Electronic Supplementary Information

Understanding Cu(II)-based systems for C(sp^3)–H bond functionalization: insights on the synthesis of aza-heterocycles

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A. Instrumentation, Materials and General Methods

NMR spectra were recorded on a Bruker Advance 300 spectrometer at 293 K (300 MHz for ^{1}H NMR, 75.4 MHz for ^{13}C NMR and 282.4 MHz for ^{19}F). Chemical shifts (δ) are reported in ppm referenced to tetramethylsilane (TMS) and coupling constants are reported in Hz. The multiplicity of signals is indicated using the following abbreviations: s = singlet, d = doublet, t = triplet, q = quadruplet, bs = broad singlet, bd = broad doublet, m = multiplet. XRD analyses were run by the technical platform of the ICT ("Institut de Chimie de Toulouse", UAR 2599). Intensity data were collected at a temperature of 193(2) K on a Bruker-AXS APEX II Quazar diffractometer (**CuA**, **Cu4B** and **4)** equipped with a 30 W air-cooled microfocus source or on a Bruker-AXS D8-Venture with a PHOTON3 detector (**6a**), using MoKα radiation (wavelength = 0.71073 Å). Phi- and omega-scans were used. The data were integrated with SAINT[1], and an empirical absorption correction with SADABS[1] was applied. The structures were solved by an intrinsic phasing method (SHELXT)[2] and refined using the least–squares method on F^2.[3] All non-H atoms were treated anisotropically. The hydrogen atoms were refined isotropically at calculated positions using a riding model. For **Cu4B**, the alkyl chain is disordered over two positions with occupancy factor values of 0.61 and 0.39. Infrared spectra were recorded using a ThermoNicolet 6700 IR Spectrometer equipped with an ATR detector. The advanced ATR correction algorithm was applied to the spectra recorded with the ATR detector. High-Resolution Mass Spectroscopy results were obtained using a GCT Premier (Waters) apparatus with desorption chemical ionization (DCI-CH_4) or electro-spray ionization (ESI) at the technical platform of the ICT ("Institut de Chimie de Toulouse", UAR 2599). Elemental analysis was carried out using a PERKIN ELMER 2400 series II analyzer. GC analyses were performed on a GC Perkin Elmer Clarus 500 with a flame ionization

[1] Bruker, *SAINT* and *SADABS*, Bruker AXS Inc., Madison, Wisconsin, USA.
[2] Sheldrick, G. M. SHELXT – Integrated space-group and crystal-structure determination. *Acta Cryst.* **2015**, *A71*, 3-8.
[3] Sheldrick, G. M. Crystal structure refinement with SHELXL. *Acta Cryst.* **2015**, *C71*, 3-8.

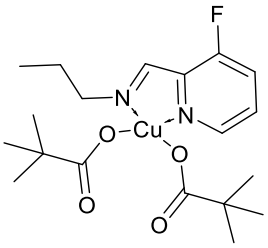
detector (FID) using a SGE BPX5 column (30 m x 0.32 mm x 0.25 mm) composed of 5% phenylmethylsiloxane and a Perkin Elmer Clarus 560 S mass spectrometer. The injector temperature was 250 °C and the flow was 2 mL/min. Voltammetric measurements were carried out with a Autolab PGStat204 Potentiostat (Metrohm) using NOVA 2.1 software. Experiments were performed at room temperature in a homemade three-electrode cell. The reference electrode consisted of a saturated calomel electrode (Biologic) with a platinum wire (homemade) counter electrode and a Pt working electrode (Metrohm). A solution of 0.1 M tetrabutylammonium hexafluorophosphate (Merck, purity ≥99.0% for electrochemical analysis) was used as electrolyte and the working electrode was polished before each measurement. Reactions under microwave activation were carried out on a microwave synthesizer CEM Discover instrument equipped with an automated CEM Explorer autosampler.

Materials. Purchased chemicals were used without further purification. The solvents used were of synthesis grade (CH_3CN, $CHCl_3$, EtOAc, AcOH, CF_3COOH, EtOH and CH_2Cl_2). $Cu(OPiv)_2$ was prepared by ion exchange $Cu(NO_3)_2 \cdot 3H_2O$ and KOPiv as detailed below.

Synthesis of $Cu(OPiv)_2$

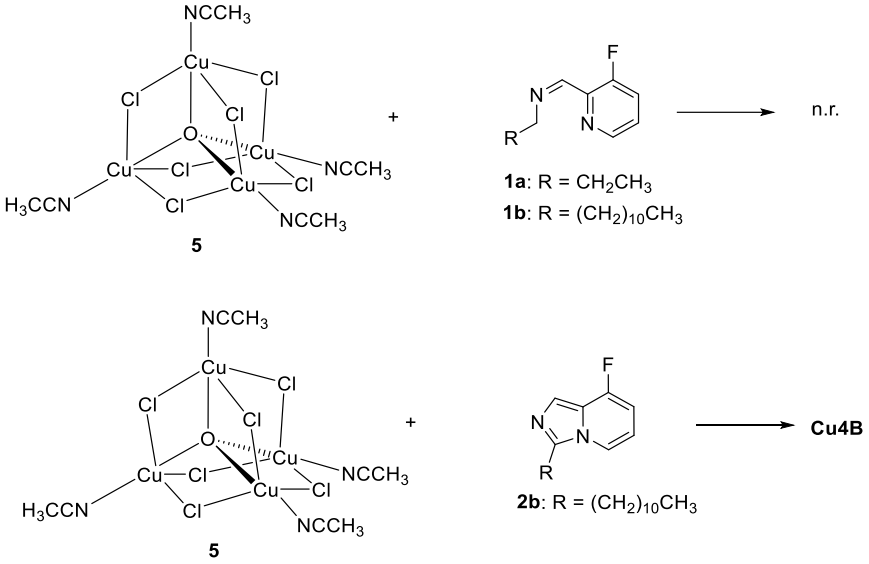
Pivalic acid (1.5 mL, 0.01 mmol) was added to a solution of $Cu(NO_3)_2 \cdot 3H_2O$ (2.416 g, 10 mmol) and KOPiv (2.804 g, 20 mmol) in EtOH (15 mL). The mixture was stirred at rt for 1 h and the solid was filtered out. The solvent was then removed under vacuum obtaining a blue-green solid, which was dissolved in pentane (20 mL) with the dropwise addition of EtOH (0.2 mL) and allowed to crystallize overnight at -10 °C obtaining a green crystalline powder (1.7030 g, 65%).[4]

[4] J.-H. Zhou, Z. Liu, Y.-Z. Li, Y. Song, X.-T. Chen, X.-Z. You, *J. Coord. Chem.* **2006**, *59*, 147.



Synthesis of Cu(OPiv)$_2$-aldimine 1a complex

Cu(OPiv)$_2$ (80.0 mg, 0.30 mmol) was added in one solid portion to a solution of aldimine **1a** (50.2 mg, 0.30 mmol) in anhydrous MeCN (2 mL) and the reaction mixture was stirred for 60 min at rt. The mixture was then filtered through a 0.2 μm PTFE filter and the solvent was removed under reduced pressure, furnishing the complex (130.5 mg, quant.) as a dark solid.



Scheme S1. Reactivity studies of **5** with **1a-b** and **2b**. A solution of **1** or **2** (0.30 mmol) and **5** (71.2 mg, 0.11 mmol) in CH_3CN (4 mL) was heated to 100 ºC for 10 min under microwave irradiation (max. 200 W).

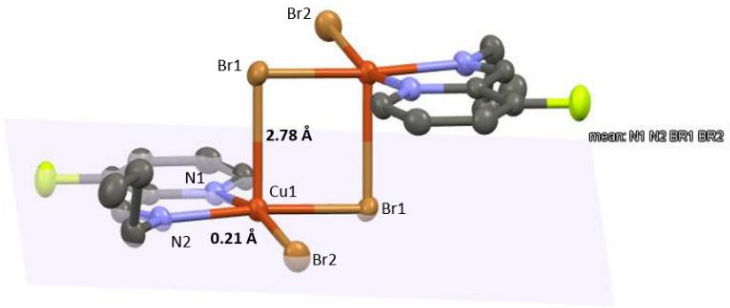


Figure S1. XRD crystal structure of complex **CuA** showing the distorted square planar arrangement around the metal center and the distances Cu1-Br1(apical) and Cu1-(N1N2Br1Br2) plane.

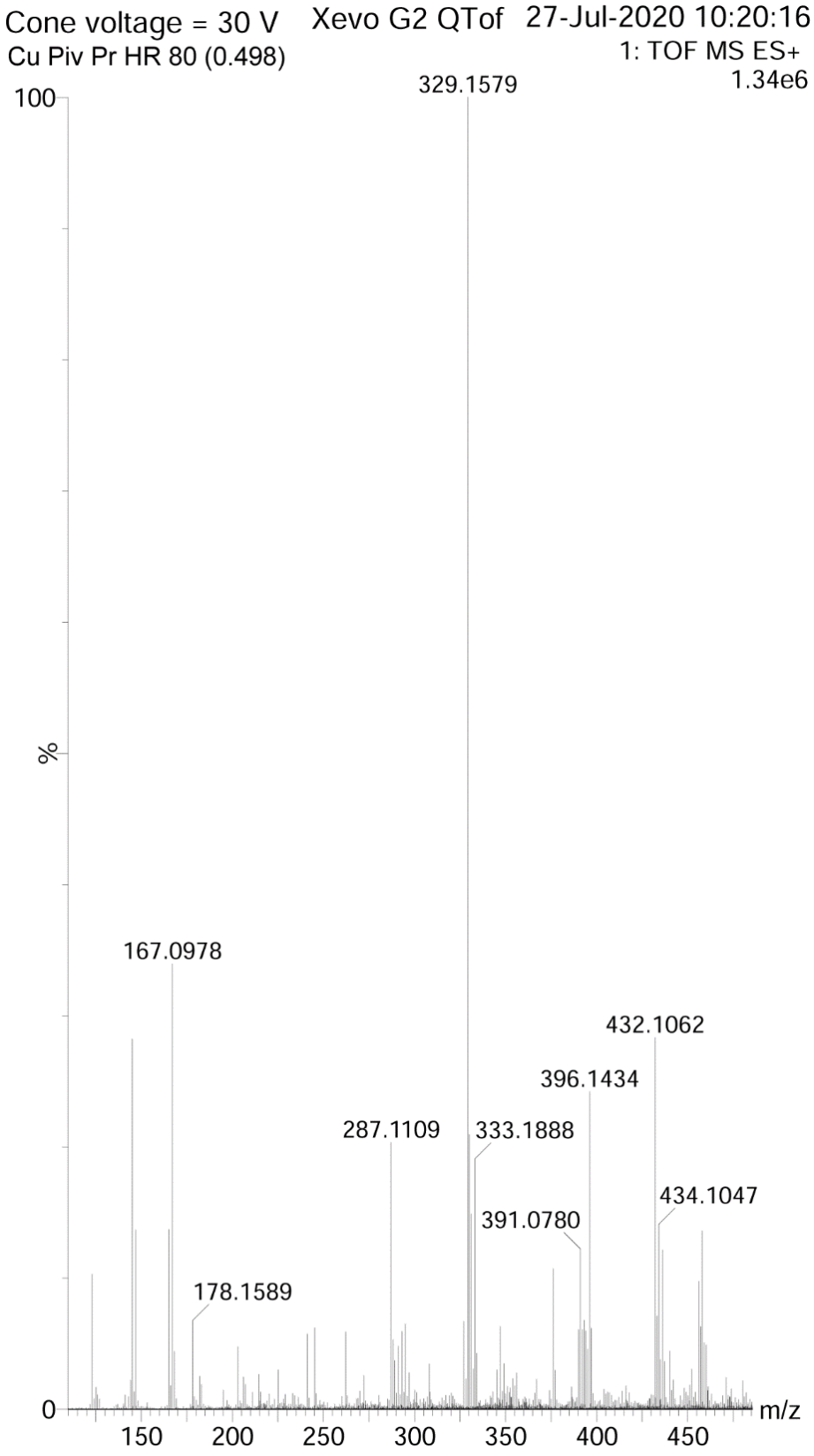


Figure S2. HRMS spectra of **1a** complexation with $Cu(OPiv)_2$ in MeCN at r.t.: bis-pivalate [$Cu(OPiv)_2$(**1a**)] species (m/z 432.1), mono-pivalate [Cu(OPiv)(**1a**)] species (m/z 330.1) and a plausible species corresponding to a C–H activation event (m/z 329).

Synthesis of preformed copper nanoparticles (CuNPs)

Copper(I) mesityl (68.5 mg; 0.375 mmol and 15 mL of poly(ethylene glycol) dimethyl ether, which was previously dried at 120 °C overnight under vacuum (PEG, M_n *ca.* 250), were placed in a Fisher-Porter bottle under argon atmosphere. After maintaining the mixture under vacuum for *ca.* 3 minutes, the mixture was pressurized with H_2 (3 bar) and heated at 120 °C for 2 h, obtaining a dark red colloidal suspension. This suspension was transferred by cannula to a centrifuge tube under argon atmosphere together with 5 mL of degassed pentane. The mixture was centrifuged (3500 rpm) for15 minutes and the supernatant removed under argon. The solid was redispersed in 3 mL of degassed THF and 9 mL of degassed pentane were added; the resulting suspension was again centrifuged (3500 rpm; 15 min). The supernatant was removed under argon and the solid dried overnight, obtaining a dark red powder (33 mg; 70% Cu by ICP-MS).

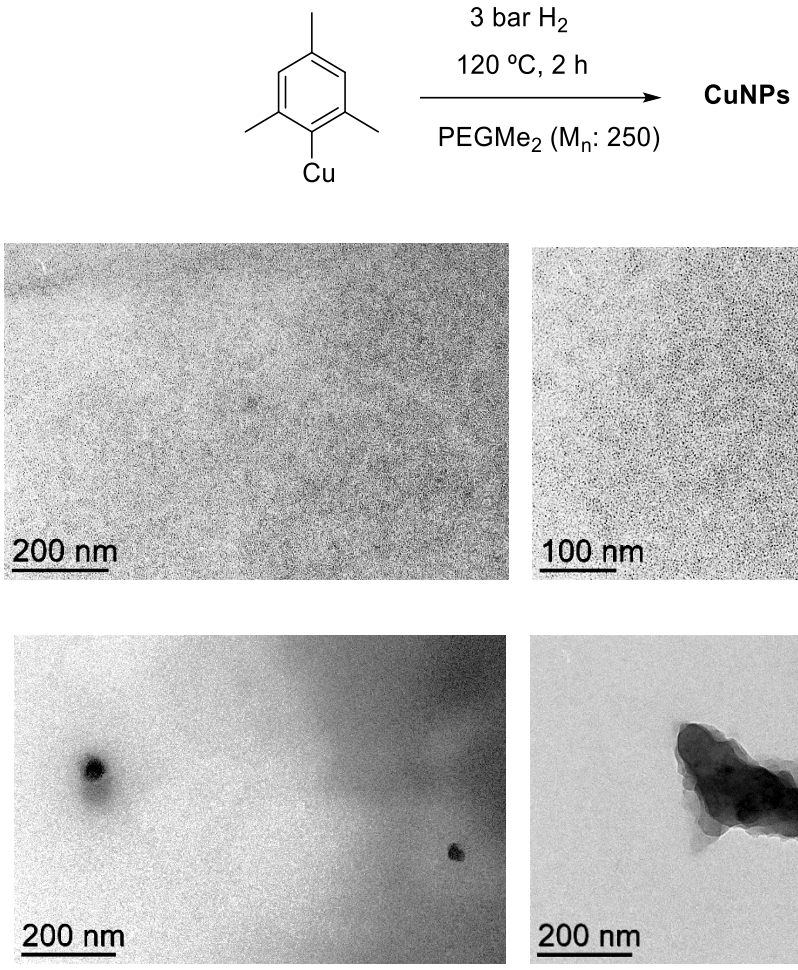
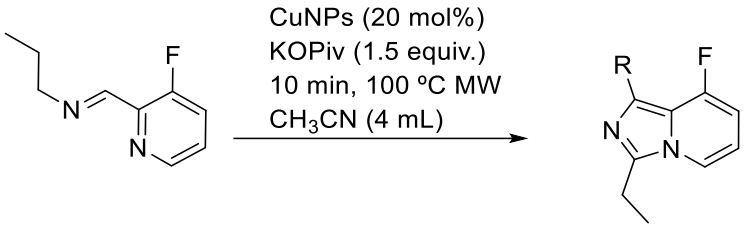


Figure S3. TOP: Synthesis of CuNPs applied in the synthesis of **2a** and **6a**. CENTER: TEM images corresponding to preformed CuNPs (d_{mean} = 1.1 ± 0.3 nm). BOTTOM: TEM images after catalytic reaction in the absence (left) and in the presence (right) of DDQ.

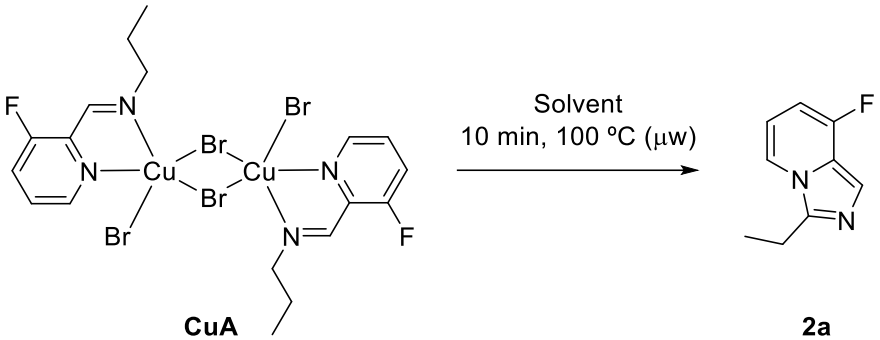


Oxidant	Yield	Conv.
None (reaction under air)	22% (R = H)	25%
DDQ (1 equiv.)	87% (R = CN)	100%

Figure S4. C–H bond functionalization reactions using Cu(0) NPs (20 mol%).

B. C–H bond functionalization: Reaction optimization tables.

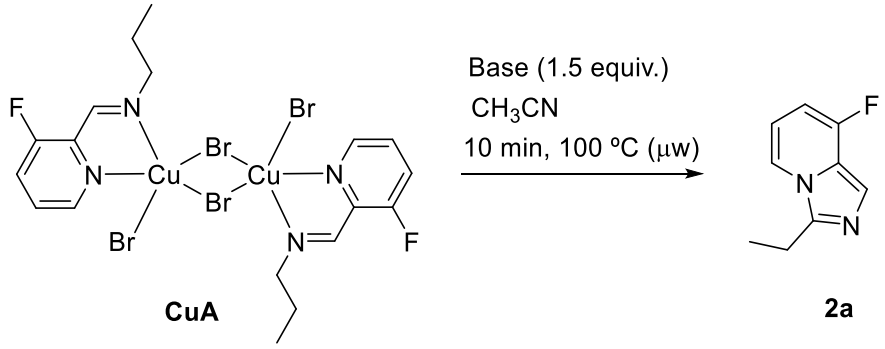
Table S1. Solvent screening for the C–H activation towards the formation of imidazo[1,5-*a*]pyridines under microwave irradiation (200 W) starting from the complex **CuA**.



Entry	Solvent	Conversion (%)[a]	Yield (%)[a]
1	$CHCl_3$	0	0
2	CH_3CN	0	0
3	Ac_2O	100	0[b]
4	AcOH-$CHCl_3$ (2:8)	5	3

[a] Reaction conditions: a solution of the $CuBr_2$-aldimine complex **CuA** (0.15 mmol, 117.0 mg) in the specified solvent (4 mL) was heated to 100 ºC for 10 min under microwave irradiation (max. 200 W). The reaction crude was diluted with CH_2Cl_2 (15 mL) and washed with tetrasodium ethylenediaminetetraacetate (3 × 15 mL, 0.4 M solution, pH 10-11). The combined organic extracts were dried with anhydrous Na_2SO_4, filtered and solvents evaporated under reduced pressure. Conversions and yields were determined by ^{19}F NMR using 4-fluorotoluene as standard. [b] A number of decomposition products was obtained, the main one being 3-fluoropyridine-2-carbaldehyde precursor (in 28%) as determined by ^{1}H NMR and ^{19}F NMR.

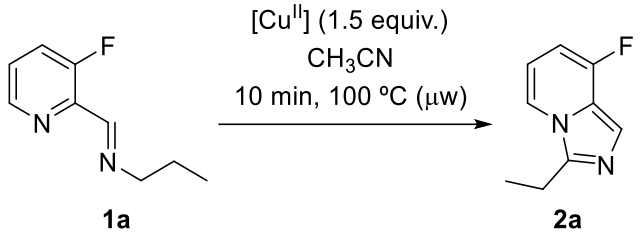
Table S2. Base effect for the C–H activation towards the formation of imidazo[1,5-*a*]pyridines under microwave irradiation (200 W) starting from the complex **CuA**.



Entry	Base	Conversion (%)[a]	2a (%)[a]
1[b]	CsOAc	8	3
2	KOAc	26	25
3	KOH	0	0
4[c]	KO^{t}Bu	100	0
5	No base	0	0

[a] Reaction conditions: general procedure C2 in CH_3CN as solvent, followed by work-up B. Conversions and yields were determined by ^{19}F NMR with 4-fluorotoluene as standard. [b] CsOAc is highly insoluble in CH_3CN. [c] Only degradation by-products were obtained in the presence of KO^{t}Bu.

Table S3. Cu(II) screening studies for C(sp^3)–H functionalization and cyclization towards the formation of imidazo[1,5-*a*]pyridines under microwave irradiation.[a]

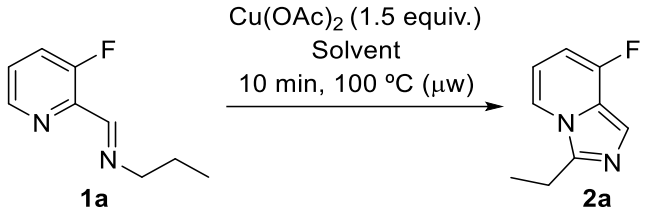


1a **2a**

Entry	[Cu^{II}]	Conversion (%)[b]	Yield (%)[b]
1	$CuBr_2$+1.5 equiv. NBu_4OAc	62	52
2	$Cu(OAc)_2$	73 (60)[c]	62 (40)[c]
3	$Cu(OOCH)_2 \cdot 4H_2O$	85	55
4	$Cu(OBz)_2$	68	14
5	$Cu(OPiv)_2$	95	83
6	$CuBr_2$	0	0
7[d]	$Cu(OPiv)_2$	>99[e]	0

[a] Reaction conditions: A solution of aldimine **1a** (0.30 mmol) and a Cu(II) salt (0.45 mmol) in CH_3CN (4 mL) was heated to 100 ºC for 10 min under microwave irradiation (max. 200 W). The reaction crude was diluted with CH_2Cl_2 (15 mL) and washed with tetrasodium ethylenediaminetetraacetate (3 × 15 mL, 0.4 M solution, pH 10-11). The combined organic extracts were dried with anhydrous Na_2SO_4, filtered and solvents evaporated under reduced pressure. [b] Conversions and yields were determined by ^{19}F NMR with 4-fluorotoluene as standard. [c] Results obtained under standard thermal conditions at 100 ºC for 8 h. [d] One-pot reaction conditions: a solution of 1-propylamine (0.30 mmol), 3-fluoro-2-pyridinecarboxaldehyde (0.30 mmol) and $Cu(OPiv)_2$ (0.45 mmol) in CH_3CN (4 mL) was heated to 100 ºC for 10 min under microwave irradiation (max. 200 W). [e] Quantitative conversion of 3-fluoro-2-pyridinecarboxaldehyde starting material.

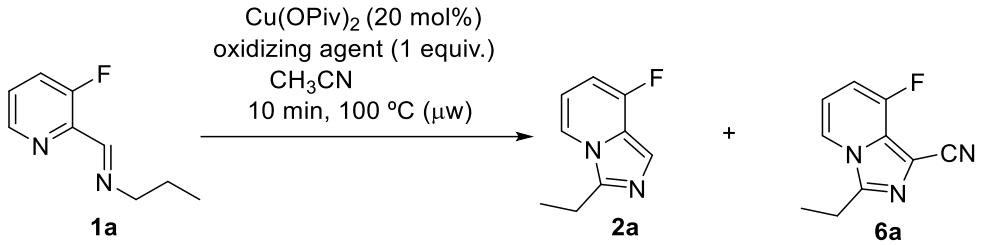
Table S4. Solvent screening studies for C–H cyclization towards the formation of imidazopyridines under microwave irradiation (max. power 200 W).

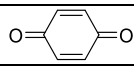
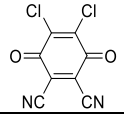
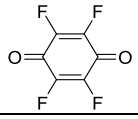
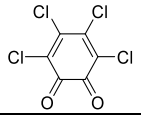
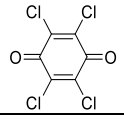
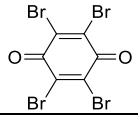
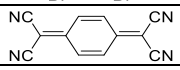
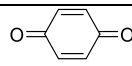


Entry	Solvent	Conversion[a] (%)	Yield[a] (%)
1	CF_3COOH	100	0
2	EtOAc	100	0
3	Glycerol	14	14
4	AcOH	75	10
5	EtOH	18	7
6	CH_3CN	70	48
7	$CHCl_3$	20	17

[a] Reaction conditions: A solution of aldimine **1a** (0.30 mmol) and $Cu(OAc)_2$ (81.7 mg, 0.45 mmol) in CH_3CN (4 mL) was heated to 100 ºC for 10 min under microwave irradiation (max. 200 W). The reaction crude was diluted with CH_2Cl_2 (15 mL) and washed with tetrasodium ethylenediaminetetraacetate (3 × 15 mL, 0.4 M solution, pH 10-11). The combined organic extracts were dried with anhydrous Na_2SO_4, filtered and solvents evaporated under reduced pressure. Conversions and yields were determined by ^{19}F NMR with 4-fluorotoluene as standard.

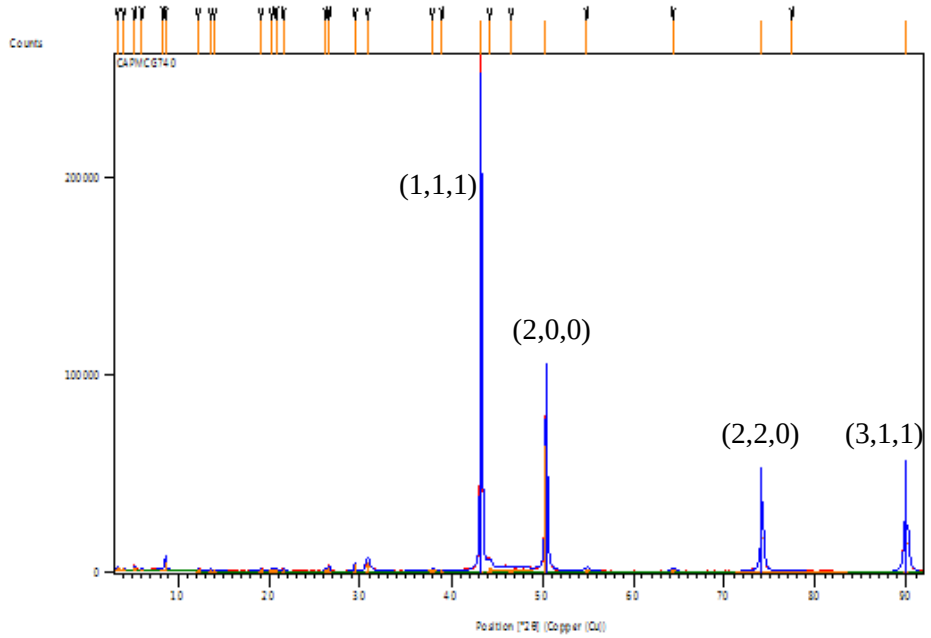
Table S5. Screening of oxidizing agents to enable the catalytic formation of imidazo[1,5-*a*]pyridines under microwave irradiation.



Entry	Oxidant	Conversion (%)[a]	Selectivity	
			2a (%)[a]	6a (%)[a]
1	Piv_2O	20	12	0
2		20	14	0
3	$K_3[Fe(CN)_6]$, dibenzo-18-crown-6	68	23	0
4		100	0	87
5		100	0	0
6		100	0	0
7		100	0	0
8		100	0	0
9		100	0	0
10	$K_3[Fe(CN)_6]$	100	0	0
11	$K_3[Fe(CN)_6]$, $PhNEt_3Cl$	100	0	0
12	$K_3[Fe(CN)_6]$, H_2O	96	0	0
13	BzOOBz	100	0	0
14	Air[b]	82	0	0
15[c]	 , Me_3SiCN	20	**2b**: 9	**6b**: 0[d]

[a] Reaction conditions: The selected oxidizing agent (0.30 mmol) was added in one solid portion to a solution of aldimine **1a** (0.30 mmol) and $Cu(OPiv)_2$ (16 mg, 0.06 mmol, 20 mol%) in CH_3CN (4 mL). The reaction mixture was heated to 100 ºC for 10 min under microwave irradiation (max. 200 W). Na_2S (14 mg, 0.18 mmol) was then added and the crude reaction mixture was stirred for 20 min under ultrasonic irradiation. The crude was then filtered through a 0.20 μm PTFE filter and solids were rinsed with CH_2Cl_2 (5 × 5 mL) and the solvent was removed under reduced pressure. Conversions and yields were determined by ^{19}F NMR with 4-fluorotoluene as standard. [b] The reaction of aldimine **1a** (0.30 mmol) and of $Cu(OPiv)_2$ (16 mg, 0.06 mmol, 20 mol%) in CH_3CN (4 mL) was carried out in a Fisher-Porter bottle under atmospheric pressure and standard heating. [c] Reaction conditions: 1,4-benzoquinone (0.30 mmol) and Me_3SiCN (0.30 mmol) were added to a solution of aldimine **1b** (0.30 mmol) and $Cu(OPiv)_2$ (16 mg, 0.06 mmol, 20 mol%) in CH_3CN (4 mL). The reaction mixture was heated to 100 ºC for 10 min under microwave irradiation (max. 200 W). [d] A cyanated by-product of m/z 317 could be detected in low yield (<5%) by GC-MS.

C. Mechanistic insights for the copper-promoted formation of 2a and 6a.



Peak List

Pos.[°2θ]	Height [cts]	FWHMLeft[°2θ]	d-spacing [Å]	Rel. Int. [%]
3.3896	951.39	0.4253	26.04479	0.43
4.0151	864.01	0.1267	21.98918	0.39
5.2255	1312.94	0.3203	16.89810	0.59
6.0427	983.18	0.1933	14.61447	0.44
8.3728	1007.27	0.8468	10.55186	0.45
8.5969	4496.64	0.0779	10.27724	2.01
12.1729	886.36	0.3768	7.26497	0.40
13.5832	663.49	0.1090	6.51370	0.30
13.9607	463.70	0.1167	6.33839	0.21
19.1157	466.99	0.5698	4.63914	0.21
20.3073	581.81	0.6604	4.36953	0.26
20.7595	1087.34	0.1030	4.27537	0.49
21.5842	737.08	0.3504	4.11384	0.33
26.2190	766.97	0.3408	3.39619	0.34
26.5860	1968.25	0.1389	3.35014	0.88
29.4255	3458.15	0.1059	3.03299	1.55
30.8344	4512.27	0.5439	2.89755	2.02
37.9203	600.76	0.8641	2.37080	0.27
38.9858	494.60	0.0474	2.30843	0.22
43.2688	223391.20	0.1443	2.08933	100.00
44.2048	2395.00	0.5090	2.04724	1.07
46.5645	1623.52	4.8301	1.94884	0.73
50.3985	63495.20	0.2287	1.80920	28.42
54.8642	1349.47	0.6942	1.67203	0.60
64.3423	861.03	0.6729	1.44671	0.39
74.0851	33528.36	0.2377	1.27870	15.01
77.4293	297.37	12.3809	1.23161	0.13
89.8933	28674.04	0.3293	1.09038	12.84

Pattern List

Visible	Ref.Code	Score	Compound Name	Displ.[°2θ]	Scale Fac.	Chem. Formula
*	96-901-2044	35	Copper	0.000	0.697	Cu4.00

Figure S5. PXRD diffractogram of Cu at solid state isolated after **2a** synthesis (blue peaks. The sharp blue lines correspond to the diffraction pattern of bulk face-centered cubic Cu(0) structure with the corresponding crystallographic plane assignments.

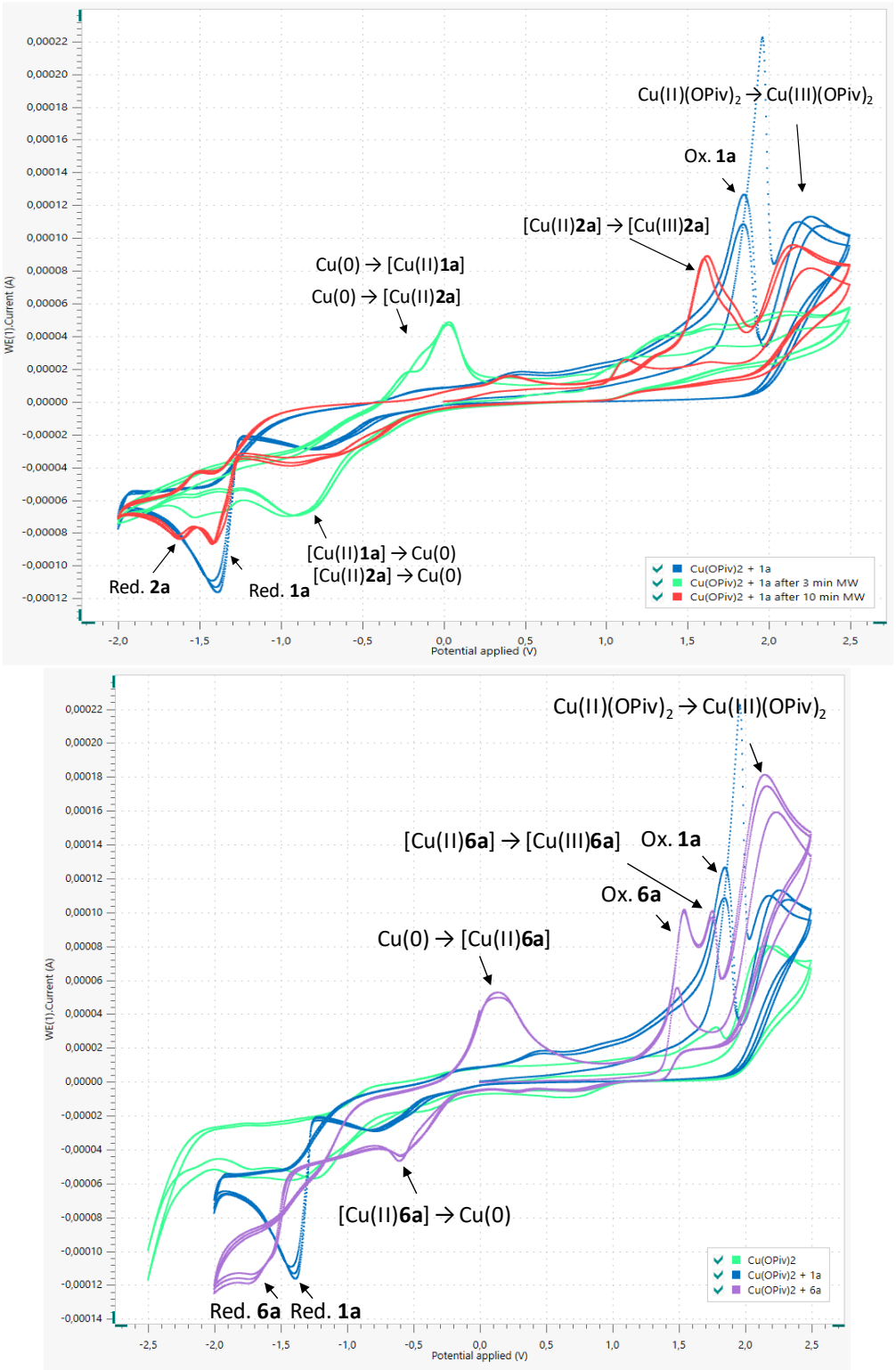
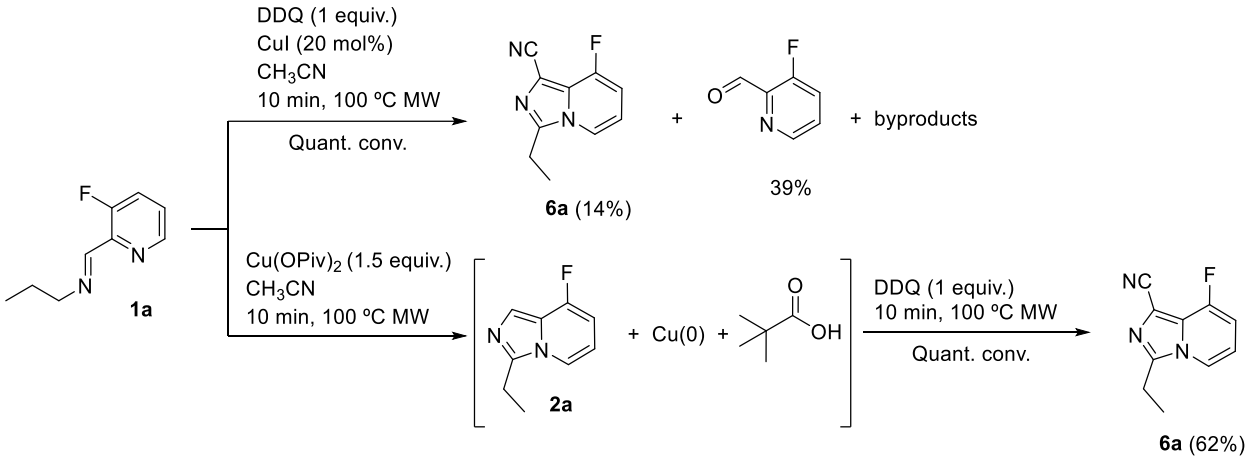


Figure S6. Stacked cyclic voltammograms. TOP: monitoring of $Cu(OPiv)_2$ and **1a** in CH_3CN at t_0 (blue), 3 min (green), and 10 min (red). BOTTOM: TOP: Control voltammograms of $Cu(OPiv)_2$ (green), a mixture of $Cu(OPiv)_2$ and **1a** (blue) and a mixture of $Cu(OPiv)_2$ and **6a** (violet) in CH_3CN. For $Cu(OAc)_2$ and its amine-based complexes, see G. Panzeri, R. Dell'Oro, V. Trifiletti, J. Parravicini, M. Acciarri, S. Binetti, L. Magagnin, *Electrochem. Commun.* **2019**, *109*, 106580.



Scheme S2. Cyanation control studies with DDQ.

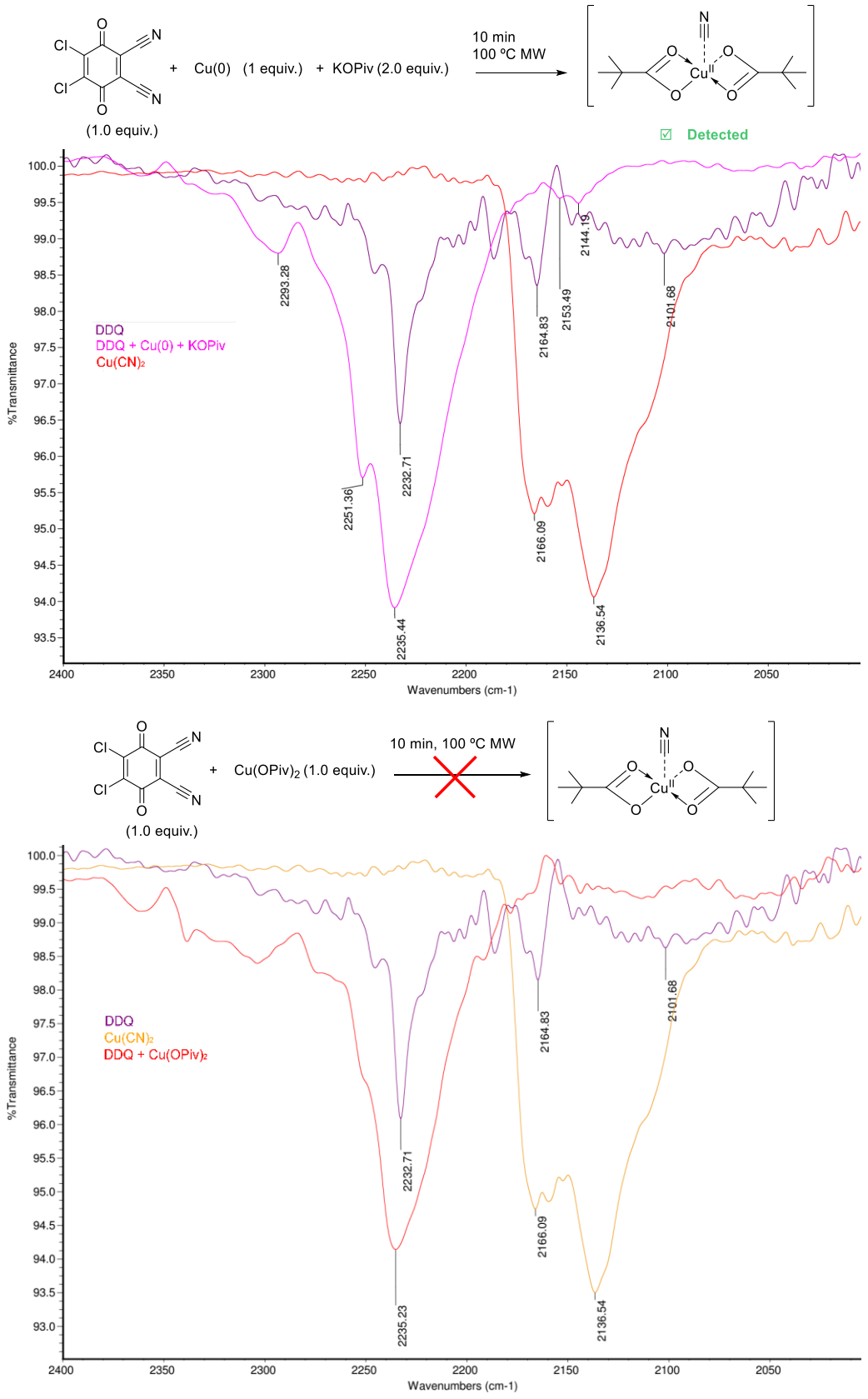
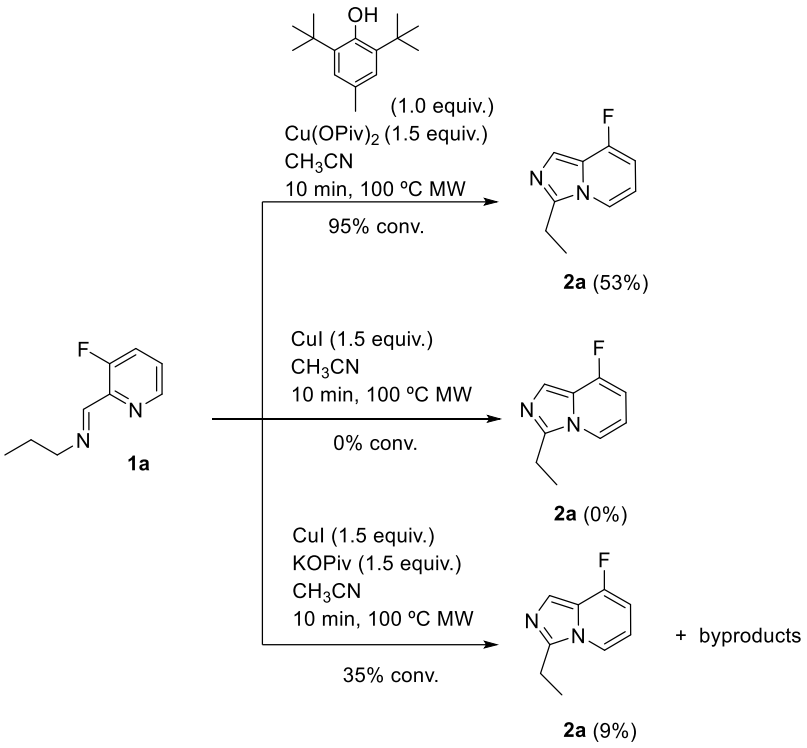
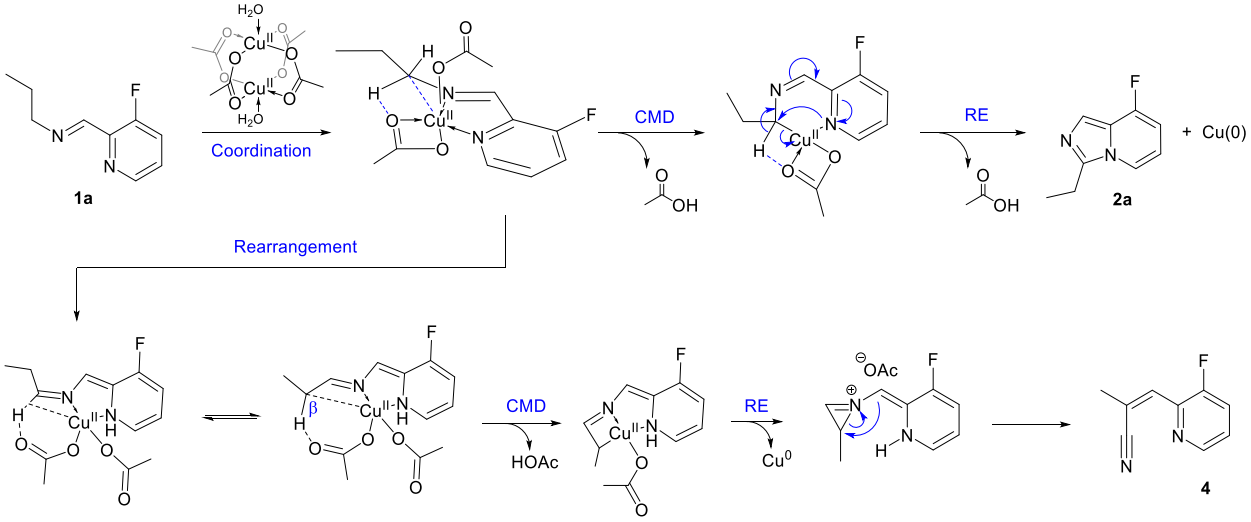


Figure S7. Formation of copper cyanide species from DDQ and copper sources. Top: Reaction control with Cu(0) and KOPiv. Bottom: Reaction control with $Cu(OPiv)_2$.

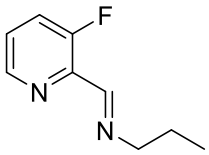


Scheme S3. Stoichiometric control studies with $Cu(OPiv)_2$ for the formation of **2a** in the presence of a radical inhibitor and control studies with CuI.

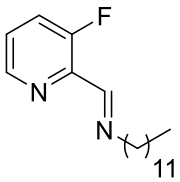


Scheme S4. A plausible reaction mechanism for the synthesis of **2a** and **4** via multiple Cu(II)-mediated C–H bond functionalizations.

D. Synthesis and characterization of compounds.

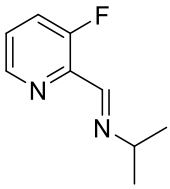


1-(3-Fluoropyridin-2-yl)-*N*-propylmethanimine (1a). Following the general procedure for the synthesis of aldimines and starting with propylamine (0.66 mL, 8.00 mmol), **1a** was obtained as a yellow oil (1.28 g, 96%) which was used without further purification. **IR** (ν in cm^{-1}) 2962, 1649, 1446, 803. **^{1}H NMR** (300 MHz, $CDCl_3$) δ_{ppm} 8.55 (s, 1H), 8.48 (dt, *J* = 4.5, 1.5 Hz, 1H), 7.42 (ddd, *J* = 10.1, 8.4, 1.4 Hz, 1H), 3.65 (t, *J* = 7.0, 2H), 1.76 (tq, *J* = 7.4, 7.0 Hz, 2H), 0.91 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (75.5 MHz, $CDCl_3$) δ_{ppm} 159.2 (d, J_{C-F}= 265.3 Hz), 155.3 (d, J_{C-F} = 3.0 Hz), 146.0 (d, J_{C-F} = 5.1 Hz), 141.8 (d, J_{C-F} = 8.1 Hz), 125.9 (d, J_{C-F} = 4.3 Hz), 124.2 (d, J_{C-F} = 18.9 Hz), 64.5, 23.7, 11.8. **^{19}F{^{1}H} NMR** (282 MHz, $CDCl_3$) δ_{ppm} -126.5. **HRMS** (DCI-CH_4) $[M+H]^+$ calculated for $C_9H_{12}N_2F$ m/z 167.0985, found m/z 167.0985.

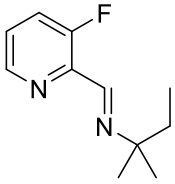


1-(3-Fluoropyridin-2-yl)-*N*-dodecylmethanimine (1b).

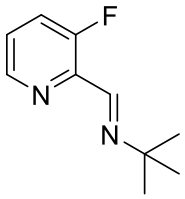
Following the general procedure for the synthesis of aldimines and starting with dodecylamine (1.4828 g, 8.00 mmol), **1b** was obtained as a yellow oil (2.2925 g, 98%) which was used without further purification. **IR** (ν in cm^{-1}) 2922, 2852, 1649, 1449, 803. **^{1}H NMR** (300 MHz, $CDCl_3$) δ_{ppm} 8.59 (s, 1H), 8.55 – 8.50 (m, 1H), 7.46 (m, 1H), 7.33 (m, 1H), 3.72 (t, *J* = 7.1 Hz, 2H), 1.77 (p, *J* = 7.1 Hz, 2H), 1.44 – 1.15 (m, 18H), 0.90 – 0.82 (t, *J* = 6.83 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ_{ppm} 159.3 (d, J_{C-F} = 265.3 Hz), 155.4 (d, J_{C-F} = 3.1 Hz), 146.2 (d, J_{C-F} = 5.3 Hz), 142.0 (d, J_{C-F} = 8.2 Hz), 126.0 (d, J_{C-F} = 4.3 Hz), 124.3 (d, J_{C-F} = 18.9 Hz), 62.9, 32.0, 30.7, 29.7, 29.6 (2 signals), 29.6, 29.5 (2 signals), 27.5, 22.8, 14.2. **^{19}F{^{1}H} NMR** (282 MHz, $CDCl_3$) δ_{ppm} -126.4. **HRMS** (DCI-CH_4) $[M+H]^+$ calculated for $C_{18}H_{30}N_2F$ m/z 293.2393, found m/z 293.2397. **Elemental Analysis** calcd. for $C_{18}H_{30}N_2F$, C: 73.93, H: 10.00, N: 9.58; found, C: 73.62, H: 10.37, N: 9.56.



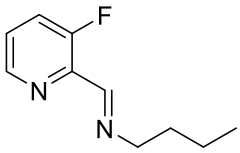
1-(3-Fluoropyridin-2-yl)-*N*-isopropylmethanimine (1c). Following the general procedure for the synthesis of aldimines and starting with isopropylamine (0.65 mL, 8.00 mmol), **1c** was obtained as a yellow oil (1.2630 g, 95%) which was used without further purification. **IR** (ν in cm^{-1}) 2971, 1646, 1444, 804, 751. **^{1}H NMR** (300 MHz, CD_3CN) δ 8.51 (d, *J* = 0.7 Hz, 1H), 8.47 (dt, *J* = 4.5, 1.5 Hz, 1H), 7.57 (ddd, *J* = 10.9, 8.4, 1.3 Hz, 1H), 7.42 (dt, *J* = 8.5, 4.3 Hz, 1H), 3.59 (dtt, *J* = 12.6, 6.2, 0.9 Hz, 1H), 1.23 (d, *J* = 6.3 Hz, 6H). **^{13}C NMR** (75 MHz, CD_3CN) δ 159.8 (d, J_{C-F} = 265.1 Hz), 155.7 (d, J_{C-F} = 5.0 Hz), 146.6 (d, J_{C-F} = 5.1 Hz), 143.2 (d, J_{C-F} = 7.8 Hz), 127.1 (d, J_{C-F} = 4.6 Hz), 125.5 (d, J_{C-F} = 19.0 Hz), 63.3, 24.3. **^{19}F{^{1}H} NMR** (282 MHz, CD_3CN) δ_{ppm} -125.4. **HRMS** (DCI-CH_4): $[M+H]^+$ calculated for $C_9H_{12}N_2F$ m/z 167.0985, found m/z 167.0990.



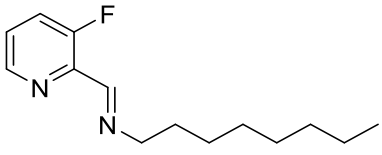
1-(3-Fluoropyridin-2-yl)-*N*-*tert*-pentylmethanimine (1d). Following the general procedure for the synthesis of aldimines and starting with *tert*-pentylamine (0.79 mL, 8.00 mmol), **1d** was obtained as a yellow oil (1.4762 g, 95%) which was used without further purification. **IR** (ν in cm^{-1}) 2967, 1646, 1446, 1179, 803. **^{1}H NMR** (300.0 MHz, $CDCl_3$) δ_{ppm} 8.59 – 8.48 (m, 2H), 7.45 (m, 1H), 7.31 (m, 1H), 1.71 (q, *J* = 7.5 Hz, 2H), 1.29 (s, 6H), 0.83 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR** (75.5 MHz, $CDCl_3$) δ_{ppm} 159.4 (d, J_{C-F} = 264.7 Hz), 150.7 (d, J_{C-F} = 2.6 Hz), 146.2 (d, J_{C-F} = 5.3 Hz), 142.8 (d, J_{C-F} = 7.9 Hz), 125.7 (d, J_{C-F} = 4.3 Hz), 124.3 (d, J_{C-F} = 18.9 Hz), 61.5, 35.5, 26.6, 8.8. **^{19}F{^{1}H} NMR** (282 MHz, $CDCl_3$) δ_{ppm} -126.8. **HRMS** (DCI-CH_4) $[M+H]^+$ calculated for $C_{11}H_{15}N_2F$ m/z 195.1298, found m/z 195.1299.



1-(3-Fluoropyridin-2-yl)-*N*-*tert*-butylmethanimine (1e). Following the general procedure for the synthesis of aldimines and starting with tert-butylamine (0.84 mL, 8.00 mmol), **1e** was obtained as a yellow oil (1.4415 g, 99%) which was used without further purification. **IR** (ν in cm^{-1}) 2969, 1651, 1285, 1263, 1250, 1226, 1211, 1181, 1158, 804. **^{1}H NMR** (300 MHz, $CDCl_3$) δ_{ppm} 8.60 (s, 1H), 8.54 (m, 1H), 7.44 (m, 1H), 7.36 – 7.27 (m, 1H), 1.34 (s, 9H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ_{ppm} 159.5 (d, J_{C-F} = 264.4 Hz), 150.1 (d, J_{C-F} = 2.3 Hz), 146.2 (d, J_{C-F} = 5.3 Hz), 142.6 (d, J_{C-F} = 7.9 Hz), 125.8 (d, J_{C-F} = 4.3 Hz), 124.2 (d, J_{C-F} = 18.9 Hz), 58.9, 29.7. **^{19}F{^{1}H} NMR** (282 MHz, $CDCl_3$) δ_{ppm} -127.1. **HRMS** (DCI-CH_4): $[M+H]^+$ calculated for $C_{10}H_{14}N_2F$ m/z 181.1141, found m/z 181.1142.

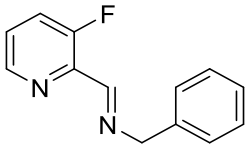


1-(3-Fluoropyridin-2-yl)-*N*-butylmethanimine (1f). Following the general procedure for the synthesis of aldimines and starting with n-butylamine (0.79 mL, 8.00 mmol), **1f** was obtained as a yellow oil (1.4416 g, 99%) which was used without further purification. **IR** (ν in cm^{-1}) 2958, 1648, 1450, 804. **^{1}H NMR** (300.0 MHz, $CDCl_3$) δ_{ppm} 8.57 (s, 1H), 8.50 (m, 1H), 7.44 (m, 1H), 7.31 (m, 1H), 3.70 (t, *J* = 7.1 Hz, 2H), 1.74 (p, *J* = 7.2 Hz, 2H), 1.36 (h, *J* = 7.4 Hz, 2H), 0.91 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ_{ppm} 159.3 (d, J_{C-F} = 265.3 Hz), 155.3 (d, J_{C-F} = 3.1 Hz), 146.1 (d, J_{C-F} = 5.3 Hz), 141.9 (d, J_{C-F} = 8.3 Hz), 125.9 (d, J_{C-F} = 4.4 Hz), 124.3 (d, J_{C-F} = 18.9 Hz), 62.5, 32.7, 20.5, 13.9. **^{19}F{^{1}H} NMR** (282 MHz, $CDCl_3$) δ_{ppm} -126.4. **HRMS** (DCI-CH_4) $[M+H]^+$ calculated for $C_{10}H_{14}N_2F$ *m/z* 181.1141, found *m/z* 181.1137.

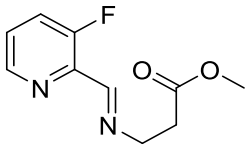


1-(3-Fluoropyridin-2-yl)-*N*-octylmethanimine (1g). Following the general procedure for the synthesis of aldimines and starting with n-octylamine (1.32 mL, 8.00

mmol), **1g** was obtained as a yellow oil (1.8906 g, 99%) which was used without further purification. **IR** (ν in cm^{-1}) 2954, 2854, 1648, 1592, 1571, 1510, 1450, 1377, 1335, 1261, 1232, 1184, 1158, 1107, 803. **^{1}H NMR** (300.0 MHz, $CDCl_3$) δ_{ppm} 8.57 (s, 1H), 8.50 (m, 1H), 7.44 (m, 1H), 7.31 (m, 1H), 3.70 (t, *J* = 7.1 Hz, 2H), 1.76 -1.30 (m, 12H), 0.91 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ_{ppm} 159.2 (d, J_{C-F} = 265.4 Hz), 155.3 (d, J_{C-F} = 3.1 Hz), 146.1 (d, J_{C-F} = 5.2 Hz), 141.9 (d, J_{C-F} = 8.2 Hz), 125.9 (d, J_{C-F} = 4.3 Hz), 124.3 (d, J_{C-F} = 18.8 Hz), 62.8, 31.9, 30.6, 29.4, 29.3, 27.4, 22.7, 14.1. **^{19}F{^{1}H} NMR** (282 MHz, $CDCl_3$) δ_{ppm} -126.4. **HRMS** (DCI-CH_4) [M+H] + calculated for $C_{14}H_{22}N_2F$ m/z 237.1767, found m/z 237.1764.

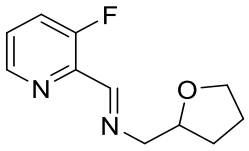


1-(3-Fluoropyridin-2-yl)-*N*-benzylmethanimine (1h). Following the general procedure for the synthesis of aldimines and starting with benzylamine (0.87 mL, 8.00 mmol), **1h** was obtained as a yellow oil (1.6454 g, 96%) which was used without further purification. **IR** (ν in cm^{-1}) 3021, 2840, 1644, 1447, 800. **^{1}H NMR** (300 MHz, CD_3CN) δ_{ppm} 8.63 (t, *J* = 1.5 Hz, 1H), 8.49 (dt, *J* = 4.5, 1.5 Hz, 1H), 7.59 (ddd, *J* = 10.9, 8.4, 1.3 Hz, 1H), 7.44 (dt, *J* = 8.5, 4.3 Hz, 1H), 7.39-7.29 (m, 5H), 4.86 (s, 2H). **^{13}C NMR** (75 MHz, CD_3CN) δ_{ppm} 159.5 (d, J_{C-F} = 265.8 Hz), 159.5 (d, J_{C-F} = 5.5 Hz), 146.6 (d, J_{C-F} = 5.2 Hz), 140.3, 129.6, 129.3 (d, J_{C-F} = 24.4 Hz), 128.9, 128.0, 127.3 (d, J_{C-F} = 4.8 Hz), 125.6 (d, J_{C-F} = 19.1 Hz), 66.5. **^{19}F{^{1}H} NMR** (282 MHz, $CDCl_3$) δ_{ppm} -124.7. **HRMS** (DCI-CH_4) $[M+H]^+$ calculated for $C_{13}H_{12}N_2F$ m/z 215.0985, found m/z 215.0988.



Methyl 3-(((3-fluoropyridin-2-yl)methylene)amino)propanoate (1i).

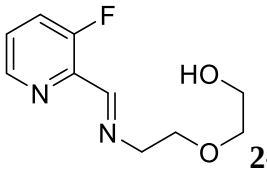
Following the general procedure for the synthesis of aldimines and starting with methyl 3-aminopropionate hydrochloride (1.2283 g, 8.8 mmol) and triethylamine (1.34 mL, 12.00 mmol), **1i** was obtained as a yellow oil (1.4961 g, 89%) which was used without further purification. **IR** (ν in cm^{-1}) 1736, 1649, 1450, 1262, 1175, 809. **^{1}H NMR** (300 MHz, CD_3CN) δ_{ppm} 8.53 (s, 1H), 8.48 (dt, *J* = 4.5, 1.5 Hz, 1H), 7.58 (ddd, *J* = 10.9, 8.5, 1.3 Hz, 1H), 7.44 (dt, *J* = 8.5, 4.3 Hz, 1H), 3.89 (t, *J* = 6.7 Hz, 2H), 3.62 (s, 3H), 2.70 (t, *J* = 6.7 Hz, 2H). **^{13}C NMR** (75 MHz, CD_3CN) δ_{ppm} 173.1, 159.9 (d, J_{C-F} = 265.6 Hz), 159.6 (d, J_{C-F} = 5.0 Hz), 146.6 (d, J_{C-F} = 5.1 Hz), 142.7 (d, J_{C-F} = 7.9 Hz), 127.4, 125.5 (d, J_{C-F} = 18.9 Hz), 58.1, 52.0, 35.7. **^{19}F{^{1}H} NMR** (282 MHz, CD_3CN) δ_{ppm} -125.2. **HRMS** (DCl-CH_4) calculated for $C_{10}H_{12}N_2O_2F$ m/z 211.0883 found 211.0885.



1-(3-Fluoropyridin-2-yl)-*N*-tetrahydrofurfurylmethanimine (1j).

Following the general procedure for the synthesis of aldimines and starting with tetrahydrofurfurylamine (0.83 mL, 8.00 mmol), **1j** was obtained as a yellow oil (1.5660 g, 94%) which was used without further purification.

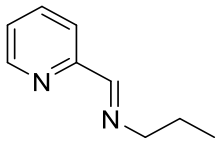
IR (ν in cm^{-1}) 2865, 1647, 1446, 1068, 806. **^{1}H NMR** (300 MHz, CD_3CN) δ_{ppm} 8.53-8.50 (m, 2H), 7.63 (ddd, *J* = 10.9, 8.4, 1.3 Hz, 1H), 7.48 (dt, *J* = 8.5, 4.3 Hz, 1H), 4.19 (qd, *J* = 6.8, 4.6 Hz, 1H), 3.88 – 3.78 (m, 2H), 3.76 – 3.65 (m, 2H), 1.98 – 1.65 (m, 4H). **^{13}C NMR** (75 MHz, CD_3CN) δ_{ppm} 159.8 (d, J_{C-F} = 265.8 Hz), 159.7 (d, J_{C-F} = 5.3 Hz), 146.6 (d, J_{C-F} = 5.2 Hz), 127.2 (d, J_{C-F} = 4.7 Hz), 125.6 (d, J_{C-F} = 19.1 Hz), 79.0, 68.5, 67.4, 30.0, 26.4. **^{19}F{^{1}H} NMR** (282 MHz, CD_3CN) δ_{ppm} -125.7. **HRMS** (ESI) [M+H]+ calculated for $C_{11}H_{14}N_2OF$ m/z 209.1085, found m/z 209.1086.



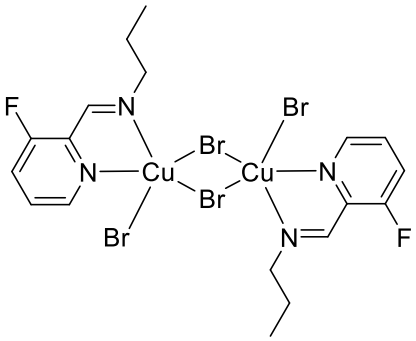
2-(2-(((3-Fluoropyridin-2-yl)methylene)amino)ethoxy)ethanol (1k).

Following the general procedure for the synthesis of aldimines and starting with 2-(2-aminoethoxy)ethanol (0.82 mL, 8.00 mmol), **1k** was obtained as a yellow oil (1.5618 g, 92%) which was used without further purification.

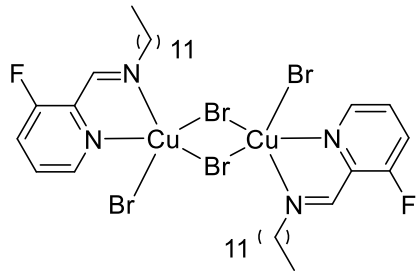
IR (ν in cm^{-1}) 3379, 2861, 1651, 1448, 1121, 1060, 806. **^{1}H NMR** (300 MHz, CD_3CN) δ_{ppm} 8.51 (t, *J* = 1.4 Hz, 1H), 8.48 (dt, *J* = 4.5, 1.5 Hz, 1H), 7.59 (ddd, *J* = 10.9, 8.4, 1.3 Hz, 1H), 7.44 (dt, *J* = 8.5, 4.3 Hz, 1H), 3.87 – 3.79 (m, 2H), 3.79 – 3.70 (m, 2H), 3.61 – 3.53 (m, 2H), 3.53 – 3.46 (m, 2H). **^{13}C NMR** (75 MHz, CD_3CN) δ_{ppm} 158.9 (d, J_{C-F} = 263.1 Hz), 159.8 (d, J_{C-F} = 5.1 Hz), 146.6 (d, J_{C-F} = 5.2 Hz), 127.3 (d, J_{C-F} = 4.7 Hz), 125.7, 125.5, 73.1, 70.9, 62.5, 61.9. **^{19}F{^{1}H} NMR** (282 MHz, CD_3CN) δ_{ppm} -125.2. **HRMS** (ESI) $[M+H]^+$ calculated for $C_{10}H_{13}N_2O_2F$ m/z 213.1034, found m/z 213.1039.



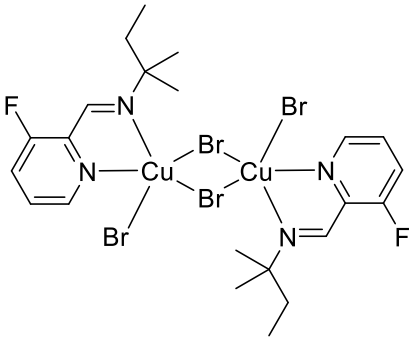
***N*-propyl-1-(pyridin-2-yl)methanimine (1a').** Following the general procedure for the synthesis of aldimines and starting with propylamine (0.66 mL, 8.00 mmol) and replacing the aldehyde by picolinaldehyde (0.8569 g, 8.00 mmol), **1a'** was obtained as a yellow oil (1.1140 g, 94%) which was used without further purification. **IR** (ν in cm^{-1}) 2962, 2930, 2874, 2834, 1650, 1587, 1567, 1468, 1436, 970, 772. **^{1}H NMR** (300 MHz, CD_3CN) δ 8.60 (ddd, *J* = 4.8, 1.8, 1.0 Hz, 1H), 8.33 (d, *J* = 0.9 Hz, 1H), 8.00 – 7.90 (m, 1H), 7.85 – 7.72 (m, 1H), 7.36 (ddd, *J* = 7.5, 4.8, 1.3 Hz, 1H), 3.60 (td, *J* = 6.9, 1.4 Hz, 2H), 1.69 (h, *J* = 7.2 Hz, 2H), 0.94 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (75 MHz, CD_3CN) δ 162.7, 155.9, 150.4, 137.6, 125.7, 121.3, 63.6, 24.7, 12.1. **HRMS** (DCI-CH_4): $[M+H]^+$ calculated for $C_9H_{13}N_2$ m/z 149.1079, found m/z 149.1085.



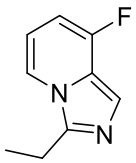
Complex $CuBr_2$-propylimine (CuA). Following the general procedure for the synthesis of $CuBr_2$-aldimine complexes and starting from 1-(3-fluoropyridin-2-yl)-*N*-propylmethanimine (**1a**) (200.0 mg, 1.20 mmol), **CuA** was obtained as a dark red powder (459.1 mg, 99%). **IR** (ν in cm^{-1}) 3675, 2988, 2900, 1638, 1604, 1582, 1459, 1248, 1119, 1065, 806. **^{1}H NMR** (300 MHz, CD_2Cl_2) δ_{ppm} 7.01 (br), 2.76 (br), 1.27 (br), 0.88 (br). **MS** (DCI-CH_4) $[M\text{-}Br^-]^+$ m/z 698.8.



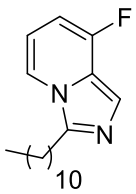
Complex $CuBr_2$-dodecylimine (CuB). Following the general procedure for the synthesis of $CuBr_2$-aldimine complexes and starting from 1-(3-fluoropyridin-2-yl)-*N*-dodecylmethanimine (**1b**) (351.0 mg, 1.20 mmol), the entitled product **CuB** (548.0 mg, 97%) was obtained as a red powder. **IR** (ν in cm^{-1}) 3041, 2921, 2852, 1645, 1458, 1288, 1242, 1117, 808. **MS** (DCI-CH_4) m/z 951.1.



Complex $CuBr_2$-*tert*-pentylimine (CuC). Following the general procedure for the synthesis of $CuBr_2$-aldimine complexes and starting from 1-(3-fluoropyridin-2-yl)-*N*-*tert*-pentylmethanimine (**1d**) (233.1 mg, 1.20 mmol), the entitled product **CuC** (401.0 mg, 80%) was obtained as a red powder. **IR** (ν in cm^{-1}) 2969, 2925, 1627, 1596, 1577, 1455, 1286, 1251, 1121, 818. **MS** (DCI-CH_4) m/z 833.8.

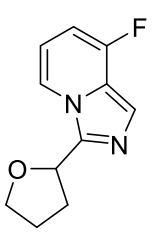


3-Ethyl-8-fluoroimidazo[1,5-*a*]pyridine (2a). Following the general procedure for stoichiometric C–H bond functionalization reactions with $Cu(OPiv)_2$ and starting with **1a** (50.0 mg, 0.30 mmol; scale-out in 4 reaction vessels). The reaction crude was treated with Na_2S (117.0 mg, 1.5 mmol) prior to the standard work-up. Column chromatography on neutral alumina and elution with pentane provided **2a** as a yellow oil (138.0 mg, 72%). **IR** (ν in cm^{-1}) 2963, 2932, 2875, 1649, 1556, 1450, 1243, 805. **^{1}H NMR** (300 MHz, $CDCl_3$) δ_{ppm} 7.52 (d, *J* = 7.0 Hz, 1H), 7.47 (s, 1H), 6.47 (td, *J* = 7.0 Hz; 5.0 Hz, 1H), 6.30 (dd, *J* = 10.3 Hz; 7.2 Hz, 1H), 2.95 (q, *J* = 7.5 Hz, 1H), 1.35 (t, *J* = 7.5 Hz, 2H). **^{13}C NMR** (75 MHz, CD_3CN) δ 153.5 (d, $J_{C\text{-}F}$ = 247.3 Hz), 142.2, 123.2 (d, $J_{C\text{-}F}$ = 39.0 Hz), 118.0 (d, $J_{C\text{-}F}$ = 4.5 Hz), 115.7 (d, $J_{C\text{-}F}$ = 4.2 Hz), 111.1 (d, $J_{C\text{-}F}$ = 7.3 Hz), 99.9 (d, $J_{C\text{-}F}$ = 17.4 Hz), 26.9, 19.7. **^{19}F{^{1}H} NMR** (282 MHz, $CDCl_3$) δ_{ppm} -123.6. **HRMS (ESI):** $[M+H]^+$ calculated for $C_9H_{10}N_2F$ m/z 164.0750, found m/z 164.0741

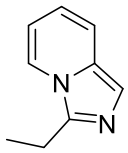


3-Undecyl-8-fluoroimidazo[1,5-*a*]pyridine (2b). Following the general procedure for stoichiometric C–H bond functionalization reactions with $Cu(OPiv)_2$ and starting with **1b** (88.3 mg, 0.30 mmol; scale-out in 3 reaction vessels). The reaction crude was treated with Na_2S (117.0 mg, 1.5 mmol) prior to the standard work-up. Column chromatography on neutral alumina and elution with pentane provided **2b** as a yellow oil (230.0 mg, 87%). **IR** (ν in cm^{-1}) 2925, 2854, 1648, 1556, 1466, 1439, 1374, 1242, 743. **^{1}H NMR** (300 MHz, $CDCl_3$) δ_{ppm} 7.52 (d, *J* = 7.0 Hz, 1H), 7.47(s, 1H), 6.47(td, *J* = 7.0 Hz; 5.0 Hz, 1H), 6.30 (dd, *J* = 10.3 Hz; 7.2 Hz, 1H), 2.96 (t, *J* = 7.7 Hz, 2H), 1.83 (m, 2H), 1.24 (m, 16H), 0.89 (t, *J* =6.6 Hz, 3H). **^{13}C NMR** (75 MHz, CD_3CN) δ_{ppm} 154.5 (d, $J_{C\text{-}F}$ = 247.5 Hz), 142.2, 124.1 (d, $J_{C\text{-}F}$ = 39.0 Hz), 119.0 (d, $J_{C\text{-}F}$ = 4.3 Hz), 116.8 (d, $J_{C\text{-}F}$ = 4.2 Hz), 112.1 (d, $J_{C\text{-}F}$ = 7.5 Hz), 100.8 (d, $J_{C\text{-}F}$ = 17.4 Hz), 32.7, 30.4, 30.3, 30.1, 30.1, 30.0, 27.9, 27.7, 27.3, 23.4, 14.4. **^{19}F{^{1}H} NMR** (282 MHz, $CDCl_3$) δ_{ppm} -123.5.

MS (EI) m/z 290.9. **HRMS (ESI):** $[M+H]^+$ calculated for $C_{18}H_{28}N_2F$ m/z 291.2231, found m/z 291.2234



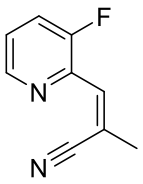
8-Fluoro-3-(tetrahydrofuran-2-yl)imidazo[1,5-*a*]pyridine (2j). Following the general procedure for stoichiometric C–H bond functionalization reactions with $Cu(OPiv)_2$ and starting with **1j** (62.5 mg, 0.30 mmol; scale-out in 4 reaction vessels). The reaction crude was treated with Na_2S (117.0 mg, 1.5 mmol) prior to the standard work-up. Column chromatography on neutral alumina and elution with cyclohexane provided **2j** as a yellow oil (170.0 mg, 69%). **IR** (ν in cm^{-1}) 2954, 2873, 1557, 1373, 1052, 753. **^{1}H NMR** (300 MHz, CD_3CN) δ_{ppm} 8.02 (dd, *J* = 7.0, 0.8 Hz, 1H), 7.41 (d, *J* = 0.9 Hz, 1H), 6.57 (td, *J* = 7.2, 5.1 Hz, 1H), 6.48 (ddd, *J* = 11.0, 7.3, 0.7 Hz, 1H), 5.27 (t, *J* = 6.9 Hz, 1H), 3.94 – 3.70 (m, 2H), 2.79 – 2.63 (m, 1H), 2.35 – 2.22 (m, 2H), 2.17 – 1.96 (m, 3H). **^{13}C NMR** (75 MHz, CD_3CN) δ_{ppm} 153.2 (d, $J_{C\text{-}F}$ = 247.5 Hz), 140.2, 119.2, 115.8 (d, $J_{C\text{-}F}$ = 4.1 Hz), 111.5 (d, $J_{C\text{-}F}$ = 7.2 Hz), 101.2, 101.0, 73.1, 68.1, 28.4, 25.6. **^{19}F{^{1}H} NMR** (282 MHz, CD_3CN) δ -126.7. **HRMS** (ESI): $[M+H]^+$ calculated for $C_{11}H_{12}N_2FO$ m/z 207.0928, found m/z 207.0927.



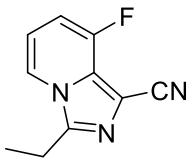
3-Ethylimidazo[1,5-a]pyridine (2a'). Following the general procedure for stoichiometric C–H bond functionalization reactions with $Cu(OPiv)_2$ and starting with *N*-propyl-1-(pyridin-2-yl)methanimine (**1a'**), **2a'** was obtained in 36% conversion (36% yield), as determined by GC-MS using 4-fluorotoluene as standard.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60 (d, *J* = 7.2 Hz, 1H), 7.30 (d, *J* = 9.1 Hz, 1H), 7.27 (s, 1H, *solvent overlap*), 6.54 (dd, *J* = 8.9, 6.5 Hz, 1H), 6.42 (t, *J* = 6.7 Hz, 1H), 2.88 (q, *J* = 7.5 Hz, 2H), 1.36 (t, *J* = 7.5 Hz, 3H). **MS** (EI) $[M+H]^+$ calculated for $C_9H_{11}N_2$ m/z 146.1 found 146.2.

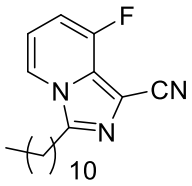
Characterization data match previous literature reports: Zeng et al. *Org. Lett*. **2014**, *16*, 6232−6235.



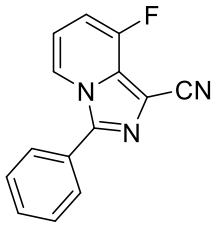
(*Z*)-3-(3-Fluoropyridin-2-yl)-2-methylacrylonitrile (4). Following the general procedure for stoichiometric C–H bond functionalization reactions with preformed $CuBr_2$-aldimine complexes and using NH_4OAc (34.7 mg, 0.45 mmol) as base in a solvent mixture of $CHCl_3$-AcOH (80:20, 4 mL) and work-up A, a crude mixture containing **2a** (traces), **3** (49%) and **4** (15%) could be determined by ^{19}F NMR with 4-fluorotoluene as standard. The product was purified by flash column chromatography using silica gel and a solvent mixture of $CHCl_3$-pentane (25:75) as eluent. **IR** (ν in cm^{-1}) 2925, 2211 (C≡N), 1432, 1243, 799. **^{1}H NMR** (300 MHz, $CDCl_3$) δ_{ppm} 8.53 (dt, *J* = 4.5, 1.4 Hz, 1H), 7.43 (ddd, *J* = 9.8, 8.4, 1.4 Hz, 1H), 7.33 (dt, *J* = 8.5, 4.3 Hz, 1H), 7.20 (p, *J* = 1.7 Hz, 1H), 2.25 (d, *J* = 1.7 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ_{ppm} 156.9 (d, J_{C-F} = 263.6 Hz), 145.4 (d, J_{C-F} = 5.4 Hz), 140.6, 133.4, 125.6, 123.3 (d, J_{C-F} = 19.0 Hz), 118.6, 112.2, 22.9. **^{19}F{^{1}H} NMR** (282 MHz, $CDCl_3$) δ_{ppm} -124.3. **HRMS** (DCI-CH_4) $[M+H]^+$ calculated for $C_9H_8FN_2$ m/z 163.0672 found 163.0669. Crystallographic data available in section **D.**



3-Ethyl-8-fluoroimidazo[1,5-*a*]pyridine-1-carbonitrile (6a). Following the general procedure for catalytic C–H bond functionalization reactions and starting with **1a** (50.0 mg, 0.30 mmol; scale-out in 4 reaction vessels), elution with cyclohexane/EtOAc/CH_3CN (100:0:0 to 40:50:10) gave a white solid (163.4 mg, 72%). **IR** (ν in cm^{-1}) 2923, 2215 (C≡N), 1564, 1271. **^{1}H NMR** (300 MHz, Methylene Chloride-d_2) δ_{ppm} 7.79 – 7.71 (m, 1H), 6.83 – 6.74 (m, 2H), 2.99 (q, *J* = 7.5 Hz, 2H), 1.44 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR** (75 MHz, Methylene Chloride-d_2) δ_{ppm} 153.2 (d, J_{C-F} = 253.2 Hz), 144.2, 119.3 (d, J_{C-F} = 5.1 Hz), 115.7, 114.4, 114.3, 106.8, 106.6, 20.7, 10.9. **^{19}F{^{1}H} NMR** (282 MHz, CD_3CN) δ -126.7. **HRMS** (DCI-CH_4) $[M+H]^+$ calculated for $C_{10}H_9FN_3$ m/z 190.0775 found 190.0786.

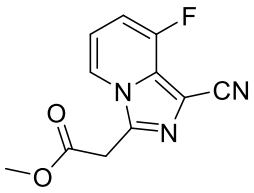


3-Undecyl-8-fluoroimidazo[1,5-*a*]pyridine-1-carbonitrile (6b). Following the general procedure for catalytic C–H bond functionalization reactions and starting with **1b** (87.7 mg, 0.30 mmol; scale out in 2 reaction vessels), elution with cyclohexane/EtOAc/CH_3CN (100:0:0 to 40:50:10) gave a white solid (140.0 mg, 74%). **IR** (ν in cm^{-1}) 2919, 2850, 2220 (C≡N), 1560, 1246. **^{1}H NMR** (300 MHz, Methylene Chloride-d_2) δ_{ppm} 7.75 (dd, J = 4.9, 2.8 Hz, 1H), 6.83 – 6.72 (m, 2H), 2.96 (t, J = 7.7 Hz, 2H), 1.85 (p, J = 7.5 Hz, 2H), 1.26 (s, 12H), 0.94 – 0.80 (m, 4H). **^{13}C NMR** (75 MHz, Methylene Chloride-d_2) δ_{ppm} 153.1 (d, $J_{C\text{-}F}$ = 253.2 Hz), 143.3, 119.2 (d, $J_{C\text{-}F}$ = 5.1 Hz), 115.6, 114.1 (d, $J_{C\text{-}F}$ = 6.7 Hz), 106.6, 106.4, 100.5 (d, $J_{C\text{-}F}$ = 4.6 Hz), 43.9, 32.3, 30.6, 30.0, 29.9, 29.7, 29.7, 29.6, 27.3, 27.1, 26.8, 23.1, 14.3. **^{19}F{^{1}H} NMR** (282 MHz, Methylene Chloride-d_2) δ -124.6. **HRMS** (DCI-CH_4) calculated for $C_{19}H_{27}FN_3$ m/z 316.2189 found 316.2193.



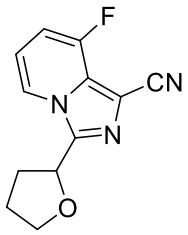
8-Fluoro-3-phenylimidazo[1,5-*a*]pyridine-1-carbonitrile (6h).

Following the general procedure for catalytic C–H bond functionalization reactions and starting with **1h** (64.3 mg, 0.30 mmol; scale out in 4 reaction vessels), elution with cyclohexane/EtOAc/CH_3CN (100:0:0 to 33:56:11) gave a white solid (230.6 mg, 81%). **IR** (ν in cm^{-1}) 2225 (C≡N), 1564, 1407. **^{1}H NMR** (300 MHz, CD_3CN) δ_{ppm} 8.27 (dd, J = 7.0, 0.7 Hz, 1H), 7.86 – 7.72 (m, 2H), 7.68 – 7.52 (m, 3H), 6.98 (ddd, J = 10.5, 7.6, 0.6 Hz, 1H), 6.87 (ddd, J = 7.6, 7.1, 4.9 Hz, 1H). **^{13}C NMR** (75 MHz, CD_3CN) δ_{ppm} 153.3 (d, $J_{C\text{-}F}$ = 250.1 Hz), 142.5, 131.2, 130.2, 129.6, 121.6 (d, $J_{C\text{-}F}$ = 5.1 Hz), 115.6 (d, $J_{C\text{-}F}$ = 6.8 Hz), 108.5 (d, $J_{C\text{-}F}$ = 16.4 Hz). **^{19}F{^{1}H} NMR** (282 MHz, CD_3CN) δ -127.2 (d, J = 6.4 Hz). **HRMS** (DCI-CH_4) $[M+H]^+$ calculated for $C_{14}H_9N_2FO$ m/z 238.0781, found m/z 238.0772.

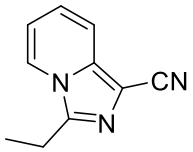


Methyl (1-cyano-8-fluoroimidazo[1,5-*a*]pyridin-3-yl)acetate (6i). Following the general procedure for catalytic C–H bond functionalization reactions and starting with **1i** (63.1 mg, 0.30 mmol; scale out in 4 reaction vessels), elution with cyclohexane/EtOAc/CH_3CN (77:19:4 to 8:77:15) gave a brown solid (152.9 mg, 55%). **IR** (ν in cm^{-1}) 2226 (C≡N), 1736, 1584, 1451, 1206.

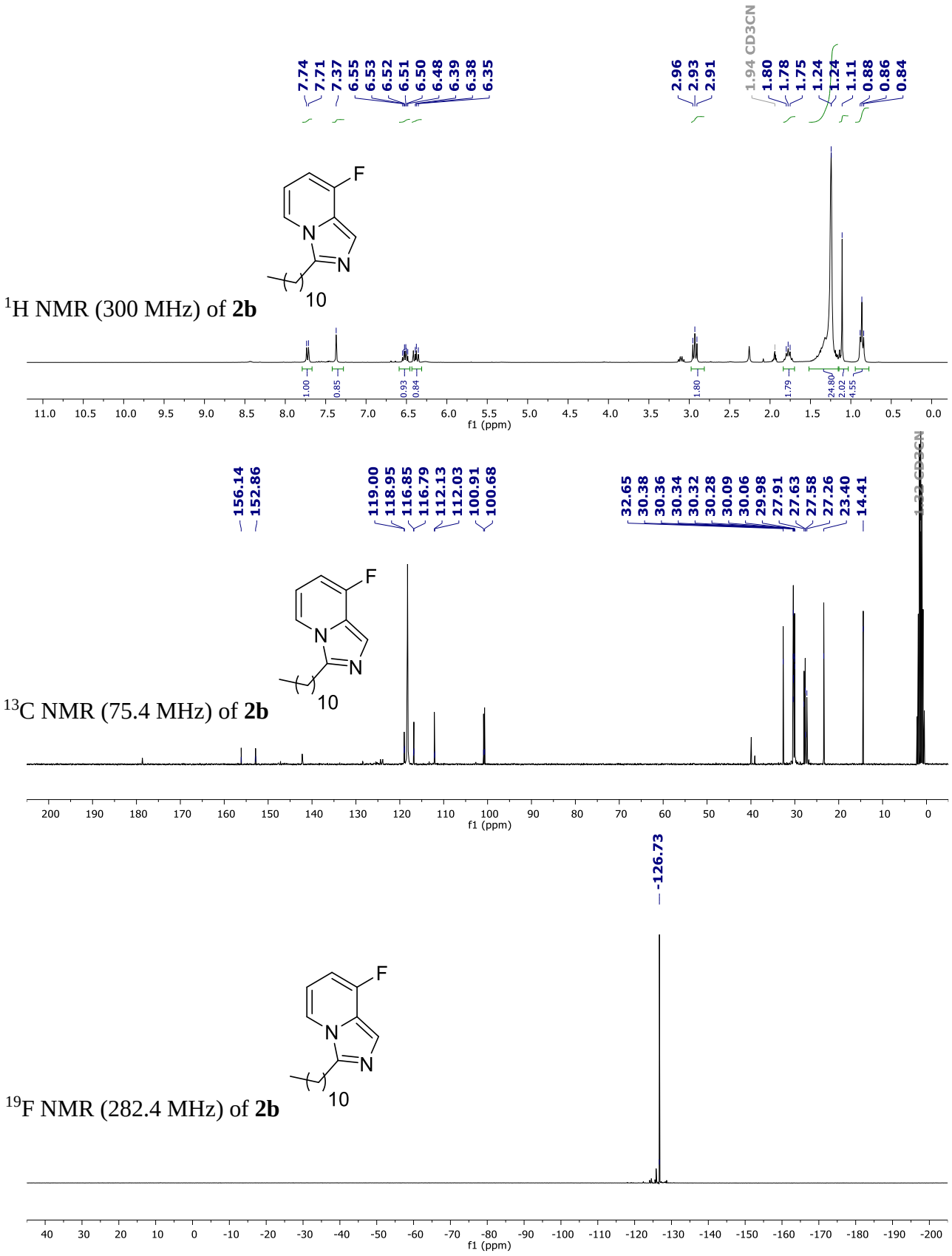
^{1}H NMR (300 MHz, CD_3CN) δ_{ppm} 8.00 (d, J = 6.8 Hz, 1H), 7.01 – 6.82 (m, 2H), 4.18 (s, 2H), 3.69 (s, 3H). **^{13}C NMR** (126 MHz, CD_3CN) δ_{ppm} 169.2, 153.1 (d, J_{C-F} = 250.1 Hz), 137.3, 130.8 (d, J_{C-F} = 36.4 Hz), 116.0, 115.1, 108.3 (d, J_{C-F} = 16.3 Hz), 100.6, 53.2, 33.9. **^{19}F{^{1}H} NMR** (282 MHz, CD_3CN) δ -127.2. **HRMS** (DCI-CH_4): $[M+H]^+$ calculated for $C_{11}H_9N_3FO_2$ m/z 234.0679, found m/z 234.0691.



8-Fluoro-3-(tetrahydrofuran-2-yl)imidazo[1,5-*a*]pyridine-1-carbonitrile (6j). Following the general procedure for catalytic C–H bond functionalization reactions and starting with **1j** (62.5 mg, 0.30 mmol; scale-out in 4 reaction vessels), elution with cyclohexane/EtOAc/CH_3CN (100:0:0 to 40:50:10) gave a white solid (190.0 mg, 69%). **IR** (ν in cm^{-1}): 3037, 2221 (C≡N), 1560, 1246. **^{1}H NMR** (300 MHz, CD_3CN) δ_{ppm} 8.26 (dd, J = 7.0, 0.7 Hz, 1H), 6.96 (ddd, J = 10.6, 7.6, 0.7 Hz, 1H), 6.88 (ddd, J = 7.6, 6.9, 5.0 Hz, 1H), 5.31 (dd, J = 7.4, 6.0 Hz, 1H), 3.97 – 3.74 (m, 2H), 2.77 – 2.59 (m, 1H), 2.32 (dddd, J = 12.4, 8.5, 7.4, 6.0 Hz, 1H), 2.13 – 1.99 (m, 2H). **^{13}C NMR** (75 MHz, CD_3CN) δ_{ppm} 152.2 (d, J_{C-F} = 249.8 Hz), 142.1, 121.3 (d, J_{C-F} = 5.2 Hz), 115.3, 114.0 (d, J_{C-F} = 6.7 Hz), 107.7 (d, J_{C-F} = 16.2 Hz), 98.9, 72.9, 68.4, 28.4, 25.3. **^{19}F{^{1}H} NMR** (282 MHz, CD_3CN) δ -127.3. **HRMS** (DCI-CH_4) $[M+H]^+$ calculated for $C_{12}H_{11}N_3FO$ m/z 232.0886, found m/z 232.0892.



3-Ethylimidazo[1,5-*a*]pyridine-1-carbonitrile (6a'). Following the general procedure for catalytic C–H bond functionalization reactions and starting with *N*-propyl-1-(pyridin-2-yl)methanimine (**1a'**) (44.5 mg, 0.3 mmol; scale-out in 4 reaction vessels), elution with cyclohexane/EtOAc/CH_3CN (100:0:0 to 40:50:10) gave a yellow solid (119.3 mg, 68%). **IR** (ν in cm^{-1}): 2218, 1533, 1456, 1277, 1220, 1078, 751. **^{1}H NMR** (300 MHz, Acetonitrile-d_3) δ 8.09 (dt, *J* = 7.2, 1.1 Hz, 1H), 7.64 (dt, *J* = 9.2, 1.2 Hz, 1H), 7.18 (ddd, *J* = 9.2, 6.6, 0.9 Hz, 1H), 6.88 (ddd, *J* = 7.1, 6.6, 1.1 Hz, 1H), 2.98 (q, *J* = 7.5 Hz, 2H), 1.38 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR** (75 MHz, Acetonitrile-d3) δ 150.6, 128.2, 124.6, 123.3, 116.4, 113.9, 113.1, 101.4, 19.5, 9.9. **HRMS** (DCI-CH_4) $[M+H]^+$ calculated for $C_{10}H_{10}N_3$ m/z 172.0875, found m/z 172.0878.



^{1}H NMR (300 MHz) of **2b**

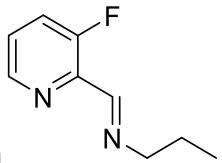
^{13}C NMR (75.4 MHz) of **2b**

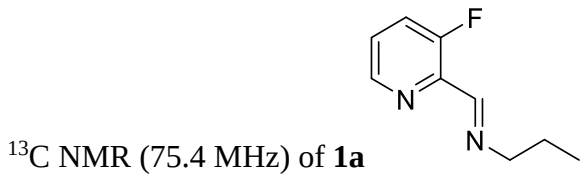
^{19}F NMR (282.4 MHz) of **2b**

Figure S8. ^{1}H, ^{13}C and ^{19}F NMR spectra of **2b** containing impurities due to the instability of the product.

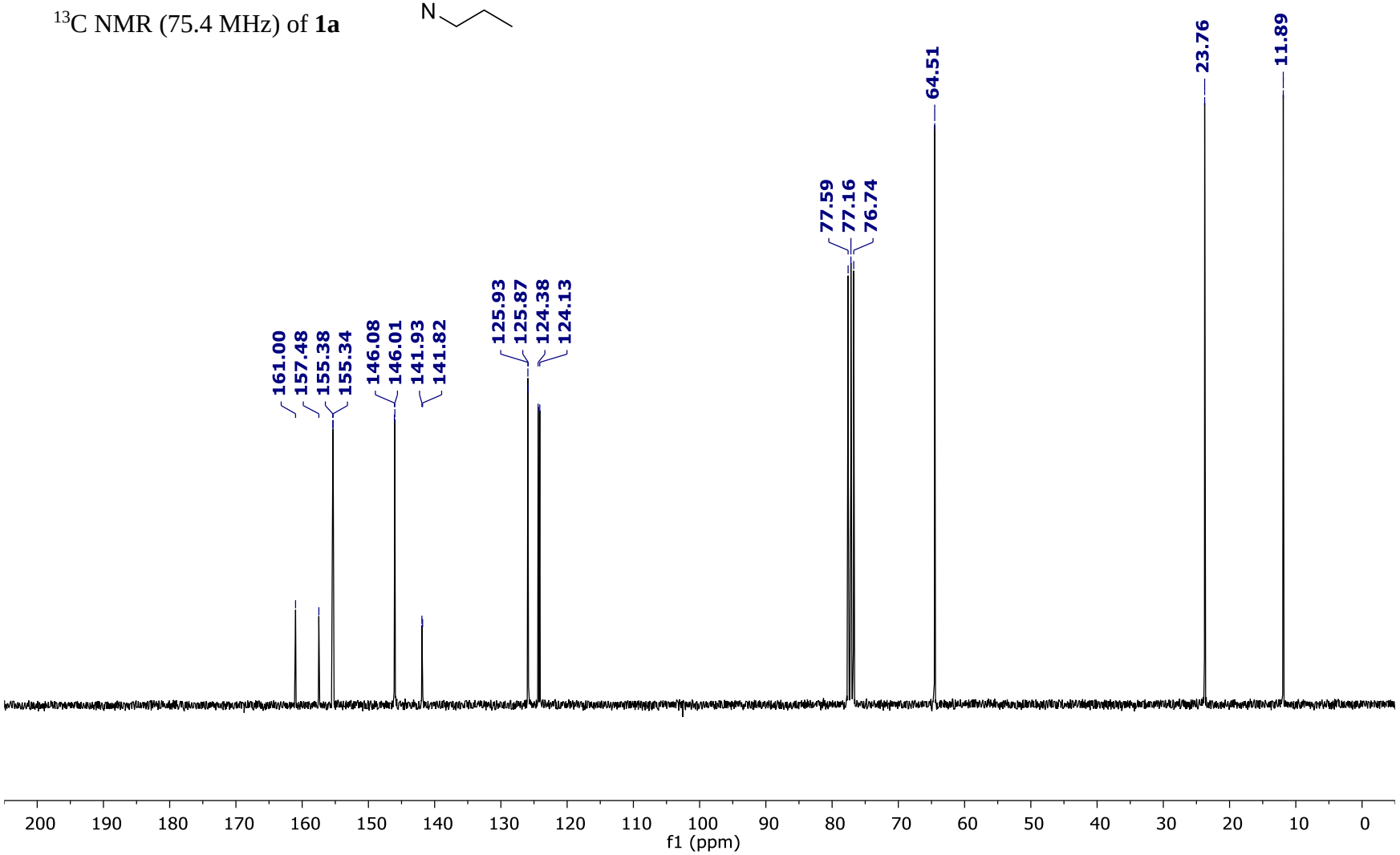
E. ^{1}H, ^{13}C, ^{19}F NMR and 2D spectra of pure compounds

^{1}H NMR (300 MHz) of **1a**

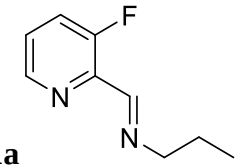


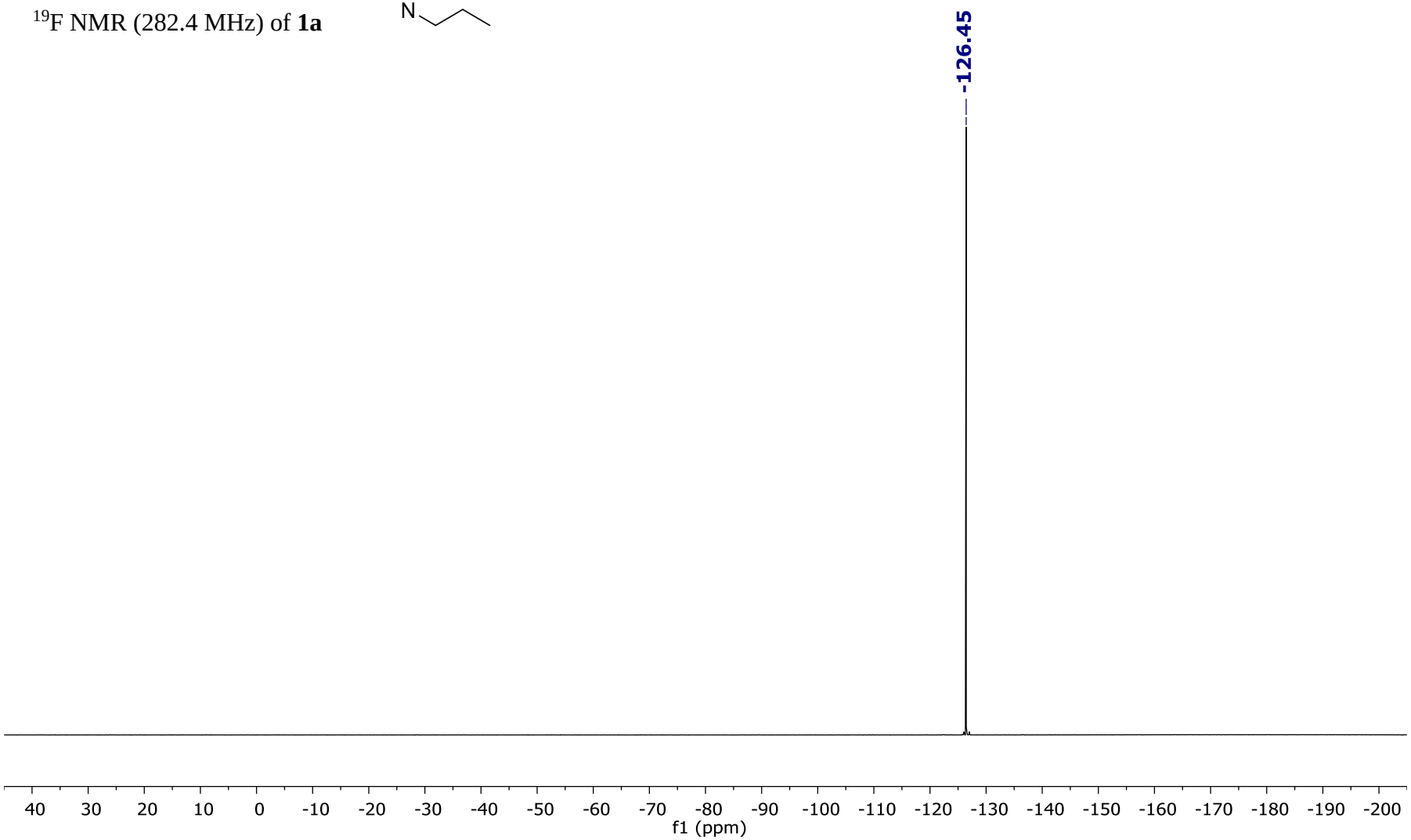


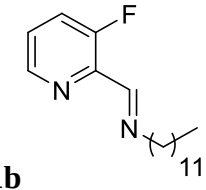
^{13}C NMR (75.4 MHz) of **1a**



^{19}F NMR (282.4 MHz) of **1a**

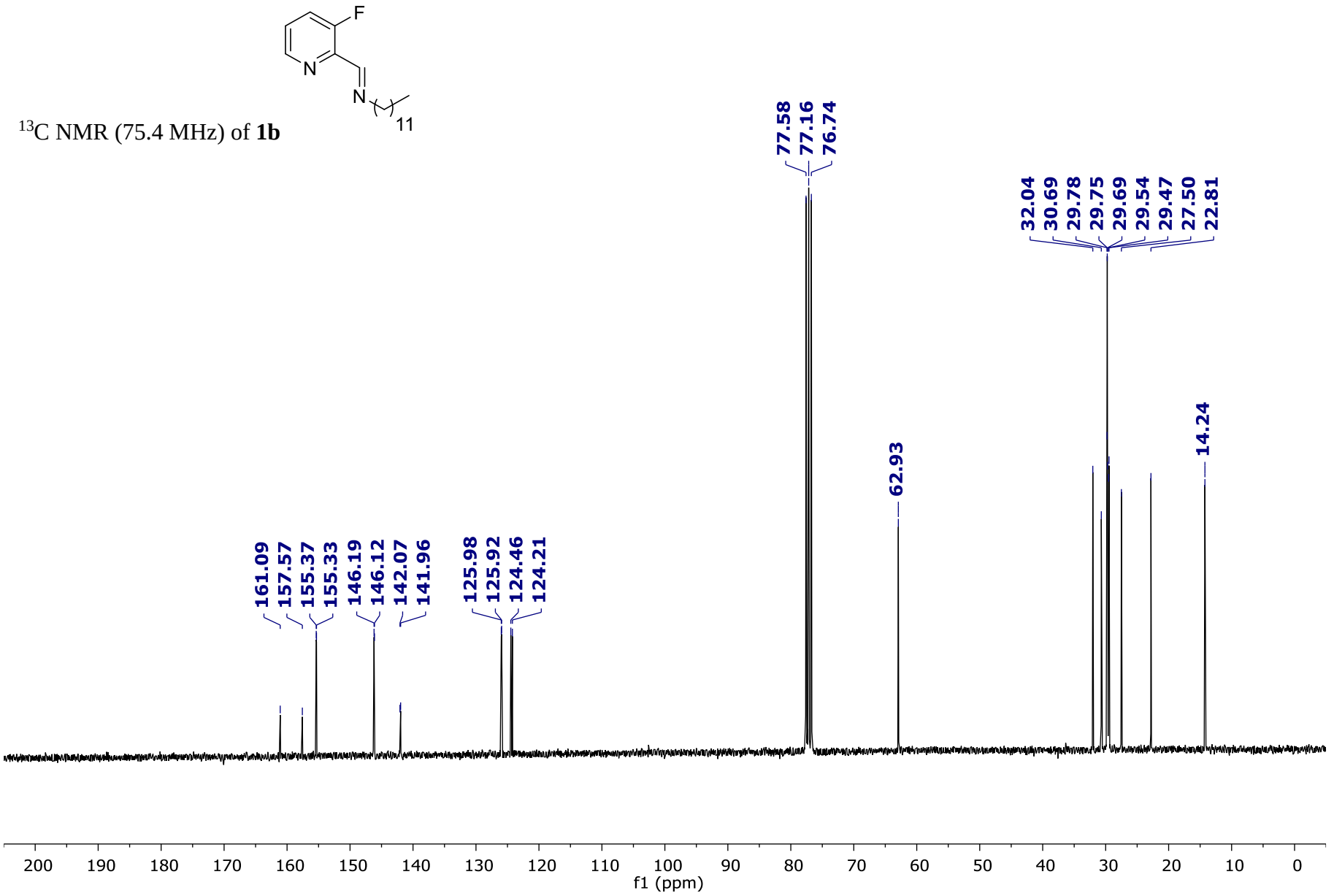


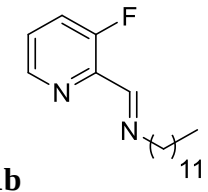




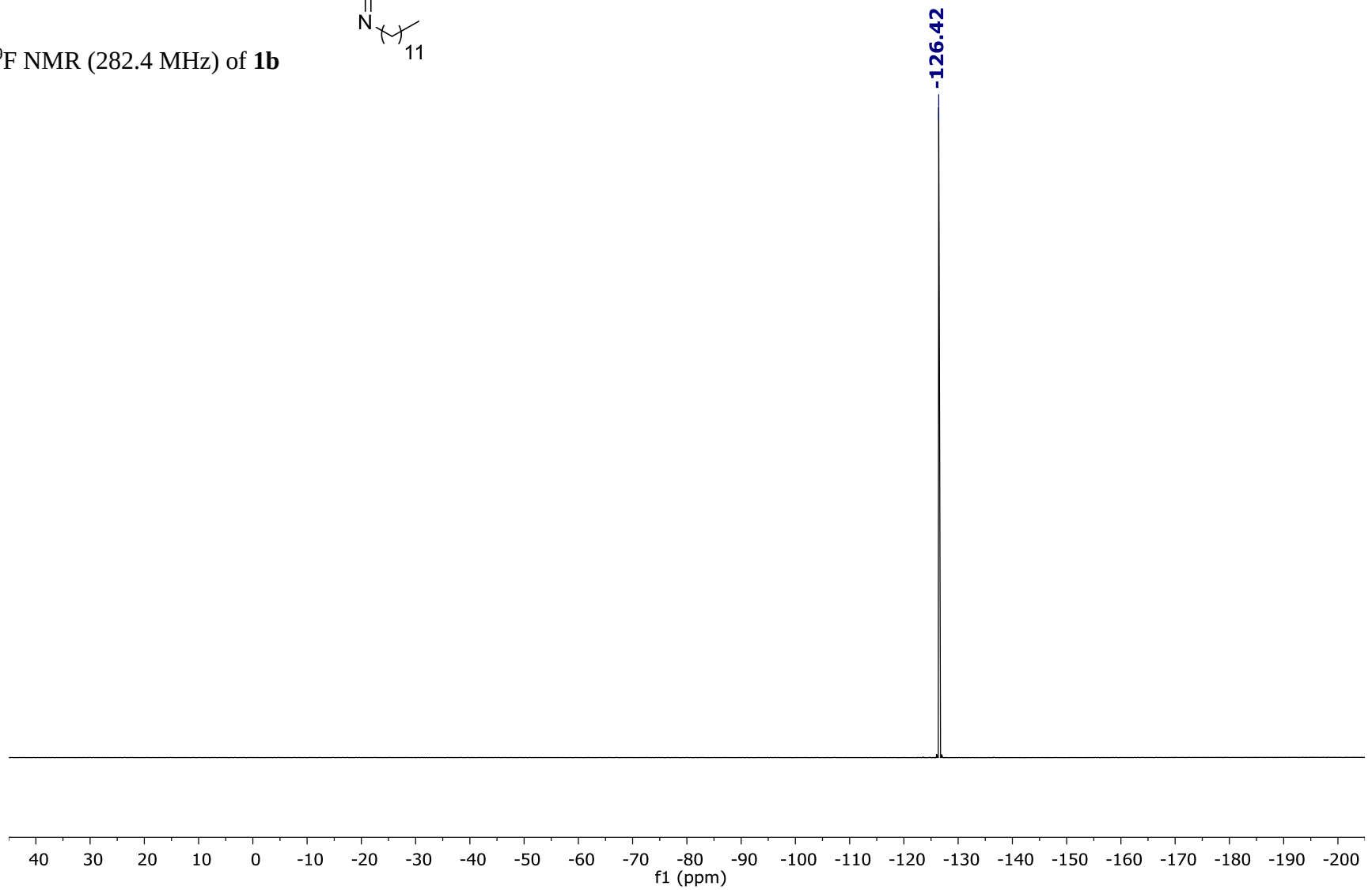
^{1}H NMR (300 MHz) of **1b**

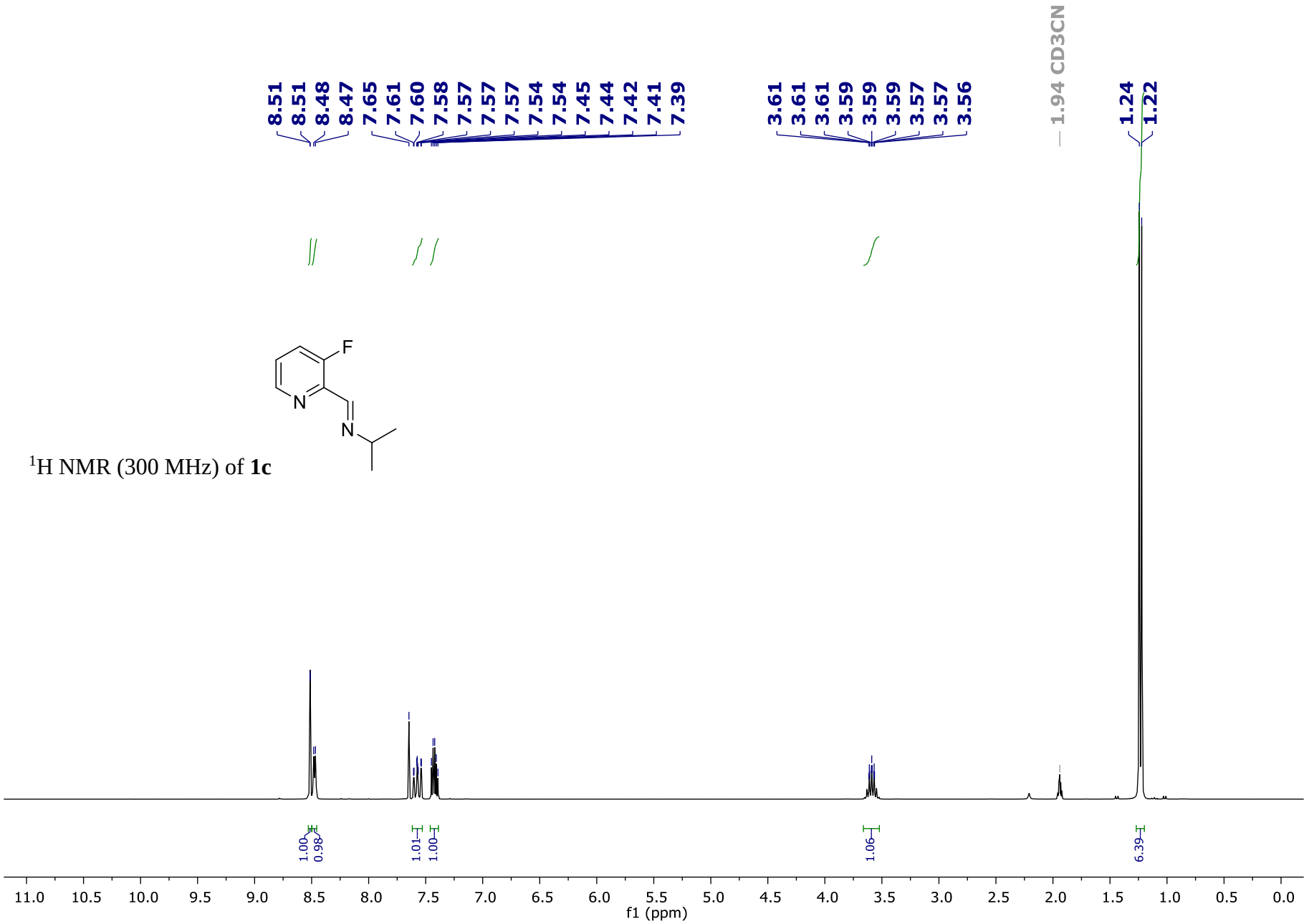
^{13}C NMR (75.4 MHz) of **1b**



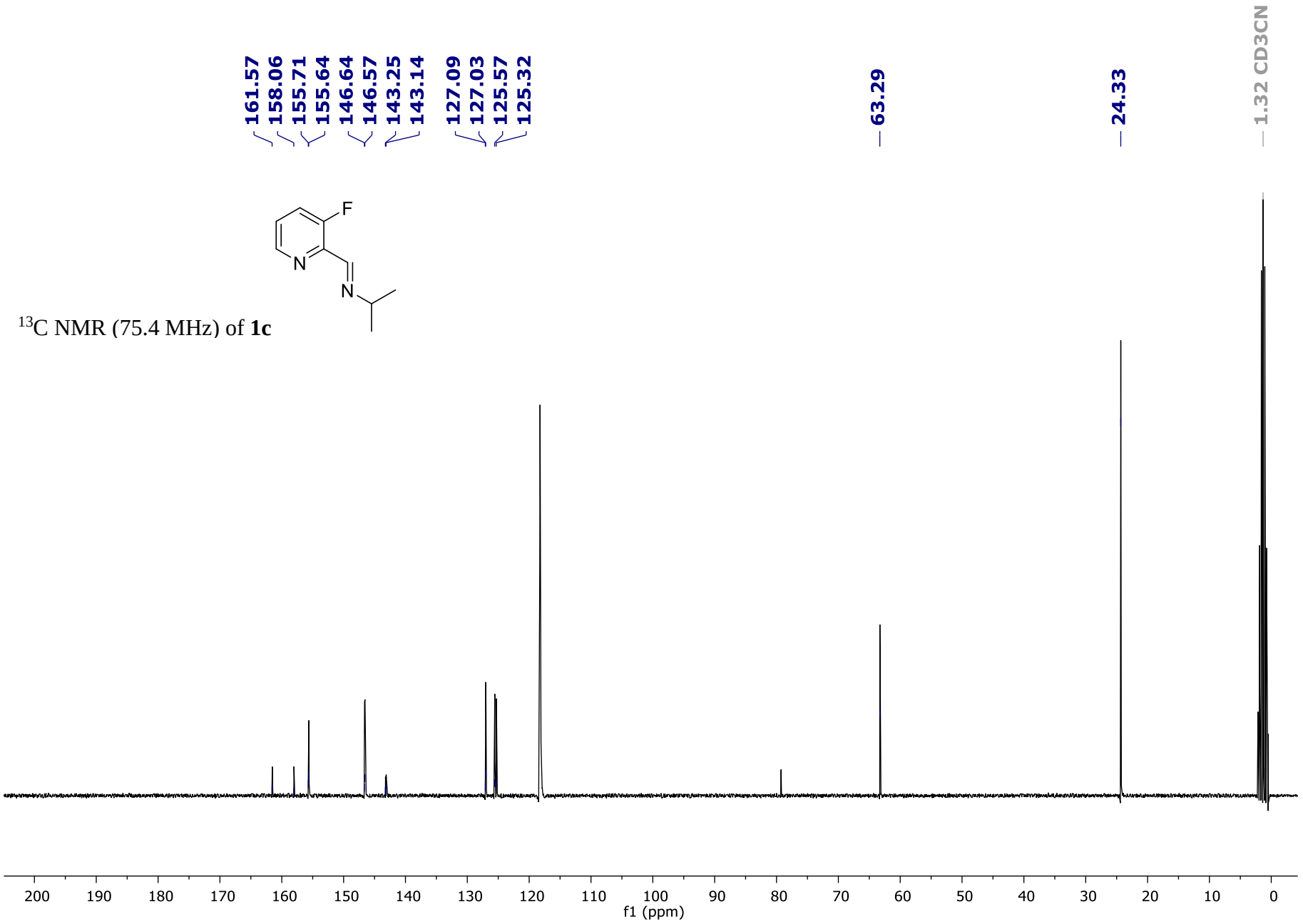


^{19}F NMR (282.4 MHz) of **1b**

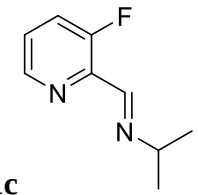




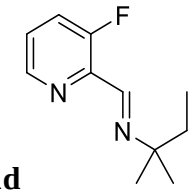
^{1}H NMR (300 MHz) of **1c**



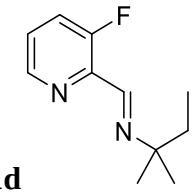
^{13}C NMR (75.4 MHz) of **1c**



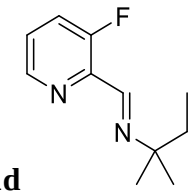
^{19}F NMR (282.4 MHz) of **1c**



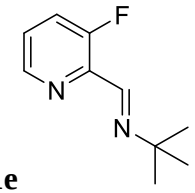
^{1}H NMR (300 MHz) of **1d**



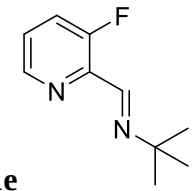
^{13}C NMR (75.4 MHz) of **1d**



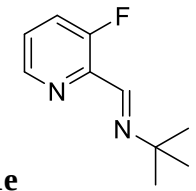
^{19}F NMR (282.4 MHz) of **1d**



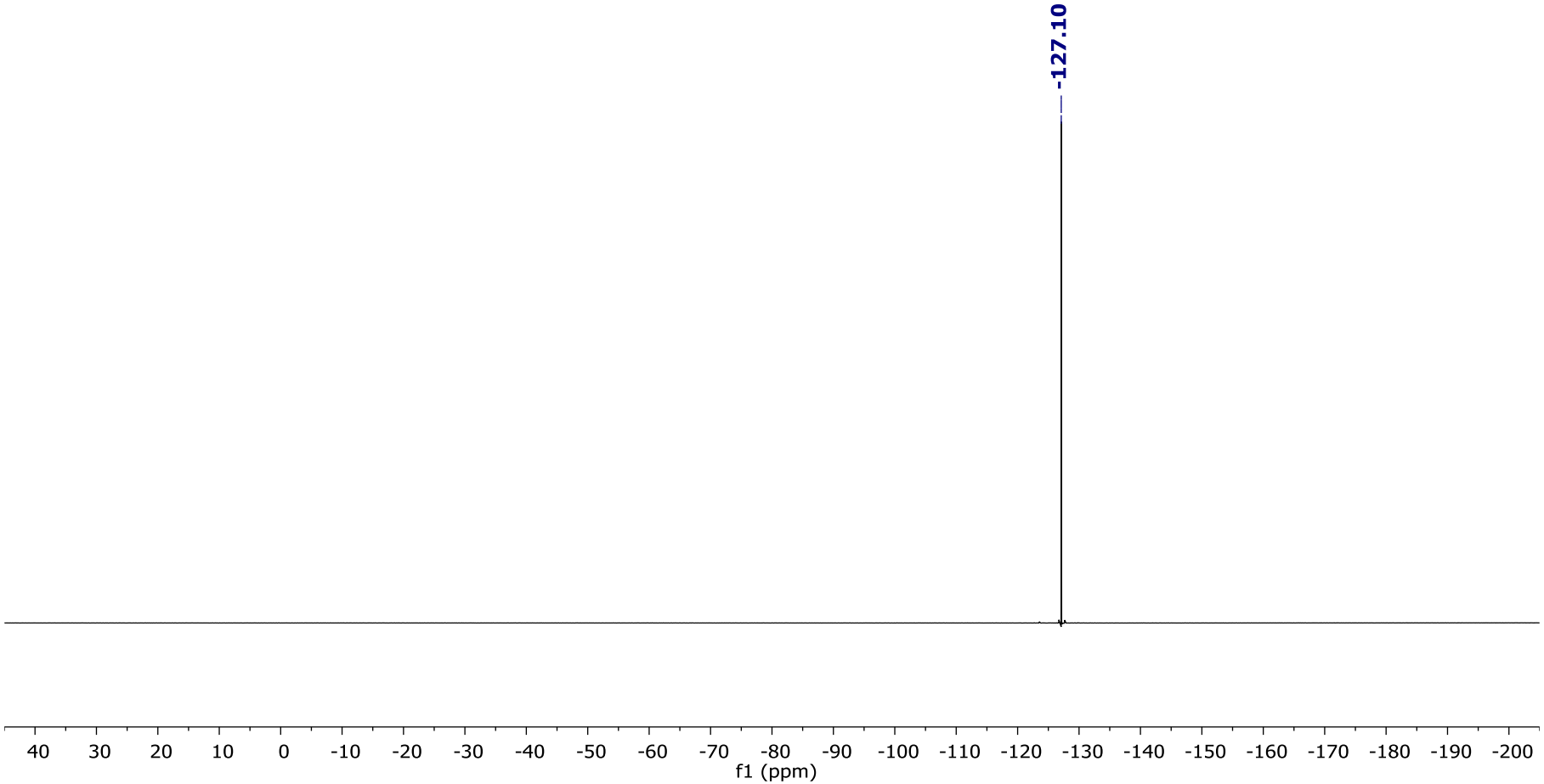
^{1}H NMR (300 MHz) of **1e**



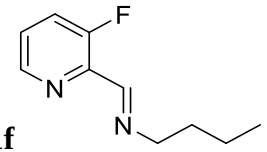
^{13}C NMR (75.4 MHz) of **1e**



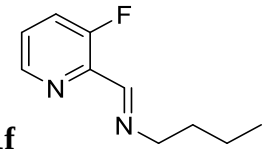
^{19}F NMR (282.4 MHz) of **1e**



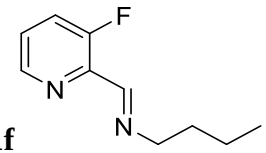
^{1}H NMR (300 MHz) of **1f**



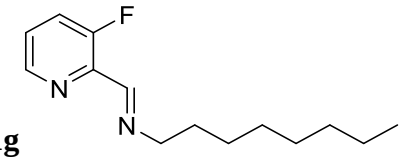
^{13}C NMR (75.4 MHz) of **1f**

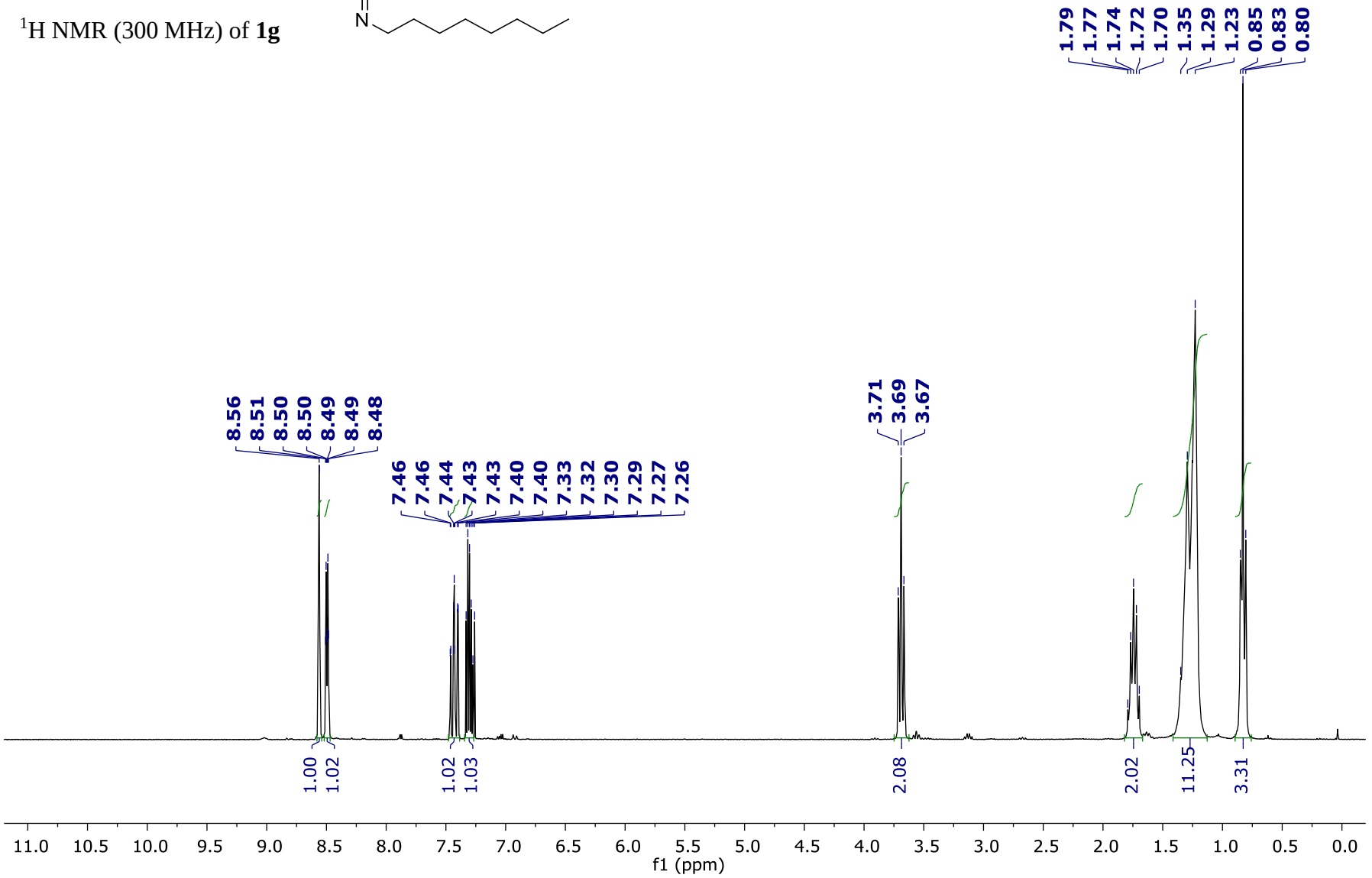


^{19}F NMR (282.4 MHz) of **1f**

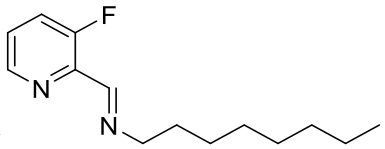


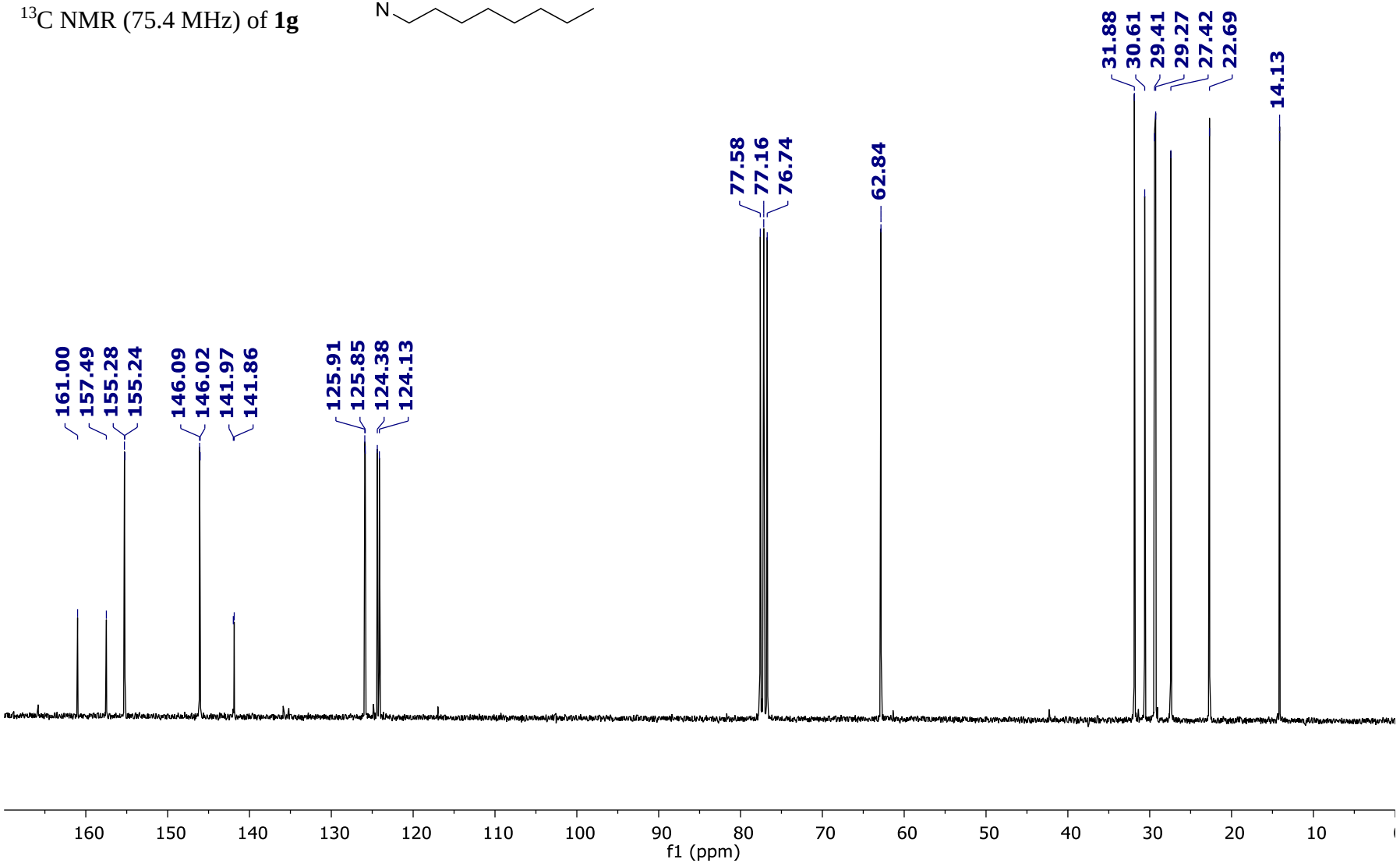
^{1}H NMR (300 MHz) of **1g**



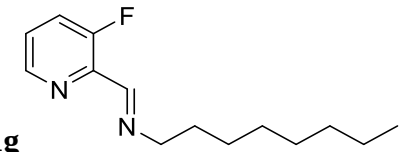


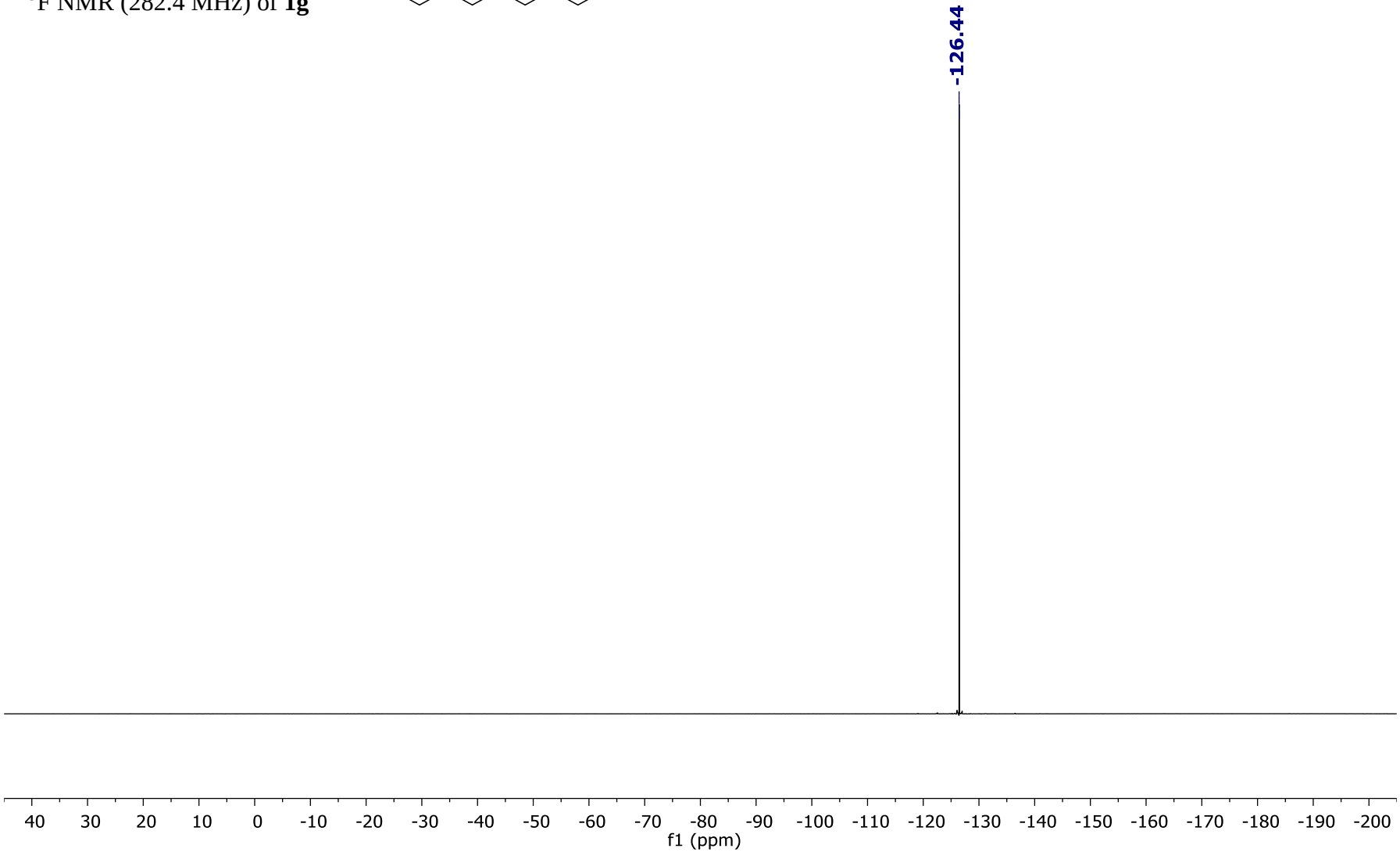
^{13}C NMR (75.4 MHz) of **1g**



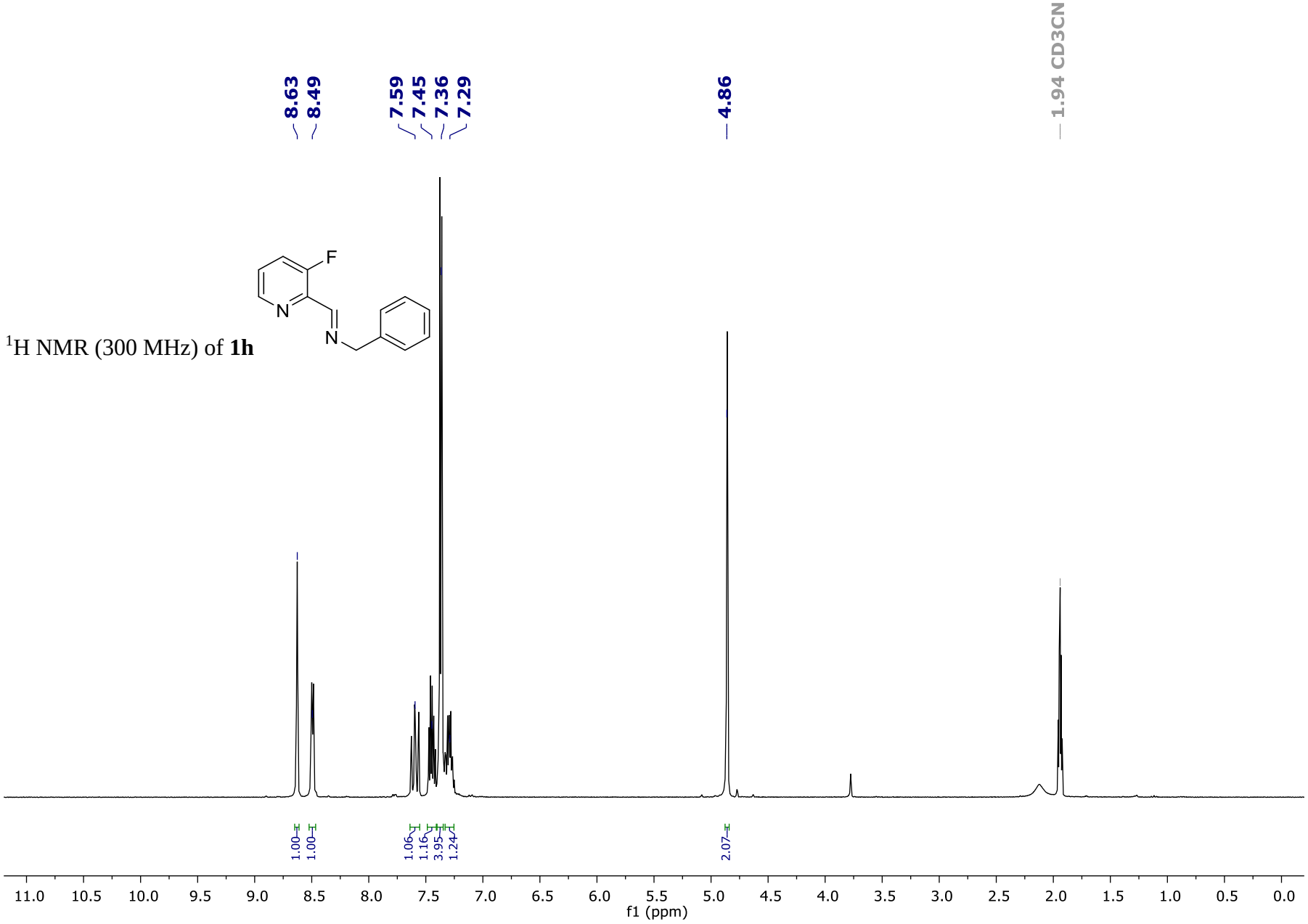


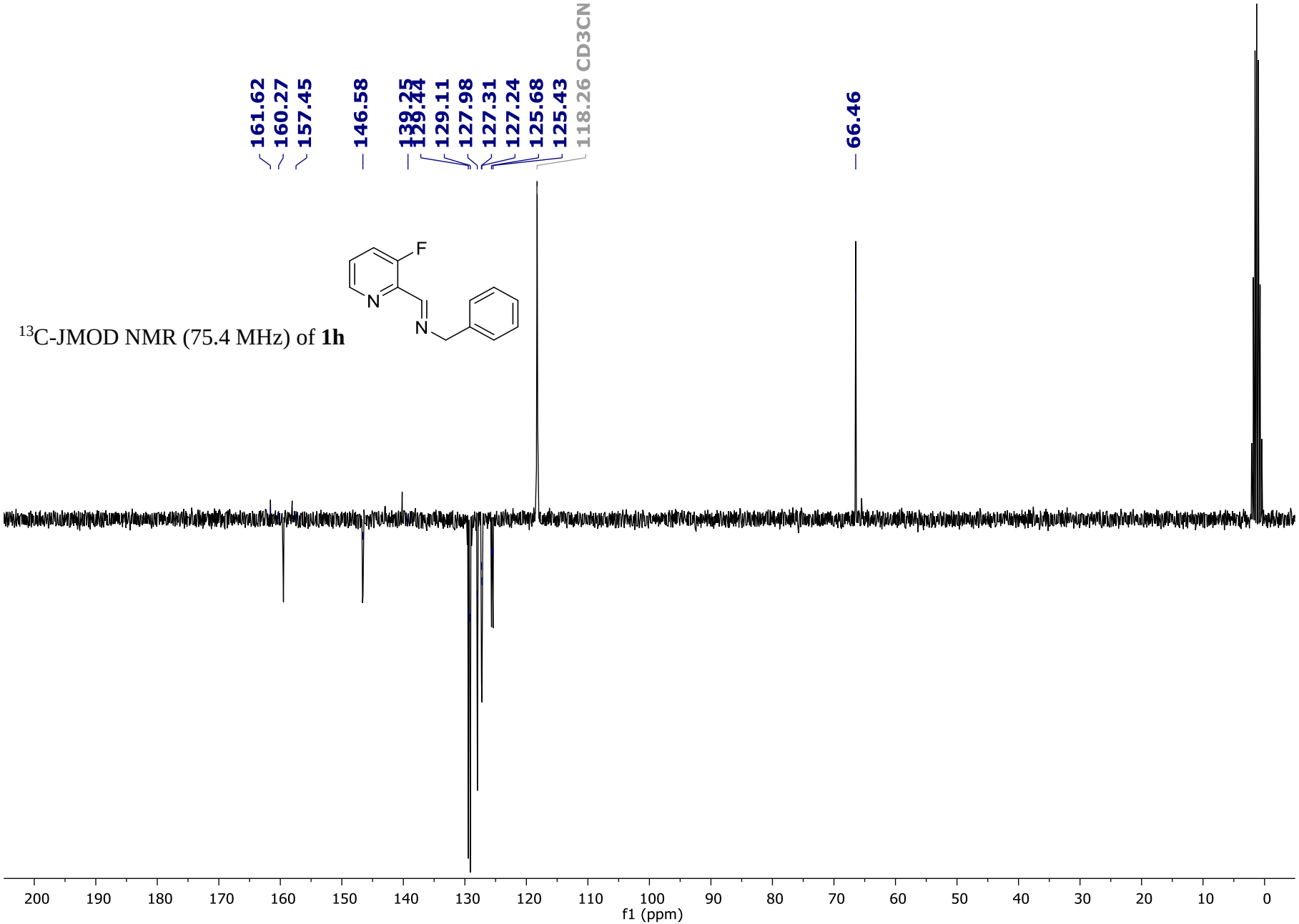
^{19}F NMR (282.4 MHz) of **1g**





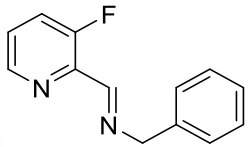
^{1}H NMR (300 MHz) of **1h**

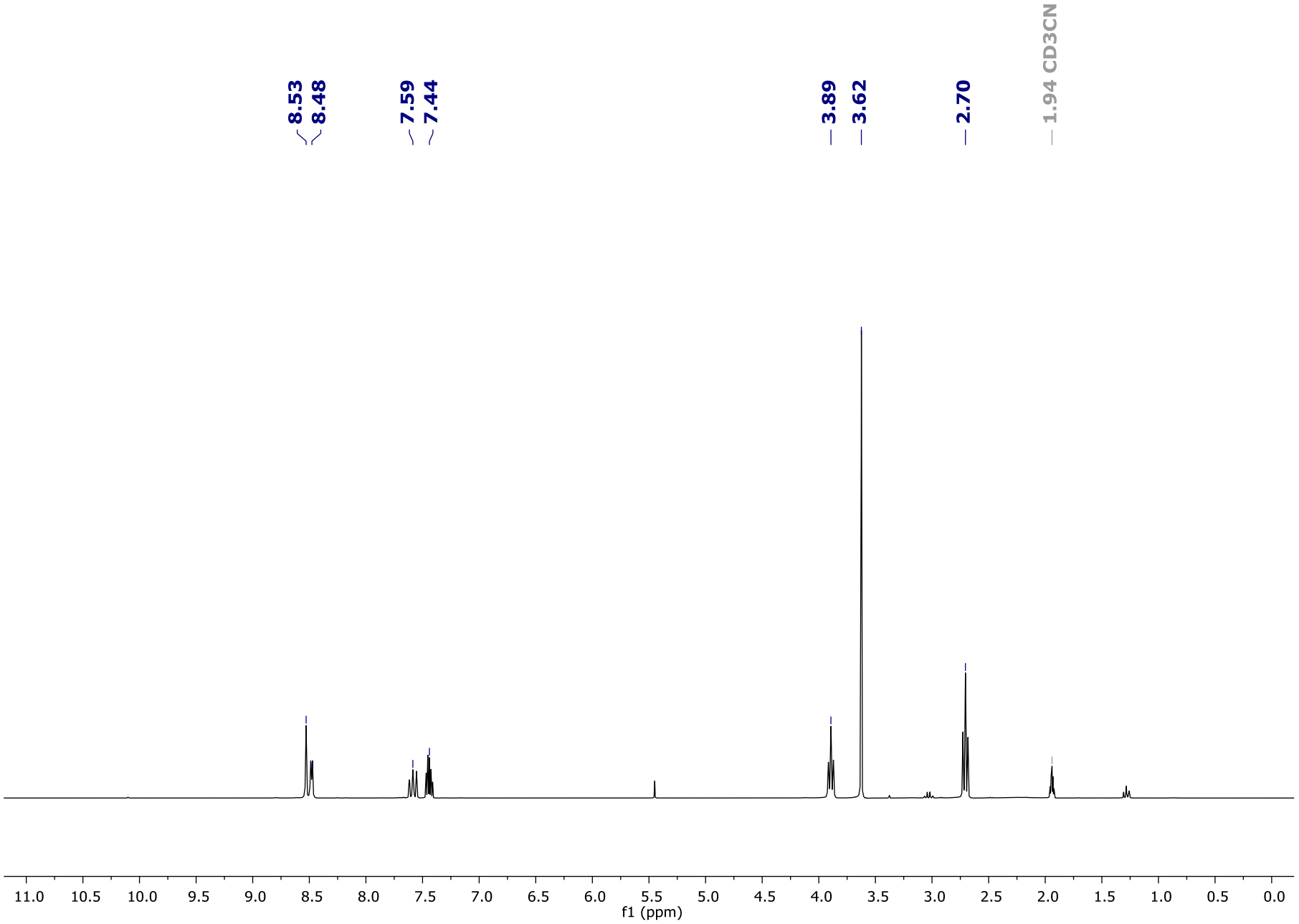


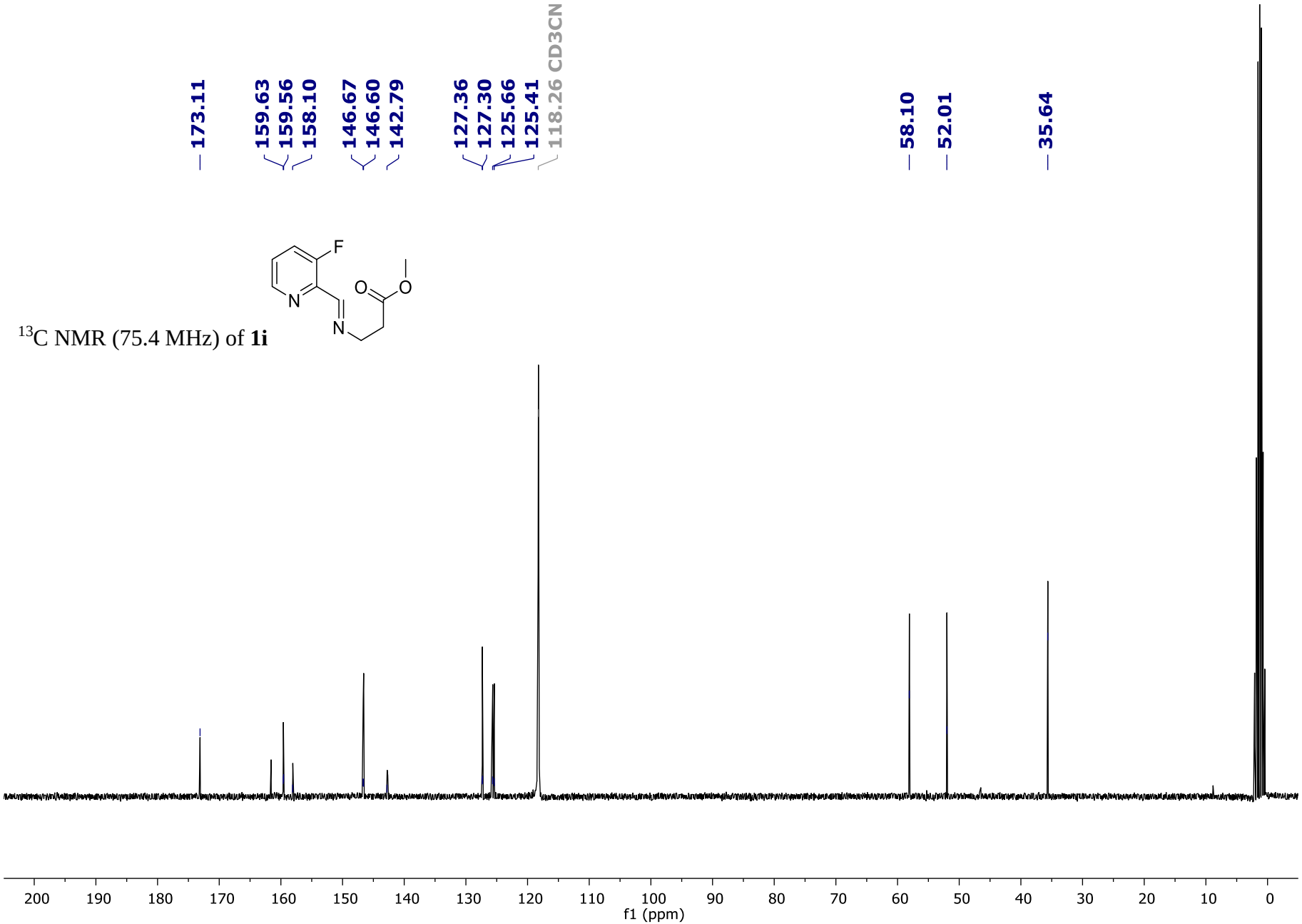


^{13}C-JMOD NMR (75.4 MHz) of **1h**

^{19}F NMR (282.4 MHz) of **1h**

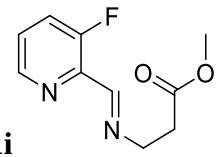


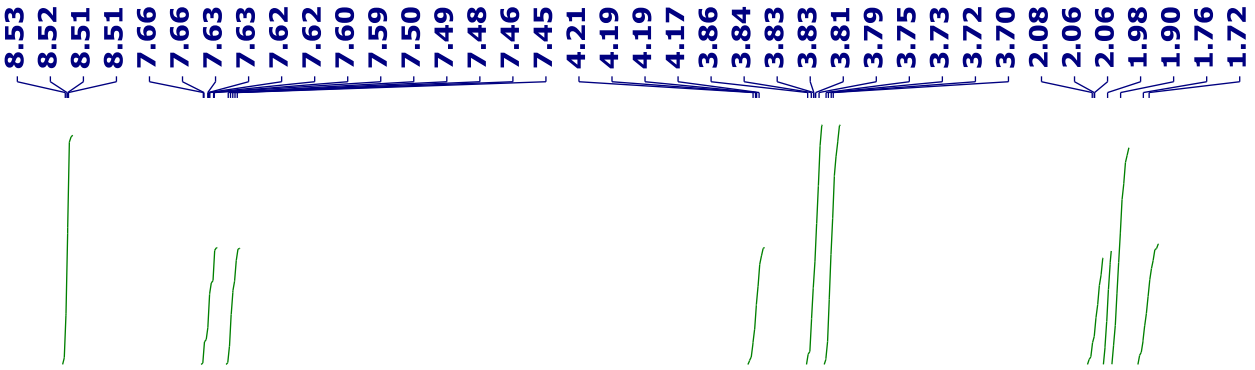

8.53
8.48
7.59
7.44
3.89
3.62
2.70
1.94 CD3CN
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

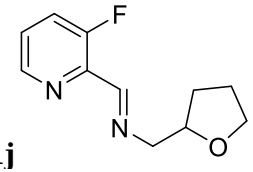


^{13}C NMR (75.4 MHz) of **1i**

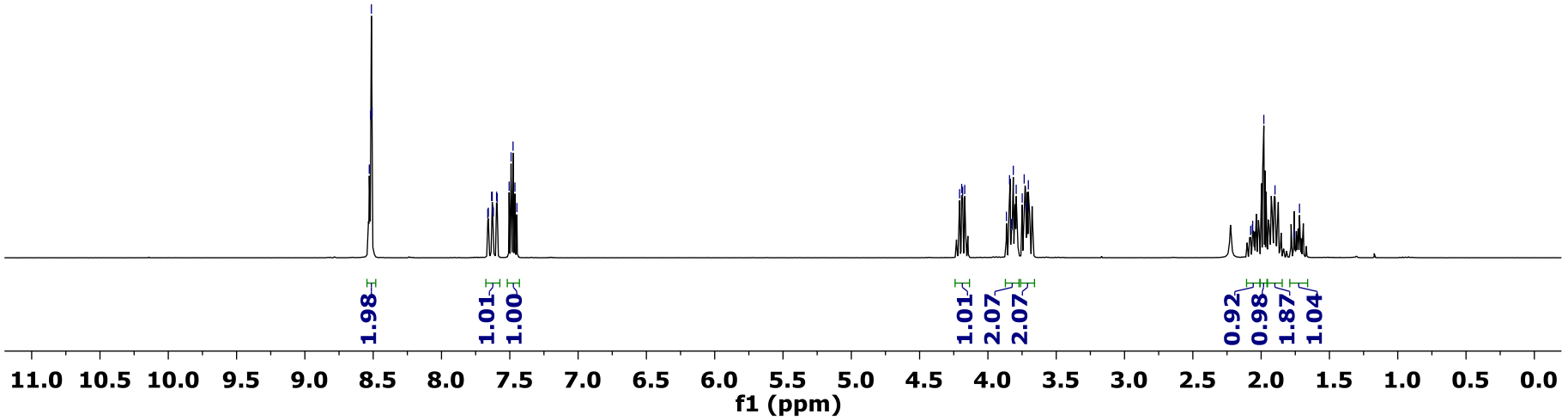
^{19}F NMR (282.4 MHz) of **1i**

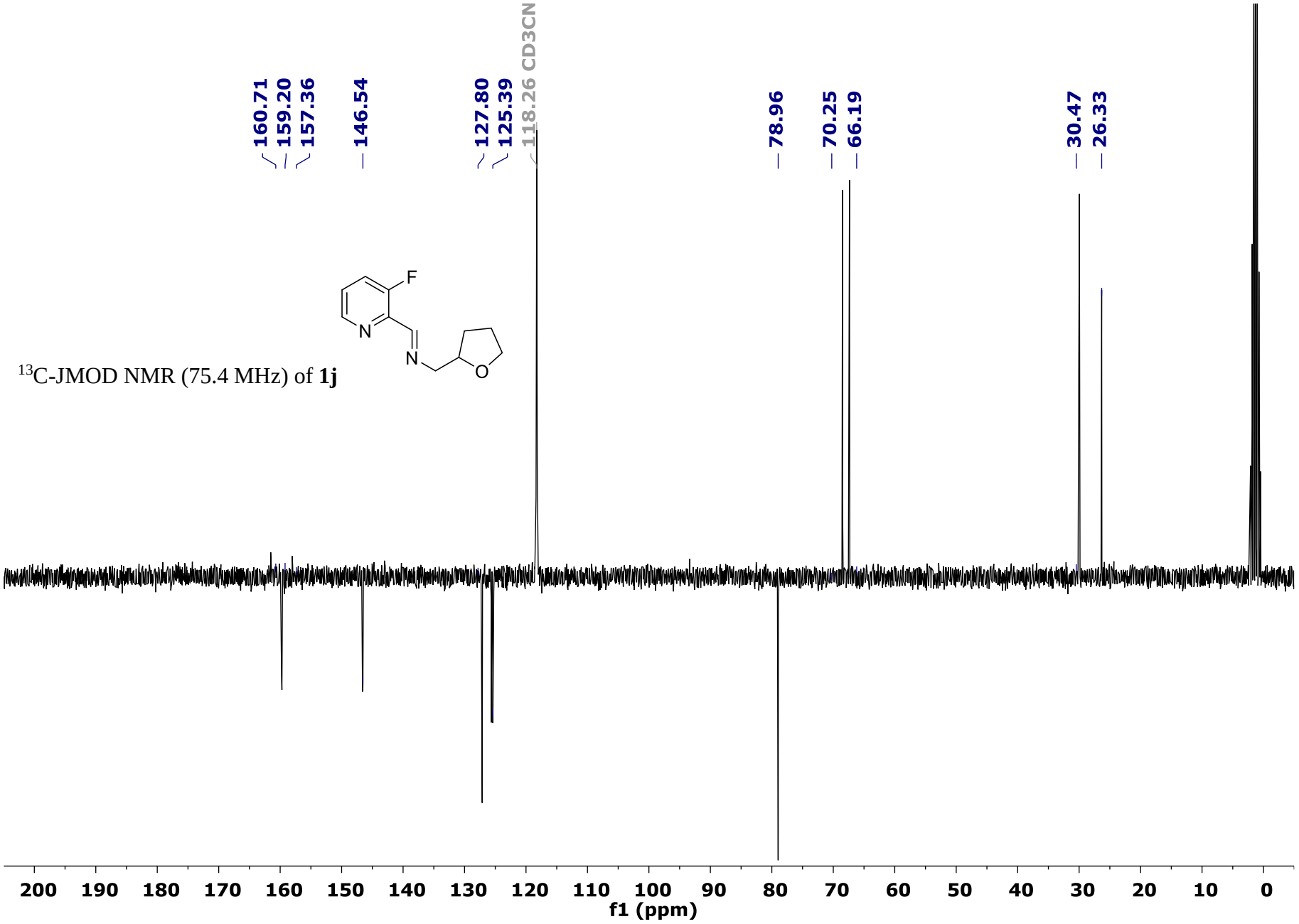






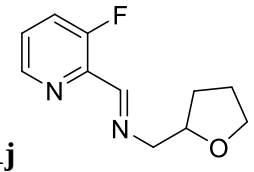
^{1}H NMR (300 MHz) of **1j**

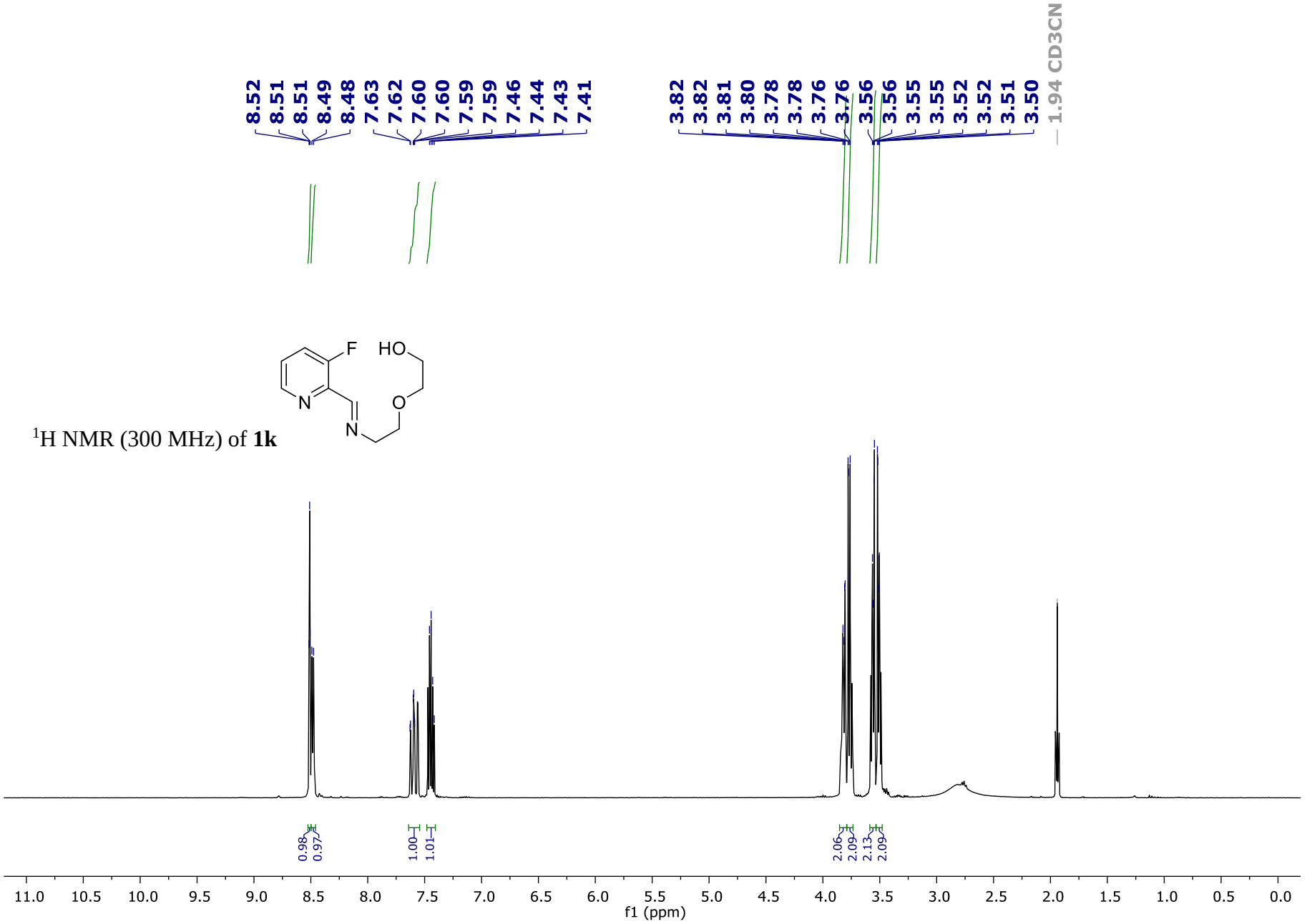




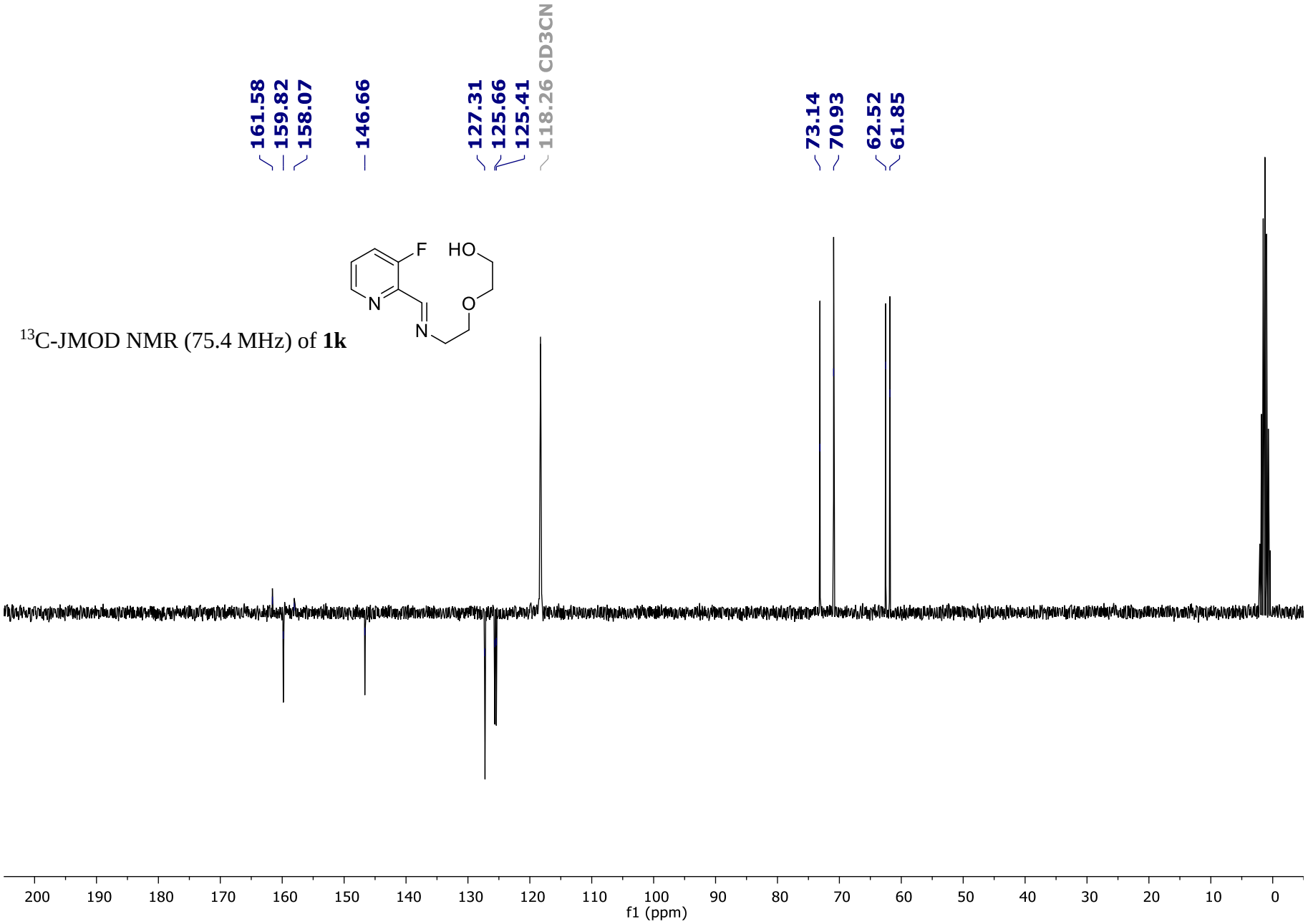
^{13}C-JMOD NMR (75.4 MHz) of **1j**

^{19}F NMR (282.4 MHz) of **1j**



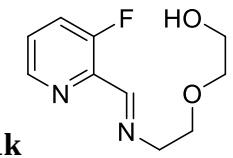


^{1}H NMR (300 MHz) of **1k**

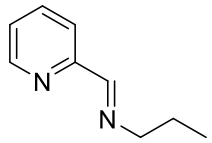


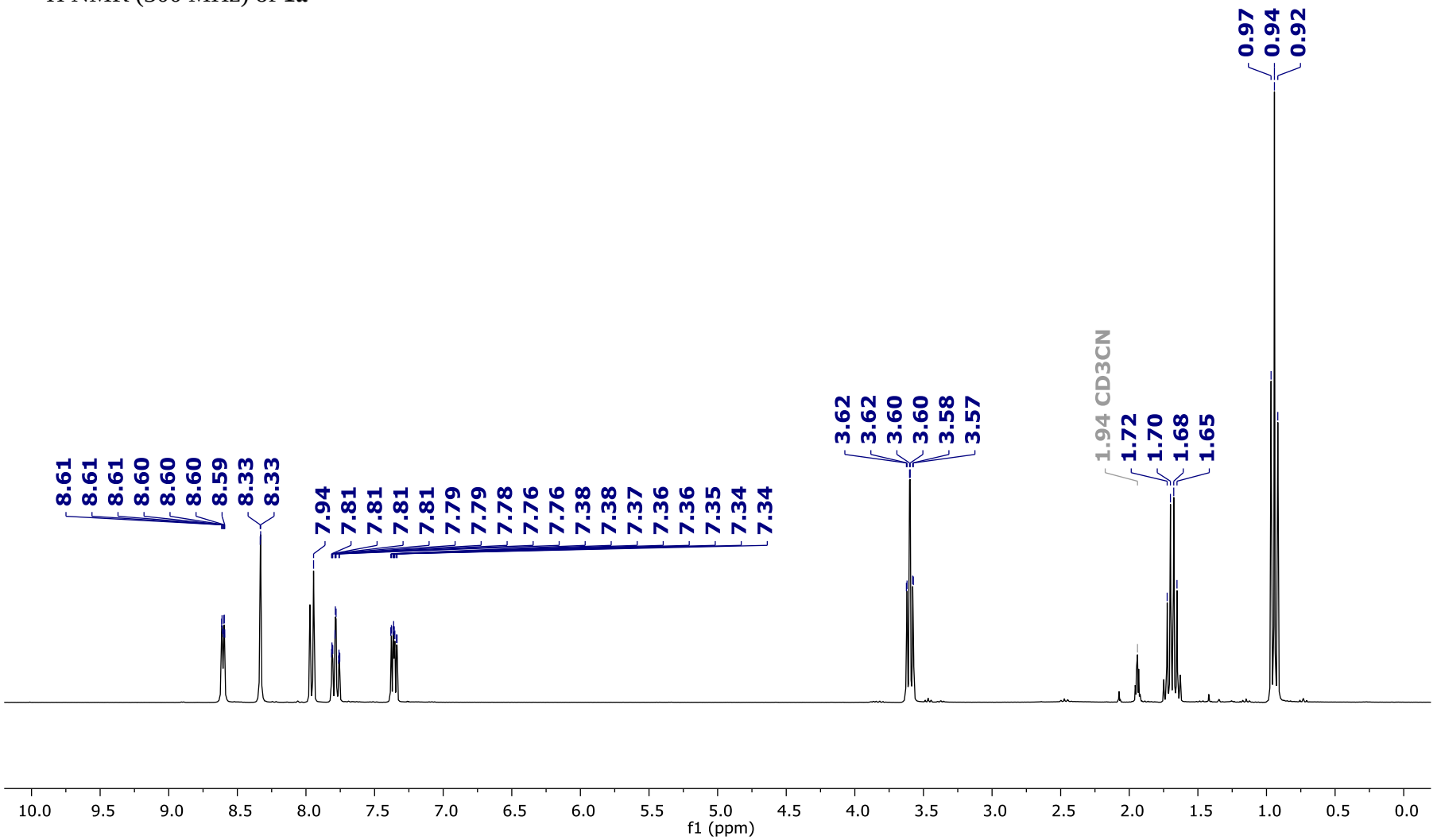
^{13}C-JMOD NMR (75.4 MHz) of **1k**

^{19}F NMR (282.4 MHz) of **1k**

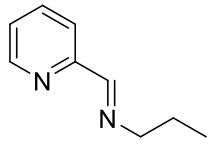


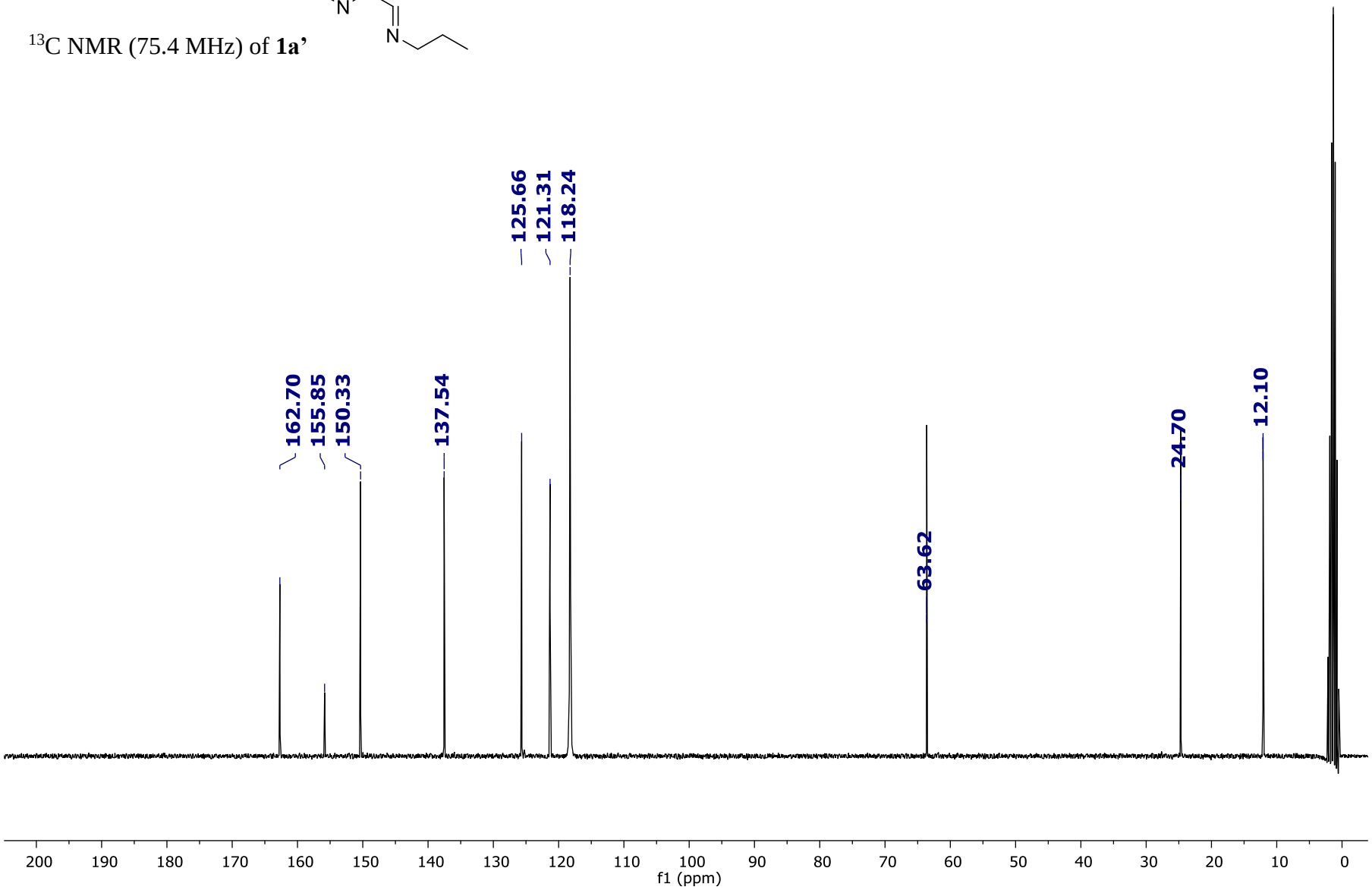
^{1}H NMR (300 MHz) of **1a'**



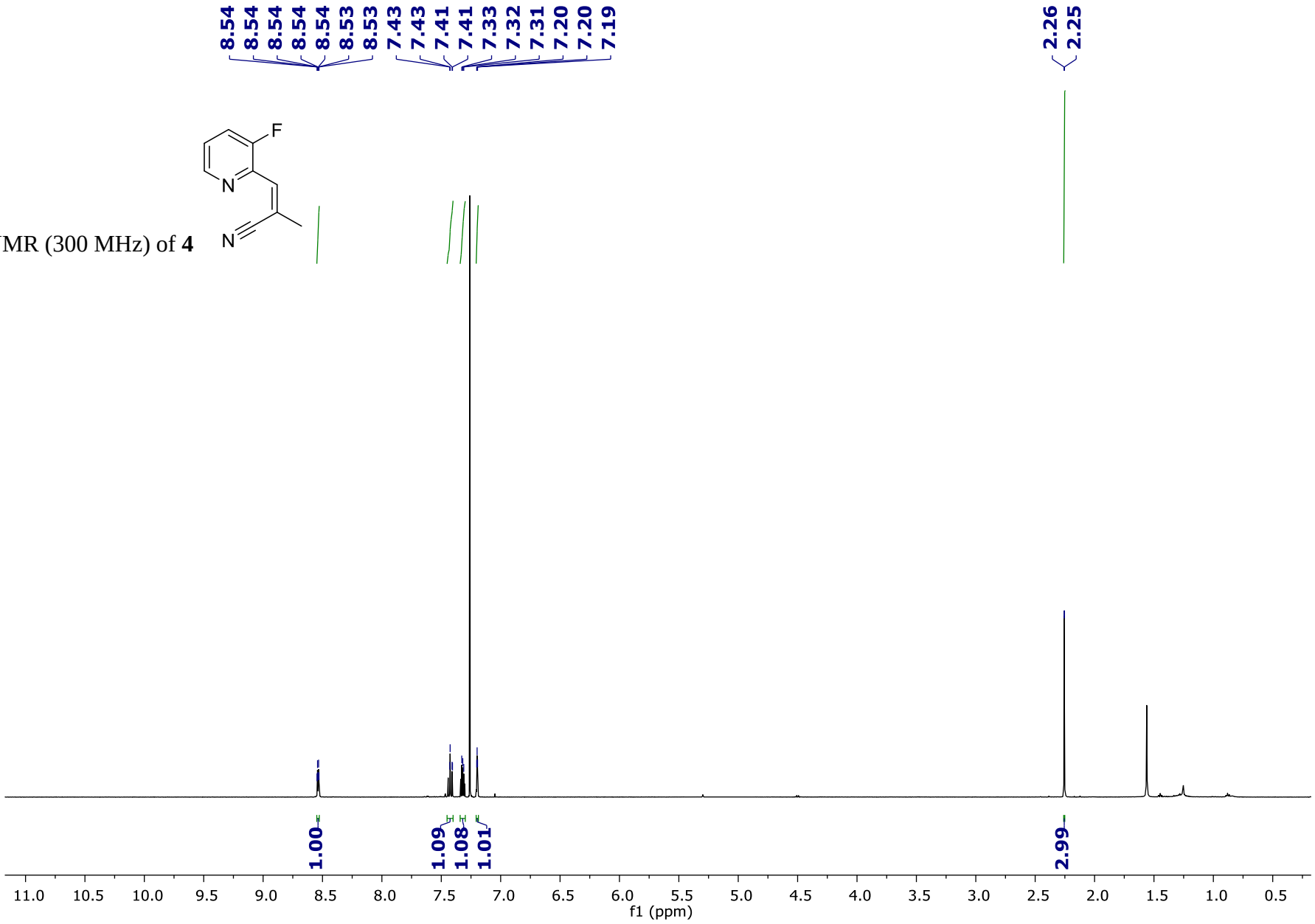


^{13}C NMR (75.4 MHz) of **1a'**

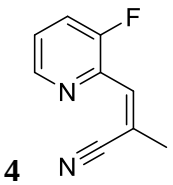




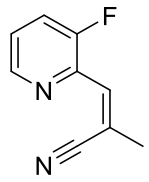
^{1}H NMR (300 MHz) of **4**



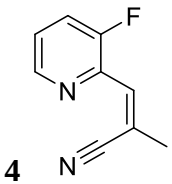
^{13}C-JMOD NMR (75.4 MHz) of **4**



^{19}F NMR (282.4 MHz) of **4**

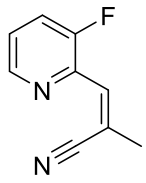


COSY of **4**


F
N
N

0
1
2
3
4
5
6
7
8
9
f1 (ppm)
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
f2 (ppm)

HSQC of **4**


F
N
N

0
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20
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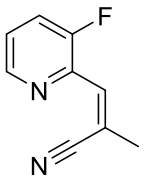
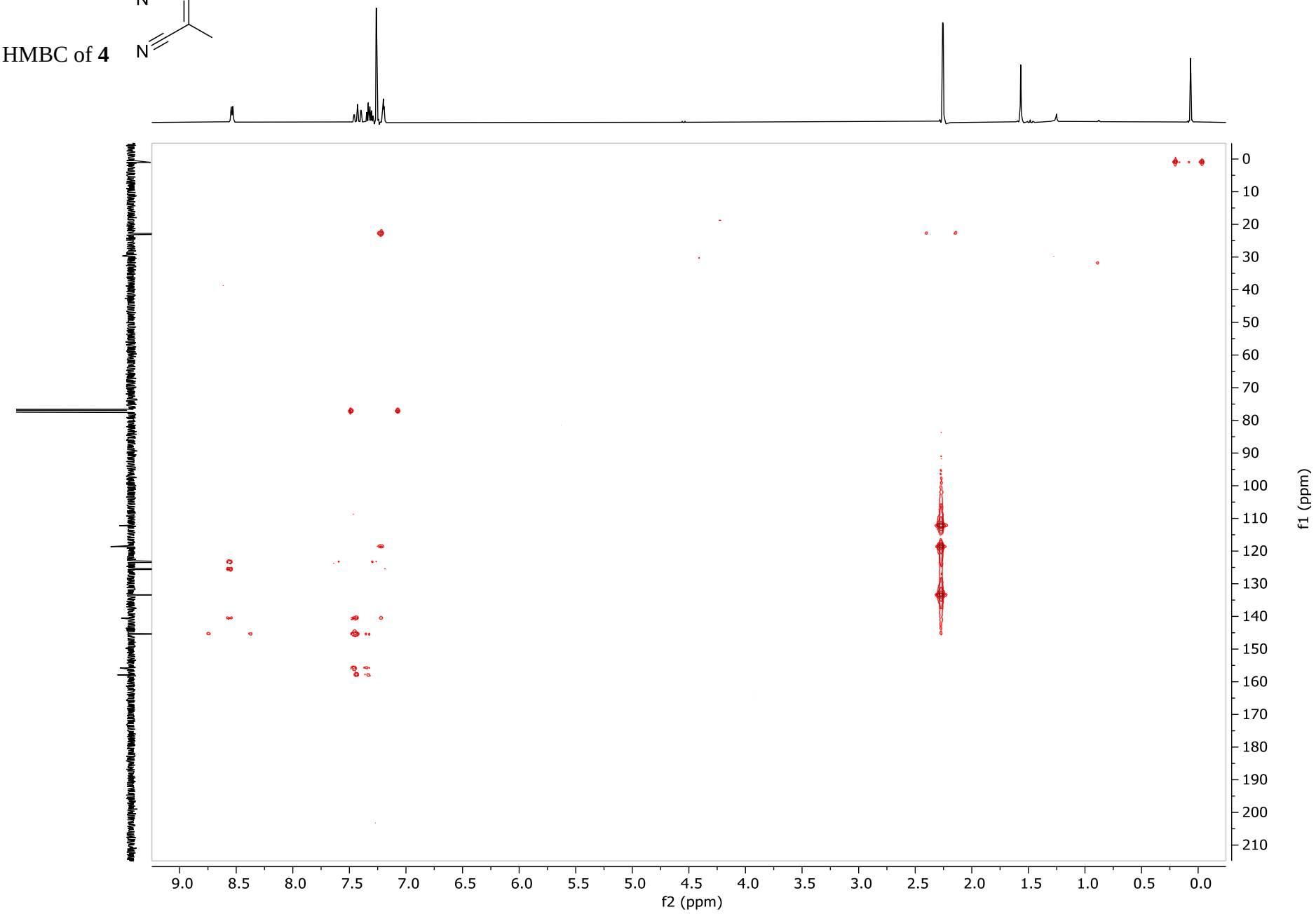
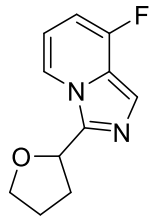
60
70
80
90
100
110
120
130
140
150
160
f1 (ppm)
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f2 (ppm)

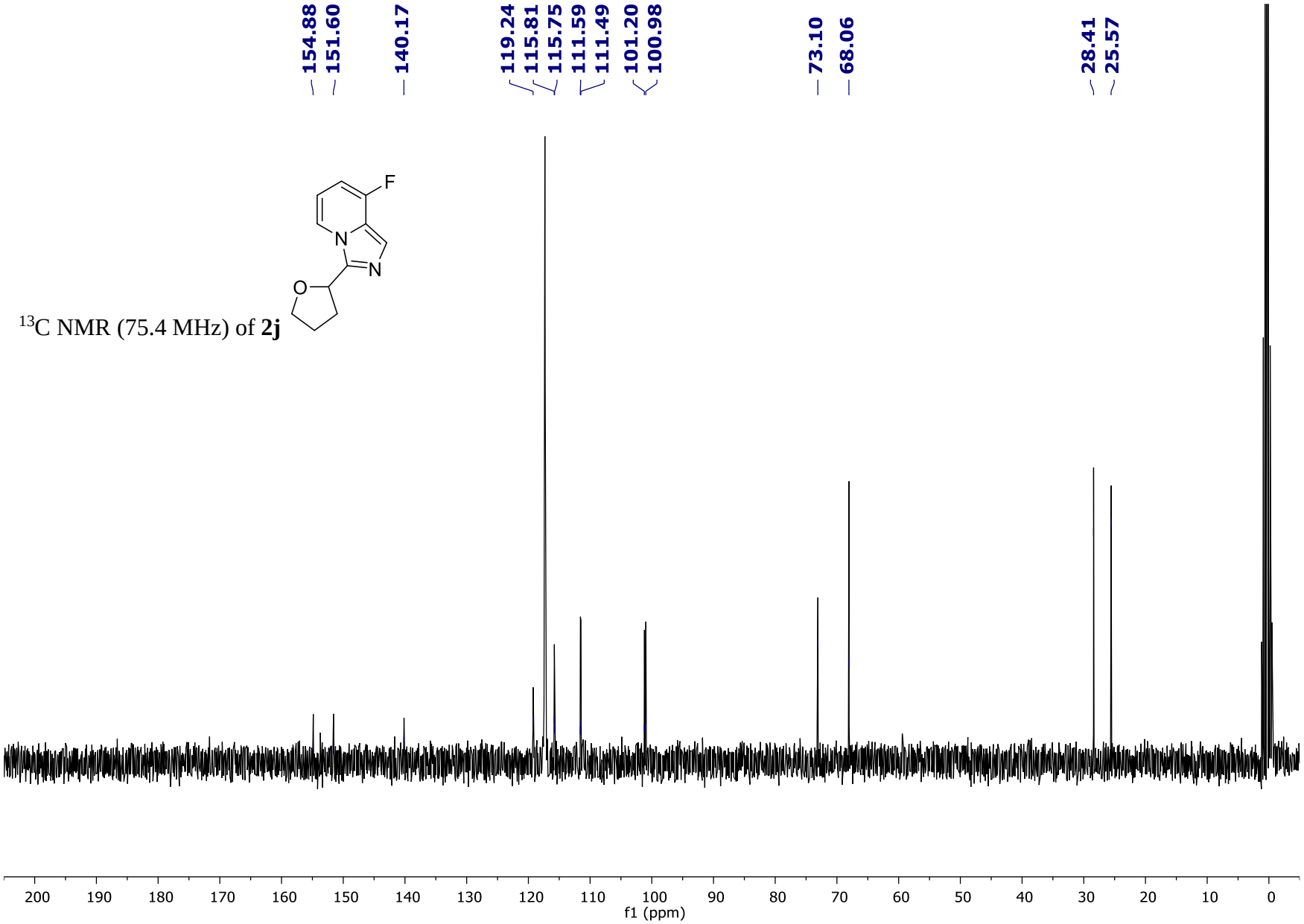
HMBC of **4**





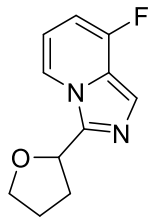
^{1}H NMR (300 MHz) of **2j**



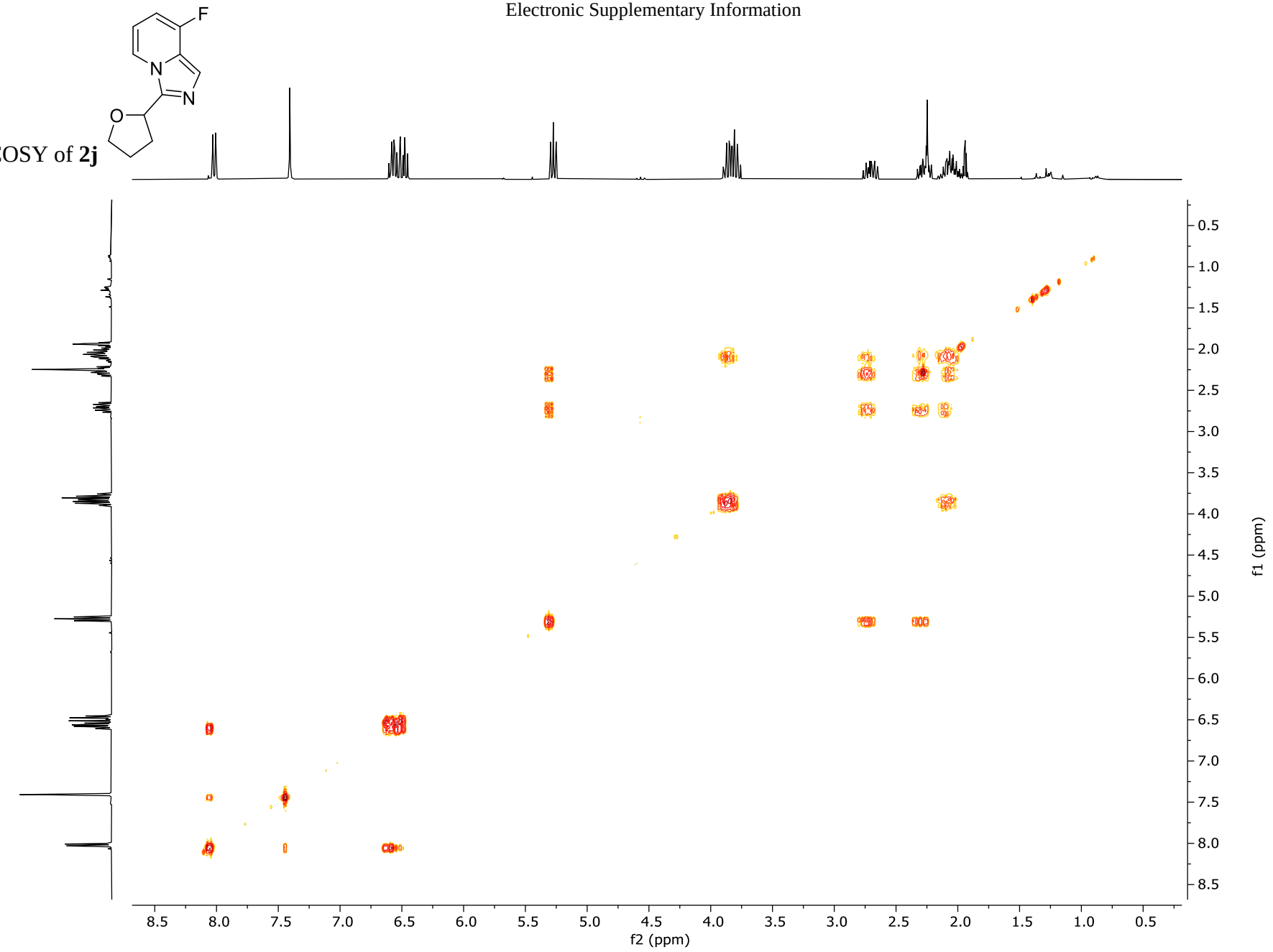


^{13}C NMR (75.4 MHz) of **2j**

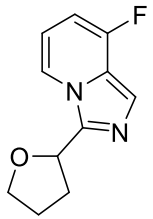
^{19}F NMR (282.4 MHz) of **2j**

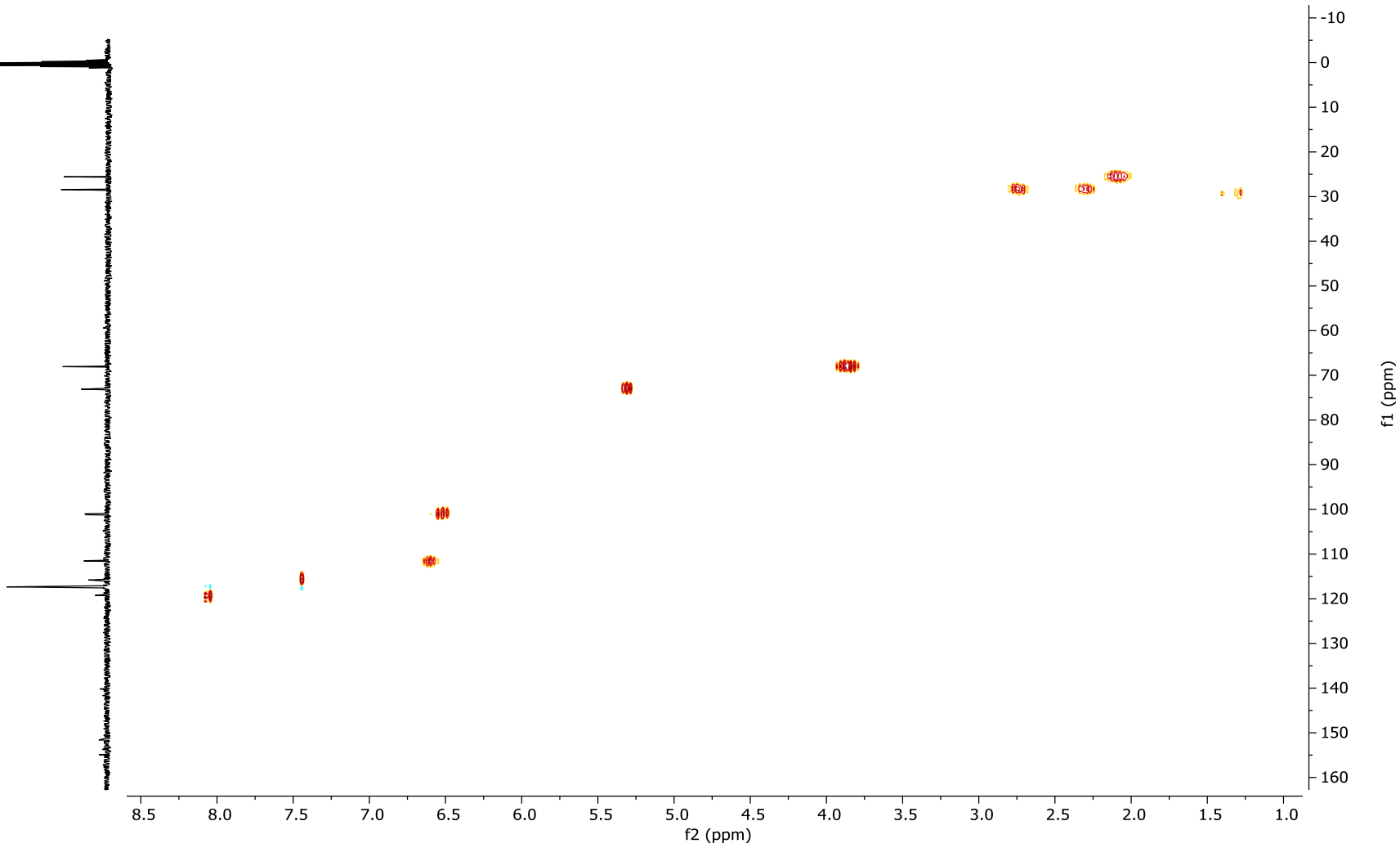


COSY of **2j**



HSQC of **2j**


F
N
N
O


-10
0
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20
30
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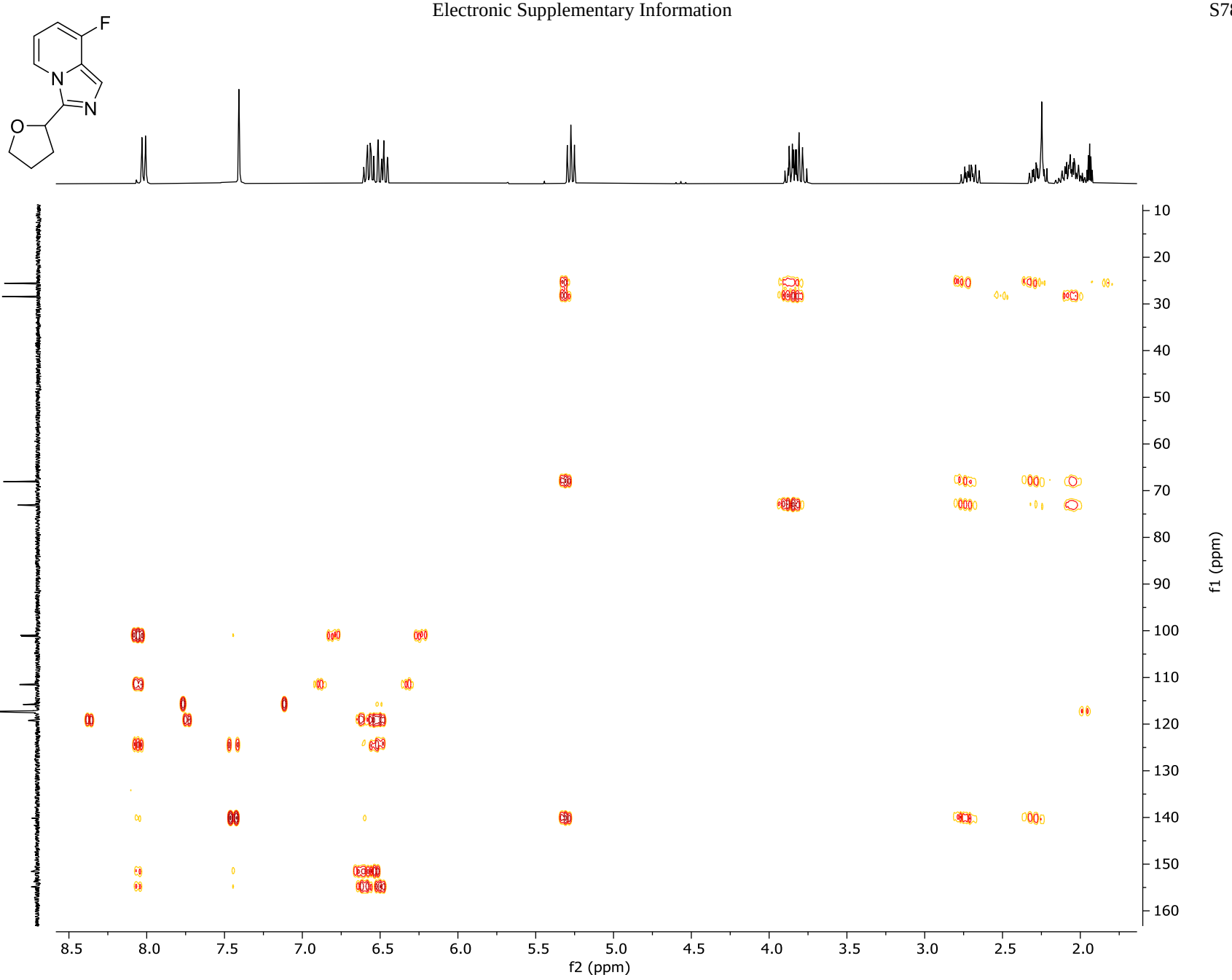
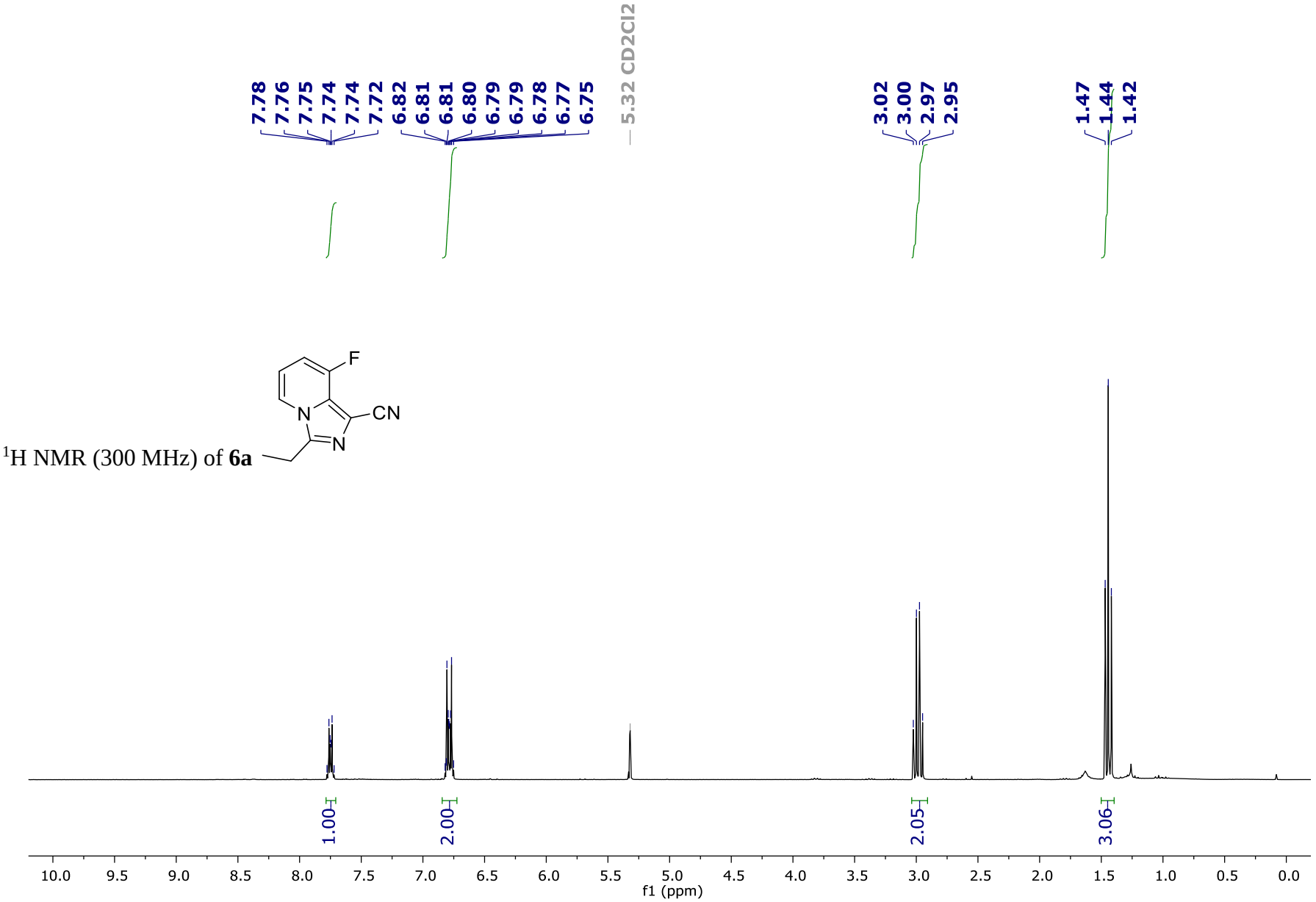
60
70
80
90
100
110
120
130
140
150
160
f1 (ppm)
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f2 (ppm)

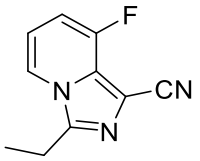
HMBC of **2j**



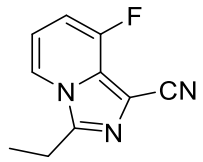


^{1}H NMR (300 MHz) of **6a**

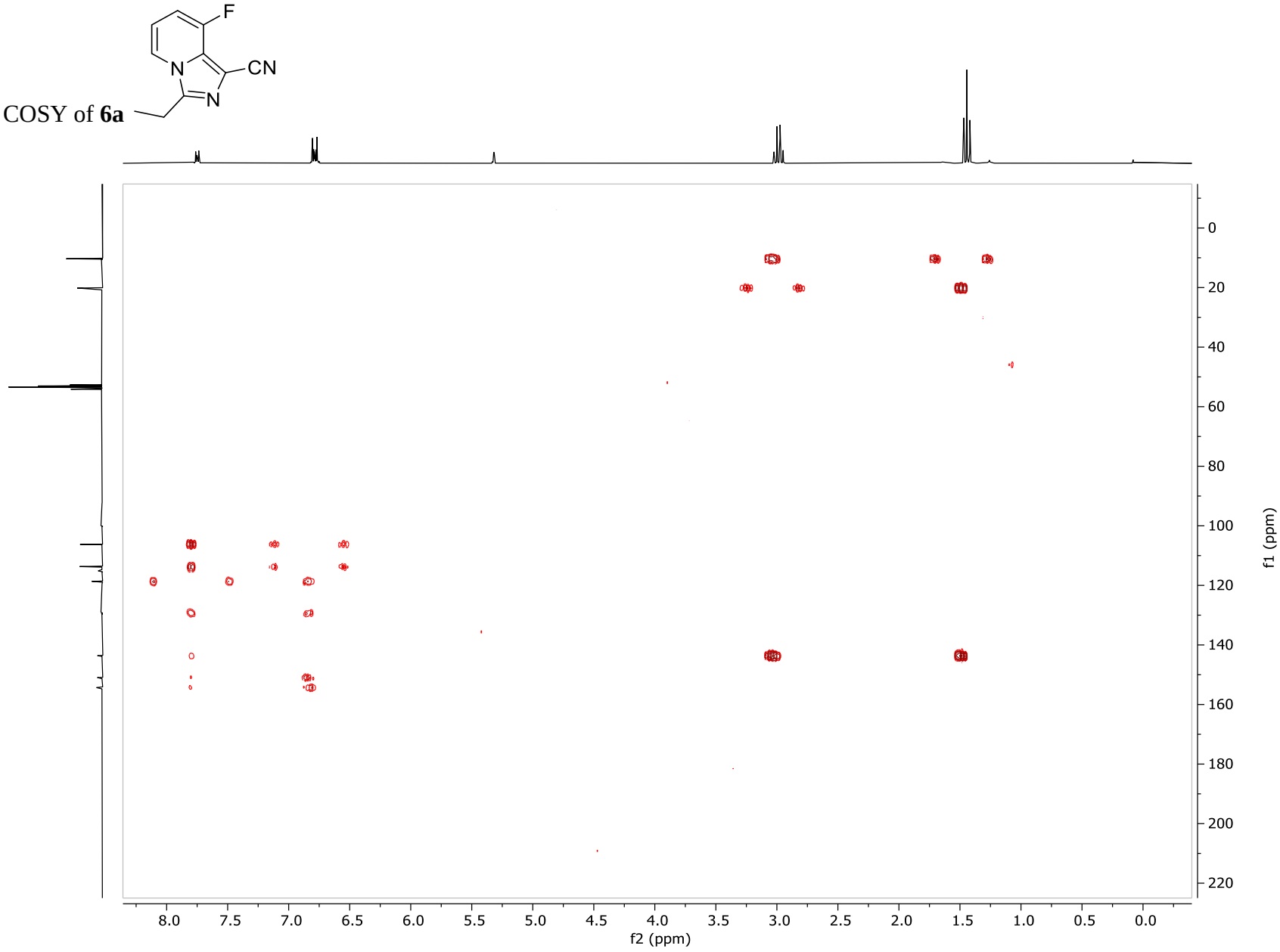
^{13}C NMR (75.4 MHz) of **6a**



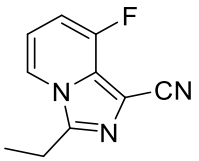
^{19}F NMR (282.4 MHz) of **6a**

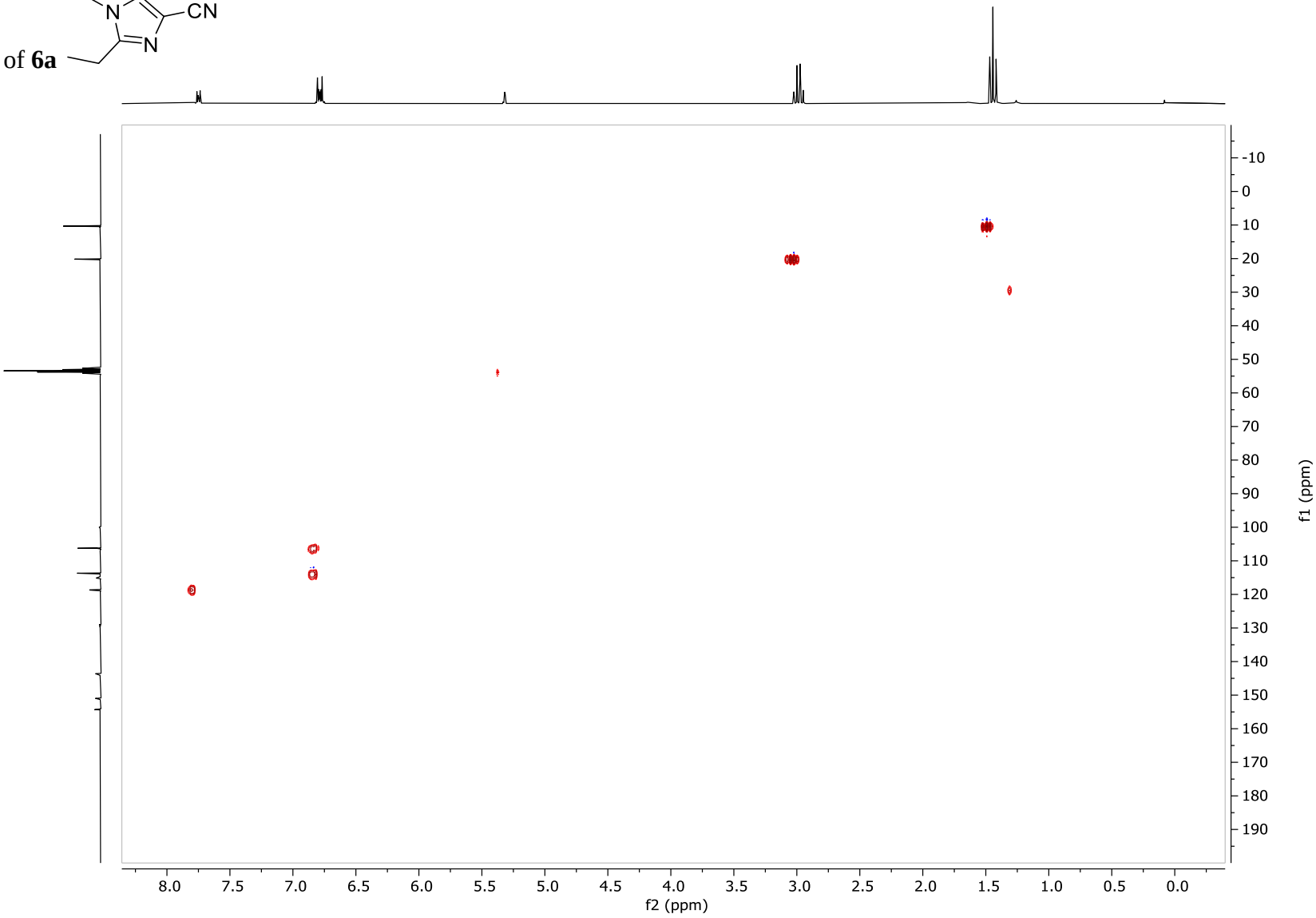


COSY of **6a**

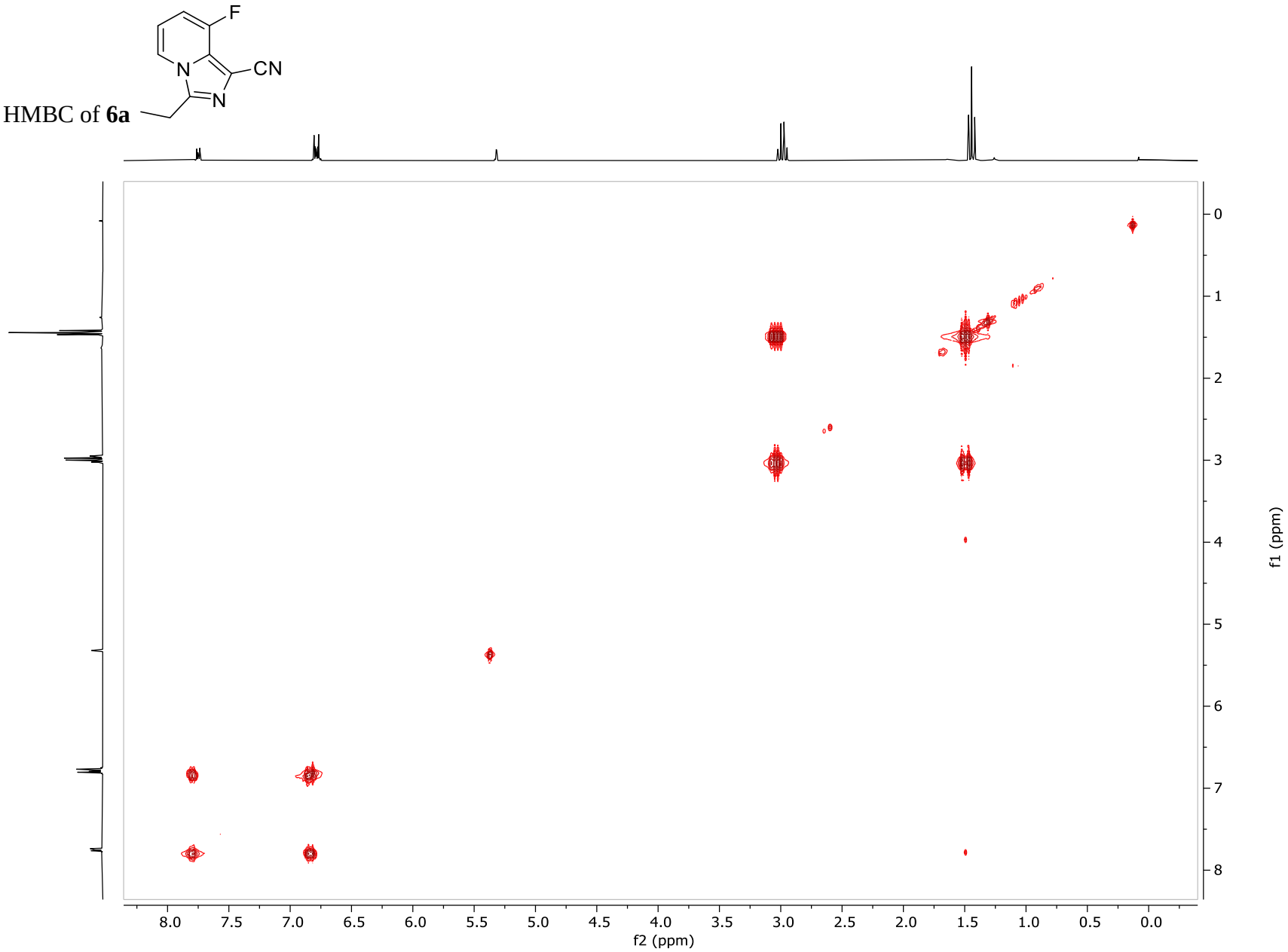


HSQC of **6a**

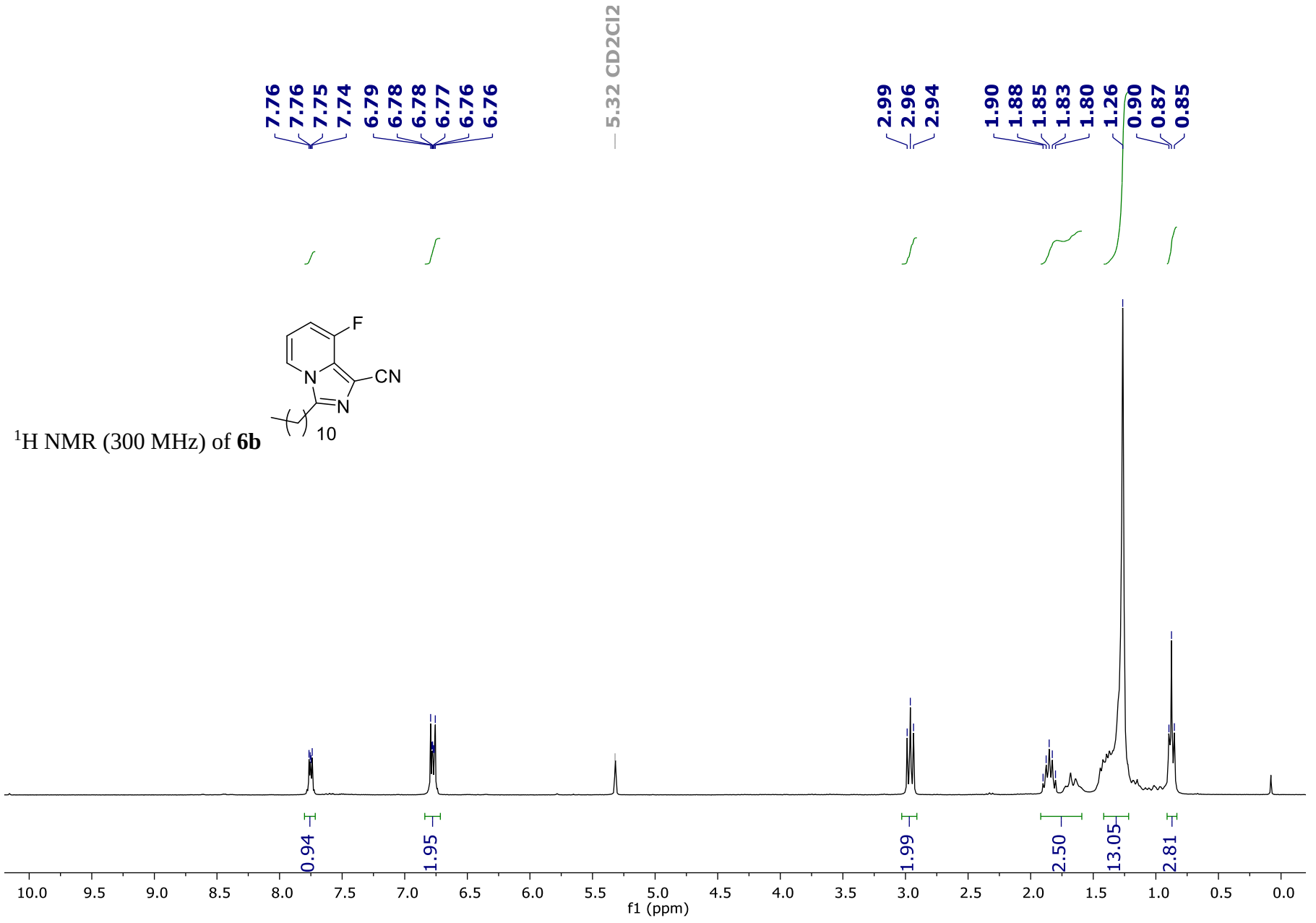

F
N
CN
N


-10
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
f1 (ppm)
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
f2 (ppm)

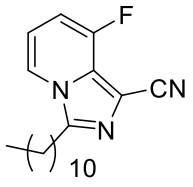
HMBC of **6a**



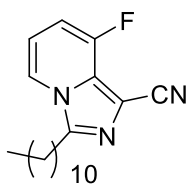
^{1}H NMR (300 MHz) of **6b**

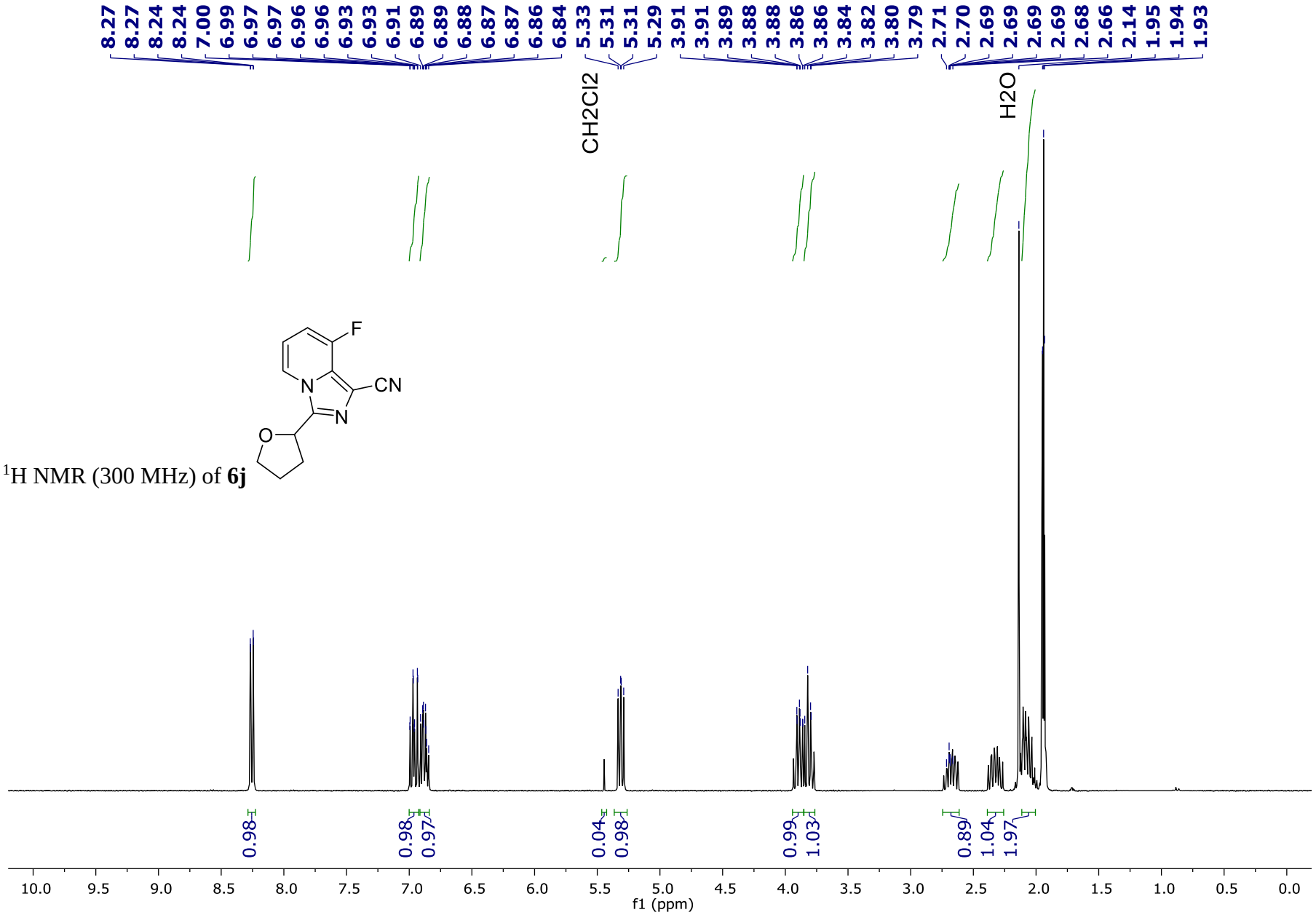


^{13}C NMR (75.4 MHz) of **6b**



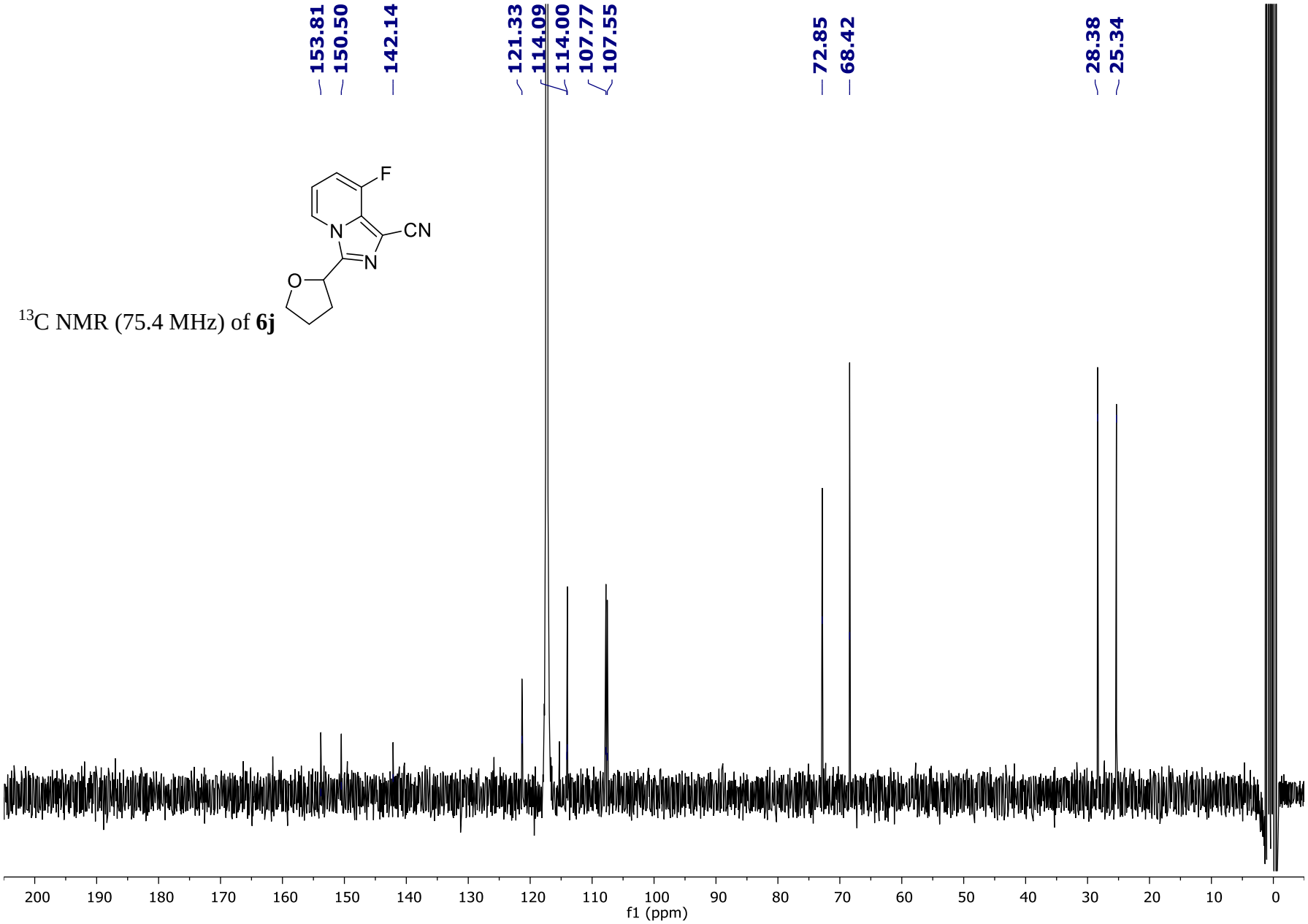
^{19}F NMR (282.4 MHz) of **6b**



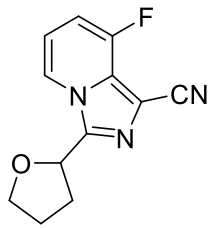


^{1}H NMR (300 MHz) of **6j**

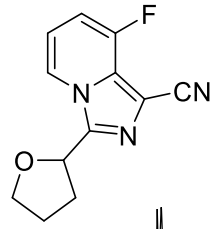
^{13}C NMR (75.4 MHz) of **6j**



^{19}F NMR (282.4 MHz) of **6j**

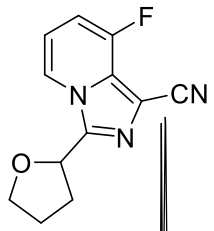


COSY of **6j**


F
N
CN
N
O

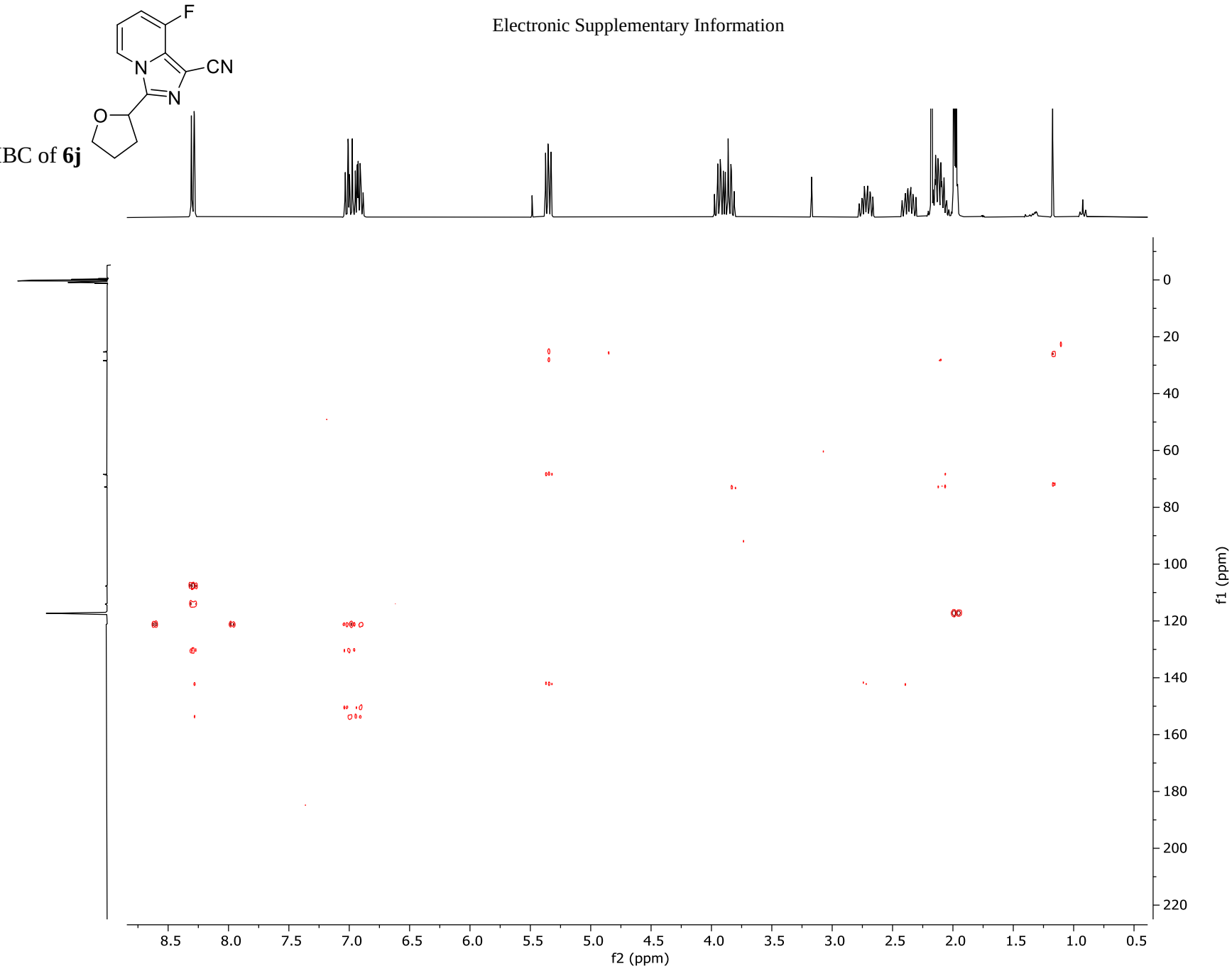
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f2 (ppm)
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
f1 (ppm)

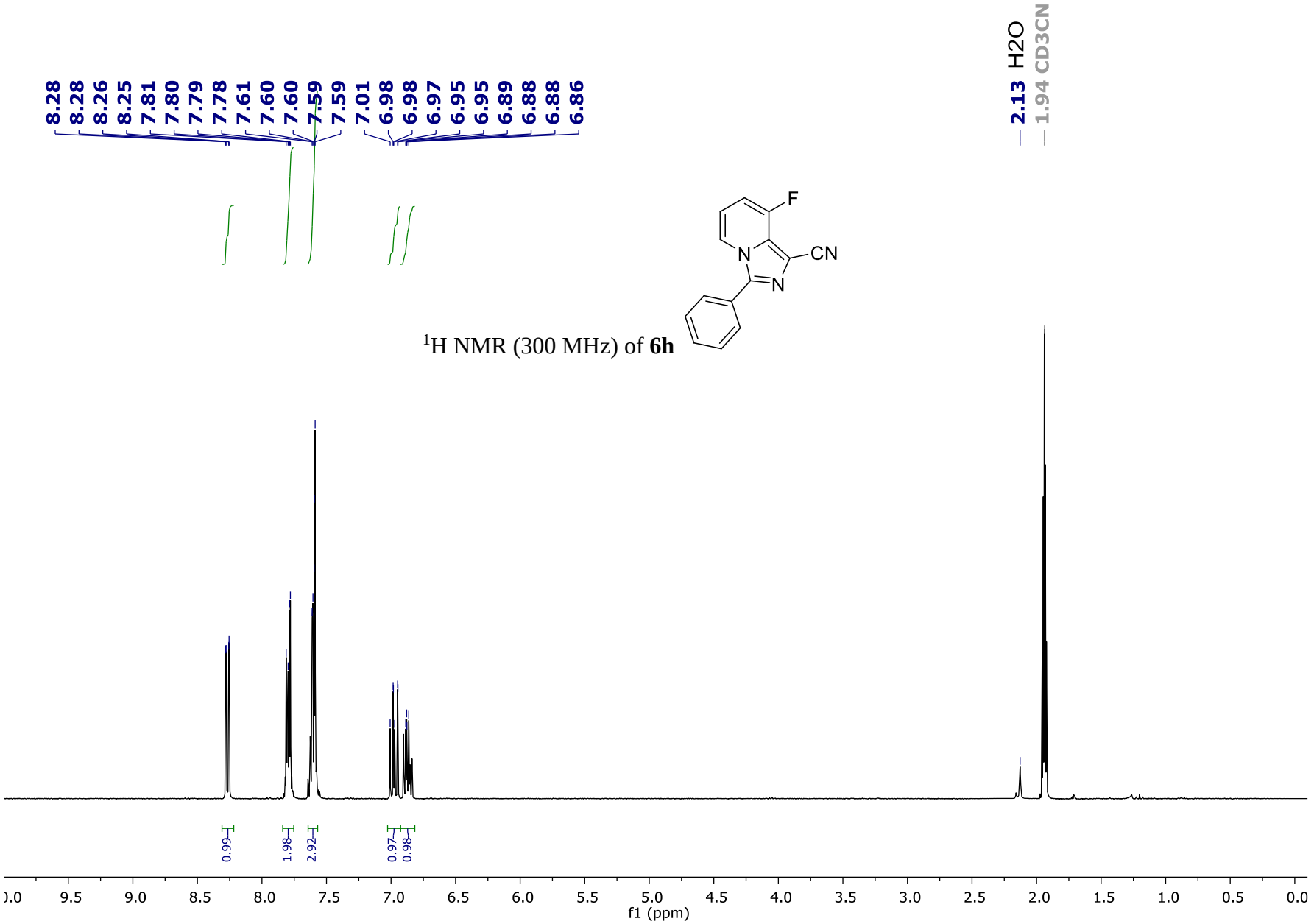
HSQC of **6j**


F
CN
N
N
O

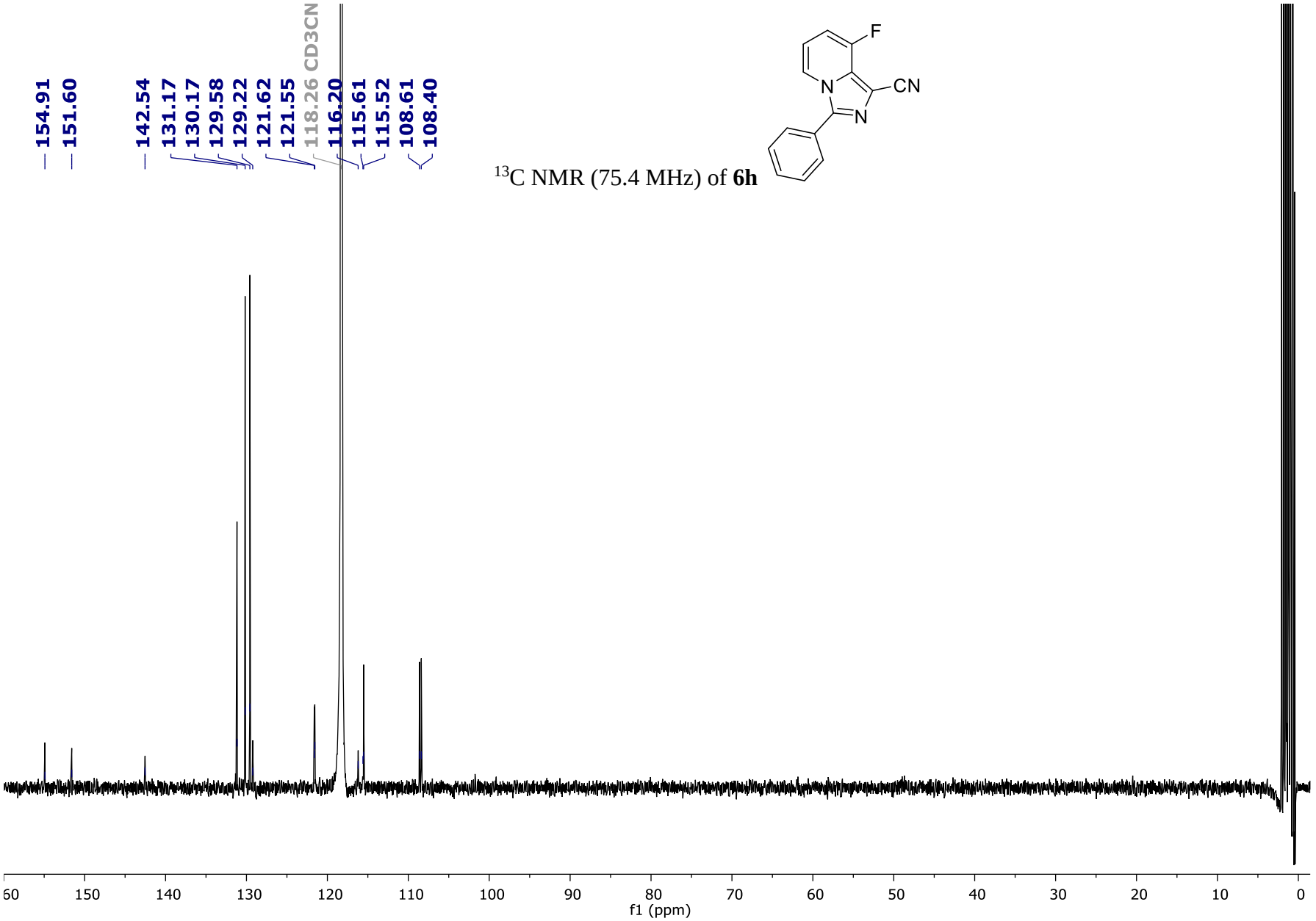
-20
-10
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
f1 (ppm)
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f2 (ppm)

HMBC of **6j**


F
CN
N
N
O
0
20
40
60
80
100
120
140
160
180
200
220
f1 (ppm)
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
f2 (ppm)

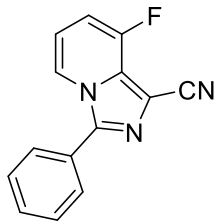


^{1}H NMR (300 MHz) of **6h**

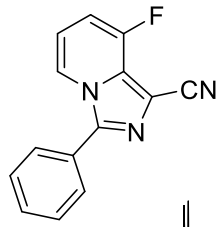


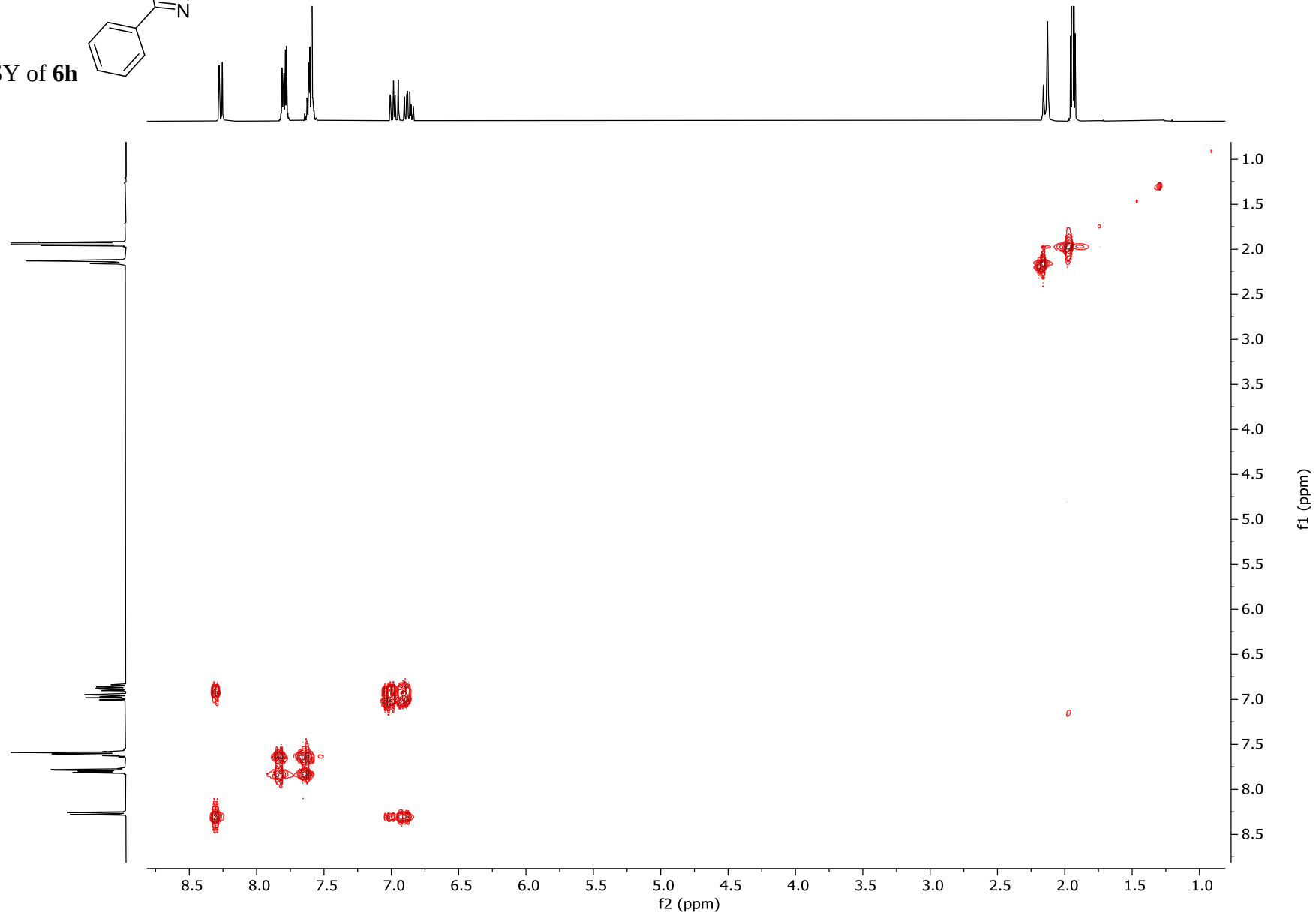
^{13}C NMR (75.4 MHz) of **6h**

^{19}F NMR (282.4 MHz) of **6h**

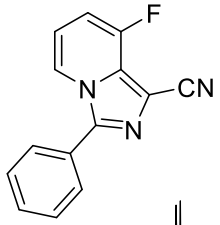


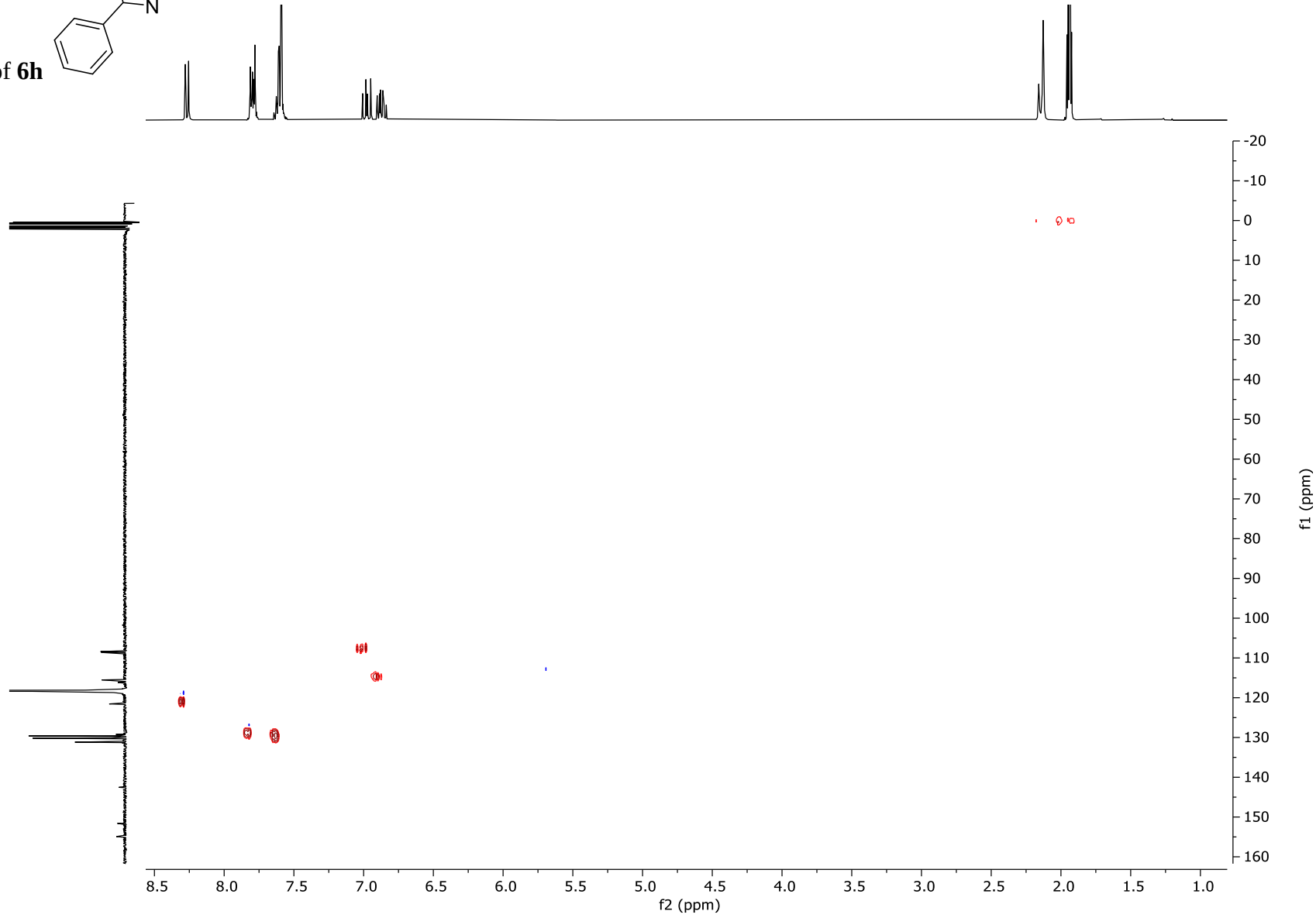
COSY of **6h**



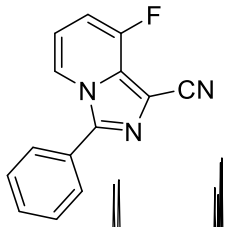


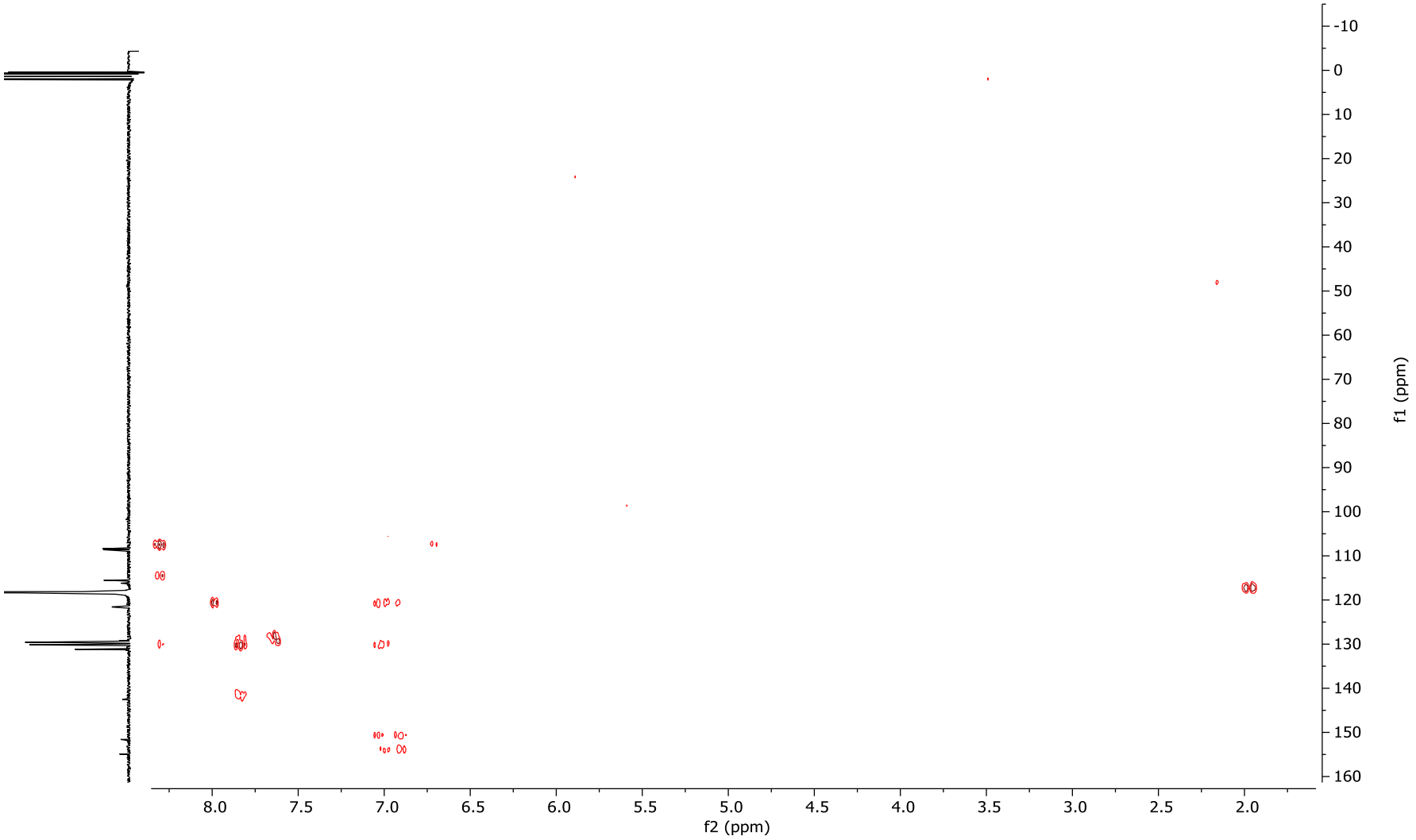
HSQC of **6h**


F
N
CN
N

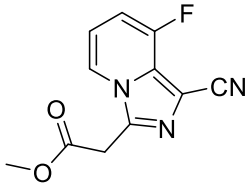

-20
-10
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
f1 (ppm)
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f2 (ppm)

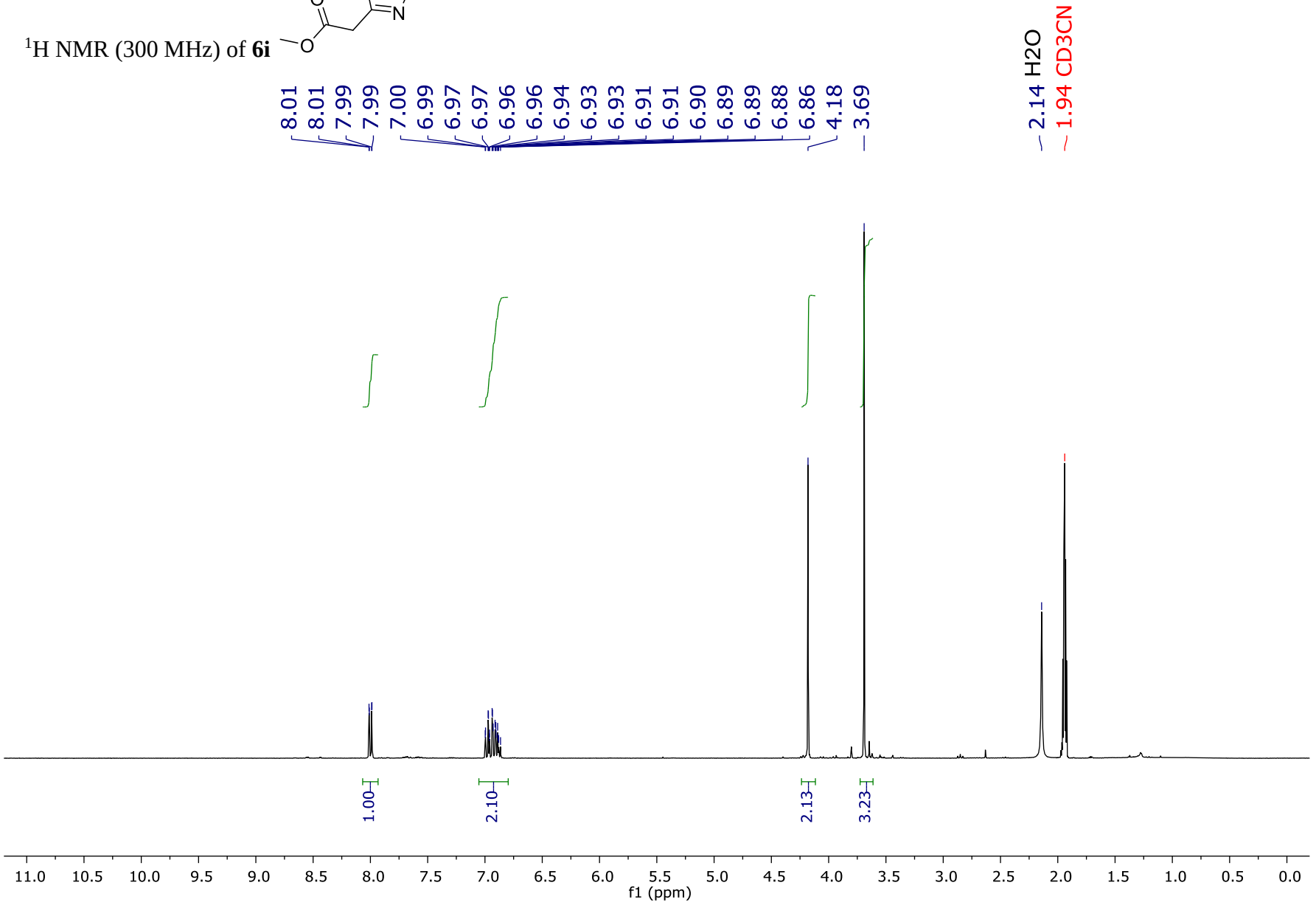
HMBC of **6h**


F
CN
N
N

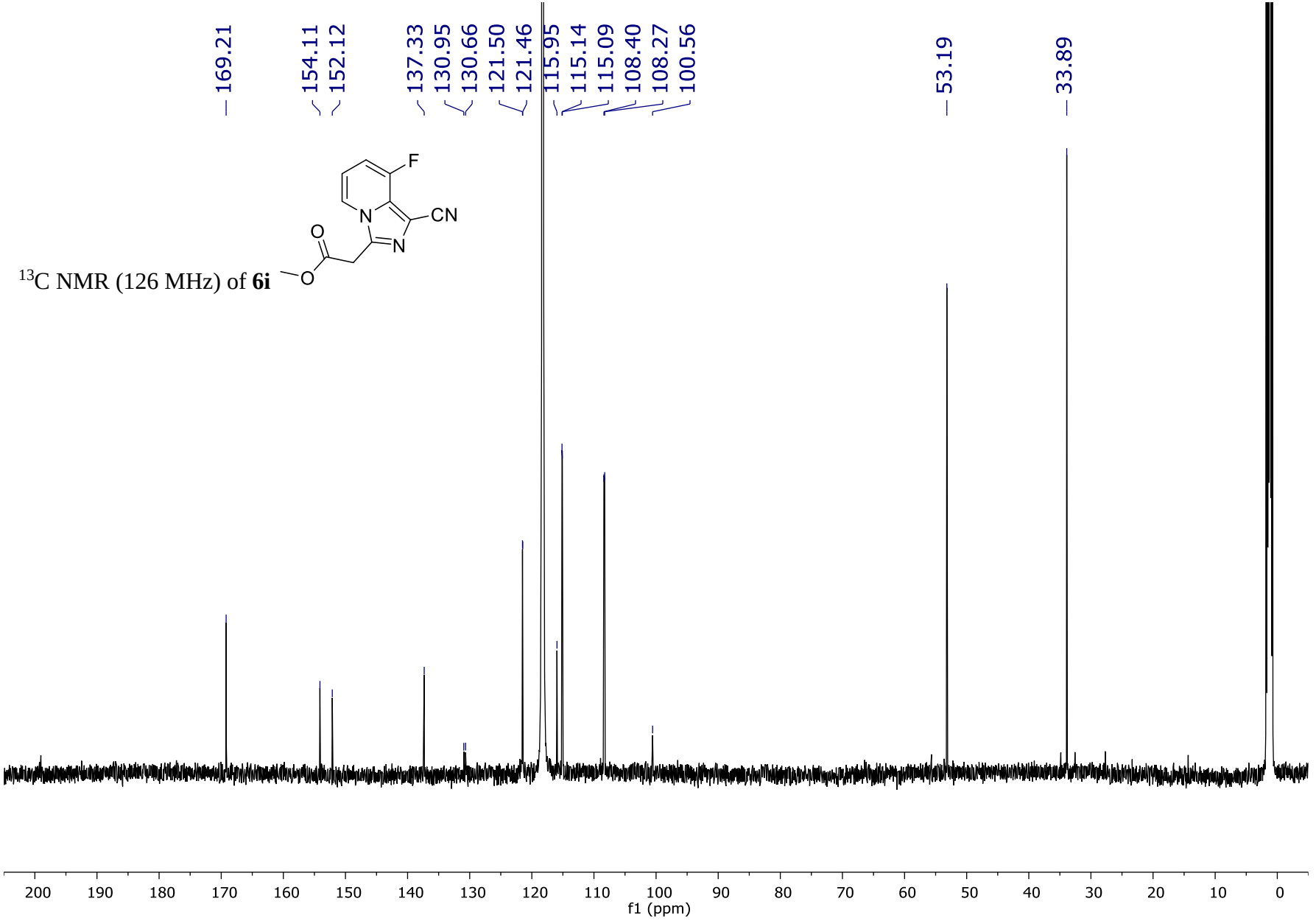

-10
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
f1 (ppm)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
f2 (ppm)

^{1}H NMR (300 MHz) of **6i**

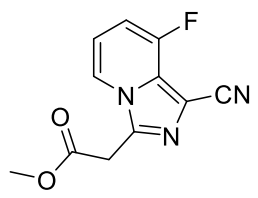




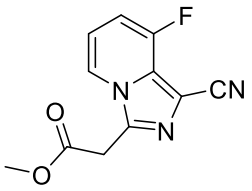
^{13}C NMR (126 MHz) of **6i**



^{19}F NMR (282.4 MHz) of **6i**

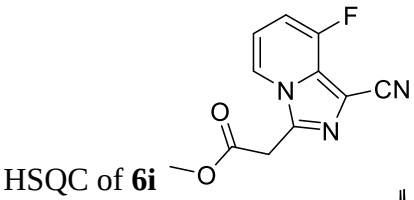


COSY of **6i**


F
N
CN
O
N
O

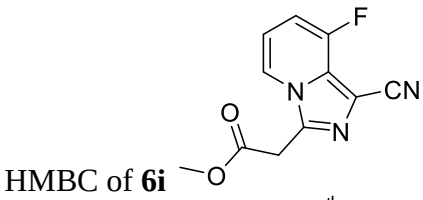
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
f1 (ppm)
8.0 7.8 7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4
f2 (ppm)

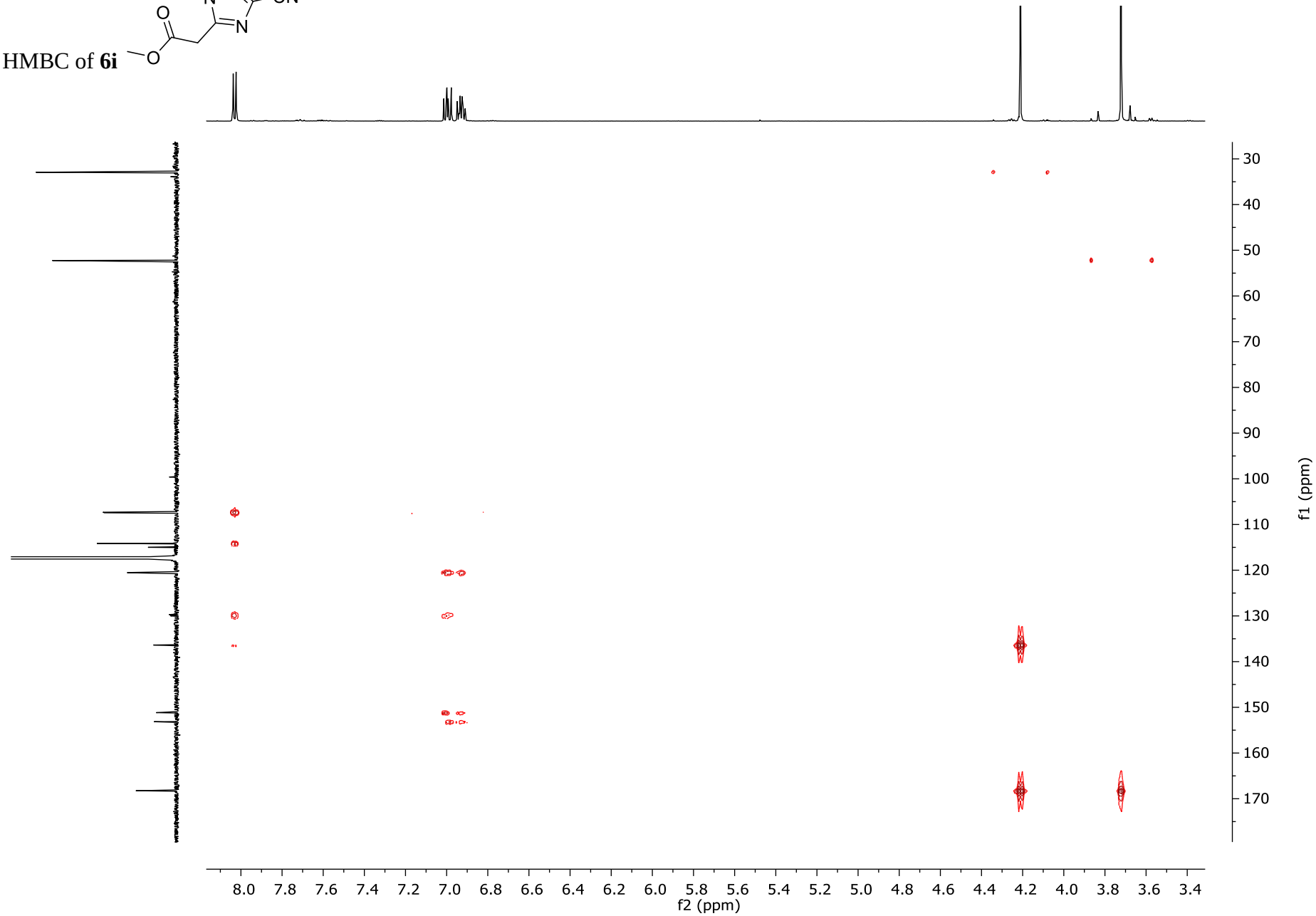
HSQC of **6i**


F
N
CN
O
N
O

30
40
50
60
70
80
90
100
110
120
130
140
f1 (ppm)
8.4 8.2 8.0 7.8 7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4
f2 (ppm)

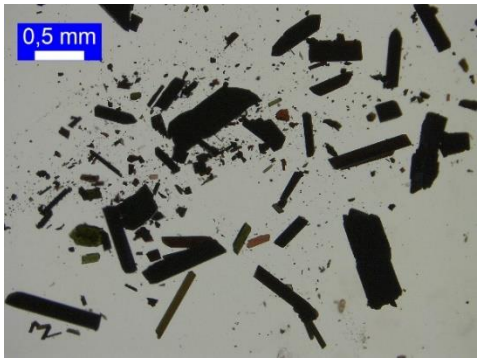
HMBC of **6i**


F
N
CN
O
N
O


30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
f1 (ppm)
8.0
7.8
7.6
7.4
7.2
7.0
6.8
6.6
6.4
6.2
6.0
5.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
f2 (ppm)

F. Crystallographic data of CuA, Cu4B, 4 and 6a.

XRD structure of **CuA**:



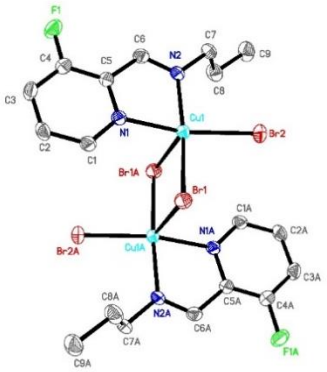
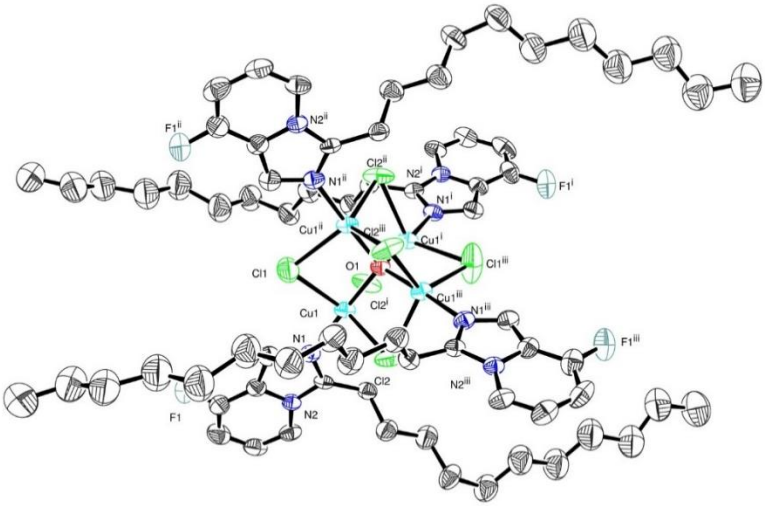


Table S6. Crystal data and structure refinement for CuA.

Empirical formula	$C_{18}H_{22}Br_4Cu_2F_2N_4$	
Formula weight	779.11	
Temperature	193(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	$P\bar{1}$	
Unit cell dimensions	a = 7.8883(6) Å	α= 71.537(2)°.
	b = 8.1714(7) Å	β= 79.335(2)°.
	c = 10.3538(8) Å	γ = 70.634(3)°.
Volume	594.83(8) $Å^3$	
Z	1	
Density (calculated)	2.175 Mg/m^3	
Absorption coefficient	8.534 mm^{-1}	
F(000)	374	
Crystal size	0.250 x 0.100 x 0.060 mm^3	
Theta range for data collection	3.269 to 27.484°.	
Index ranges	-10<=h<=10, -10<=k<=10, -13<=l<=11	
Reflections collected	16362	
Independent reflections	2720 [R(int) = 0.0347]	
Completeness to theta = 25.242°	99.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7457 and 0.4616	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2720 / 0 / 137	
Goodness-of-fit on F^2	1.068	
Final R indices [I>2sigma(I)]	R1 = 0.0209, wR2 = 0.0451	
R indices (all data)	R1 = 0.0288, wR2 = 0.0473	
Largest diff. peak and hole	0.357 and -0.394 $e.Å^{-3}$	

XRD structure of **Cu4B**:



Molecule [Symmetry codes : (i)0.5-y,-0.5+x,0.5-z ; (ii) 1-x,y,z ; (iii) 0.5+y,0.5-x,0.5-z]

Table S7. Crystal data and structure refinement for Cu4B.

Empirical formula	$C_{72}H_{108}Cl_6Cu_4F_4N_8O_1$	
Formula weight	1644.56	
Temperature	193(2) K	
Wavelength	0.71073 A	
Crystal system, space group	tetragonal, I -4	
Unit cell dimensions	a = 11.5858(4) A	alpha = 90 deg.
	b = 11.5858(4) A	beta = 90 deg.
	c = 29.2335(13) A	gamma = 90 deg.
Volume	3924.0(3) A^3	
Z, Calculated density	2, 1.392 Mg/m^3	
Absorption coefficient	1.329 mm^{-1}	
F(000)	1716	
Crystal size	0.16 x 0.10 x 0.08 mm	
Theta range for data collection	1.39 to 26.40 deg.	
Limiting indices	-14<=h<=14, -11<=k<=14, -36<=l<=34	
Reflections collected / unique	15162 / 4023 [R(int) = 0.0503]	
Completeness to theta = 26.40	99.4 %	
Max. and min. transmission	0.7454 and 0.6526	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4023 / 386/ 316	
Goodness-of-fit on F^2	1.040	
Final R indices [I>2sigma(I)]	R1 = 0.0452, wR2 = 0.1045	
R indices (all data)	R1 = 0.0673, wR2 = 0.1152	
Absolute structure parameter	-0.024(9)	
Largest diff. peak and hole	0.584 and -0.595 $e.A^{-3}$	

XRD structure of **4**:

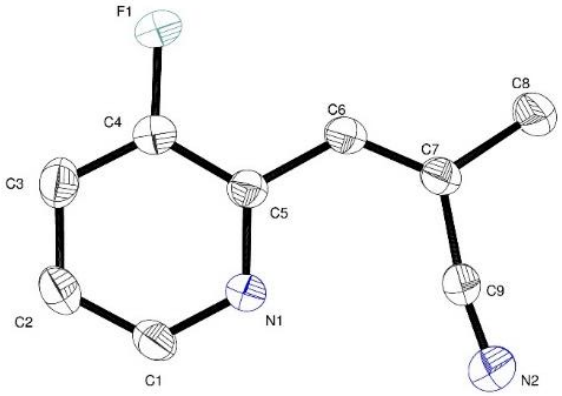
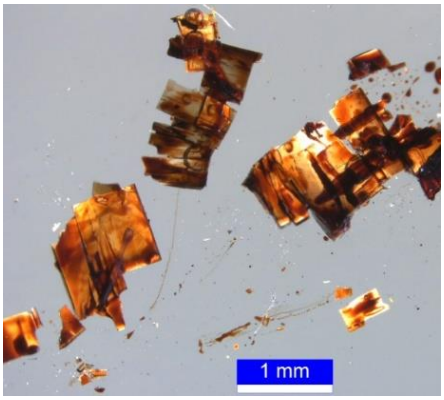


Table S8. Crystal data and structure refinement for 4.

Empirical formula	$C_9H_7FN_2$	
Formula weight	162.17	
Temperature	193(2) K	
Wavelength	0.71073 A	
Crystal system, space group	Monoclinic, *P* $2_1/c$	
Unit cell dimensions	a = 9.9462(8) A	alpha = 90 deg.
	b = 11.8055(9) A	beta = 109.811(5) deg.
	c = 7.1741(7) A	gamma = 90 deg.
Volume	792.53(12) A^3	
Z, Calculated density	4, 1.359 Mg/m^3	
Absorption coefficient	0.100 mm^{-1}	
F(000)	336	
Crystal size	0.200 x 0.080 x 0.060 mm	
Theta range for data collection	2.778 to 25.345 deg.	
Limiting indices	-11<=h<=11, -14<=k<=14, -8<=l<=8	
Reflections collected / unique	17537 / 1444 [R(int) = 0.0588]	
Completeness to theta = 25.242	99.2 %	
Max. and min. transmission	0.7465 and 0.6711	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1444 / 0 / 110	
Goodness-of-fit on F^2	1.175	
Final R indices [I>2sigma(I)]	R1 = 0.0771, wR2 = 0.2489	
R indices (all data)	R1 = 0.0835, wR2 = 0.2555	
Largest diff. peak and hole	0.399 and -0.345 $e.A^{-3}$	

XRD structure of **6a**:



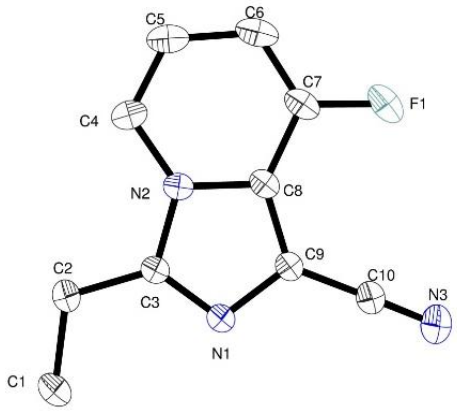


Table S9. Crystal data and structure refinement for 6a.

Empirical formula	$C_{10}H_8FN_3$	
Formula weight	189.19	
Temperature	193(2) K	
Wavelength	0.71073 A	
Crystal system, space group	Orthorhombic, I b a m	
Unit cell dimensions	a = 15.8734(6) A	alpha = 90 deg.
	b = 17.3509(7) A	beta = 90 deg.
	c = 6.6216(3) A	gamma = 90 deg.
Volume	1823.71(13) A^3	
Z, Calculated density	8, 1.378 Mg/m^3	
Absorption coefficient	0.101 mm^{-1}	
F(000)	784	
Crystal size	0.200 x 0.100 x 0.080 mm	
Theta range for data collection	4.026 to 34.987 deg.	
Limiting indices	-25<=h<=21, -27<=k<=27, -10<=l<=10	
Reflections collected / unique	32011 / 2099 [R(int) = 0.0337]	
Completeness to theta =	25.242 97.4 %	
Refinement method	Full-matrix least-squares on F^2	
Max. and min. transmission	0.7469 and 0.7010	
Data / restraints / parameters	2099 / 0 / 92	
Goodness-of-fit on F^2	1.083	
Final R indices [I>2sigma(I)]	R1 = 0.0398, wR2 = 0.1093	
R indices (all data)	R1 = 0.0471, wR2 = 0.1184	
Largest diff. peak and hole	0.396 and -0.266 $e.A^{-3}$	