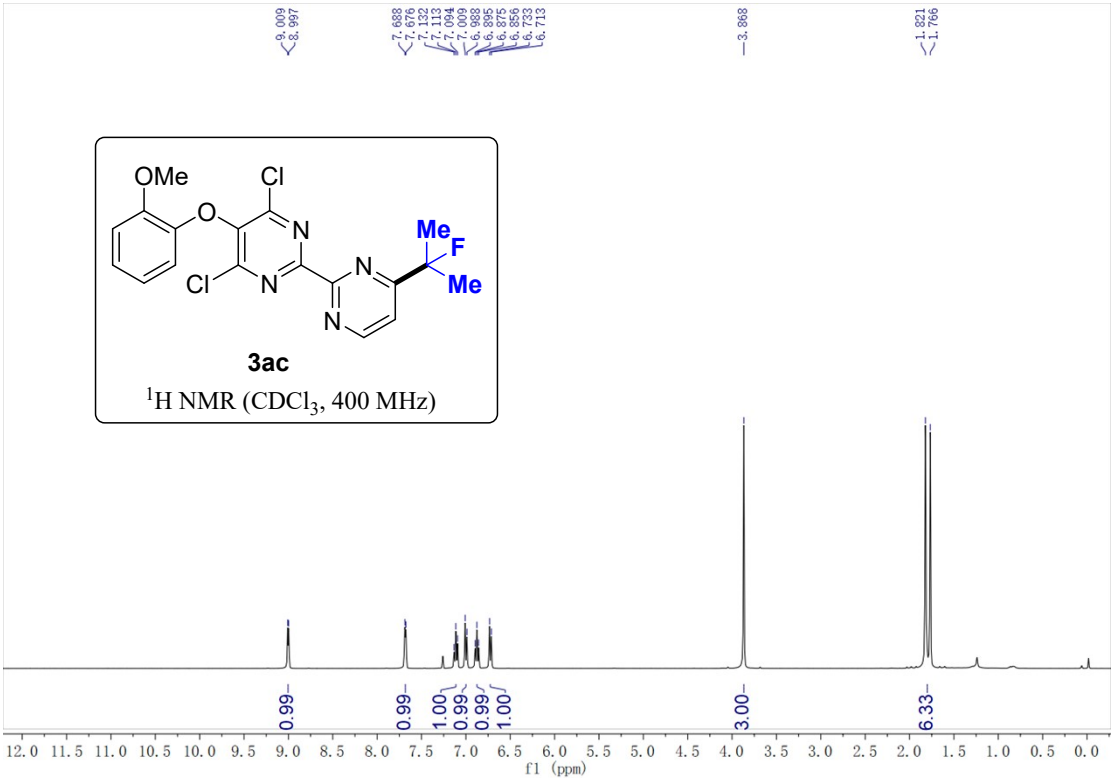

-145.25
-145.31
-145.36
-145.42
-145.48
-145.54
-145.60
f1 (ppm)
N
N
Me
F
Me
3aa
^{19}F NMR (CDCl$_3$, 376 MHz)
f1 (ppm)

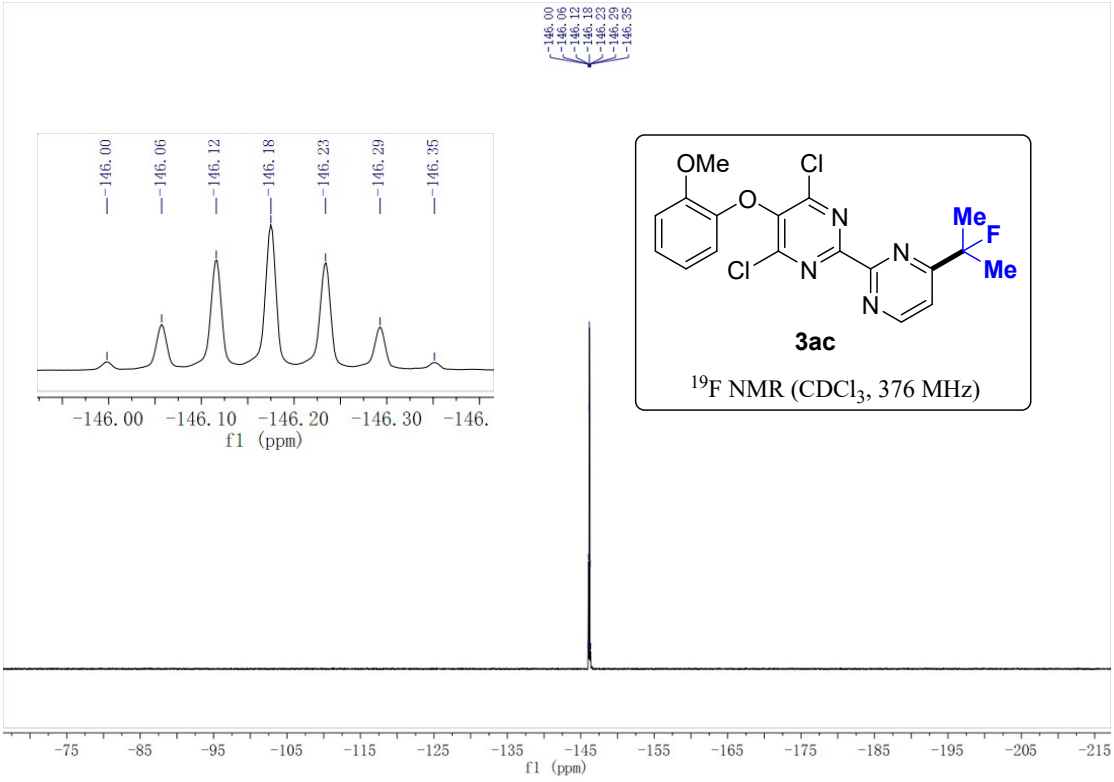

158.37
158.10
141.86
141.82
141.76
141.14
141.13
130.12
129.74
129.26
129.21
97.67
96.00
77.32
77.00
76.68
27.81
27.58
N
N
Me
F
Me
3aa
13C NMR (CDCl3, 100 MHz)
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

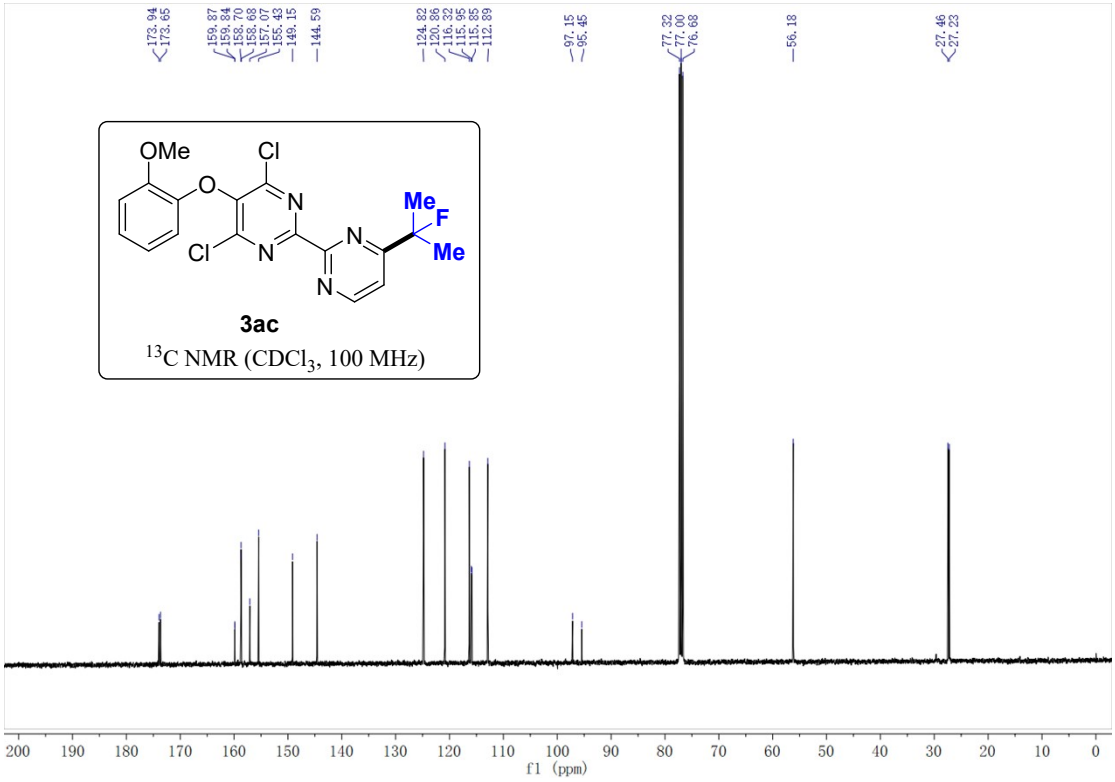

8.002
7.981
7.730
7.712
7.693
7.674
7.656
2.938
2.924
1.907
1.852
N
N
Me
Me
F
Me
3ab
1H NMR (CDCl3, 400 MHz)
1.96
2.00
3.00
6.21
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

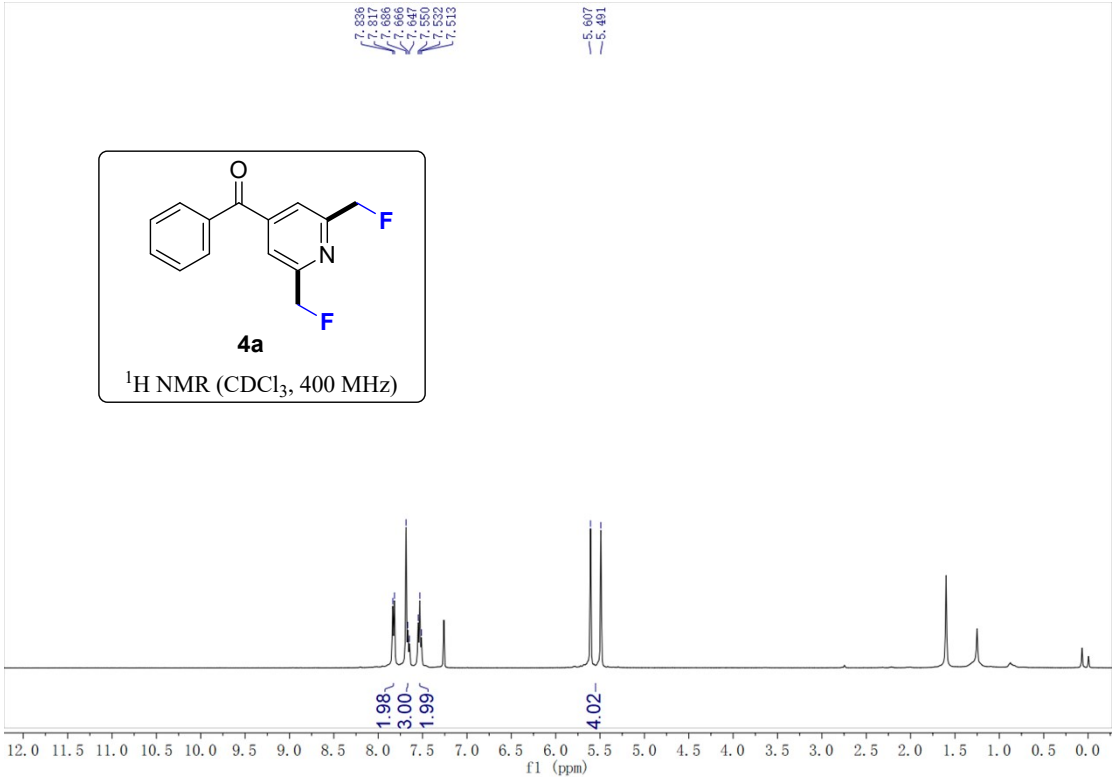

Me
Me
F
Me
3ab
19F NMR (CDCl3, 376 MHz)
f1 (ppm)

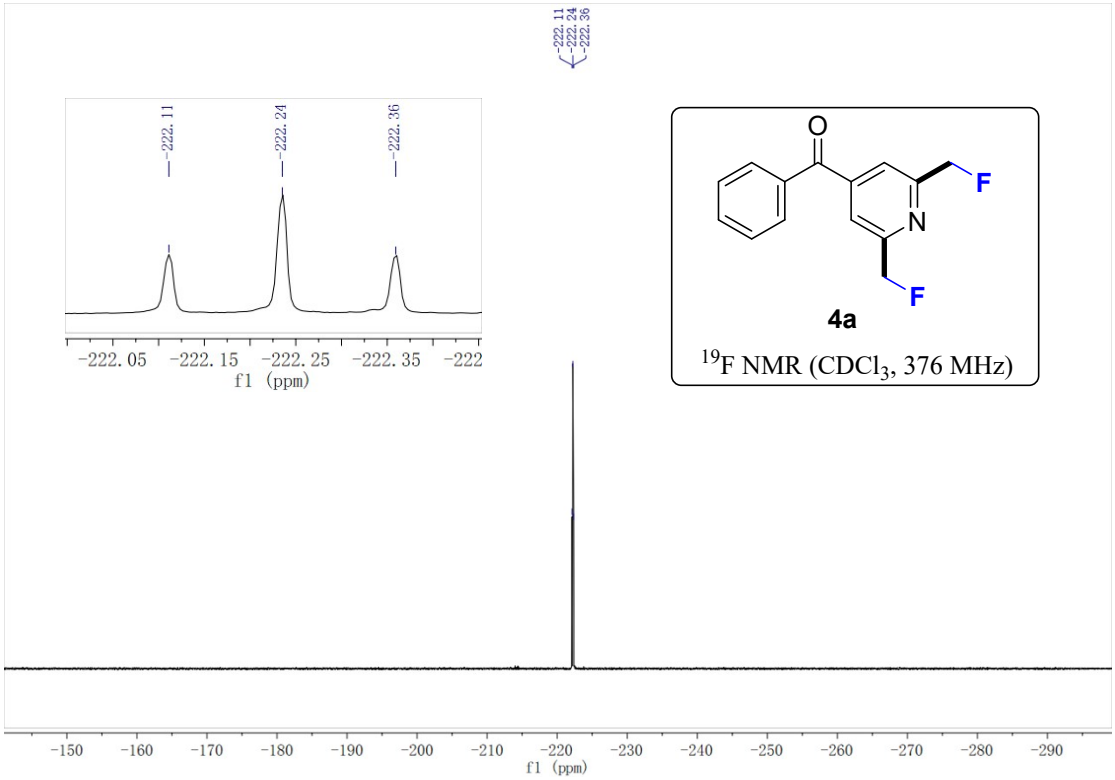

Me
Me
F
Me
3ab
13C NMR (CDCl3, 100 MHz)
f1 (ppm)

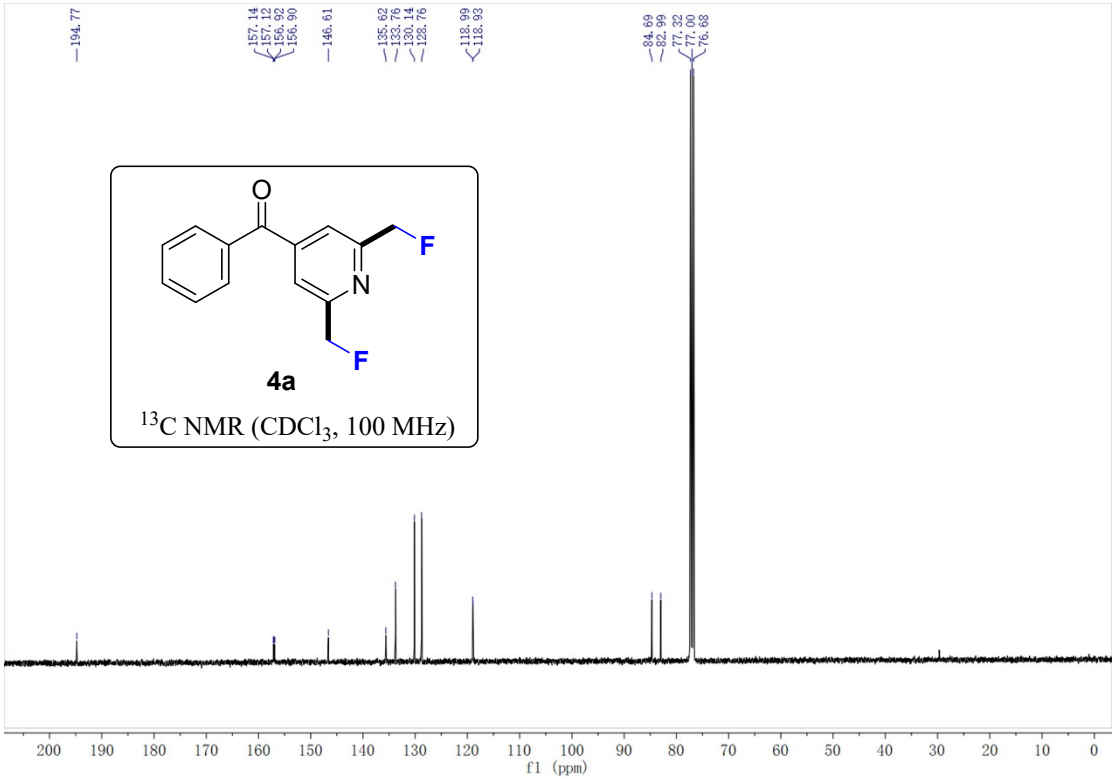

9.009
8.997
7.688
7.676
7.132
7.113
7.094
7.090
6.988
6.895
6.875
6.856
6.733
6.713
3.868
1.821
1.766
OMe
Cl
O
N
Cl
N
N
N
Me
F
Me
3ac
^{1}H NMR ($CDCl_3$, 400 MHz)
0.99
0.99
1.00
0.99
0.99
1.00
3.00
6.33
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

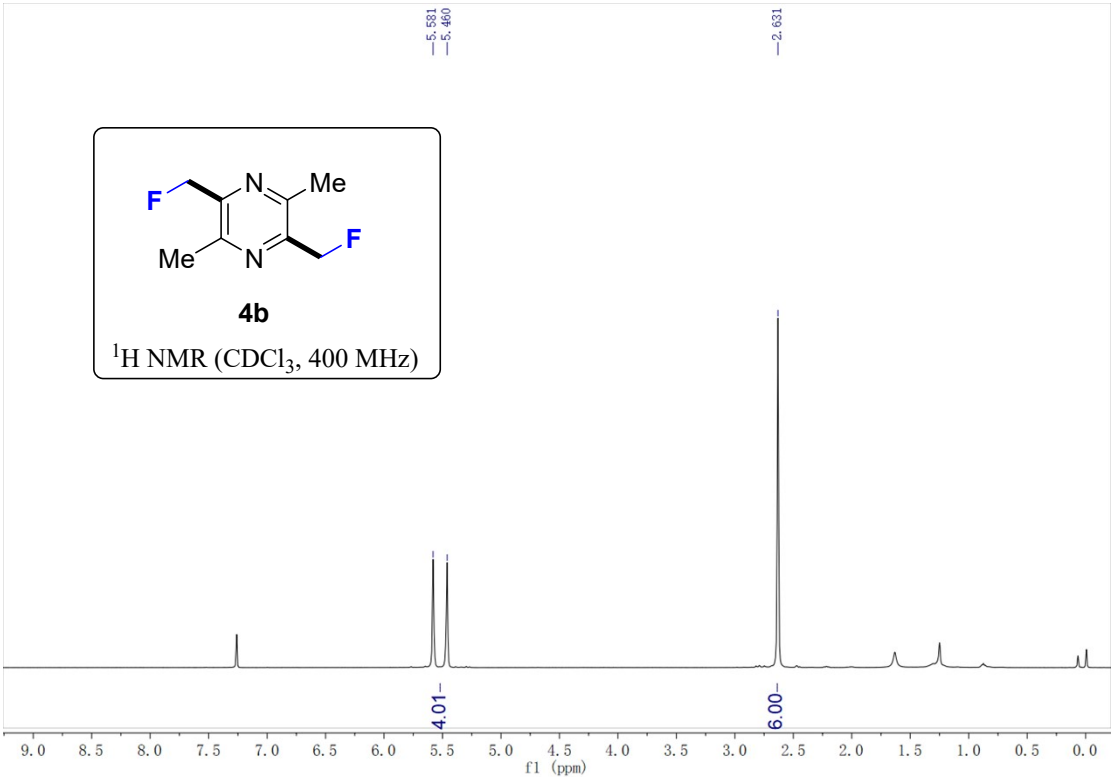

146.00
146.06
146.12
146.18
146.23
146.29
146.35
−146.00
−146.06
−146.12
−146.18
−146.23
−146.29
−146.35
−146.00 −146.10 −146.20 −146.30 −146.
f1 (ppm)
OMe
Cl
O
N
Cl
N
N
N
Me
F
Me
3ac
^{19}F NMR ($CDCl_3$, 376 MHz)
−75 −85 −95 −105 −115 −125 −135 −145 −155 −165 −175 −185 −195 −205 −215
f1 (ppm)

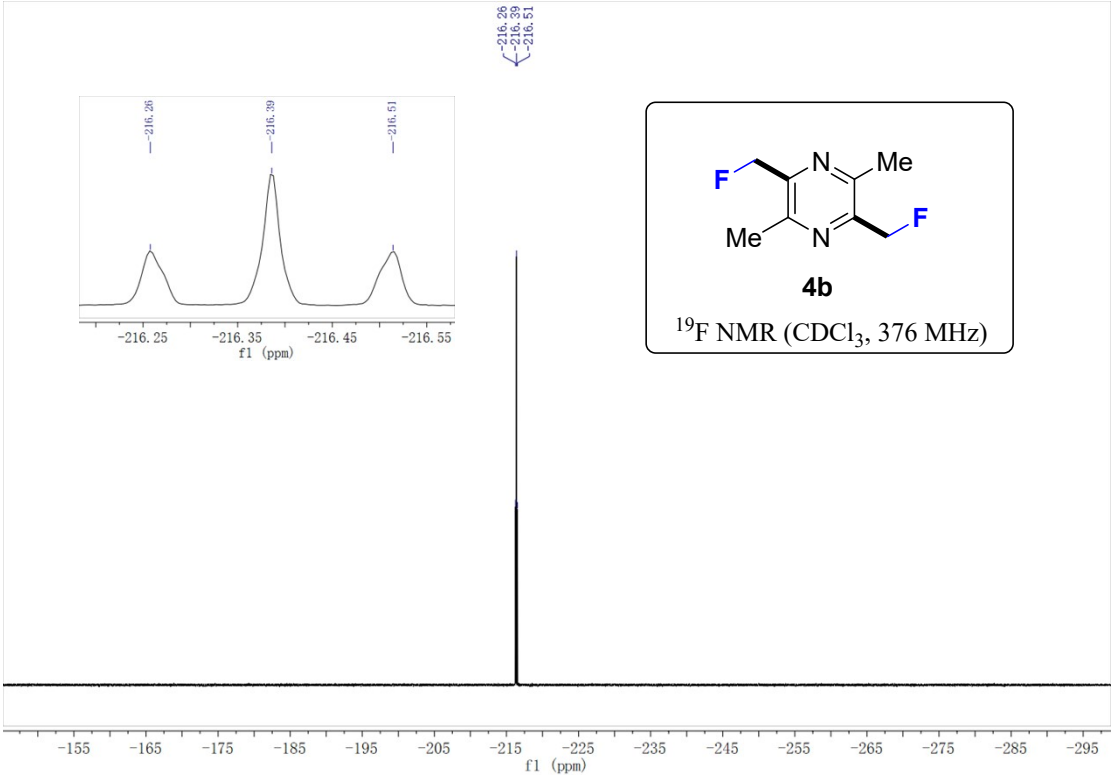

173.94
173.65
159.87
159.84
158.70
158.68
157.07
155.43
149.15
144.59
124.82
120.86
116.32
115.95
115.85
112.89
97.15
95.45
77.32
77.00
76.68
56.18
27.46
27.23
OMe
Cl
O
N
Me
F
Me
Cl
N
N
N
3ac
13C NMR (CDCl3, 100 MHz)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

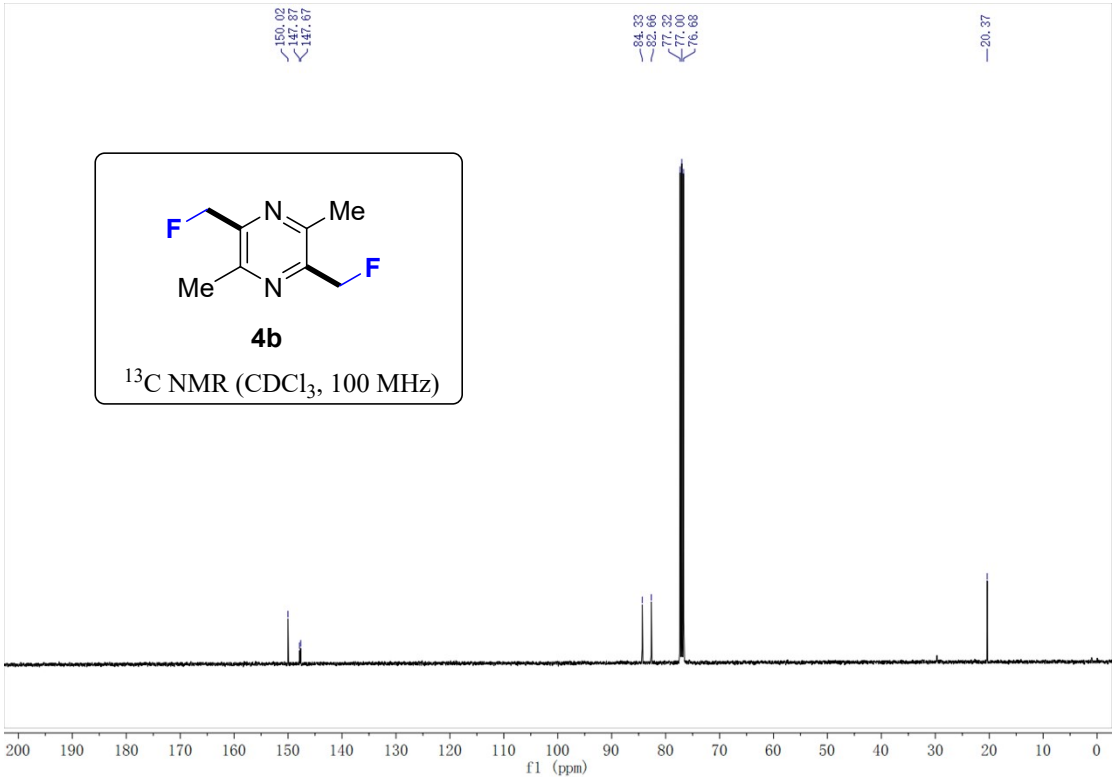

7.836
7.817
7.686
7.666
7.647
7.550
7.532
7.513
5.607
5.491
O
F
N
F
4a
1H NMR (CDCl3, 400 MHz)
1.98
3.00
1.99
4.02
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

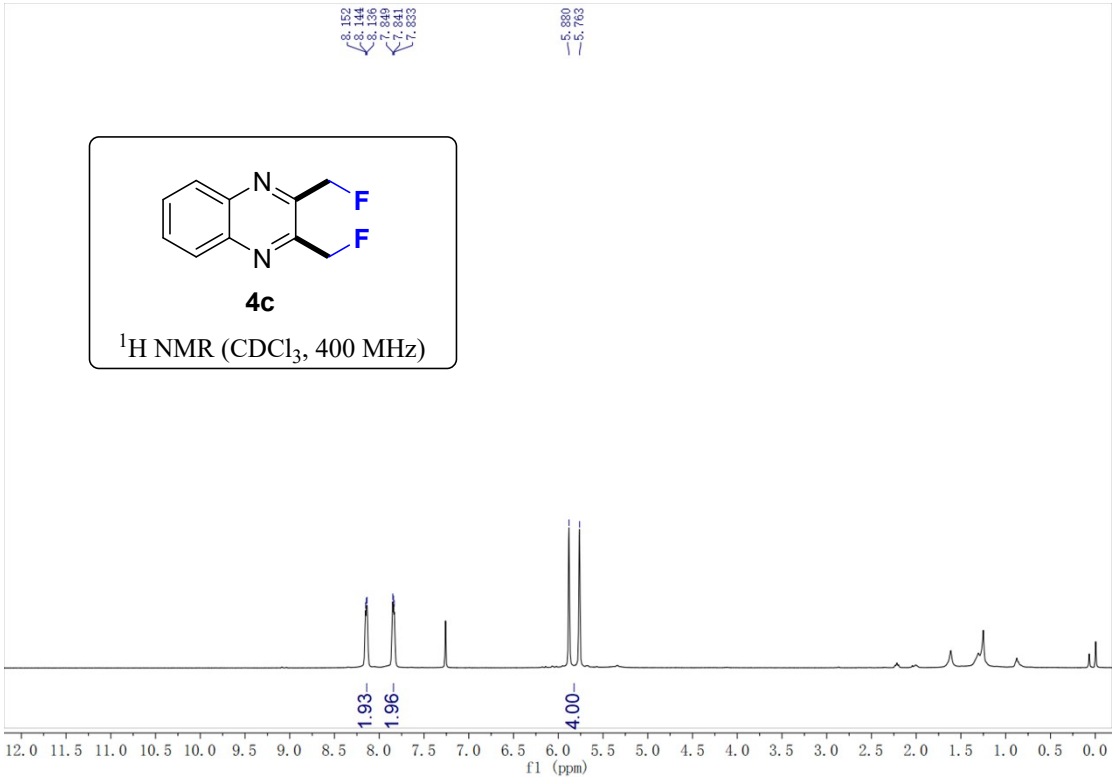

-222.11
-222.24
-222.36
-222.11
-222.24
-222.36
-222.05
-222.15
-222.25
-222.35
-222
f1 (ppm)
O
F
N
F
4a
19F NMR (CDCl3, 376 MHz)
-150
-160
-170
-180
-190
-200
-210
-220
-230
-240
-250
-260
-270
-280
-290
f1 (ppm)

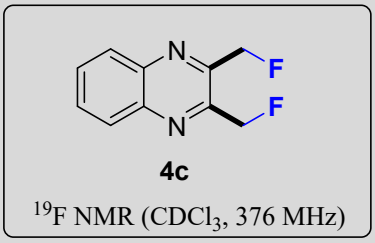

194.77
157.14
157.12
156.92
156.90
146.61
135.62
133.76
130.14
128.76
118.99
118.93
84.69
82.99
77.32
77.00
76.68
O
F
N
F
4a
13C NMR (CDCl3, 100 MHz)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


5.581
5.460
2.631
F
N
Me
Me
N
F
4b
1H NMR (CDCl3, 400 MHz)
4.01
6.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


216.26
216.39
216.51
216.26
216.39
216.51
216.25 216.35 216.45 216.55
f1 (ppm)
F
N
Me
Me
N
F
4b
19F NMR (CDCl3, 376 MHz)
155 165 175 185 195 205 215 225 235 245 255 265 275 285 295
f1 (ppm)

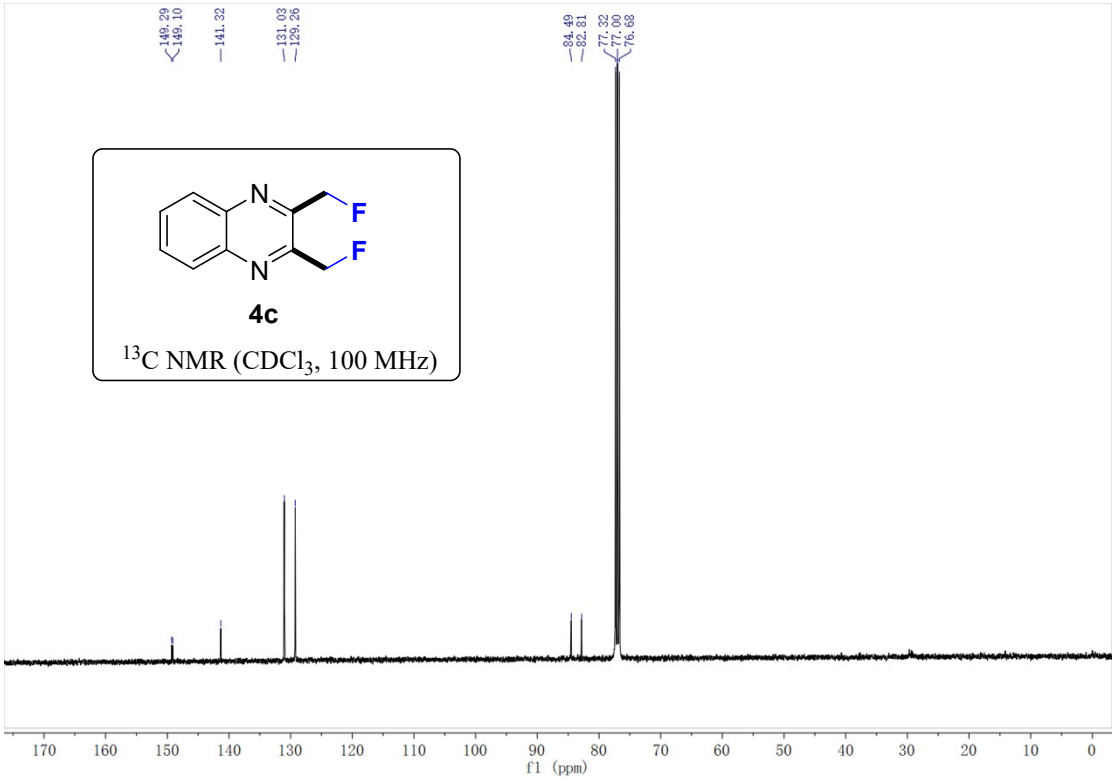

150.02
147.87
147.67
84.33
82.66
77.32
77.00
76.68
20.37
F
N
Me
Me
N
F
4b
^{13}C NMR (CDCl$_3$, 100 MHz)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.152
8.144
8.136
7.849
7.841
7.833
5.880
5.763
N
F
F
N
4c
^{1}H NMR (CDCl$_3$, 400 MHz)
1.93
1.96
4.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)



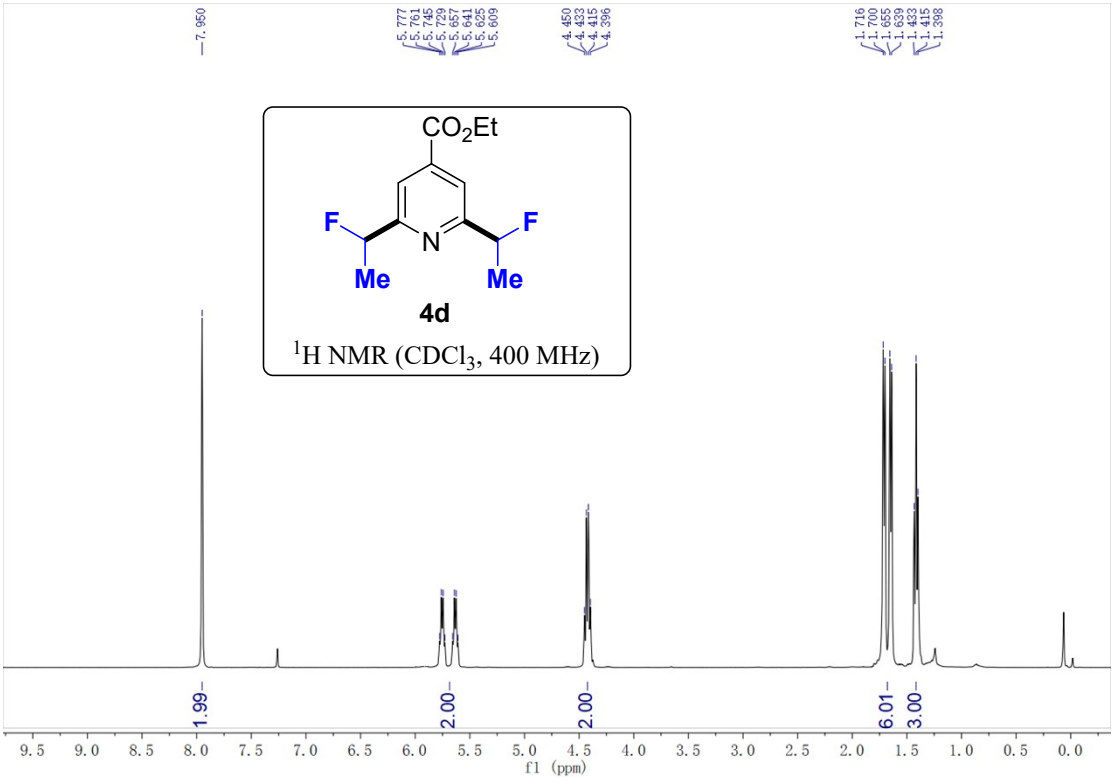
4c

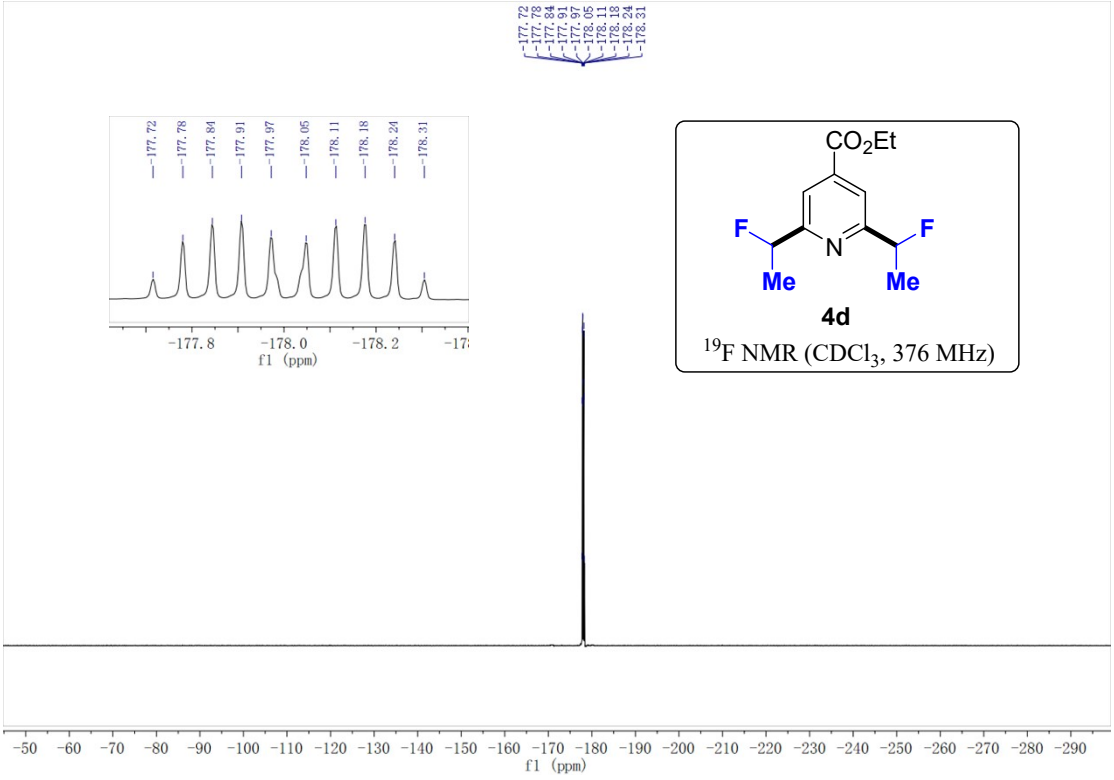
^{19}F NMR ($CDCl_3$, 376 MHz)

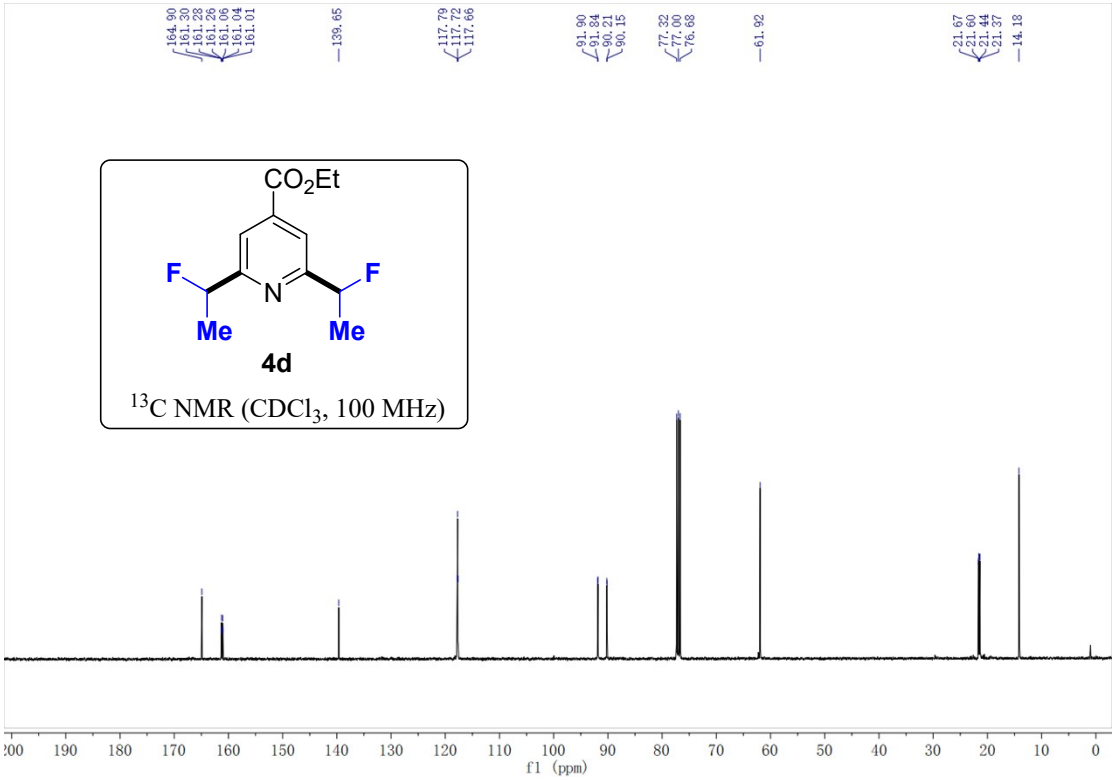


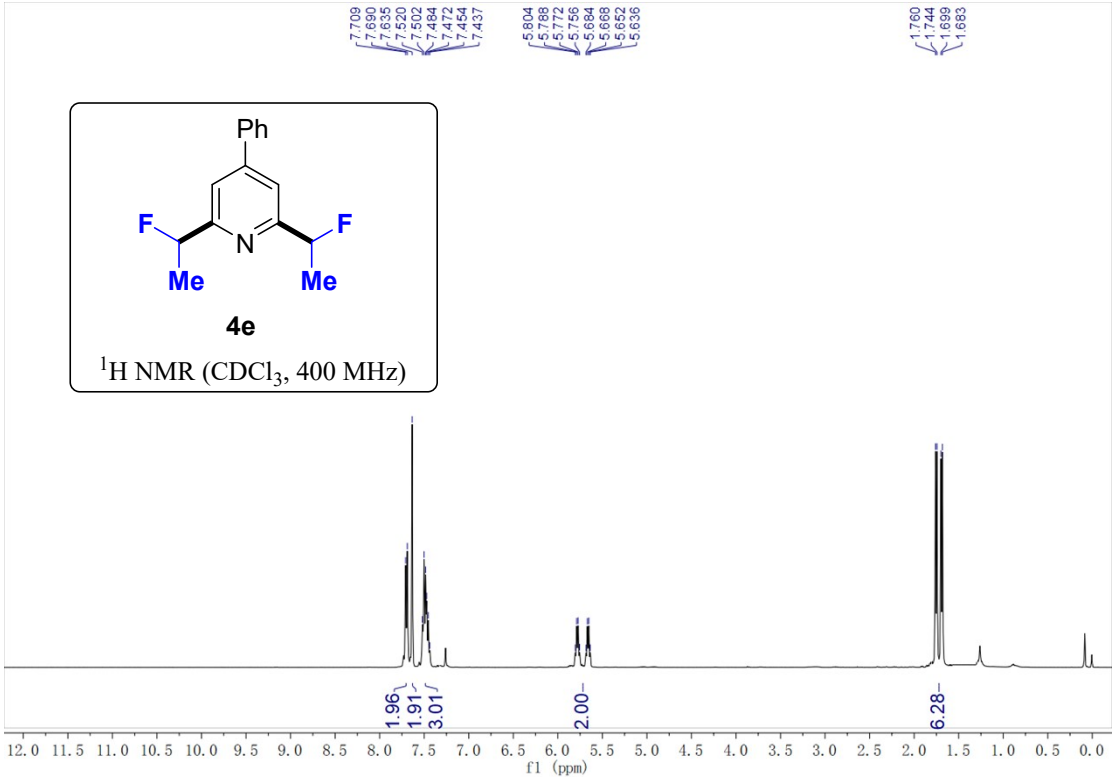
4c

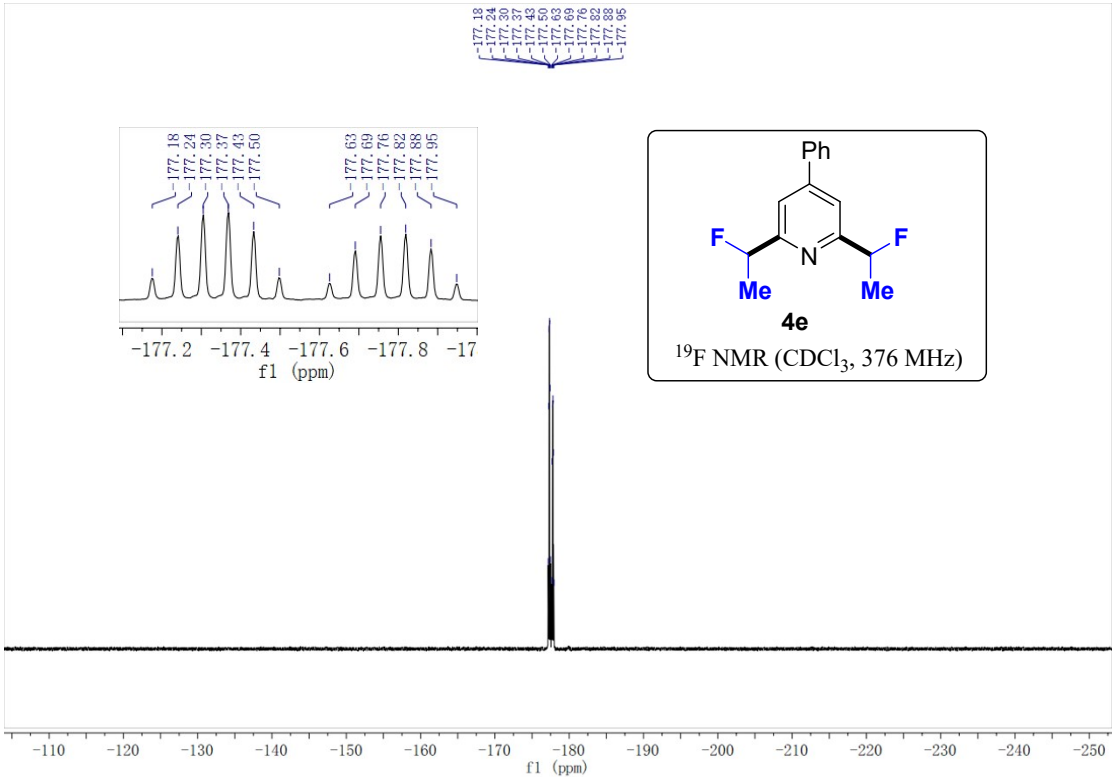
^{13}C NMR ($CDCl_3$, 100 MHz)

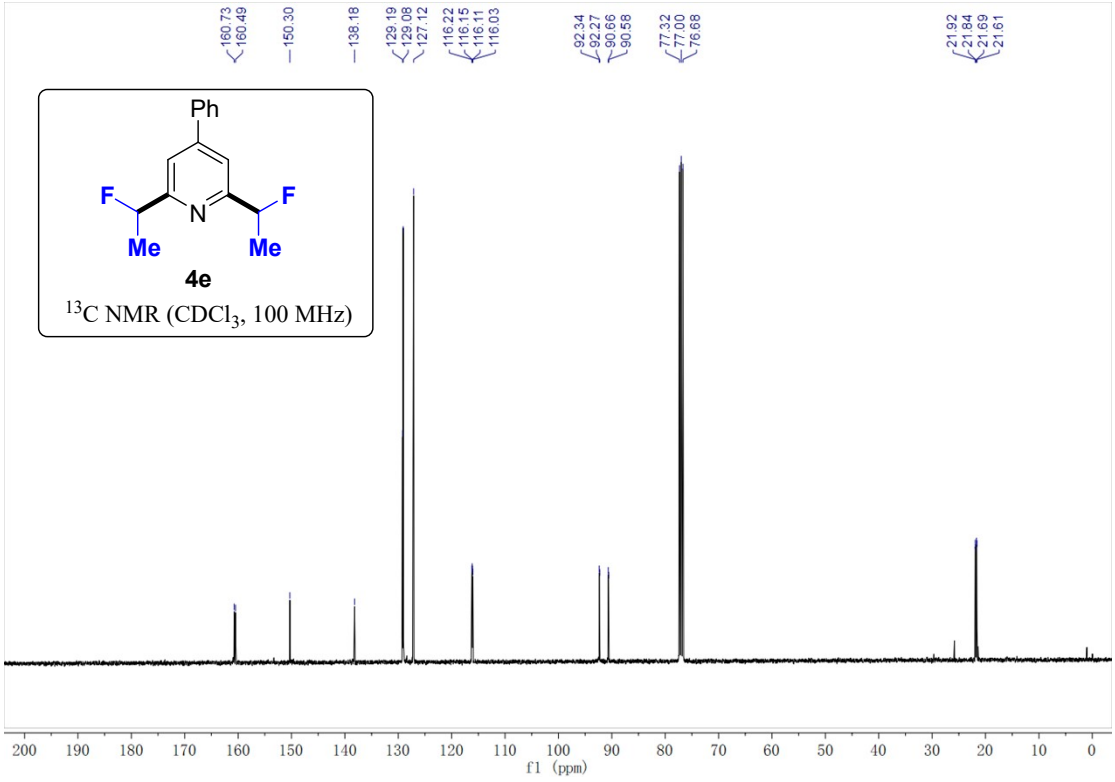

7.960
5.777
5.761
5.745
5.729
5.657
5.641
5.625
5.609
4.450
4.433
4.415
4.396
1.716
1.700
1.655
1.639
1.433
1.415
1.398
CO2Et
F
N
F
Me
Me
4d
1H NMR (CDCl3, 400 MHz)
1.99
2.00
2.00
6.01
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

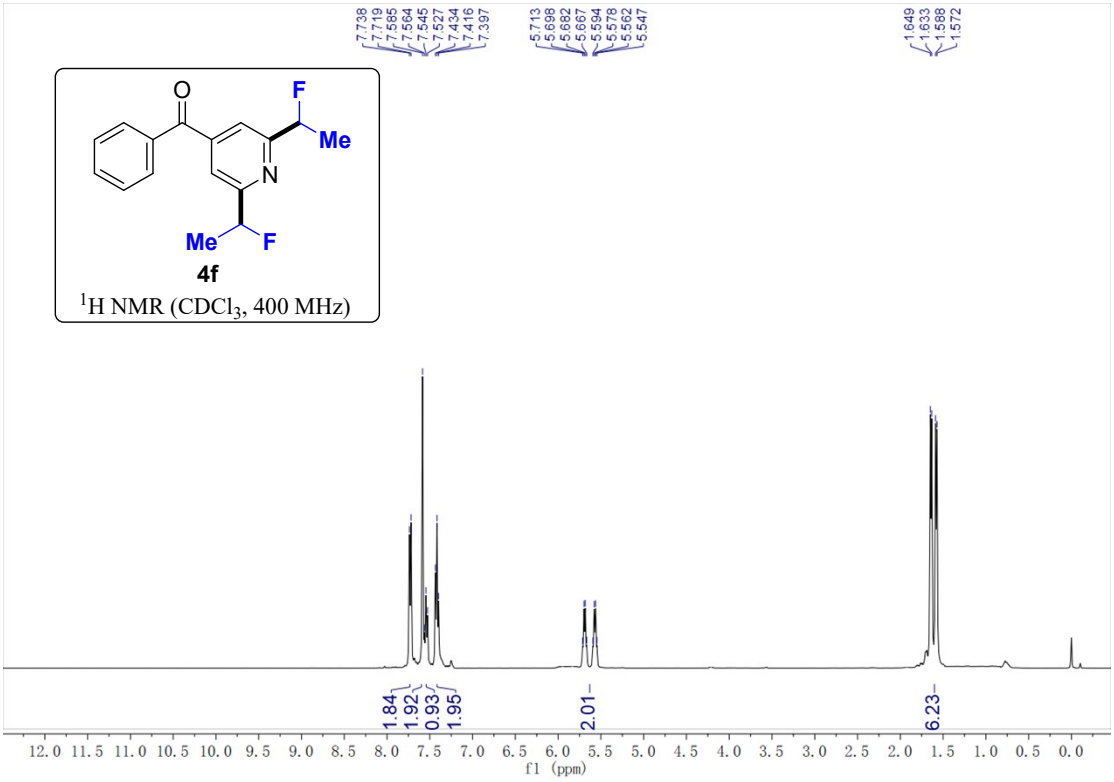

177.72
177.78
177.84
177.91
177.97
178.05
178.11
178.18
178.24
178.31
−177.8
−178.0
−178.2
f1 (ppm)
CO2Et
F
N
F
Me
Me
4d
19F NMR (CDCl3, 376 MHz)
−50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210 −220 −230 −240 −250 −260 −270 −280 −290
f1 (ppm)

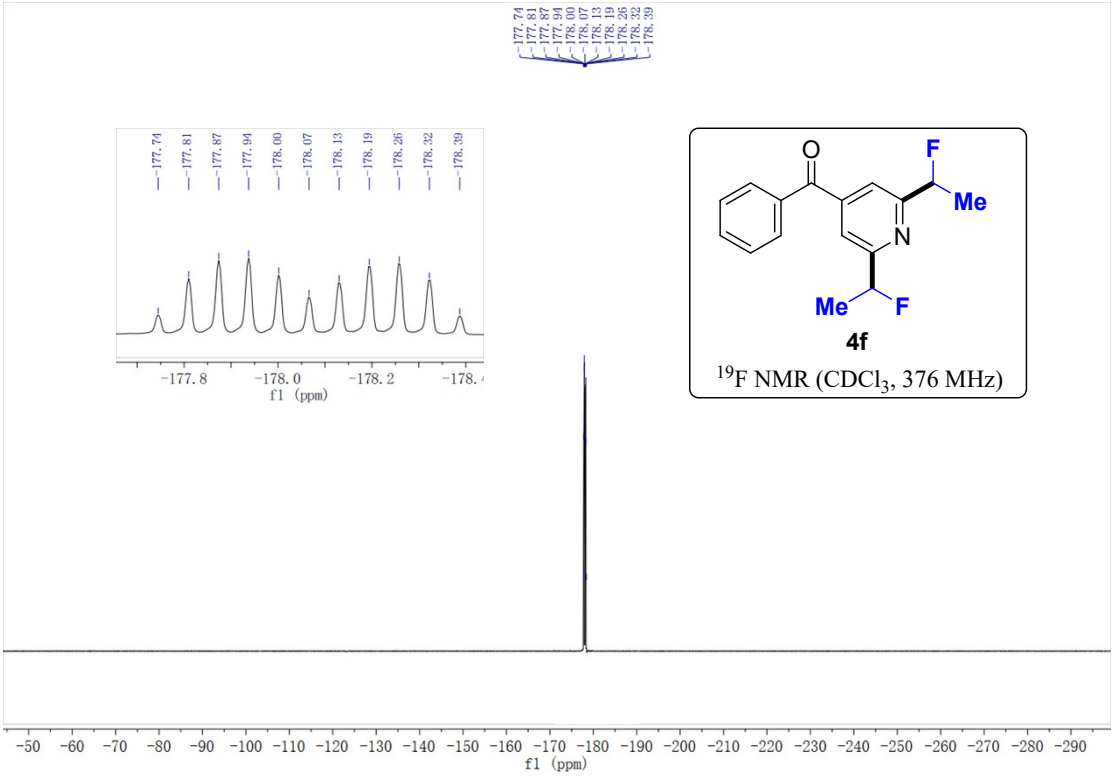

164.90
161.30
161.28
161.26
161.06
161.04
161.01
139.65
117.79
117.72
117.66
91.90
91.84
90.21
90.15
77.32
77.00
76.68
61.92
21.67
21.60
21.44
21.37
14.18
CO2Et
F
N
F
Me
Me
4d
13C NMR (CDCl3, 100 MHz)
f1 (ppm)

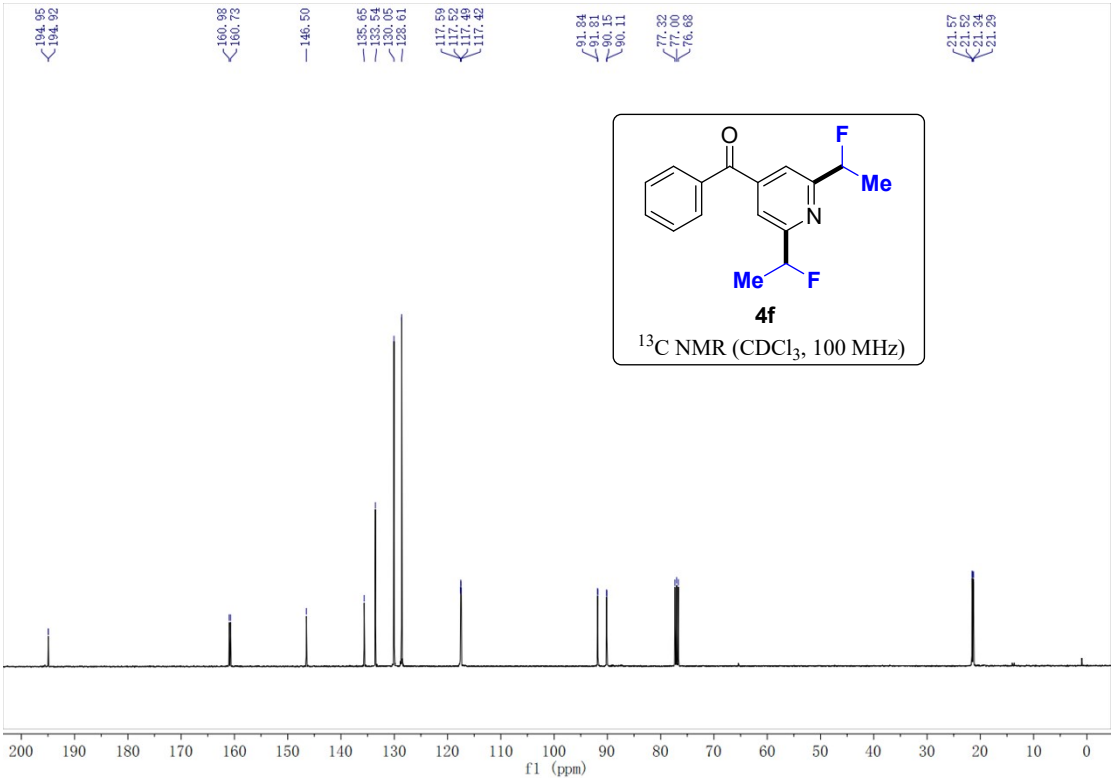

7.709
7.690
7.635
7.520
7.502
7.484
7.472
7.454
7.437
5.804
5.788
5.772
5.756
5.684
5.668
5.652
5.636
1.760
1.744
1.699
1.683
Ph
F
N
F
Me
Me
4e
1H NMR (CDCl3, 400 MHz)
1.96
1.91
3.01
2.00
6.28
f1 (ppm)

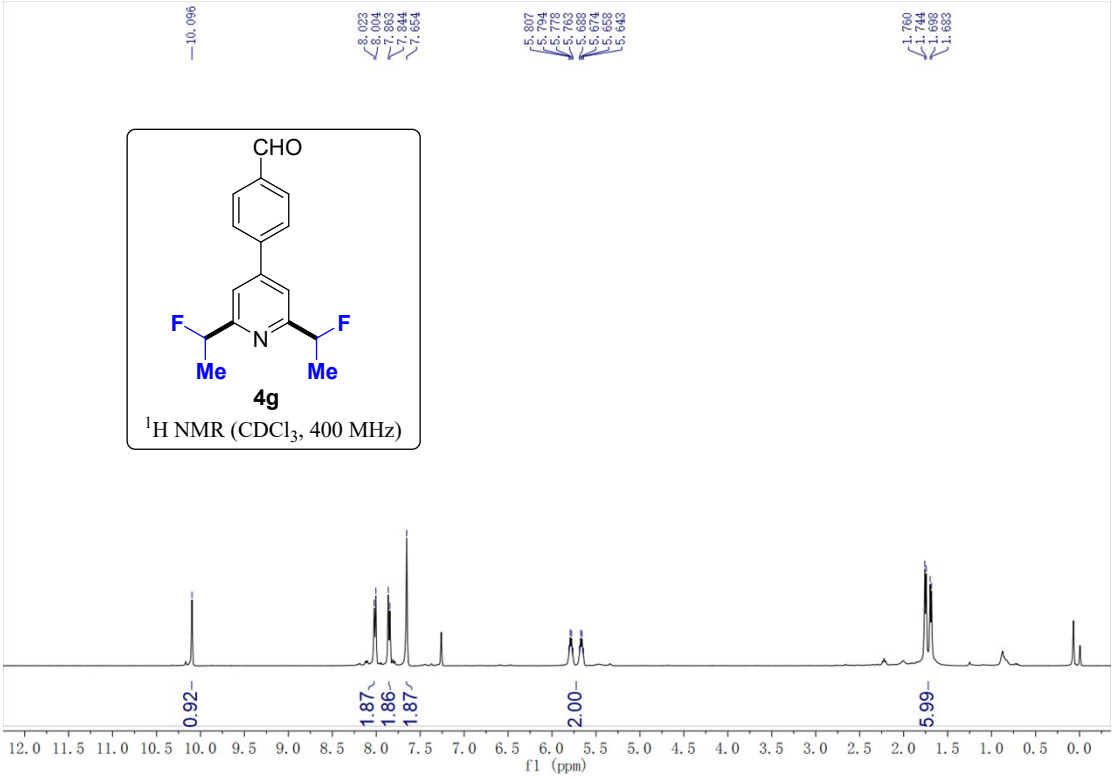

Ph
F
F
N
Me
Me
4e
^{19}F NMR ($CDCl_3$, 376 MHz)
f1 (ppm)

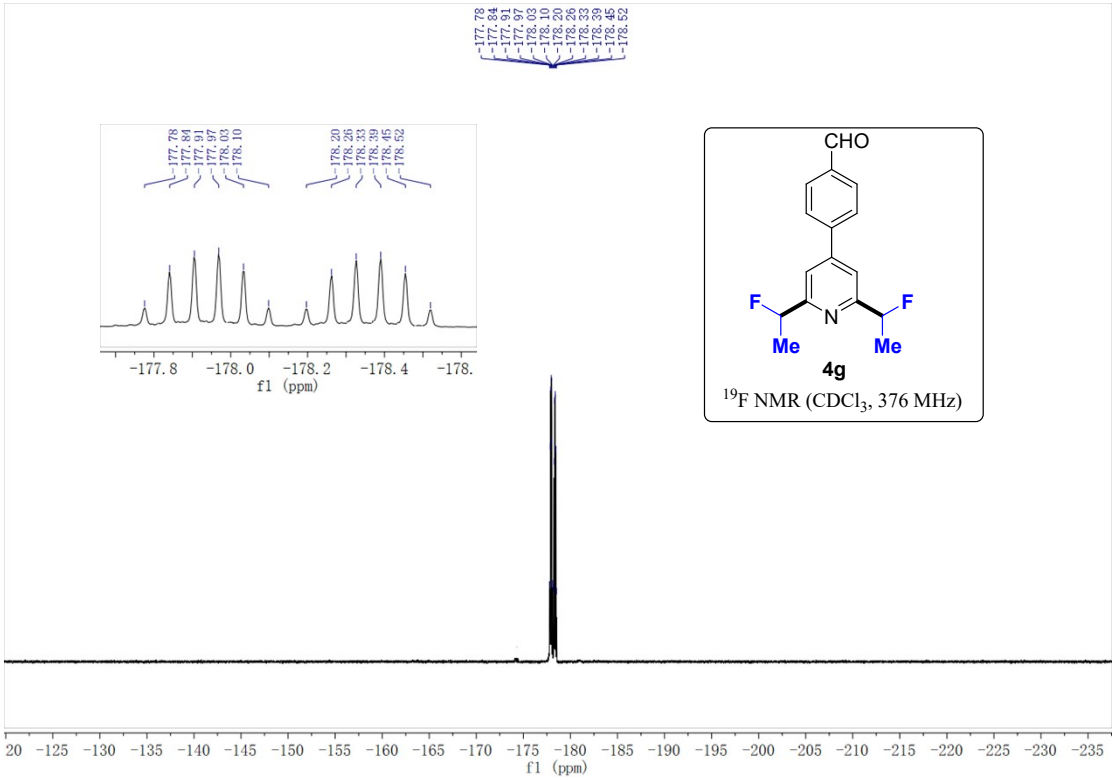

Ph
F
F
N
Me
Me
4e
^{13}C NMR ($CDCl_3$, 100 MHz)
f1 (ppm)

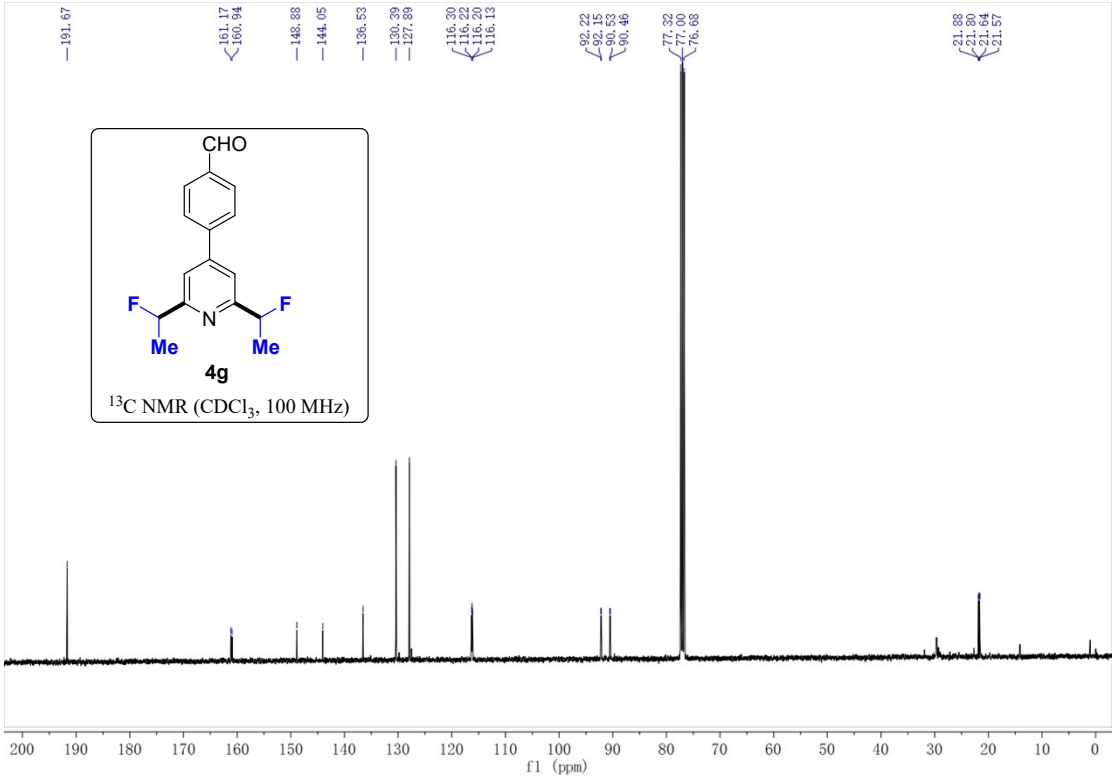

4f
1H NMR (CDCl3, 400 MHz)
1.84
1.92
0.93
1.95
2.01
6.23
f1 (ppm)

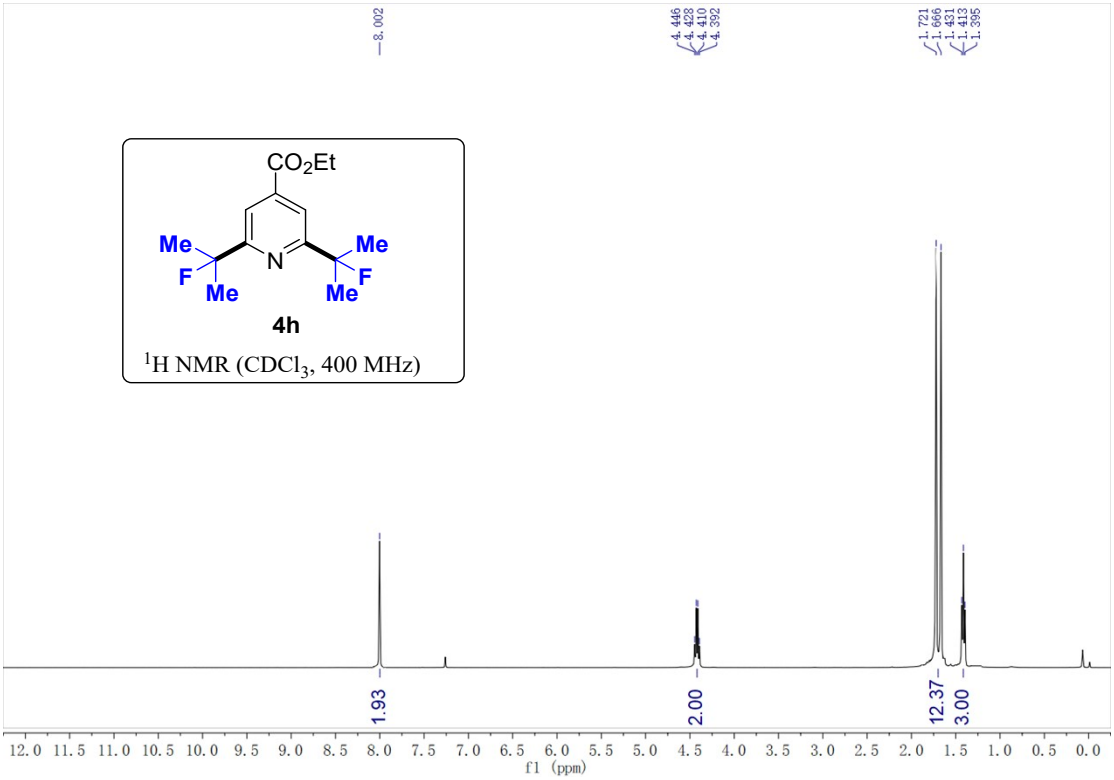

4f
19F NMR (CDCl3, 376 MHz)
f1 (ppm)

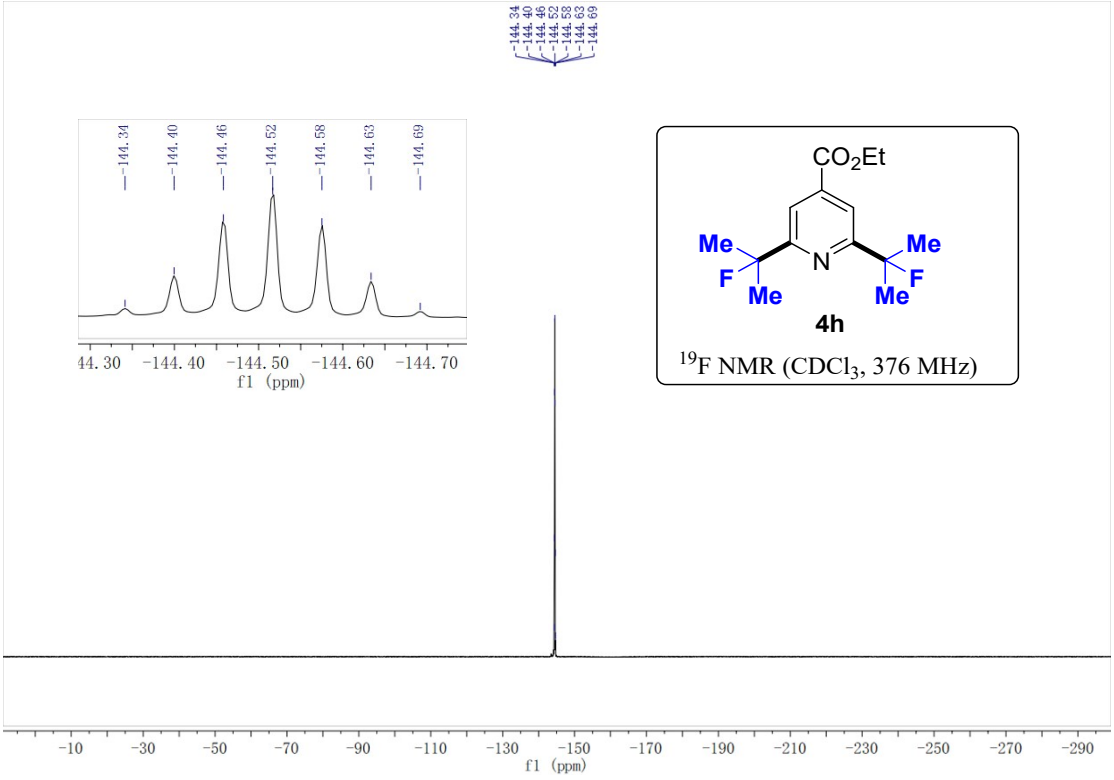

194.95
194.92
160.98
160.73
146.50
135.65
133.54
130.05
128.61
117.59
117.52
117.49
117.42
91.84
91.81
90.15
90.11
77.32
77.00
76.68
21.57
21.52
21.34
21.29
O
F
Me
N
Me
F
4f
13C NMR (CDCl3, 100 MHz)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

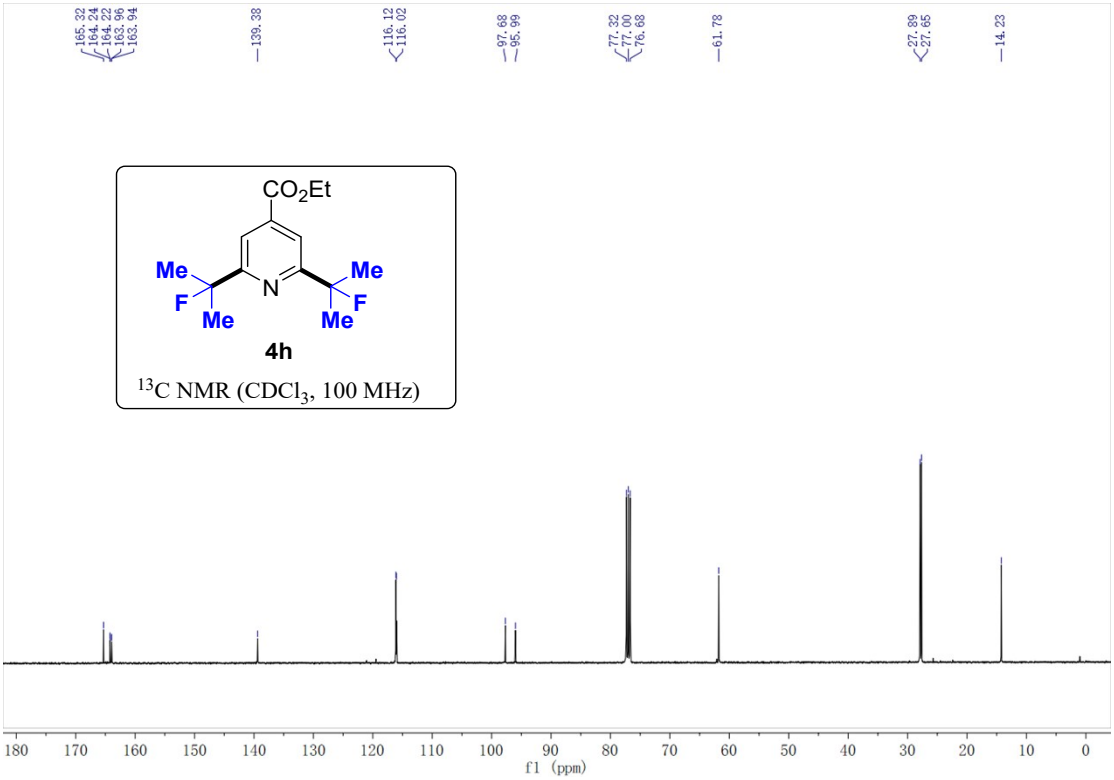

10.096
8.023
8.004
7.863
7.844
7.654
5.807
5.794
5.778
5.763
5.688
5.674
5.658
5.643
1.760
1.744
1.698
1.683
CHO
F
N
F
Me
Me
4g
1H NMR (CDCl3, 400 MHz)
0.92
1.87
1.86
1.87
2.00
5.99
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

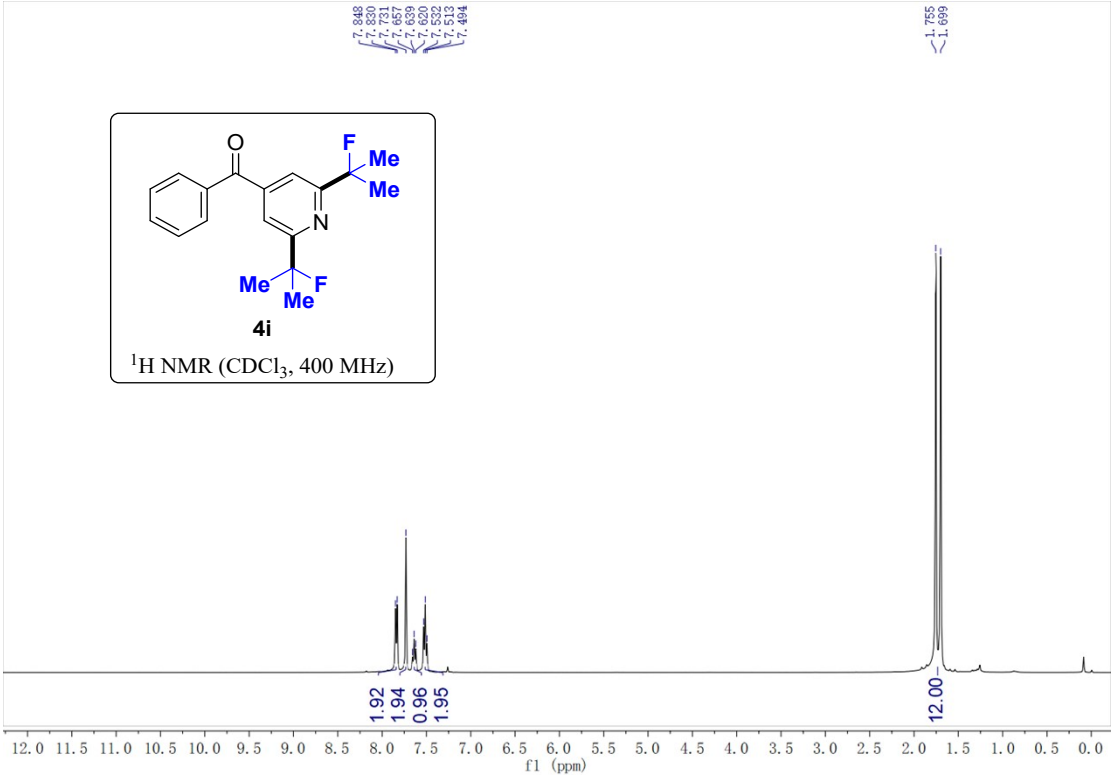

177.78
177.84
177.91
177.97
178.03
178.10
178.20
178.26
178.33
178.39
178.45
178.52
CHO
F
N
F
Me
Me
4g
19F NMR (CDCl3, 376 MHz)
f1 (ppm)

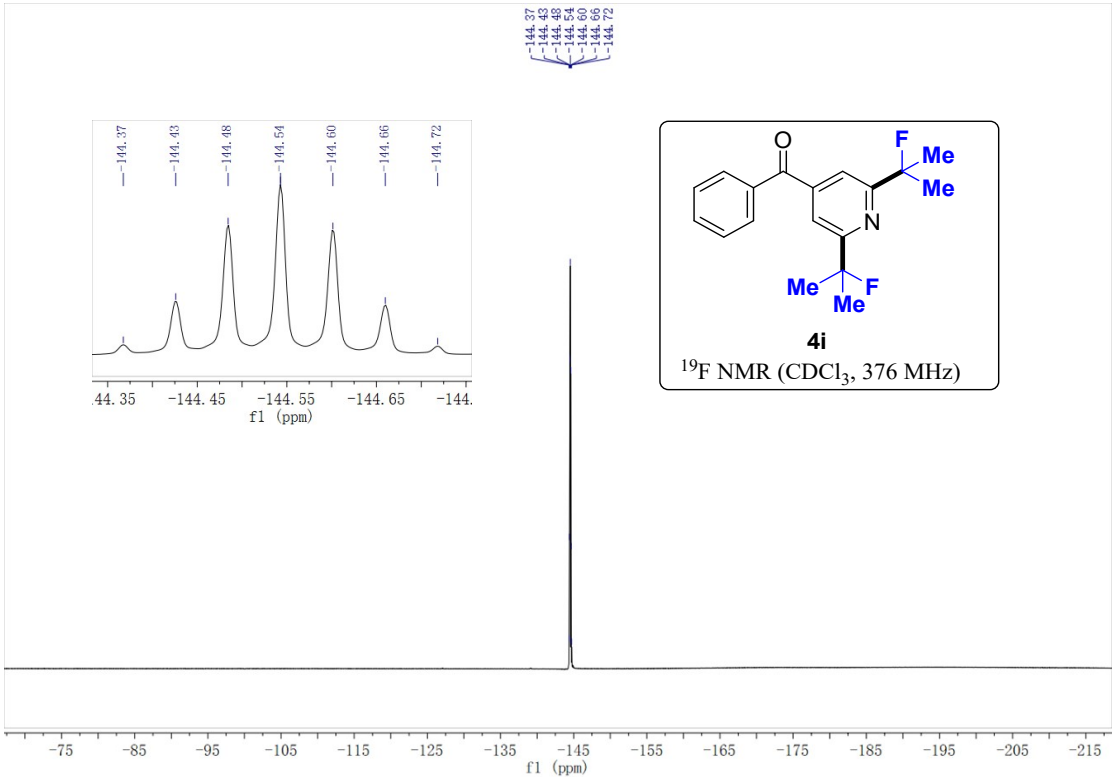

191.67
161.17
160.94
148.88
144.05
136.53
130.39
127.89
116.30
116.22
116.20
116.13
92.22
92.15
90.53
90.46
77.32
77.00
76.68
21.88
21.80
21.64
21.57
CHO
F
N
F
Me
Me
4g
13C NMR (CDCl3, 100 MHz)
f1 (ppm)

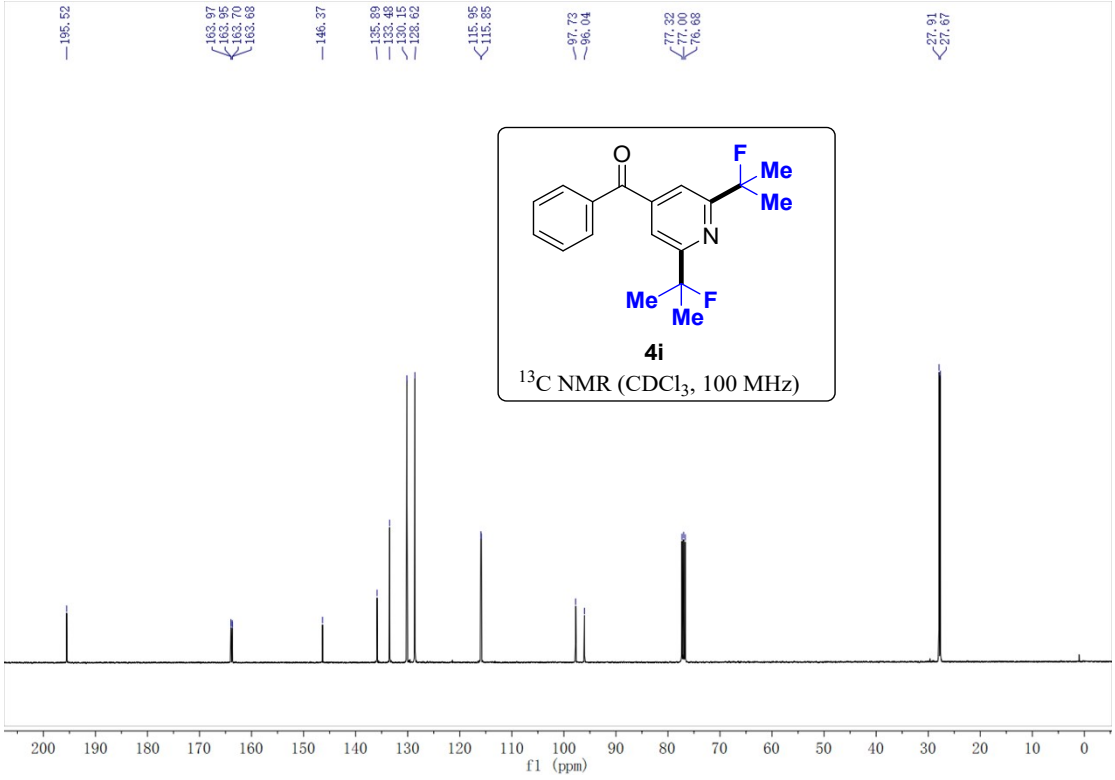

8.002
4.446
4.428
4.410
4.392
1.721
1.666
1.431
1.413
1.395
CO2Et
Me
F
Me
Me
F
Me
N
4h
1H NMR (CDCl3, 400 MHz)
1.93
2.00
12.37
3.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

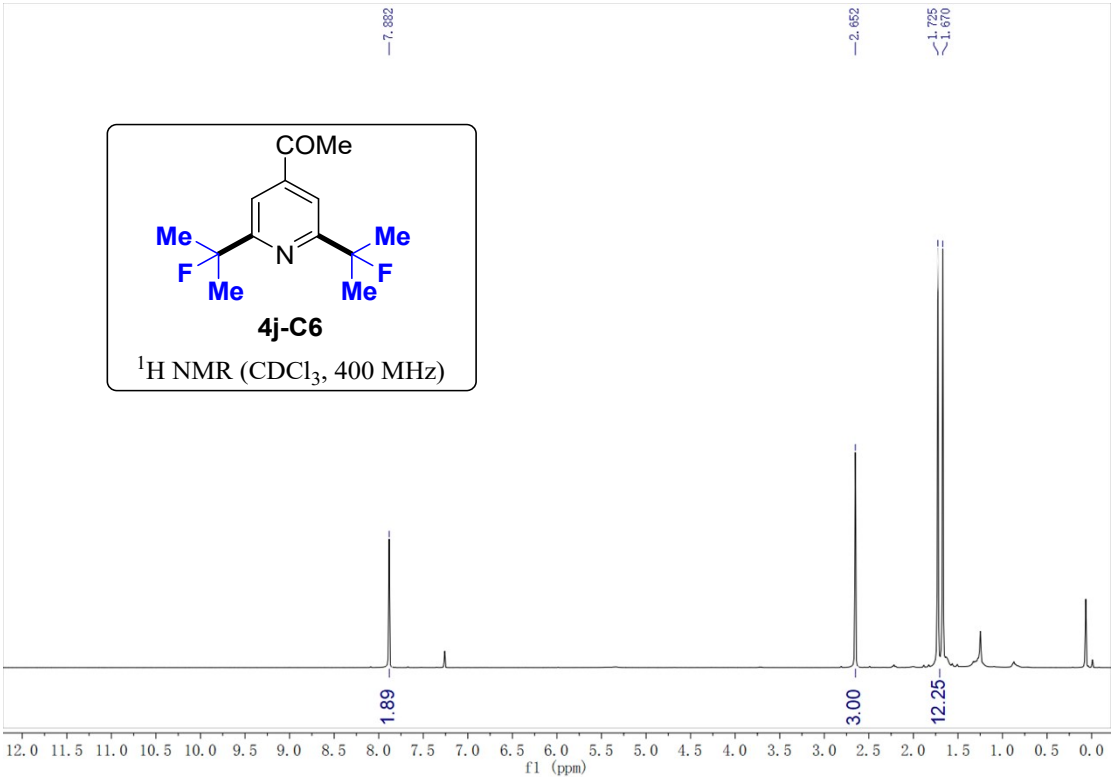

-144.34
-144.40
-144.46
-144.52
-144.58
-144.63
-144.69
44.30 -144.40 -144.50 -144.60 -144.70
f1 (ppm)
CO2Et
Me
F
Me
Me
F
Me
N
4h
19F NMR (CDCl3, 376 MHz)
-10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230 -250 -270 -290
f1 (ppm)

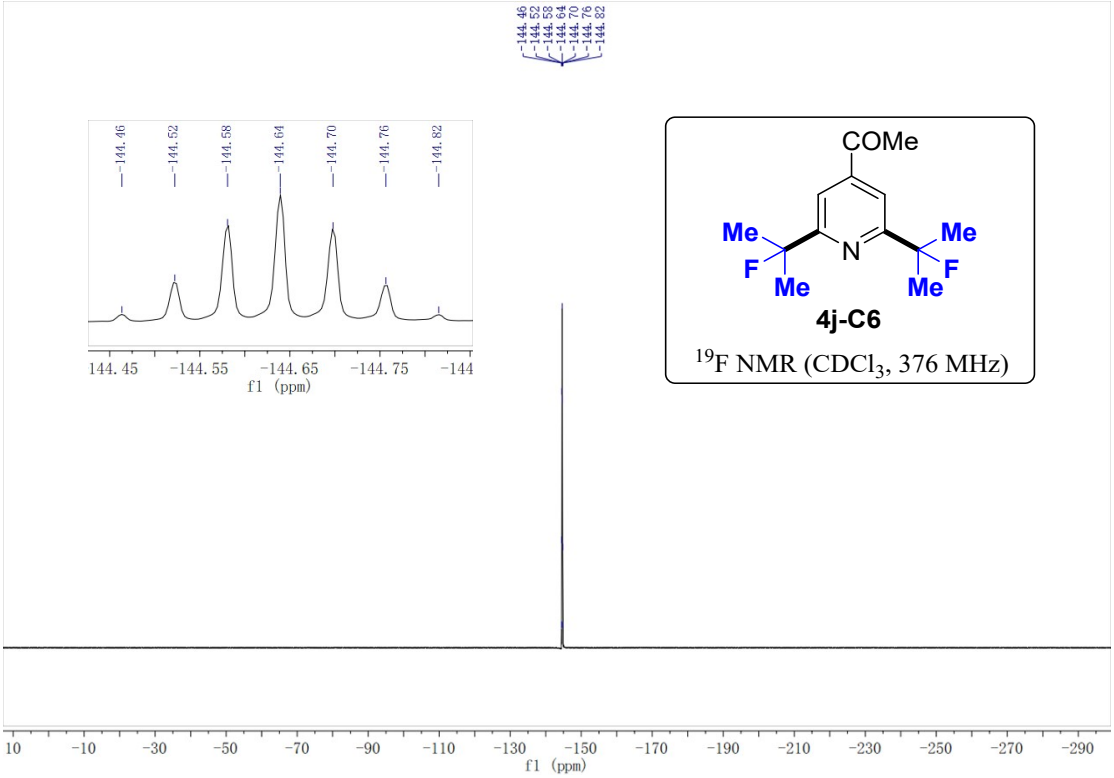

165.32
164.24
164.22
163.96
163.94
139.38
116.12
116.02
97.68
95.99
77.32
77.00
76.68
61.78
27.89
27.85
14.23
CO2Et
Me
F
Me
N
Me
F
Me
4h
13C NMR (CDCl3, 100 MHz)
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

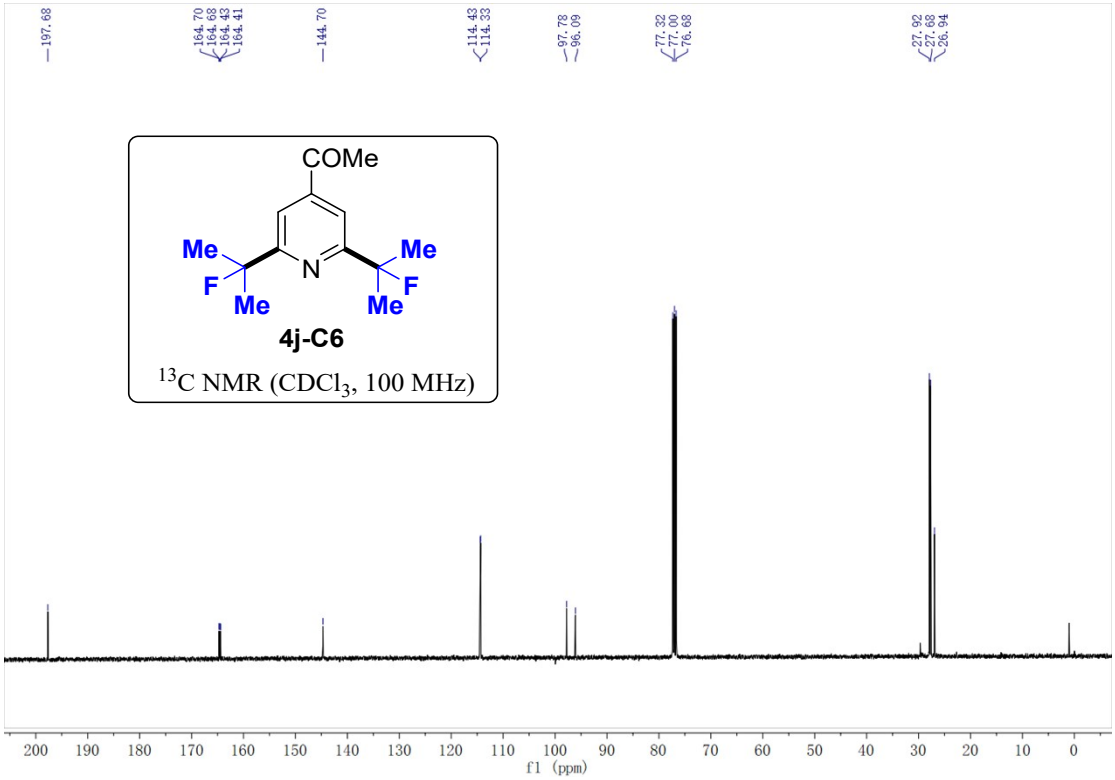

7.848
7.830
7.731
7.657
7.639
7.620
7.532
7.513
7.494
1.755
1.699
O
F
Me
Me
N
Me
F
Me
4i
1H NMR (CDCl3, 400 MHz)
1.92
1.94
0.96
1.95
12.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

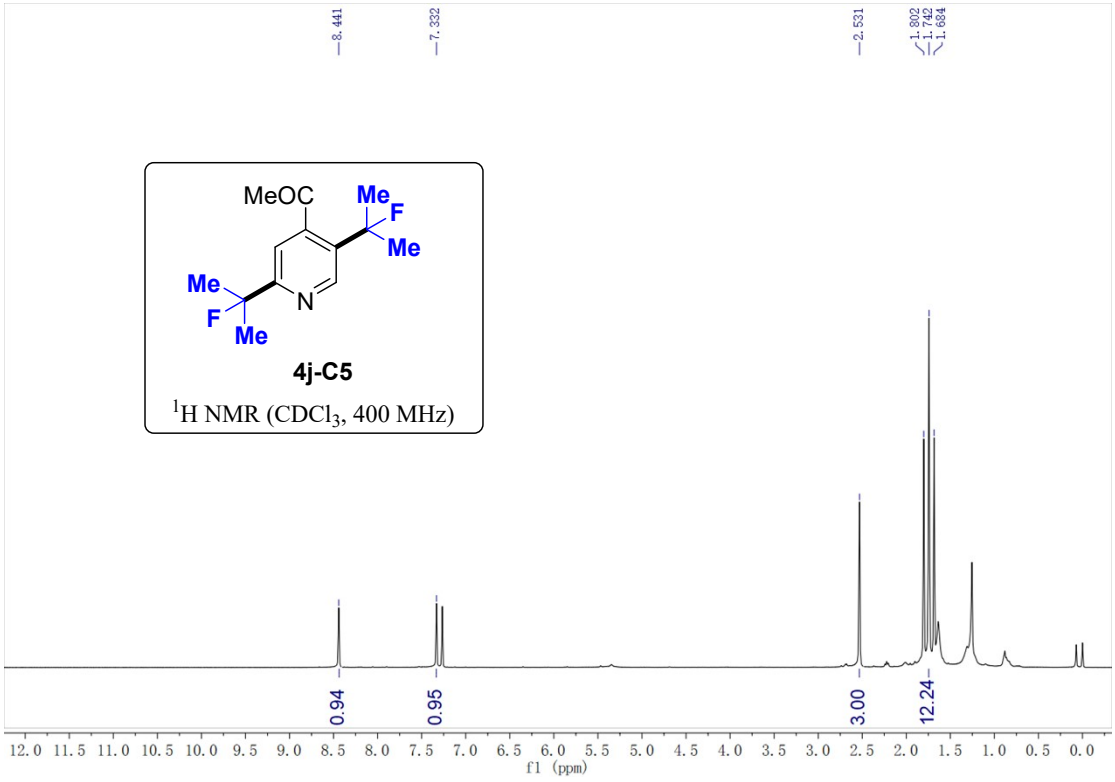

-144.37
-144.43
-144.48
-144.54
-144.60
-144.66
-144.72
f1 (ppm)
O
F
Me
Me
N
Me
F
Me
4i
19F NMR (CDCl3, 376 MHz)

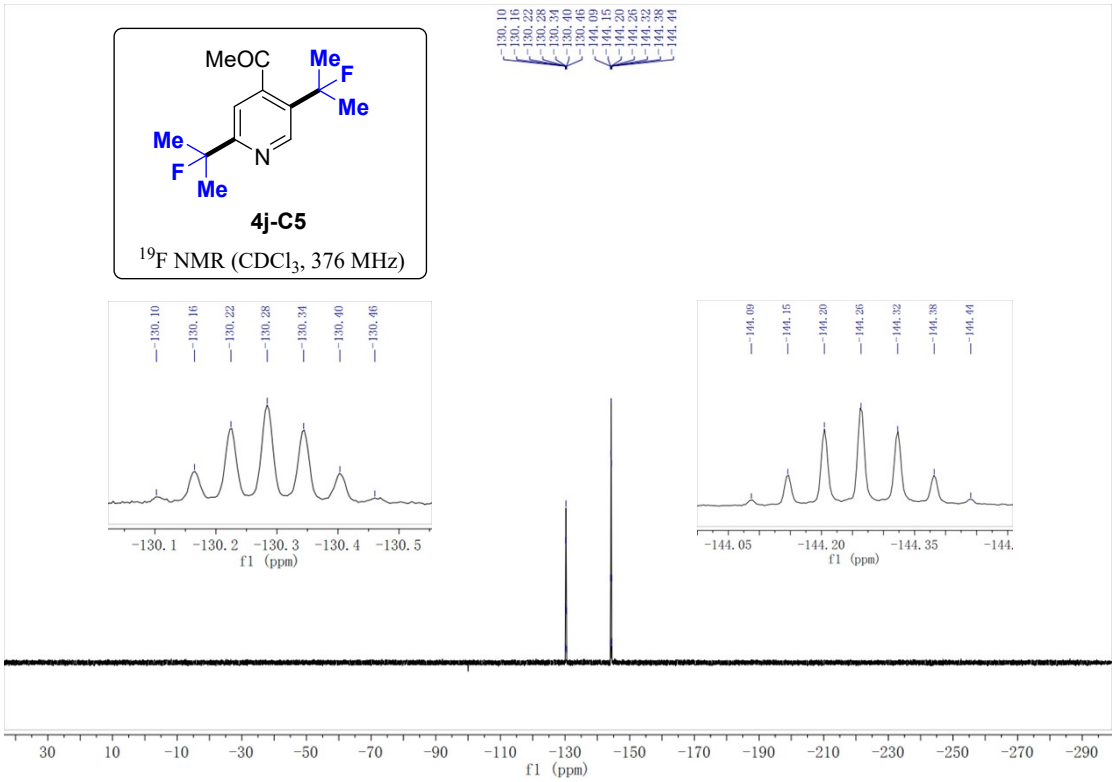

195.52
163.97
163.95
163.70
163.68
146.37
135.89
133.48
130.15
128.62
115.95
115.85
97.73
96.04
77.32
77.00
76.68
27.91
27.67
f1 (ppm)
O
F
Me
Me
N
Me
F
Me
4i
13C NMR (CDCl3, 100 MHz)

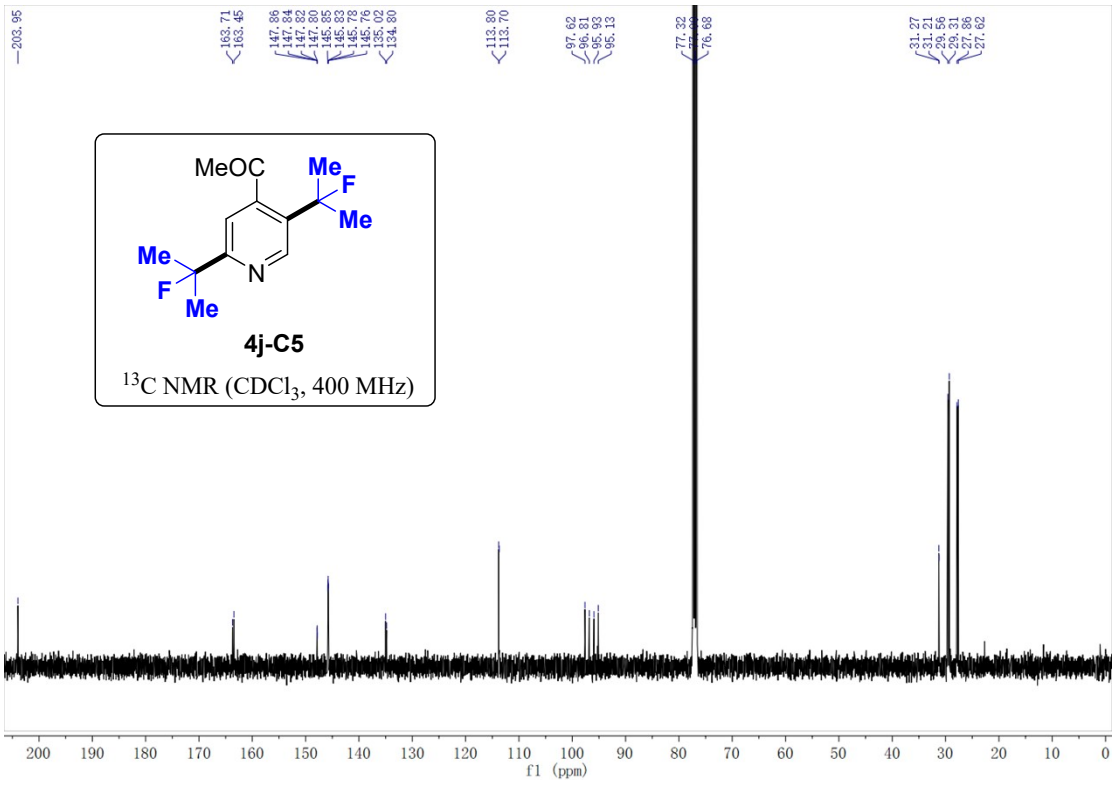

7.882
2.652
1.725
1.670
COMe
Me
F
Me
N
Me
F
Me
4j-C6
1H NMR (CDCl3, 400 MHz)
1.89
3.00
12.25
f1 (ppm)

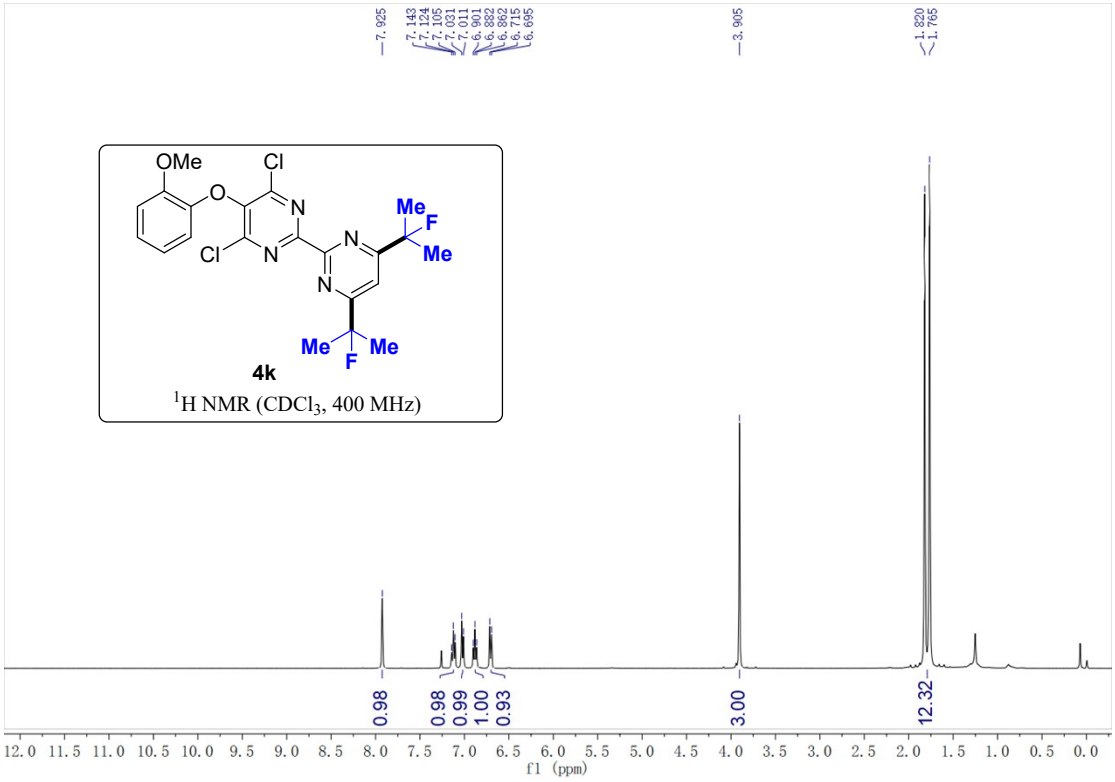

144.46
144.52
144.58
144.64
144.70
144.76
144.82
144.45
144.55
144.65
144.75
f1 (ppm)
COMe
Me
F
Me
N
Me
F
Me
4j-C6
19F NMR (CDCl3, 376 MHz)
f1 (ppm)


197.68
164.70
164.63
164.43
164.41
144.70
114.43
114.33
97.78
96.09
77.32
77.00
76.68
27.92
27.68
26.94
COMe
Me
F
Me
N
Me
F
Me
4j-C6
13C NMR (CDCl3, 100 MHz)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

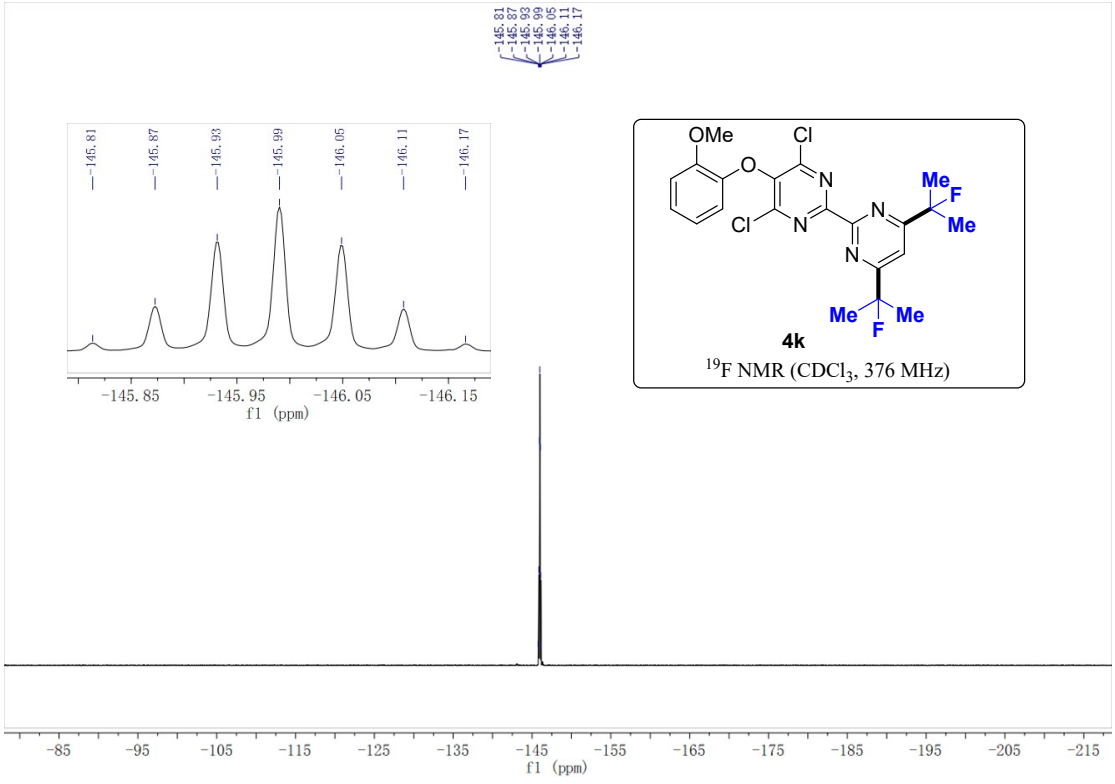

8.441
7.332
2.531
1.802
1.742
1.684
MeOC
Me
F
Me
Me
F
Me
N
4j-C5
1H NMR (CDCl3, 400 MHz)
0.94
0.95
3.00
12.24
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


MeOC
Me
F
Me
Me
F
Me
N
4j-C5
19F NMR (CDCl3, 376 MHz)
f1 (ppm)

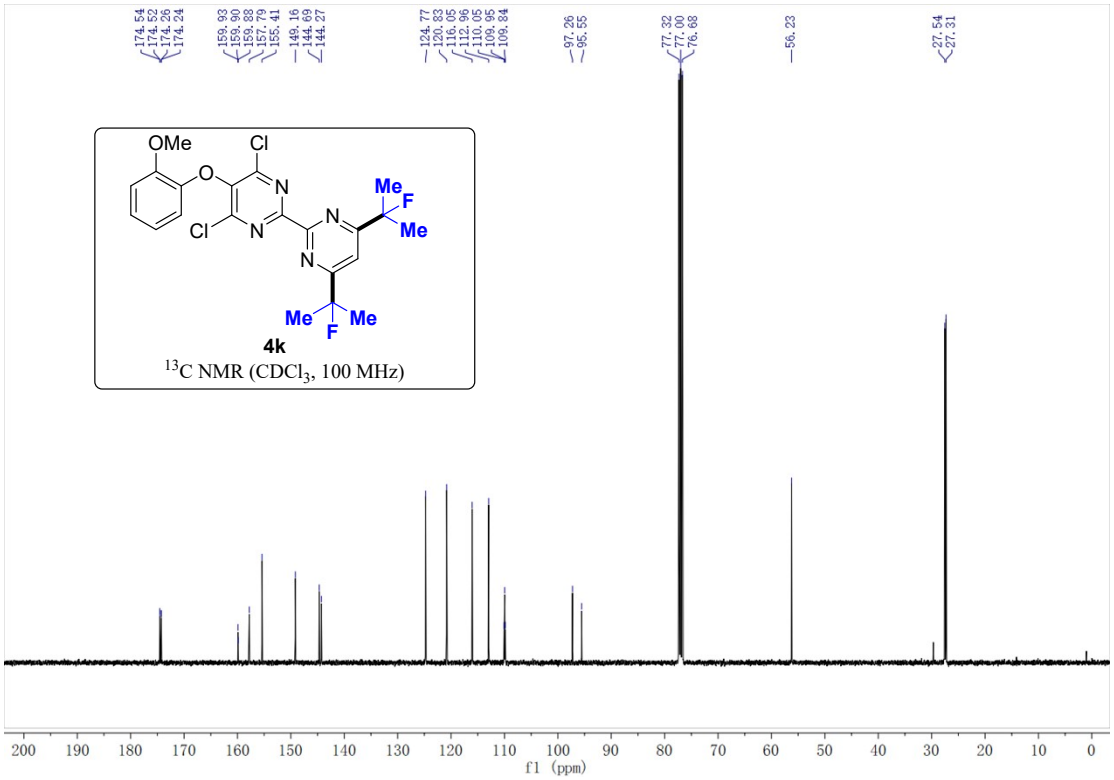

MeOC
Me
F
Me
Me
F
Me
N
4j-C5
13C NMR (CDCl3, 400 MHz)
f1 (ppm)



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



^{19}F NMR ($CDCl_3$, 376 MHz)


174.54
174.52
174.26
174.24
159.93
159.90
159.88
157.79
155.41
149.16
144.69
144.27
124.77
120.83
116.05
112.06
110.05
109.95
109.84
97.26
95.55
77.32
77.00
76.68
56.23
27.54
27.31
OMe
Cl
O
N
Cl
N
N
N
Me
F
Me
Me
F
Me
4k
13C NMR (CDCl3, 100 MHz)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)