Pd-Catalyzed annulation of imidazo[1,2-a]pyridines with coumarins and indoles: Synthesis of benzofuran and indole fused heterocycles

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Experimental Section:

General: All commercially available chemicals and reagents were used without any further purification unless otherwise indicated. ^{1}H and ^{13}C {H} NMR spectra were recorded at 600/500, and 150/125 MHz, respectively. The spectra were recorded in $CDCl_3$ as solvent. Multiplicity was indicated as follows: s (singlet); d (doublet); t (triplet); m (multiplet); dd (doublet of doublets), etc. and coupling constants (J) were given in Hz. Chemical shifts are reported in ppm relative to TMS as an internal standard for ^{1}H NMR. ^{19}F NMR (564 MHz) chemical shifts were reported in ppm (δ) (CF_3COOH as an outside standard). The peaks around delta values of ^{1}H NMR (7.26), and ^{13}C {H} NMR (77.0) are deuterated solvent chloroform, [δ value around (1.5) in ^{1}H NMR is of water]. Mass spectra were obtained using electron impact (EI) ionization method. Progress of the reactions were monitored by thin layer chromatography (TLC). All products were purified through column chromatography using silica gel 100-200 mesh size using hexane/ethyl acetate as eluent, unless otherwise indicated.

General procedure for the synthesis of 2-phenylimidazo[1,2-a]pyridine (1a)[1]:

470 mg (5.0 mmol) of 2-aminopyridine, 1200 mg (10 mmol) of acetophenone, CuI 5 mol% (47 mg; 0.25 mmol), $BF_3 \cdot Et_2O$ (45–50% purity); 10 mol%, (0.5 mmol) and DMF (2 mL) were placed in a 25-mL double-necked round-bottomed flask. The mixture was heated in oil bath at 60 ˚C for 24 h under an oxygen atmosphere (balloon). After completion of the reaction, it was allowed to attain to room temperature and then the mixture was poured into 20 mL of sodium carbonate solution. The product was extracted with DCM (50 mL X 3) and dried with anhydrous Na_2SO_4. Removal of the solvent under reduced pressure and the left residue that was purified through column chromatography using silica gel (30% EtOAc/hexane) to afford **1a**; yield: 0.799 g (82%) experimental data also matched with reported literature and the same method was applied for all the reported starting substrates.[1]

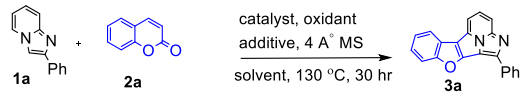
General procedure for the synthesis of 1-phenylbenzofuro[3,2-a]imidazo[5,1,2-cd]indolizine (3a):

To a reaction tube equipped with a magnetic stir bar, added 2-phenylimidazo[1,2-a]pyridine (**1a**) (39 mg, 0.20 mmol), coumarin (**2a**) (58.4 mg, 0.40 mmol), Copper(II) trifluoroacetate hydrate (115.8 mg, 0.40 mmol), 1,10 Phenanthroline monohydrate (19.8 mg, 0.50 mmol) and $Pd(OAc)_2$(8.96 mg, 0.02 mmol) and charged with 4º MS in 1.5 mL of dry DMF solvent. The mixture was heated in an oil bath at 130 ºC in a closed tube. Reaction was monitored by TLC, after completion of the reaction; it was allowed to attain room temperature. Then the mixture was poured into 20 mL of water and the product was extracted with EtOAc. The combined organic layers were dried over anhydrous Na_2SO_4 and

solvent was removed under vacuum. The crude residue left out was purified by silica gel column chromatography using 15 % EtOAc/hexane to afford **3a** (49.2 mg; 80 % yield).

General procedure for the synthesis of 6-methyl-1-phenyl-6H-imidazo[5',1',2':3,4,5]indolizino[1,2-b]indole (5a): To a reaction tube equipped with a magnetic stir bar, added 2-phenylimidazo[1,2-a]pyridine (**1a**) (39 mg, 0.20 mmol), 1-methyl-1H-indole (**4a**) (52.4 mg, 0.40 mmol), Copper(II) trifluoroacetate hydrate (115.8 mg, 0.40 mmol), 1,10 Phenanthroline monohydrate (19.8 mg, 0.50 mmol), $Pd(OAc)_2$ (8.96 mg, 0.02 mmol) and Cs_2CO_3 (130 mg; 0.40 mmol) in 1.5 mL of dry DMF solvent. The mixture was heated in an oil bath at 130 °C in a closed tube. Reaction was monitored by TLC, after completion of the reaction; it was allowed to attain room temperature. Then the mixture was poured into 20 mL of water and the product was extracted with EtOAc. The combined organic layers were dried over anhydrous Na_2SO_4 and solvent was removed under vacuum. The crude residue was purified by silica gel column chromatography using 30 % EtOAc/hexane to afford **5a** (46.8 mg; 75 % yield).

Table S1: Optimization conditions for 3a[a]

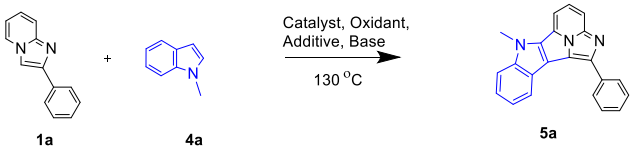


1a 2a 3a

S. No.	Catalyst	Oxidant	Additive (mmol)	Yield (%)
1	$Pd(OAc)_2$	$Cu(OAc)_2.H_2O$	-	trace
2	$Pd(OAc)_2$	$Cu(OAc)_2.H_2O$	KOtBu(0.40)	25
3	$Pd(OAc)_2$	$Cu(OAc)_2.H_2O$	NaOtBu(0.40)	30
4	$Pd(OAc)_2$	$Cu(OAc)_2.H_2O$	DMAP(0.40)	35
5	$Pd(OAc)_2$	$Cu(OAc)_2.H_2O$	Cs_2CO_3(0.40)	nr
6	$Pd(OAc)_2$	$Cu(OAc)_2.H_2O$	DBU(0.40)	nr
7	$Pd(OAc)_2$	$Cu(TFA)_2.H_2O$	KOtBu(0.40)	40
8	$Pd(OAc)_2$	$Cu(TFA)_2.H_2O$	NaOtBu(0.40)	42
9	$Pd(OAc)_2$	$Cu(TFA)_2.H_2O$	DMAP(0.40)	35
10	$Pd(OAc)_2$	$Cu(TFA)_2.H_2O$	Cs_2CO_3(0.40)	nr
11	$Pd(OAc)_2$	$Cu(TFA)_2.H_2O$	DBU(0.40)	nr
12	$PdCl_2(PPh_3)_2$	$Cu(TFA)_2.H_2O$	phen(0.05)	nr
13	$PdCl_2$	$Cu(TFA)_2.H_2O$	phen(0.05)	nr
14	$PdBr_2$	$Cu(TFA)_2.H_2O$	phen(0.05)	nr
15	PdI_2	$Cu(TFA)_2.H_2O$	phen(0.05)	nr
16	$Pd(TFA)_2$	$Cu(TFA)_2.H_2O$	phen(0.05)	50
17	-	$Cu(TFA)_2.H_2O$	phen(0.05)	nr

[a]Reaction Conditions **1a** (0.20 mmol), **2a** (0.40 mmol), catalyst (0.02 mmol), Oxidant (0.40 mmol), Additive, 4 Aº MS, DMF (1.5 ml) 130 °C, 30 hr.

Table S2: Optimization conditions for 5a[a]



1a 4a 5a

S. No.	Base (equiv)	Yield (%)
1	K_2CO_3 (2)	50
2	$NaHCO_3$ (2)	45
3	Na_2CO_3 (2)	40
4	DBU (2)	nr
5	NaH (2)	55
6	**Cs_2CO_3 (2)**	**75**
7	Cs_2CO_3 (2)	70[b]
8	Cs_2CO_3 (2)	50[c]

[a]Reaction Conditions **1a** (0.20 mmol), **4a** (0.40 mmol), Catalyst $Pd(OAc)_2$ (0.02 mmol), Oxidant $Cu(TFA)_2.H_2O$(0.40 mmol), Additive phen (0.05 mmol), Base (0.40 mmol),[b]Reaction under N_2 atm,[c]Reaction under O_2 atm, 130 °C, 36 h.

Further we explored this reaction conditions with the indole derivatives (Table S2). Initially we applied same reaction condition with the indole derivatives which is same for the coumarin derivatives. But unfortunately we did not get any annulated product. After adding base to the reaction, the reaction proceeds. So base is major requirement for obtaining the annulated product. Then we optimized the reaction with different bases such as K_2CO_3, $NaHCO_3$, Na_2CO_3, DBU and NaH but we did not get affective yield for the annulated product (entry 1 to 5). Upon changing the base to the Cs_2CO_3 we got 75% of the desired annulated product (entry 6). Again when we performed the reaction in presence of nitrogen and oxygen atmosphere, it does not improve the yield of reaction (entry 7 and 8).

Scheme S1: Mechanistic pathway for 5a

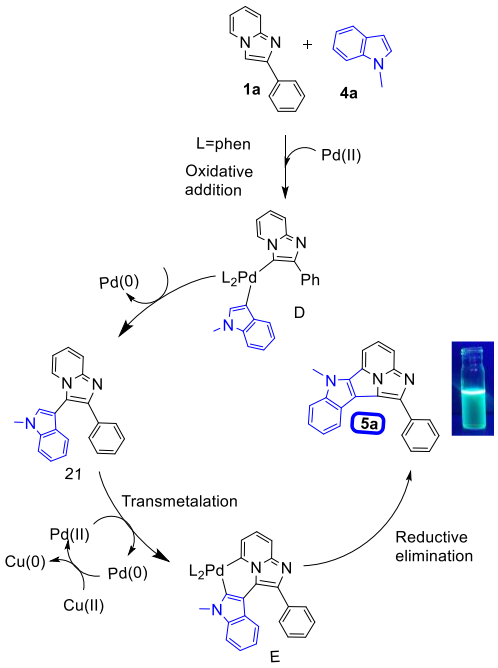
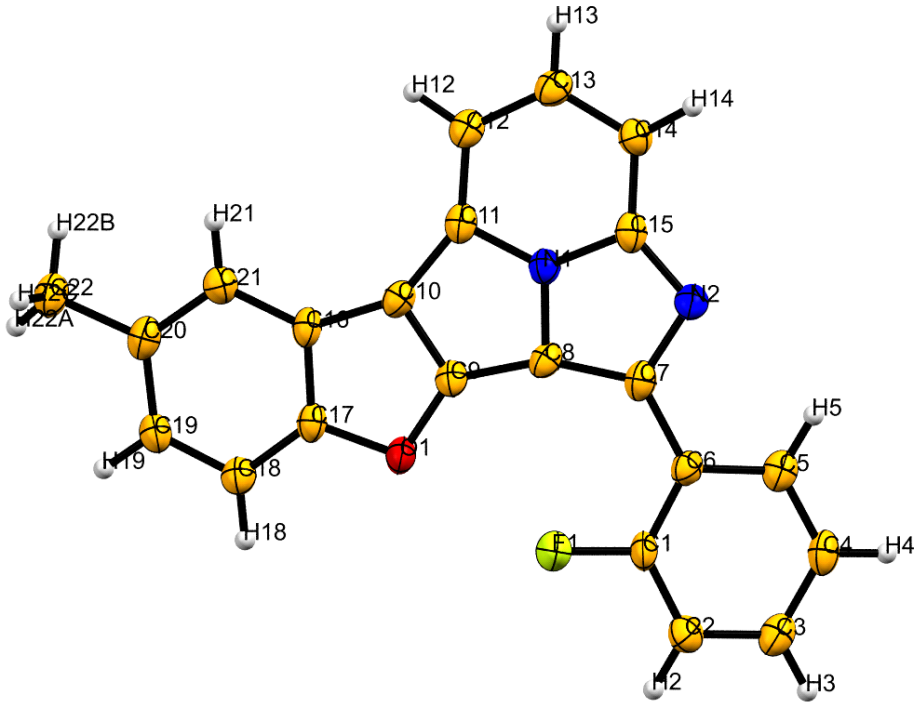
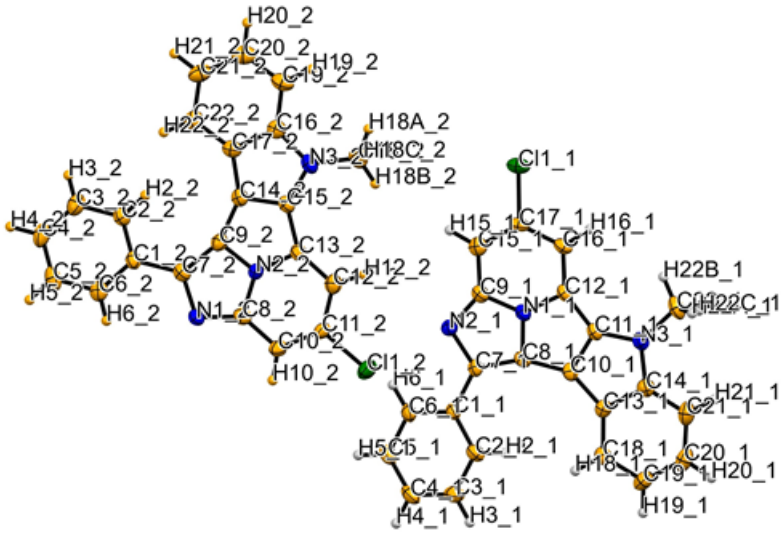


Fig. S1. Thermal ellipsoid plot for the crystal structure 3aa



Single crystal XRD of 3aa CCDC:2124566

Fig. S2 Thermal ellipsoid plot for the crystal structure 5e



Single crystal XRD of 5e (CCDC: 2124567)

Crystal Data and Refinement Parameters

Experimental: X-ray part

Crystal of suitable size was selected for the organic compound, immersed in partone oil and then mounted on the tip of a glass fiber using epoxy resin. Intensity data for all four crystals were collected at 100 and 150 K using graphite monochromatised MoKα (α = 0.71073Å) radiation on diffractometer equipped with CCD area detector. The data integration and reduction were processed.[1] An empirical absorption correction was applied to the collected reflections.[2] The structures were solved by direct methods[3] and refined on F^2 by the full-matrix least-squares technique [4] package. Graphics are generated.[5,6] Non-hydrogen atoms were refined anisotropically till convergence is reached and the hydrogen atoms of the organic compound is stereochemically fixed. Crystallographic parameters for the compound is given in Table S4.

1. Sheldrick, G. M.; SAINT 5.1 ed.; Siemens Industrial Automation Inc.: Madison, WI, 1995.
2. SADABS, Empirical Absorption Correction Program; University of Göttingen: Göttingen, Germany 1997.
3. Sheldrick, G. M.; SHELXTL Reference Manual: Version 5.1; Bruker AXS: Madison, WI 1997.
4. Sheldrick, G.M. SHELXL-97: Program for Crystal Structure Refinement; University of Göttingen: Göttingen, Germany (1997).
5. A.L.Spek, Acta Cryst. 2009, D65, 148-155
6. Mercury 1.3, Supplied with Cambridge Structural Database; CCDC: Cambridge, U.K., (2003).

Table S3. Crystal Data and Refinement Parameters for Compounds **3aa** and **5e**

Identification code	**3aa**	**5e**
Empirical formula	$C_{22}H_{14}ClN_3$	$C_{22}H_{13}FN_2O$
Formula weight	355.81	340.34
Temperature/K	150(2)	100(2)
Crystal system	monoclinic	Monoclinic
Space group	Pc	$P2_1/n$
a/Å	17.667(2)	11.213(4)
b/Å	13.2247(15)	7.512(2)
c/Å	7.1270(7)	18.352(6)
α/°	90	90
β/°	98.212(5)	95.058(11)
γ/°	90	90
Volume/Å^3	1648.1(3)	1539.7(9)
Z	4	4
ρ_{calc}g/cm^3	1.434	1.468
μ/mm^{-1}	0.242	0.100
F(000)	736.0	704.0
Crystal size/mm^3	0.226 × 0.125 × 0.027	0.206 × 0.111 × 0.024
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.862 to 55.152	4.102 to 47.194
Index ranges	$-22 \le h \le 22$, $-17 \le k \le 17$, $-7 \le l \le 9$	$-12 \le h \le 12$, $-8 \le k \le 8$, $-20 \le l \le 18$
Reflections collected	33131	17598
Independent reflections	7145 [R_{int} = 0.1367, R_{sigma} = 0.1106]	2315 [R_{int} = 0.1495, R_{sigma} = 0.0953]
Data/restraints/parameters	7145/2/471	2315/0/236
Goodness-of-fit on F^2	0.999	1.085
Final R indexes [I>=2σ (I)]	R_1 = 0.0548, wR_2 = 0.1116	R_1 = 0.0607, wR_2 = 0.1552
Final R indexes [all data]	R_1 = 0.1066, wR_2 = 0.1328	R_1 = 0.1202, wR_2 = 0.1928
Largest diff. peak/hole / e Å^{-3}	0.30/-0.34	0.26/-0.32

Photo Physical Data

Due to the highly fluorescence characteristic nature of the annulated products, we studied the photo physical properties of the hetero fused derivatives by recording the uv-visible and fluorescence spectra at low concentration of 10 µM in DCM solution of the selected fluorophores. All the spectra were recorded by exciting at the respective wavelength and the fluorophore molecules showed emission spectra in the visible region 506-580 nm. These scaffolds may find applications as chemo sensors in the fields of molecular imaging, bioorganic chemistry, molecular recognition, analytical chemistry, materials chemistry and as well as in medicinal chemistry and biology.[2]

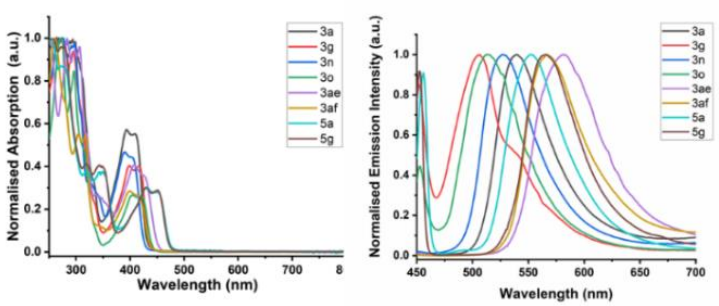


Fig. S3 Normalized **(a)** absorption and **(b)** emission spectra of selected annulated products

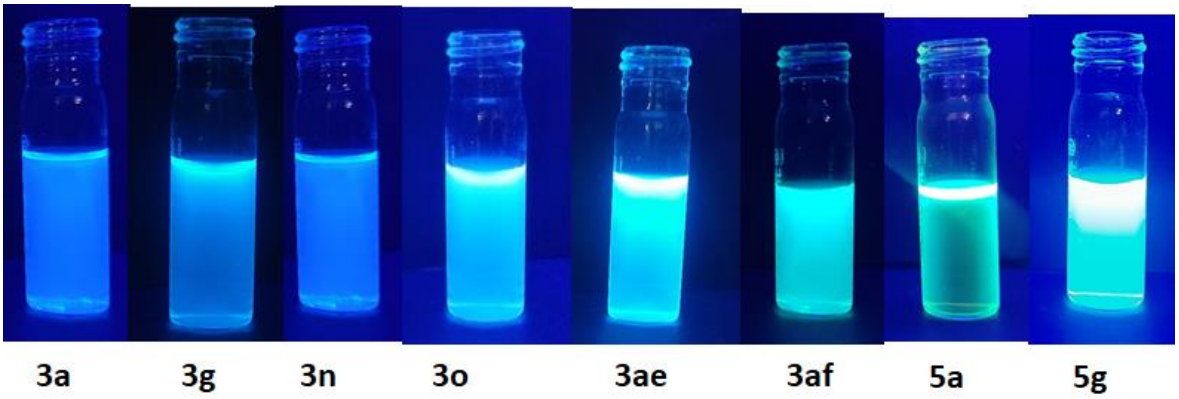


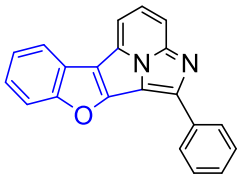
Fig. S4 Digital photograph of the fluorescent imidazopyridines in DCM under UV light

Table S4. Spectral properties of selected imidazopyridines in DCM at room temperature (10 μM solution):

Comp	$\lambda_{abs(max)}$ nm	$\lambda_{ex(max)}$ nm	$\lambda_{em(max)}$ nm	Δ_{stokes} nm
3a	394	394	539	145
3g	398	398	506	108
3n	390	390	527	137
3o	403	403	514	111
3ae	408	408	580	172
3af	398	398	567	169
5a	430	430	552	122
5g	430	430	565	135

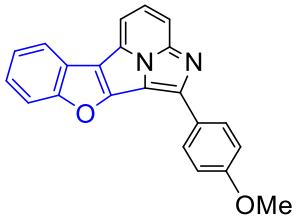
Characterization data:

1-phenylbenzofuro[3,2-a]imidazo[5,1,2-cd]indolizine (3a):



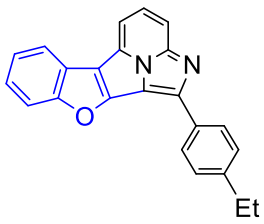
(Eluent: 15% EtOAc/hexane); 80% yield (49.2 mg); yellow solid, Mp: 208-210 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.59 (d, J = 8.1 Hz, 2H), 8.08 – 7.98 (m, 4H), 7.80 (d, J = 8.1 Hz, 1H), 7.66 (t, J = 7.5 Hz, 2H), 7.53 (t, J = 7.5 Hz, 1H), 7.50 – 7.42 (m, 2H).^{13}C NMR (150 MHz, $CDCl_3$) δ 159.6, 150.9, 147.6, 141.1, 132.9, 130.0, 129.1, 128.0, 127.0, 124.8, 124.5, 124.0, 122.9, 119.9, 115.1, 112.7, 111.0, 110.7, 110.6. HRMS-ESI (m/z) $[M+H]^+$calcd. For $C_{21}H_{13}N_2O$: 309.1023; Found: 309.1018.

7-methoxybenzofuro[3'',2'':3',4']naphtho[1',2':4,5]imidazo[1,2-a]pyridine (3b):



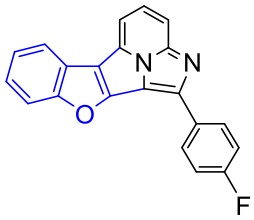
(Eluent: 20% EtOAc/hexane); 60% yield (40.5 mg); yellow solid, Mp: 255-257 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.53 (d, J = 9.2 Hz, 2H), 8.01 (d, J = 5.8 Hz, 4H), 7.79 (d, J = 7.9 Hz, 1H), 7.51 – 7.42 (m, 2H), 7.18 (d, J = 8.1 Hz, 2H), 3.95 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 161.3, 159.8, 129.7, 126.9, 125.7, 124.7, 124.5, 124.1, 120.0, 114.7, 112.8, 110.5, 110.4, 55.5. HRMS-ESI (m/z) $[M+H]^+$calcd. For $C_{22}H_{15}N_2O_2$: 339.1129; Found: 339.1143.

1-(4-ethylphenyl)benzofuro[3,2-a]imidazo[5,1,2-cd]indolizine (3c):



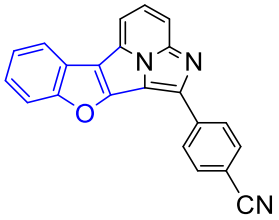
(Eluent: 15% EtOAc/hexane); 73% yield (49.0 mg); yellow solid, Mp: 215-217 °C; δ ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.48 (d, J = 7.9 Hz, 2H), 8.00 (p, J = 7.5, 7.0 Hz, 4H), 7.77 (d, J = 7.9 Hz, 1H), 7.48 (d, J = 7.9 Hz, 2H), 7.44 (q, J = 7.3 Hz, 2H), 2.80 (q, J = 7.9 Hz, 2H), 1.37 (s, 3H).^{13}C NMR (150 M Hz, $CDCl_3$) δ 159.7, 151.1, 148.1, 146.6, 141.3, 130.4, 128.8, 128.1, 126.9, 124.8, 124.5, 124.1, 123.1, 120.0, 115.0, 112.8, 110.8, 110.6, 110.5, 28.9, 15.4. HRMS-ESI (m/z) $[M+H]^+$calcd. For $C_{23}H_{17}N_2O$: 337.1336; Found: 337.1348.

1-(4-fluorophenyl)benzofuro[3,2-a]imidazo[5,1,2-cd]indolizine (3d):



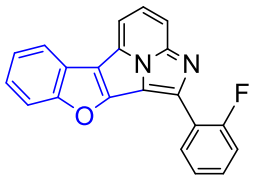
Eluent: 15% EtOAc/hexane); 63% yield (41.0 mg); yellow solid, Mp:270-272 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.51 (dd, J = 8.6, 5.3 Hz, 2H), 8.03 – 7.92 (m, 4H), 7.78 – 7.73 (m, 1H), 7.45 (p, J = 7.2, 6.6 Hz, 2H), 7.31 (t, J = 8.6 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 164.7 (d, $J_{C,F}$ = 249 Hz), 163.0, 159.7, 150.8, 146.6, 141.1, 129.9 (d, $J_{C,F}$ = 7.5 Hz), 129.3, 127.1, 124.9, 124.6, 124.2, 123.0, 120.0, 116.4 (d, $J_{C,F}$ = 21 Hz), 115.2, 112.7, 111.1, 110.8, 110.3; ^{19}F NMR (564 MHz, $CDCl_3$) δ -110.21 (s, 1F); HRMS-ESI (m/z) $[M+Na]^+$ calcd. For $C_{21}H_{11}FN_2ONa$: 349.0748; Found: 349.0738.

4-(benzofuro[3,2-a]imidazo[5,1,2-cd]indolizin-1-yl)benzonitrile (3e):



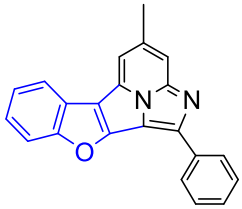
(Eluent: 30% EtOAc/hexane); 65% yield (43.2 mg); yellow solid, Mp:215-217 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.61 (d, J = 8.0 Hz, 2H), 8.07 (q, J = 5.2, 4.7 Hz, 3H), 8.01 (d, J = 5.8 Hz, 1H), 7.89 (d, J = 8.0 Hz, 2H), 7.80 (d, J = 7.8 Hz, 1H), 7.52 – 7.46 (m, 2H).^{13}C NMR (150 MHz, $CDCl_3$) δ 159.8, 150.7, 144.7, 141.1, 137.2, 132.9, 128.2, 127.8, 125.4, 125.1, 124.4, 122.8, 120.2, 118.8, 116.1, 112.9, 112.8, 112.2, 111.7. HRMS-ESI (m/z) $[M+H]^+$calcd. For $C_{22}H_{12}N_3O$: 334.0975; Found: 334.0983.

1-(2-fluorophenyl)benzofuro[3,2-a]imidazo[5,1,2-cd]indolizine (3f)



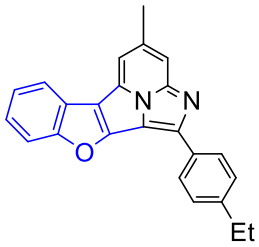
(Eluent: 10% EtOAc/hexane); 65% yield (42.3 mg); yellow solid, Mp:255-257 °C ; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.68 – 8.62 (m, 1H), 8.08 (d, J = 5.5 Hz, 1H), 8.03 (d, J = 3.3 Hz, 2H), 7.98 (d, J = 7.5 Hz, 1H), 7.78 (d, J = 7.5 Hz, 1H), 7.50 (q, J = 7.2, 6.1 Hz, 1H), 7.45 (dd, J = 9.8, 6.4 Hz, 2H), 7.39 (q, J = 9.9, 8.8 Hz, 2H).; ^{13}C NMR (150 MHz, $CDCl_3$) δ 161.8 (d, $J_{C,F}$ = 252 Hz), 159.6, 152.0, 140.4 (d, $J_{C,F}$ = 25.5 Hz), 131.4, 131.3, 130.1, 127.2, 125.1, 124.8, 124.7, 124.6, 124.0, 122.7, 121.4, 121.4, 121.4, 119.9, 116.3 (d, $J_{C,F}$ = 21 Hz), 115.7, 112.9, 111.3, 110.6; ^{19}F NMR (564 MHz, $CDCl_3$) δ -113.28 (s, 1F); HRMS-ESI (m/z) $[M+H]^+$calcd. For $C_{21}H_{12}FN_2O$: 327.0929; Found: 327.0950.

4-methyl-1-phenylbenzofuro[3,2-a]imidazo[5,1,2-cd]indolizine (3g) :



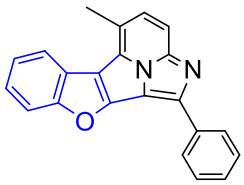
(Eluent: 15% EtOAc/hexane); 69% yield (44.4 mg); yellow solid, Mp:215-217 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.55 (dd, J = 7.8, 1.4 Hz, 2H), 7.97 (dd, J = 7.3, 1.9 Hz, 1H), 7.84 (d, J = 16.3 Hz, 2H), 7.81 – 7.76 (m, 1H), 7.64 (t, J = 7.7 Hz, 2H), 7.54 – 7.49 (m, 1H), 7.49 – 7.41 (m, 2H), 2.87 (s, 3H).^{13}C NMR (150 MHz, $CDCl_3$) δ 159.7, 151.3, 147.5, 141.2, 138.7, 133.1, 129.8, 129.2, 128.0, 124.4, 124.1, 123.2, 119.9, 114.6, 112.8, 112.2, 111.4, 110.4, 23.0. HRMS-ESI (m/z) $[M+Na]^+$calcd. For $C_{22}H_{14}N_2NaO$: 345.0999; Found: 345.0978.

1-(4-ethylphenyl)-4-methylbenzofuro[3,2-a]imidazo[5,1,2-cd]indolizine (3h) :



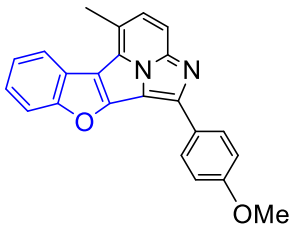
(Eluent: 10% EtOAc/hexane); 73% yield (51.1 mg); yellow solid, Mp:210-212 ℃ ; ^{1}H NMR (600 MHz, CDCl3)δ 8.46 (d, J = 7.9 Hz, 2H), 7.96 (d, J = 7.6 Hz, 1H), 7.83 (s, 1H), 7.80 (s, 1H), 7.77 (d, J = 7.4 Hz, 1H), 7.47 (d, J = 7.8 Hz, 2H), 7.46 – 7.39 (m, 2H), 2.85 (s, 3H), 2.79 (q, J = 7.4 Hz, 2H), 1.35 (t, J = 7.5 Hz, 3H).^{13}C NMR (150 MHz, $CDCl_3$) δ 159.6, 151.2, 147.8, 146.4, 141.2, 138.5, 130.5, 128.7, 128.0, 124.2, 124.2, 124.0, 123.1, 119.8, 114.3, 112.7, 111.9, 111.1, 110.1, 28.9, 23.0, 15.4. Anal. calcd for $C_{24}H_{18}N_2O$: C, 82.26; H, 5.18; N, 7.99; found: C, 95.88; H, 14.29; N, 4.97.

5-methyl-1-phenylbenzofuro[3,2-a]imidazo[5,1,2-cd]indolizine (3i)



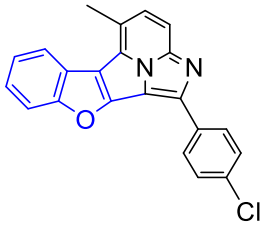
(Eluent: 15% EtOAc/hexane); 67% yield (43.1 mg); yellow solid, Mp:210-212 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.55 (d, J = 7.2 Hz, 2H), 7.97 (d, J = 7.8 Hz, 1H), 7.86 (s, 1H), 7.83 (s, 1H), 7.78 (d, J = 7.8 Hz, 1H), 7.64 (t, J = 7.5 Hz, 2H), 7.51 (t, J = 7.4 Hz, 1H), 7.48 – 7.41 (m, 2H), 2.87 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 159.7, 151.4, 147.6, 141.2, 138.6, 133.1, 129.8, 129.2, 128.0, 124.4, 124.1, 123.2, 119.9, 114.6, 112.8, 112.2, 111.4, 110.4, 23.0. HRMS-ESI (m/z) $[M+Na]^+$calcd. For $C_{22}H_{14}N_2ONa$: 345.0989; Found: 345.0999.

1-(4-methoxyphenyl)-5-methylbenzofuro[3,2-a]imidazo[5,1,2-cd]indolizine (3j)



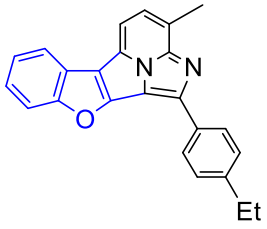
(Eluent:30% EtOAc/hexane); 69% yield (48.5 mg); yellow solid, Mp: 270-272 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.41 (d, J = 8.5 Hz, 2H), 7.93 – 7.88 (m, 1H), 7.80 (d, J = 8.0 Hz, 1H), 7.71 – 7.64 (m, 2H), 7.41 – 7.34 (m, 2H), 7.13 (d, J = 8.1 Hz, 2H), 3.94 (s, 3H), 3.00 (s, 3H).^{13}C NMR (150 MHz, $CDCl_3$) δ 161.0, 159.6, 149.9, 147.1, 139.9, 129.3, 128.8, 125.9, 124.2, 124.0, 123.8, 123.0, 121.3, 120.0, 114.7, 114.5, 112.6, 110.3, 109.8, 55.4, 18.6. HRMS-ESI (m/z) $[M+H]^+$calcd. For $C_{23}H_{17}N_2O_2$: 353.1285; Found: 353.1282.

1-(4-chlorophenyl)-5-methylbenzofuro[3,2-a]imidazo[5,1,2-cd]indolizine (3k)



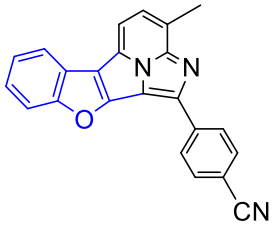
(Eluent: 10% EtOAc/hexane); 61% yield (43.4 mg); yellow solid, Mp: 200-202 ℃, ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.39 (d, J = 8.0 Hz, 2H), 8.00 – 7.93 (m, 1H), 7.87 (d, J = 8.2 Hz, 1H), 7.74 (dd, J = 8.7, 4.0 Hz, 2H), 7.57 (d, J = 8.0 Hz, 2H), 7.47 – 7.41 (m, 2H), 3.06 (s, 3H).^{13}C NMR (150 MHz, $CDCl_3$) δ 159.7, 149.9, 145.5, 139.7, 135.5, 131.7, 129.3, 128.9, 124.6, 124.4, 124.1, 122.9, 122.1, 120.1, 115.3, 112.8, 111.2, 110.4, 18.7. HRMS-ESI (m/z) $[M+H]^+$calcd. For $C_{22}H_{14}ClN_2O$: 357.0790; Found: 357.0795.

1-(4-ethylphenyl)-3-methylbenzofuro[3,2-a]imidazo[5,1,2-cd]indolizine (3l) :



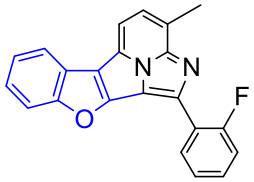
(Eluent: 10% EtOAc/hexane); 67% yield (46.9 mg); yellow solid, Mp: 230-237 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.50 (d, J = 7.9 Hz, 2H), 7.98 (d, J = 6.8 Hz, 1H), 7.91 (d, J = 7.6 Hz, 1H), 7.78 (t, J = 6.9 Hz, 2H), 7.53 – 7.40 (m, 4H), 3.03 (s, 3H), 2.79 (d, J = 7.6 Hz, 2H), 1.35 (t, J = 7.5 Hz, 3H).^{13}C NMR (150 MHz, $CDCl_3$) δ 159.7, 146.8, 146.2, 141.0, 130.7, 128.7, 128.0, 127.6, 124.3, 123.9, 123.3, 123.1, 122.2, 119.9, 114.9, 112.7, 110.7, 28.9, 16.2, 15.4. Anal. calcd for $C_{14}H_{18}N_2O$: C, 82.26; H, 5.18; N, 7.99; found: C, 63.40; H, 7.547; N, 7.73.

4-(3-methylbenzofuro[3,2-a]imidazo[5,1,2-cd]indolizin-1-yl)benzonitrile (3m) :



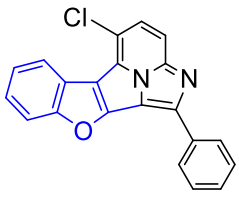
(Eluent: 10% EtOAc/hexane); 66% yield (45.8 mg); yellow solid, Mp: 210-212 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.58 (d, J = 8.4 Hz, 2H), 8.00 – 7.96 (m, 1H), 7.93 (d, J = 7.5 Hz, 1H), 7.86 (d, J = 8.1 Hz, 2H), 7.82 – 7.75 (m, 2H), 7.47 (dt, J = 6.2, 2.8 Hz, 2H), 3.00 (s, 3H).^{13}C NMR (150 MHz, $CDCl_3$) δ 159.7, 150.1, 143.3, 140.8, 137.5, 132.8, 128.2, 128.1, 124.9, 124.2, 123.8, 123.5, 122.9, 120.1, 118.9, 116.0, 112.8, 112.4, 111.9, 111.8, 16.2. HRMS-ESI (m/z) $[M+H+Na]^+$calcd. For $C_{23}H_{14}N_3NaO$: 371.1030; Found: 371.1046.

1-(2-fluorophenyl)-3-methylbenzofuro[3,2-a]imidazo[5,1,2-cd]indolizine (3n) :



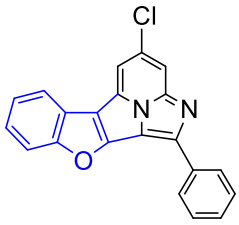
(Eluent: 20% EtOAc/hexane); 63% yield (42.8 mg); yellow solid, Mp: 218-220 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.69 – 8.64 (m, 1H), 7.98 – 7.92 (m, 1H), 7.88 (d, J = 7.9 Hz, 1H), 7.76 (d, J = 7.6 Hz, 2H), 7.51 – 7.45 (m, 1H), 7.45 – 7.33 (m, 4H), 3.02 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 161.6 (d, $J_{C,F}$ = 252 Hz), 159.5, 151.5, 140.1, 138.9, 131.0 (d, $J_{C,F}$ = 9.0 Hz), 130.2, 127.6, 124.7, 124.4, 123.8, 123.3, 122.9, 122.6, 121.7, 121.6, 119.8, 116.0 (d, $J_{C,F}$ = 22.5 Hz), 115.6, 112.8, 110.7, 16.2; ^{19}F NMR (564 MHz, $CDCl_3$) δ -112.56 (s, 1F); HRMS-ESI (m/z) $[M+H]^+$calcd. For $C_{22}H_{14}FN_2O$: 341.1085. Found: 341.1085.

5-chloro-1-phenylbenzofuro[3,2-a]imidazo[5,1,2-cd]indolizine (3o):



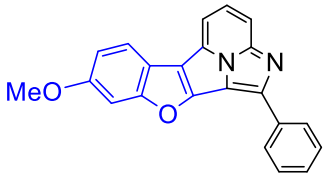
(Eluent: 15% EtOAc/hexane); 77% yield (52.6 mg); yellow solid; Mp: 255-257 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.52 – 8.48 (m, 2H), 8.00 (s, 2H), 7.95 – 7.90 (m, 1H), 7.79 – 7.74 (m, 1H), 7.67 – 7.61 (m, 2H), 7.56 – 7.51 (m, 1H), 7.49 – 7.42 (m, 2H).; ^{13}C NMR (150 MHz, $CDCl_3$) δ 159.8, 151.7, 149.2, 140.8, 133.6, 132.4, 130.4, 129.2, 128.1, 125.0, 124.4, 124.3, 122.6, 120.0, 115.1, 112.9, 111.6, 111.2, 110.8. Anal. calcd for $C_{21}H_{11}ClN_2O$: C, 73.58; H, 3.23; N, 8.17; found: C, 62.72; H, 9.362; N, 8.01.

4-chloro-1-phenylbenzofuro[3,2-a]imidazo[5,1,2-cd]indolizine (3p) :



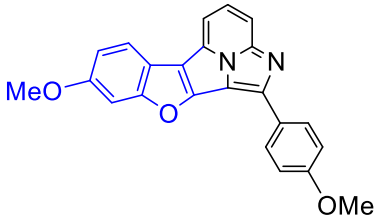
(Eluent: 10% EtOAc/hexane); 79% yield (54.0 mg); yellow solid, Mp: 270-272 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.48 (d, J = 7.1 Hz, 2H), 8.14 – 8.09 (m, 1H), 7.88 (s, 2H), 7.72 (dd, J = 6.1, 3.0 Hz, 1H), 7.63 (t, J = 8.0 Hz, 2H), 7.55 – 7.50 (m, 1H), 7.42 (h, J = 3.4 Hz, 2H).; ^{13}C NMR (150 MHz, $CDCl_3$) δ 159.8, 150.4, 148.8, 139.8, 132.5, 130.3, 129.2, 128.0, 127.6, 125.1, 124.2, 122.9, 122.3, 121.1, 118.0, 115.0, 112.6, 111.2. Anal. calcd for $C_{21}H_{11}ClN_2O$: C, 73.58; H, 3.23; N, 8.17; found: C, 61.02; H, 9.340; N, 7.56.

8-methoxy-1-phenylbenzofuro[3,2-a]imidazo[5,1,2-cd]indolizine (3q) :



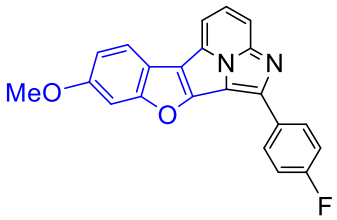
(Eluent: 30% EtOAc/hexane); 72% yield (48.6 mg); yellow solid; Mp: 235-237 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.52 (d, J = 7.8 Hz, 2H), 7.99 (d, J = 7.9 Hz, 1H), 7.97 – 7.89 (m, 2H), 7.76 (d, J = 8.1 Hz, 1H), 7.62 (t, J = 7.4 Hz, 2H), 7.50 (t, J = 7.5 Hz, 1H), 7.28 (s, 1H), 7.01 (d, J = 8.3 Hz, 1H), 3.92 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 160.8, 157.9, 150.6, 147.2, 141.0, 133.1, 129.8, 129.1, 127.9, 126.7, 124.7, 119.9, 116.2, 115.2, 112.1, 111.0, 110.8, 110.7, 98.0, 77.2, 77.0, 76.8, 55.8. HRMS-ESI (m/z) $[M+H]^+$ calcd. For $C_{22}H_{15}N_2O_2$: 339.1129; Found: 339.1123.

8-methoxy-1-(4-methoxyphenyl)benzofuro[3,2-a]imidazo[5,1,2-cd]indolizine (3r) :



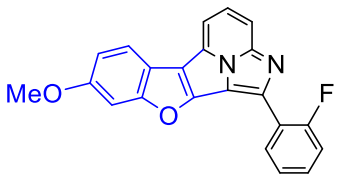
(Eluent: 40% EtOAc/hexane); 73% yield (53.7 mg); yellow liquid, Mp: 230-232 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.52 – 8.47 (m, 2H), 7.97 (d, J = 3.3 Hz, 3H), 7.84 (d, J = 8.3 Hz, 1H), 7.34 (d, J = 2.3 Hz, 1H), 7.16 (d, J = 8.6 Hz, 2H), 7.07 (dd, J = 8.4, 2.2 Hz, 1H), 3.95 (d, J = 2.3 Hz, 6H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 161.1, 160.8, 157.9, 150.6, 147.4, 141.2, 129.5, 126.6, 125.8, 124.5, 120.0, 116.4, 114.9, 114.6, 112.0, 110.4, 110.3, 110.2, 98.1, 55.9, 55.4. HRMS-ESI (m/z) $[M+H]^+$calcd. For $C_{23}H_{17}N_2O_3$: 369.1234; Found: 369.1239.

1-(4-fluorophenyl)-8-methoxybenzofuro[3,2-a]imidazo[5,1,2-cd]indolizine (3s) :



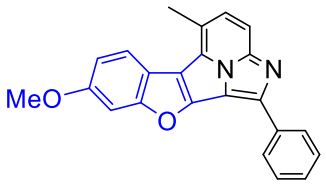
(Eluent: 20% EtOAc/hexane); 73% yield (51.9 mg); yellow solid, Mp: 234-237 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.48 – 8.43 (m, 2H), 7.98 – 7.87 (m, 3H), 7.75 (d, J = 8.2 Hz, 1H), 7.30 – 7.25 (m, 3H), 7.02 (dd, J = 8.2, 2.3 Hz, 1H), 3.93 (s, 3H).^{13}C NMR (150 MHz, $CDCl_3$) δ 164.6 (d, $J_{C,F}$ = 249 Hz), 160.7, 158.0, 150.3, 146.0, 141.0, 129.8 (d, $J_{C,F}$ = 9.0 Hz), 129.3, 126.8, 124.6, 120.0, 116.3 (d, $J_{C,F}$ = 22.5 Hz), 115.2, 112.1, 110.9, 110.7, 110.4, 98.0, 55.8; ^{19}F NMR (564 MHz, $CDCl_3$) δ -110.47 (s, 1F); HRMS-ESI (m/z) $[M+H]^+$calcd. For $C_{22}H_{14}FN_2O_2$: 357.1034; Found: 357.1025.

. **1-(2-fluorophenyl)-8-methoxybenzofuro[3,2-a]imidazo[5,1,2-cd]indolizine (3t) :**



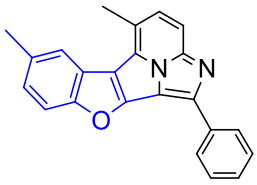
(Eluent: 30% EtOAc/hexane); 64% yield (45.5 mg); yellow solid, Mp: 225-227 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.62 (t, J = 7.6 Hz, 1H), 8.02 (d, J = 8.0 Hz, 1H), 7.99 – 7.91 (m, 2H), 7.77 (d, J = 8.4 Hz, 1H), 7.52 – 7.44 (m, 1H), 7.40 – 7.33 (m, 2H), 7.29 (s, 1H), 7.04 – 6.99 (m, 1H), 3.91 (s, 3H).^{13}C NMR (150 MHz, $CDCl_3$) δ 161.6 (d, $J_{C,F}$ = 250 Hz), 159.9, 158.0, 151.4, 140.2, 139.7, 131.2, 131.1, 130.0, 126.8, 124.8 (d, $J_{C,F}$ = 21.0 Hz), 121.5, 121.4, 119.9, 116.1, 115.9 (d, $J_{C,F}$ = 7.5 Hz), 115.7, 112.2, 111.1, 110.5, 97.9, 55.8; ^{19}F NMR (564 MHz, $CDCl_3$) δ -113.43 (s, 1F); HRMS-ESI (m/z) $[M+Na]^+$calcd. For $C_{22}H_{13}FN_2O_2Na$: 379.0854; Found: 379.0845.

8-methoxy-5-methyl-1-phenylbenzofuro[3,2-a]imidazo[5,1,2-cd]indolizine (3u)



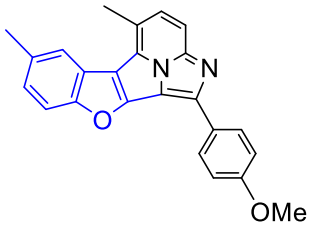
(Eluent: 30% EtOAc/hexane); 72% yield (50.6 mg); yellow solid, Mp:257-258 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.54 – 8.49 (m, 2H), 7.81 – 7.76 (m, 3H), 7.62 (t, J = 7.7 Hz, 2H), 7.49 (t, J = 7.2 Hz, 1H), 7.32 (d, J = 2.3 Hz, 1H), 7.05 (dd, J = 8.1, 2.3 Hz, 1H), 3.94 (s, 3H), 2.84 (s, 3H).^{13}C NMR (150 MHz, $CDCl_3$) δ 160.7, 157.9, 150.9, 147.0, 141.0, 138.3, 133.2, 129.7, 129.1, 127.9, 124.2, 119.9, 116.4, 114.6, 112.2, 112.1, 111.3, 110.5, 98.1, 55.9, 23.0. HRMS-ESI (m/z) [M+Na]+calcd. For $C_{23}H_{16}N_2NaO_2$: 375.1104; Found: 375.1098.

5,7-dimethyl-1-phenylbenzofuro[3,2-a]imidazo[5,1,2-cd]indolizine (3v):



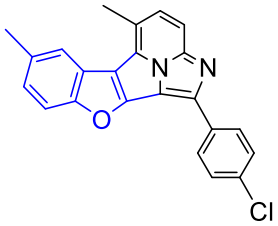
(Eluent: 20% EtOAc/hexane); 70% yield (47.0 mg); yellow solid; Mp:227-228 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.49 (d, J = 7.4 Hz, 2H), 7.76 (d, J = 12.3 Hz, 2H), 7.68 (s, 1H), 7.64 – 7.57 (m, 3H), 7.50 (t, J = 7.0 Hz, 1H), 7.19 (d, J = 8.3 Hz, 1H), 2.82 (s, 3H), 2.54 (s, 3H).^{13}C NMR (150 MHz, $CDCl_3$) δ 158.0, 151.4, 147.2, 141.0, 138.5, 133.7, 133.1, 129.7, 129.1, 127.9, 125.4, 124.3, 123.0, 119.9, 114.4, 112.1, 112.0, 111.2, 110.4, 23.0, 21.5. Anal. calcd for $C_{23}H_{16}N_2O$: C, 82.12; H, 4.79; N, 8.33; found: C, 64.36; H, 4.83 N, 7.83.

1-(4-methoxyphenyl)-5,7-dimethylbenzofuro[3,2-a]imidazo[5,1,2-cd]indolizine (3w):



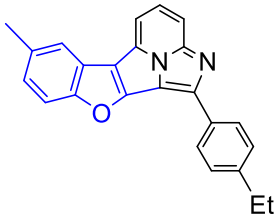
(Eluent: 25% EtOAc/hexane); 69% yield (50.5 mg); yellow solid, Mp:207-209 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.49 (d, J = 8.0 Hz, 2H), 7.87 (d, J = 8.1 Hz, 1H), 7.80 – 7.73 (m, 2H), 7.64 (d, J = 8.1 Hz, 1H), 7.23 (d, J = 8.7 Hz, 1H), 7.16 (d, J = 8.4 Hz, 2H), 3.94 (s, 3H), 3.11 (s, 3H), 2.57 (s, 3H).^{13}C NMR (150 MHz, $CDCl_3$) δ 161.0, 158.2, 158.2, 150.4, 150.4, 147.1, 140.0, 133.6, 129.4, 128.9, 125.9, 125.4, 124.3, 123.1, 121.4, 120.2, 114.6, 112.2, 110.3, 55.4, 21.6, 18.8. Anal. calcd for $C_{24}H_{18}N_2O_2$: C, 78.67; H, 4.95; N, 7.65; found: C, 73.84; H, 6.43; N, 14.23.

1-(4-chlorophenyl)-5,7-dimethylbenzofuro[3,2-a]imidazo[5,1,2-cd]indolizine (3x)



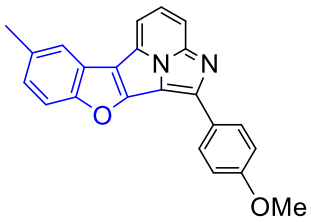
(Eluent: 15% EtOAc/hexane); 70% yield (51.8 mg); yellow solid, Mp: 215-217 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.34 (d, J = 8.0 Hz, 2H), 7.81 (d, J = 7.9 Hz, 1H), 7.70 – 7.62 (m, 2H), 7.54 (d, J = 7.9 Hz, 3H), 7.18 (d, J = 8.3 Hz, 1H), 3.00 (s, 3H), 2.53 (s, 3H).^{13}C NMR (150 MHz, $CDCl_3$) δ 158.0, 150.0, 145.2, 139.6, 135.4, 133.6, 131.7, 129.3, 129.2, 128.9, 125.6, 124.3, 122.7, 121.9, 120.1, 115.1, 112.2, 111.0, 110.4, 21.5, 18.7. HRMS-ESI (m/z) $[M+H]^+$calcd. For $C_{23}H_{16}ClN_2O$: 371.0946; Found: 371.0975.

1-(4-ethylphenyl)-7-methylbenzofuro[3,2-a]imidazo[5,1,2-cd]indolizine (3y) :



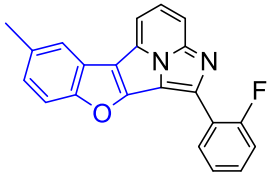
(Eluent: 15% EtOAc/hexane); 79 % yield (55.3 mg); yellow solid, Mp: 215-217 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.48 (d, J = 7.3 Hz, 2H), 8.04 – 7.96 (m, 3H), 7.78 (s, 1H), 7.64 (d, J = 9.0 Hz, 1H), 7.48 (d, J = 7.9 Hz, 2H), 7.23 (d, J = 8.6 Hz, 1H), 2.79 (d, J = 7.9 Hz, 2H), 2.57 (s, 3H), 1.35 (d, J = 16.0 Hz, 3H).; ^{13}C NMR (150 MHz, $CDCl_3$) δ 158.1, 151.3, 147.9, 146.6, 141.2, 133.8, 130.5, 128.7, 128.1, 126.9, 125.5, 124.9, 123.0, 120.1, 115.0, 112.2, 110.7, 110.5, 28.9, 21.5, 15.4. Anal. calcd for $C_{24}H_{18}N_2O$: C, 82.26; H, 5.18; N, 7.99; found: C, 62.93; H, 9.036; N, 7.85.

1-(4-methoxyphenyl)-7-methylbenzofuro[3,2-a]imidazo[5,1,2-cd]indolizine (3z) :



(Eluent: 30% EtOAc/hexane); 67 % yield (47.1 mg); yellow solid, Mp: 218-220 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.48 (d, J = 8.3 Hz, 2H), 7.98 – 7.91 (m, 3H), 7.73 (s, 1H), 7.61 (d, J = 8.0 Hz, 1H), 7.20 (d, J = 8.5 Hz, 1H), 7.15 (d, J = 8.0 Hz, 2H), 3.94 (s, 3H), 2.55 (s, 3H).; ^{13}C NMR (150 MHz, $CDCl_3$) δ 161.2, 158.1, 151.1, 147.8, 141.3, 133.7, 129.6, 126.7, 125.7, 125.4, 124.7, 123.1, 120.0, 114.6, 112.1, 110.3, 110.2, 110.1, 55.4, 21.5. HRMS-ESI (m/z) $[M+H]^+$calcd. For $C_{23}H_{17}N_2O_2$: 353.1285; Found: 353.1291.

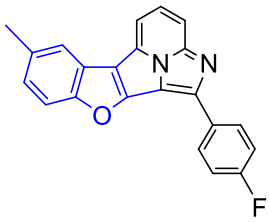
1-(2-fluorophenyl)-7-methylbenzofuro[3,2-a]imidazo[5,1,2-cd]indolizine (3aa) :



(Eluent: 15% EtOAc/hexane); 60% yield (40.8 mg);yellow solid, Mp: 218-220 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.61 (t, J = 7.4 Hz, 1H), 8.00 (d, J = 8.1 Hz, 1H), 7.96 (d, J = 7.9 Hz, 1H), 7.91 (d, J = 7.7 Hz, 1H), 7.67 (s, 1H), 7.57 (d, J = 8.1 Hz, 1H), 7.48 (q, J = 7.0 Hz, 1H), 7.40 – 7.32 (m, 2H), 7.17 (d, J = 8.2 Hz, 1H), 2.52 (s, 3H).; ^{13}C NMR (150 MHz, $CDCl_3$) δ 161.7 (d, $J_{C,F}$ = 252.0 Hz), 160.0, 158.0, 152.1, 140.3 (d, $J_{C,F}$ = 43.5 Hz), 133.5, 131.3 (d, $J_{C,F}$ = 7.5 Hz), 130.1, 127.0, 125.6, 125.1, 124.7, 124.7, 122.6, 121.5, 121.4, 119.9, 116.1 (d, $J_{C,F}$ = 21.0 Hz), 115.6, 112.7, 112.6, 112.2, 111.1, 110.3,

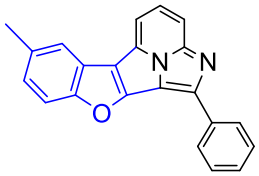
21.5; ^{19}F NMR (564 MHz, $CDCl_3$) δ -113.78 (s, 1F); HRMS-ESI (m/z) $[M+H]^+$calcd. For $C_{22}H_{14}FN_2O$: 341.1085; Found: 341.1090.

1-(4-fluorophenyl)-7-methylbenzofuro[3,2-a]imidazo[5,1,2-cd]indolizine (3ab)



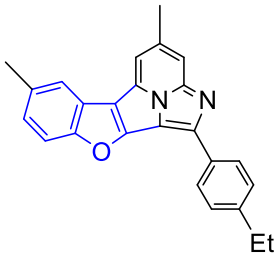
(Eluent: 10% EtOAc/hexane); 68% yield (46.2 mg); yellow solid, Mp: 210-212 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.53 (dd, J = 8.6, 5.2 Hz, 2H), 8.00 (td, J = 5.6, 2.4 Hz, 3H), 7.78 (s, 1H), 7.64 (d, J = 9.1 Hz, 1H), 7.35 – 7.30 (m, 2H), 7.24 (d, J = 8.9 Hz, 2H), 2.57 (s, 3H).; ^{13}C NMR (150 MHz, $CDCl_3$) δ 164.7 (d, $J_{C,F}$ = 249.0 Hz), 163.0, 158.2, 151.1, 146.4, 141.1, 133.9, 129.9 (d, $J_{C,F}$ = 9.0 Hz), 129.3, 127.1, 125.7, 125.0, 122.9, 120.2, 116.4 (d, $J_{C,F}$ = 22.5 Hz), 115.2, 112.2, 111.0, 110.7, 110.5, 21.5; ^{19}F NMR (564 MHz, $CDCl_3$) δ -110.30 (s, 1F); HRMS-ESI (m/z) $[M+H]^+$calcd. For $C_{22}H_{14}FN_2O$: 341.1085; Found: 341.1086.

7-methyl-1-phenylbenzofuro[3,2-a]imidazo[5,1,2-cd]indolizine (3ac) :



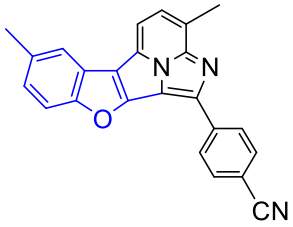
(Eluent: 10% EtOAc/hexane); 68% yield (43.7 mg); yellow solid, Mp: 210-212 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.69 – 8.64 (m, 1H), 7.98 – 7.92 (m, 1H), 7.88 (d, J = 7.9 Hz, 1H), 7.76 (d, J = 7.6 Hz, 2H), 7.51 – 7.45 (m, 1H), 7.45 – 7.33 (m, 4H), 3.02 (s, 3H).^{13}C NMR (150 MHz, $CDCl_3$) δ 161.6, 159.9, 159.5, 151.5, 140.1, 138.9, 131.0, 131.0, 130.2, 127.6, 124.7, 124.4, 123.8, 123.3, 122.9, 122.6, 121.7, 121.6, 119.8, 116.0, 115.9, 115.6, 112.8, 110.7, 16.2. HRMS-ESI (m/z) $[M+H]^+$calcd. For $C_{22}H_{15}N_2O$:323.1179; Found: 323.1177.

1-(4-ethylphenyl)-4,7-dimethylbenzofuro[3,2-a]imidazo[5,1,2-cd]indolizine (3ad) :



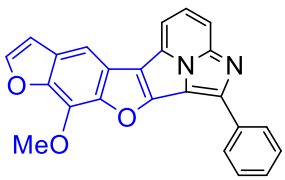
(Eluent: 10% EtOAc/hexane); 73% yield (53.1 mg); yellow solid, Mp: 205-207 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.45 (d, J = 7.4 Hz, 2H), 7.81 (d, J = 12.7 Hz, 2H), 7.76 (s, 1H), 7.64 (d, J = 8.0 Hz, 1H), 7.47 (d, J = 7.7 Hz, 2H), 7.22 (d, J = 8.6 Hz, 1H), 2.85 (s, 3H), 2.78 (q, J = 7.5 Hz, 2H), 2.57 (s, 3H), 1.34 (d, J = 15.9 Hz, 4H).; ^{13}C NMR (150 MHz, $CDCl_3$) δ 158.1, 151.6, 147.6, 146.4, 141.2, 138.5, 133.7, 130.6, 128.7, 128.0, 125.3, 124.4, 123.2, 120.0, 114.3, 112.2, 111.9, 111.0, 28.9, 23.0, 21.5, 15.4. HRMS-ESI (m/z) $[M+H]^+$calcd. For $C_{25}H_{21}N_2O$:365.1649; Found: 365.1648.

4-(3,7-dimethylbenzofuro[3,2-a]imidazo[5,1,2-cd]indolizin-1-yl)benzonitrile (3ae) :



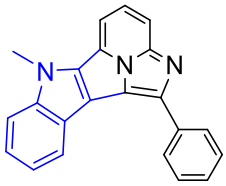
(Eluent: 25% (EtOAc/hexane); 68% yield (49.0 mg) yellow solid, Mp: 230-232 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.57 (d, J = 8.5 Hz, 2H), 7.89 (d, J = 7.5 Hz, 1H), 7.85 (d, J = 8.1 Hz, 2H), 7.77 (d, J = 7.5 Hz, 1H), 7.75 (d, J = 1.7 Hz, 1H), 7.62 (d, J = 8.3 Hz, 1H), 7.26 – 7.23 (m, 1H), 2.99 (s, 3H), 2.57 (s, 3H).; ^{13}C NMR (150 MHz, $CDCl_3$) δ 158.1, 150.3, 143.2, 140.7, 137.6, 133.9, 132.8, 128.1, 128.1, 125.9, 123.7, 123.6, 122.8, 120.2, 119.0, 115.9, 112.3, 112.3, 112.0, 111.6, 21.5, 16.2. Anal. calcd for $C_{24}H_{15}N_3O$: C, 79.76; H, 4.18; N, 11.63; found: C, 57.78; H, 9.463; N, 8.83.

10-methoxy-1-phenylfuro[3',2':5,6]benzofuro[3,2-a]imidazo[5,1,2-cd]indolizine (3af) :



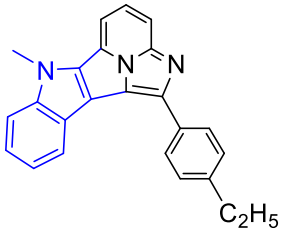
(Eluent: 15% (EtOAc/hexane); 60% yield (45.3 mg); yellow solid, Mp: 290-292 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.58 (d, J = 7.5 Hz, 2H), 8.03 (dt, J = 9.7, 7.8 Hz, 3H), 7.74 (d, J = 2.7 Hz, 2H), 7.65 (t, J = 7.5 Hz, 2H), 7.53 (d, J = 7.3 Hz, 1H), 6.93 (d, J = 2.2 Hz, 1H), 4.57 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 151.5, 148.1, 147.7, 145.9, 143.5, 141.2, 133.0, 131.8, 130.0, 129.2, 128.1, 127.1, 127.0, 125.0, 121.5, 115.2, 111.1, 110.8, 110.7, 106.9, 103.5, 61.2. HRMS-ESI (m/z) $[M+H]^+$calcd. For $C_{24}H_{15}N_2O_3$:379.1078; Found: 379.1078.

6-methyl-1-phenyl-6H-imidazo[5',1',2':3,4,5]indolizino[1,2-b]indole (5a) :



(Eluent: 30% (EtOAc/hexane); 75% yield (48.1 mg); yellow solid, Mp: 270-272 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.58 – 8.49 (m, 2H), 8.31 (d, J = 8.0 Hz, 1H), 8.06 (d, J = 7.9 Hz, 1H), 7.94 (dd, J = 18.3, 7.5 Hz, 2H), 7.69 (t, J = 7.6 Hz, 2H), 7.53 (dt, J = 24.2, 8.3 Hz, 3H), 7.42 – 7.33 (m, 1H), 4.21 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 145.6, 142.7, 139.7, 136.1, 135.0, 129.0, 128.9, 128.5, 124.9, 124.3, 121.5, 121.3, 120.2, 119.6, 117.0, 114.5, 111.6, 110.1, 108.2, 31.9. HRMS-ESI (m/z) $[M+H]^+$calcd. For $C_{22}H_{16}N_3$:322.1325; Found: 322.1339.

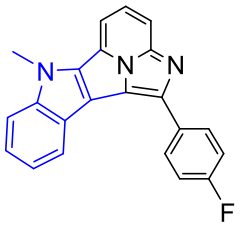
1-(4-ethylphenyl)-6-methyl-6H-imidazo[5',1',2':3,4,5]indolizino[1,2-b]indole (5b) :



(Eluent: 30% (EtOAc/hexane); 69% yield (48.1 mg); yellow solid, Mp: 200-202 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.46 (d, J = 8.0 Hz, 2H), 8.35 (d, J = 8.0 Hz, 1H), 8.05 (d, J = 8.1 Hz, 1H), 7.97 (d, J = 7.4 Hz, 1H), 7.58 (d, J = 8.4 Hz, 1H), 7.52 (dd, J = 14.1, 7.7 Hz, 3H), 7.38 (t, J = 7.5 Hz, 1H), 4.24 (s, 3H), 2.83 (q, J = 7.7 Hz, 2H), 1.38 (t, J = 7.6 Hz, 3H).^{13}C NMR (150 MHz, $CDCl_3$) δ 145.7, 145.3, 142.6, 139.6, 135.9, 132.3, 128.5, 128.4, 124.6, 124.1, 121.4, 120.9, 120.0, 119.5, 116.6, 114.4, 111.2,

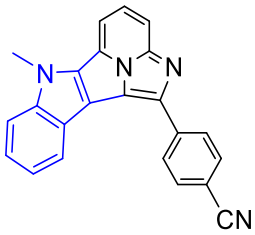
110.0, 107.9, 31.7, 28.9, 15.5. Anal. calcd for $C_{24}H_{19}N_3$: C, 82.49; H, 5.48; N, 12.03; found: C, 94.97; H, 8.786; N, 12.43.

1-(4-fluorophenyl)-6-methyl-6H-imidazo[5',1',2':3,4,5]indolizino[1,2-b]indole (5c) :



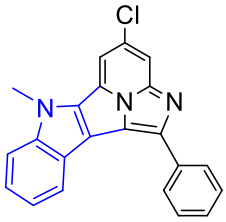
(Eluent: 30 % (EtOAc/hexane); 65% yield (44.0 mg); yellow solid, Mp: 240-242 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.49 – 8.43 (m, 2H), 8.20 (d, J = 8.0 Hz, 1H), 8.03 (d, J = 7.8 Hz, 1H), 7.95 – 7.87 (m, 2H), 7.55 (d, J = 8.2 Hz, 1H), 7.50 (t, J = 7.6 Hz, 1H), 7.40 – 7.33 (m, 3H), 4.18 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 164.2 (d, $J_{C,F}$ = 247.5 Hz), 162.6, 144.4, 142.7, 139.6, 136.1, 131.2, 130.2 (d, $J_{C,F}$ = 9.0 Hz), 125.0, 124.3, 121.2, 120.2, 119.5, 116.6, 116.3 (d, $J_{C,F}$ = 22.5 Hz), 114.3, 111.5, 110.2, 108.2, 31.9; ^{19}F NMR (564 MHz, $CDCl_3$) δ -112.23 (s, 1F); Anal. calcd for $C_{22}H_{14}FN_3$: C, 77.86; H, 4.16; N, 12.38; found: C, 61.61; H, 13.344; N, 7.91.

4-(6-methyl-6H-imidazo[5',1',2':3,4,5]indolizino[1,2-b]indol-1-yl)benzonitrile (5d) :



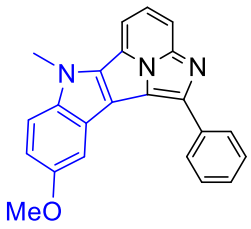
(Eluent: 30 % (EtOAc/hexane); 64% yield (44.2 mg); yellow solid, Mp: 230-232 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.59 – 8.55 (m, 2H), 8.17 (d, J = 7.9 Hz, 1H), 8.07 (d, J = 7.8 Hz, 1H), 8.00 – 7.90 (m, 4H), 7.58 (d, J = 8.2 Hz, 1H), 7.53 (t, J = 7.6 Hz, 1H), 7.40 (t, J = 7.4 Hz, 1H), 4.22 (s, 3H).^{13}C NMR (150 MHz, $CDCl_3$) δ 142.7, 142.3, 139.6, 139.3, 136.6, 132.7, 128.6, 125.9, 124.6, 121.8, 121.0, 120.6, 119.4, 119.0, 117.8, 112.5, 111.8, 110.4, 108.9, 32.0. Anal. calcd for $C_{23}H_{14}N_4$: C, 79.75; H, 4.07; N, 16.17; found: C, 87.72; H, 6.830; N, 13.33.

5-chloro-6-methyl-1-phenyl-6H-imidazo[5',1',2':3,4,5]indolizino[1,2-b]indole (5e) :



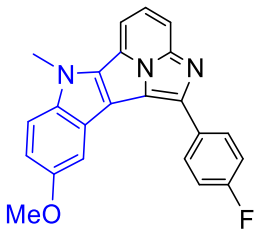
(Eluent: 30% (EtOAc/hexane); 63% yield (44.7 mg); yellow solid, Mp: 230-232 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.50 – 8.46 (m, 2H), 8.27 (d, J = 7.9 Hz, 1H), 8.01 (s, 1H), 7.93 (s, 1H), 7.69 (t, J = 7.7 Hz, 2H), 7.58 – 7.49 (m, 3H), 7.40 – 7.35 (m, 1H), 4.17 (s, 3H).^{13}C NMR (150 MHz, $CDCl_3$) δ 146.9, 142.9, 139.2, 135.4, 134.4, 131.2, 129.3, 129.1, 128.4, 124.9, 121.6, 120.6, 120.5, 119.4, 117.1, 115.6, 111.3, 110.2, 108.9, 31.9. Anal. calcd for $C_{22}H_{14}ClN_3$: C, 74.26; H, 3.97; N, 11.81; found: C, 63.32; H, 10.245; N, 7.94.

9-methoxy-6-methyl-1-phenyl-6H-imidazo[5',1',2':3,4,5]indolizino[1,2-b]indole (5f) :



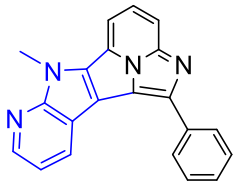
(Eluent: 30% (EtOAc/hexane); 75% yield (52.6 mg); yellow solid, Mp: 220-222 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.47 – 8.36 (m, 2H), 7.96 (d, J = 8.0 Hz, 1H), 7.81 (td, J = 7.7, 1.5 Hz, 1H), 7.77 (dd, J = 7.5, 2.1 Hz, 1H), 7.66 – 7.59 (m, 3H), 7.54 – 7.48 (m, 1H), 7.32 (dd, J = 9.0, 1.9 Hz, 1H), 7.08 (dt, J = 8.9, 1.7 Hz, 1H), 4.01 (d, J = 2.4 Hz, 3H), 3.93 (s, 3H).^{13}C NMR (150 MHz, $CDCl_3$) δ 154.1, 144.7, 139.5, 137.8, 136.3, 135.0, 128.8, 128.4, 124.7, 121.2, 119.5, 116.8, 114.3, 113.8, 111.4, 110.8, 107.7, 103.0, 55.6, 31.8. HRMS-ESI (m/z) $[M+H]^+$calcd. For $C_{23}H_{18}N_3O$:352.1445; Found: 352.1447.

1-(4-fluorophenyl)-9-methoxy-6-methyl-6H-imidazo[5',1',2':3,4,5]indolizino[1,2-b]indole (5g) :



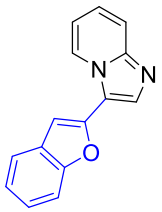
(Eluent: 30% (EtOAc/hexane); 63% yield (46.4 mg); yellow solid, Mp: 260-262 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.38 (dd, J = 8.5, 5.6 Hz, 2H), 7.96 (d, J = 8.0 Hz, 1H), 7.82 (dt, J = 15.2, 7.4 Hz, 2H), 7.53 (d, J = 2.5 Hz, 1H), 7.36 (d, J = 9.0 Hz, 1H), 7.31 (t, J = 8.5 Hz, 2H), 7.10 (dd, J = 8.9, 2.5 Hz, 1H), 4.05 (s, 3H), 3.93 (s, 3H).^{13}C NMR (150 MHz, $CDCl_3$) δ 164.2 (d, $J_{C,F}$ = 247.5 Hz), 154.2, 143.7, 139.6, 137.8, 136.5, 131.3, 130.1 (d, $J_{C,F}$ = 7.5 Hz), 124.9, 121.4, 119.5, 116.6, 116.0 (d, $J_{C,F}$ = 21.0 Hz), 114.3, 113.8, 111.4, 110.9, 107.9, 103.0, 55.7, 31.9; ^{19}F NMR (564 MHz, $CDCl_3$) δ -112.32 (s, 1F); HRMS-ESI (m/z) $[M+H]^+$calcd. For $C_{23}H_{17}FN_3O$:370.1351; Found: 370.1350.

6-methyl-1-phenyl-6H-imidazo[5,1,2-cd]pyrido[3',2':4,5]pyrrolo[2,3-a]indolizine (5h) :



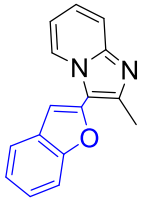
(Eluent: 40% (EtOAc/hexane); 60% yield (38.6 mg); yellow solid, Mp: 200-202 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.60 – 8.54 (m, 2H), 8.53 – 8.46 (m, 2H), 8.10 (d, J = 8.1 Hz, 1H), 8.04 (d, J = 7.5 Hz, 1H), 7.96 (t, J = 7.8 Hz, 1H), 7.69 (t, J = 7.7 Hz, 2H), 7.58 – 7.51 (m, 1H), 7.33 (dd, J = 7.8, 4.8 Hz, 1H), 4.33 (s, 3H).^{13}C NMR (150 MHz, $CDCl_3$) δ 152.0, 145.9, 144.9, 139.8, 135.0, 134.6, 129.2, 129.1, 128.2, 125.2, 121.1, 117.1, 116.1, 113.1, 112.2, 111.7, 109.1, 30.3. Anal. calcd for $C_{21}H_{14}N_4$: C, 78.24; H, 4.38; N, 17.38; found: C, 86.30; H, 8.368; N, 15.67.

3-(benzofuran-2-yl)imidazo[1,2-a]pyridine (9) :



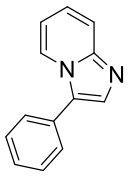
(Eluent: 30% (EtOAc/hexane); 70% yield (32.7 mg); yellow solid, Mp: 190-192 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.78 (d, J = 6.9 Hz, 1H), 8.08 (s, 1H), 7.73 (d, J = 9.0 Hz, 1H), 7.62 (dd, J = 7.5, 1.4 Hz, 1H), 7.57 (d, J = 8.1 Hz, 1H), 7.36 – 7.26 (m, 3H), 7.02 – 6.93 (m, 2H).^{13}C NMR (150 MHz, $CDCl_3$) δ 154.4, 146.8, 134.3, 128.5, 125.5, 125.1, 124.4, 123.4, 120.8, 118.3, 113.4, 111.1, 102.2.

3-(benzofuran-2-yl)-2-methylimidazo[1,2-a]pyridine (12) :



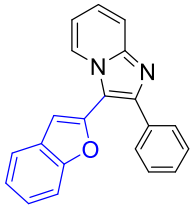
(Eluent: 30% (EtOAc/hexane); 45% yield (22.3 mg); brown solid, Mp: 200-202 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.74 (dd, J = 6.9, 1.2 Hz, 1H), 7.66 – 7.59 (m, 2H), 7.57 (dt, J = 8.2, 1.0 Hz, 1H), 7.35 – 7.28 (m, 2H), 7.26 – 7.23 (m, 1H), 6.92 – 6.86 (m, 2H), 2.67 (d, J = 1.0 Hz, 3H).

3-phenylimidazo[1,2-a]pyridine (18)[3] :



(Eluent: 15% (EtOAc/hexane); white solid, Mp 98-100 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.30 (d, J = 6.9 Hz, 1H), 7.71 – 7.63 (m, 2H), 7.57 – 7.45 (m, 4H), 7.39 (t, J = 7.2 Hz, 1H), 7.16 (dd, J = 9.1, 6.6 Hz, 1H), 6.77 (t, J = 6.8 Hz, 1H).^{13}C NMR (150 MHz, $CDCl_3$) δ145.9, 132.2, 129.0, 128.0, 127.9, 127.8, 125.5, 124.1, 123.1, 118.0, 112.3.

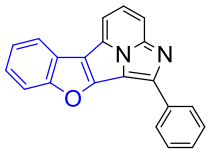
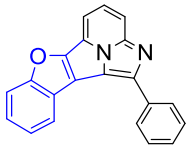
3-(benzofuran-2-yl)-2-phenylimidazo[1,2-a]pyridine (20) :



(Eluent: 15% (EtOAc/hexane); yellow solid, Mp: 206-208 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.49 (d, J = 6.9 Hz, 1H), 7.81 (d, J = 7.2 Hz, 2H), 7.72 (d, J = 8.8 Hz, 1H), 7.61 (d, J = 7.7 Hz, 1H), 7.57 (d, J = 8.2 Hz, 1H), 7.37 (dt, J = 12.9, 7.0 Hz, 4H), 7.31 (d, J = 8.9 Hz, 2H), 6.92 – 6.86 (m, 2H).^{13}C NMR (150 MHz, $CDCl_3$) δ 155.0, 146.4, 145.9, 133.9, 128.6, 128.6, 128.4, 125.9, 125.3, 124.9, 123.4, 121.3, 117.8, 113.2, 112.0, 111.5, 107.6. HRMS-ESI (m/z) $[M+H]^{+}$calcd. For $C_{21}H_{14}N_2ONa$:333.0999; Found: 333.0989.

1-phenylbenzofuro[3,2-a]imidazo[5,1,2-cd]indolizine and

1-phenylbenzofuro[2,3-a]imidazo[5,1,2-cd]indolizine (3a and 3a') :

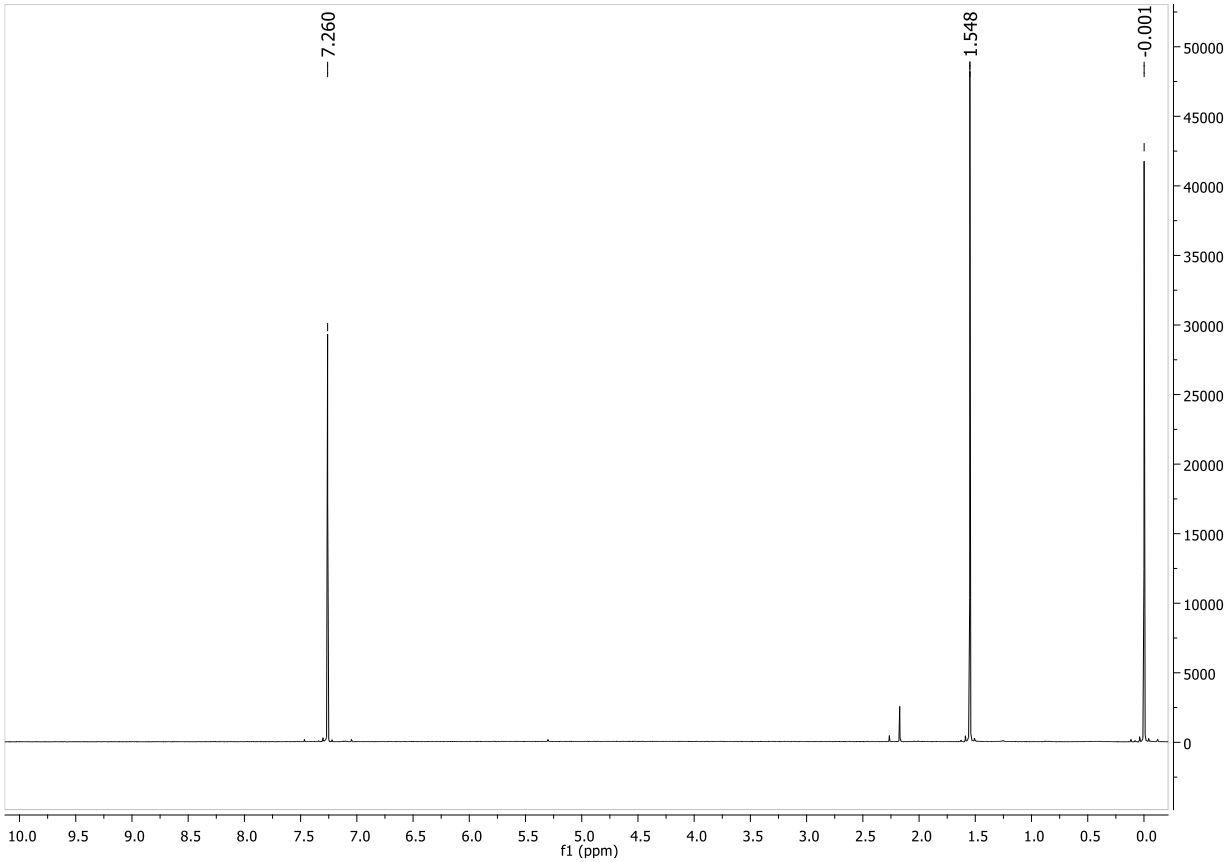



(Eluent: 15% (EtOAc/hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.64 – 8.61 (m, 1H), 8.60 – 8.56 (m, 3H), 8.37 (d, J = 7.9 Hz, 1H), 8.23 – 8.16 (m, 5H), 8.13 – 8.09 (m, 1H), 8.04 – 7.98 (m, 1H), 7.83 – 7.79 (m, 2H), 7.75 (t, J = 7.8 Hz, 3H), 7.70 – 7.64 (m, 2H), 7.64 – 7.61 (m, 2H), 7.59 – 7.53 (m, 3H), 7.51 – 7.48 (m, 1H).

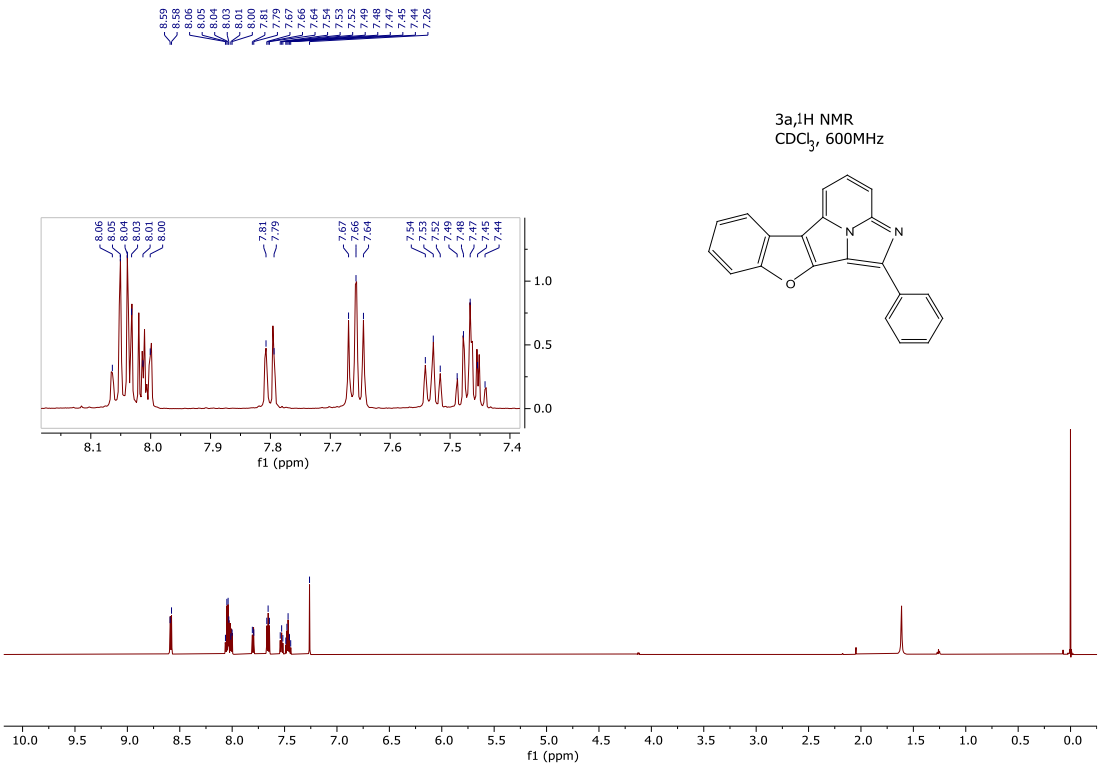
References:

1. D. C. Mohan, R. R. Donthiri, S. N. Rao, S. Adimurthy, *Adv. Synth. Catal.* 2013, **355**, 2217 – 222.
2. D. Cao, Z. Liu, P. Verwilst, S. Koo, P. angjili, J. S. Kim, W, Lin, *Chem. Rev*. 2019, **119**, 10403.
3. D. A. Babar, H. B. Rode, *Eur. J. Org. Chem*. 2020, 1823–1827.

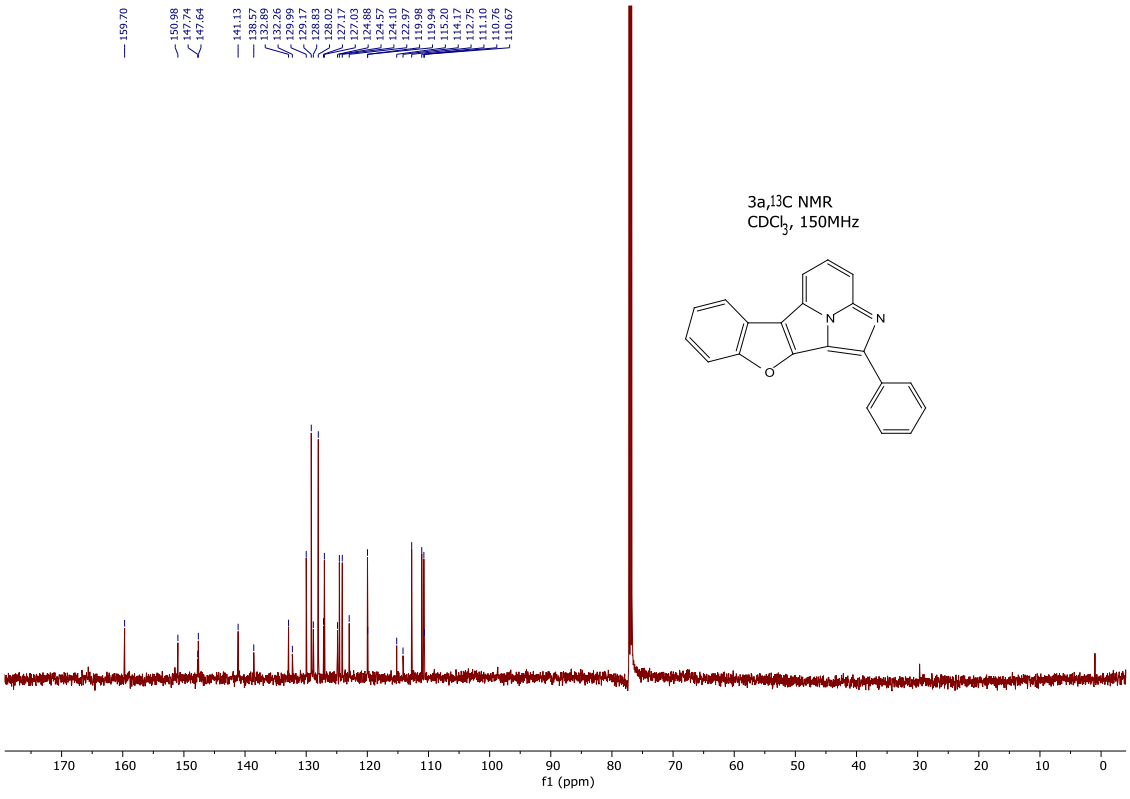
^{1}H NMR and ^{13}C NMR Spectra



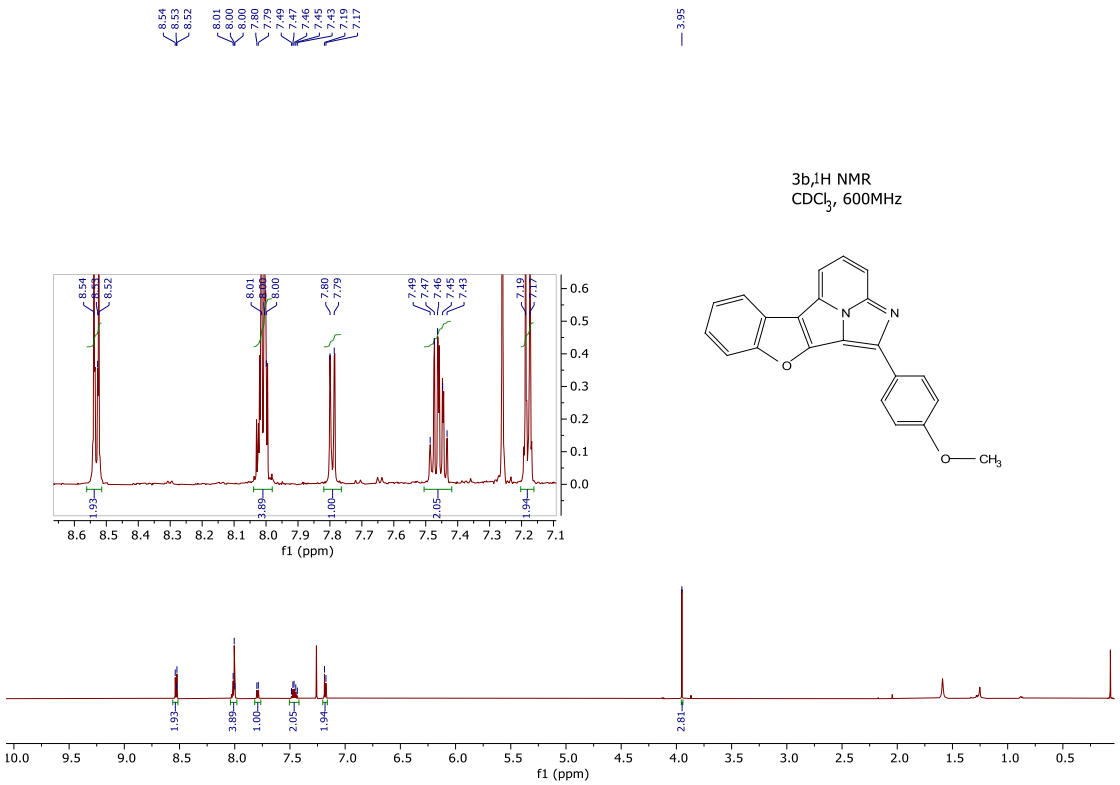
^{1}H NMR of $CDCl_3$



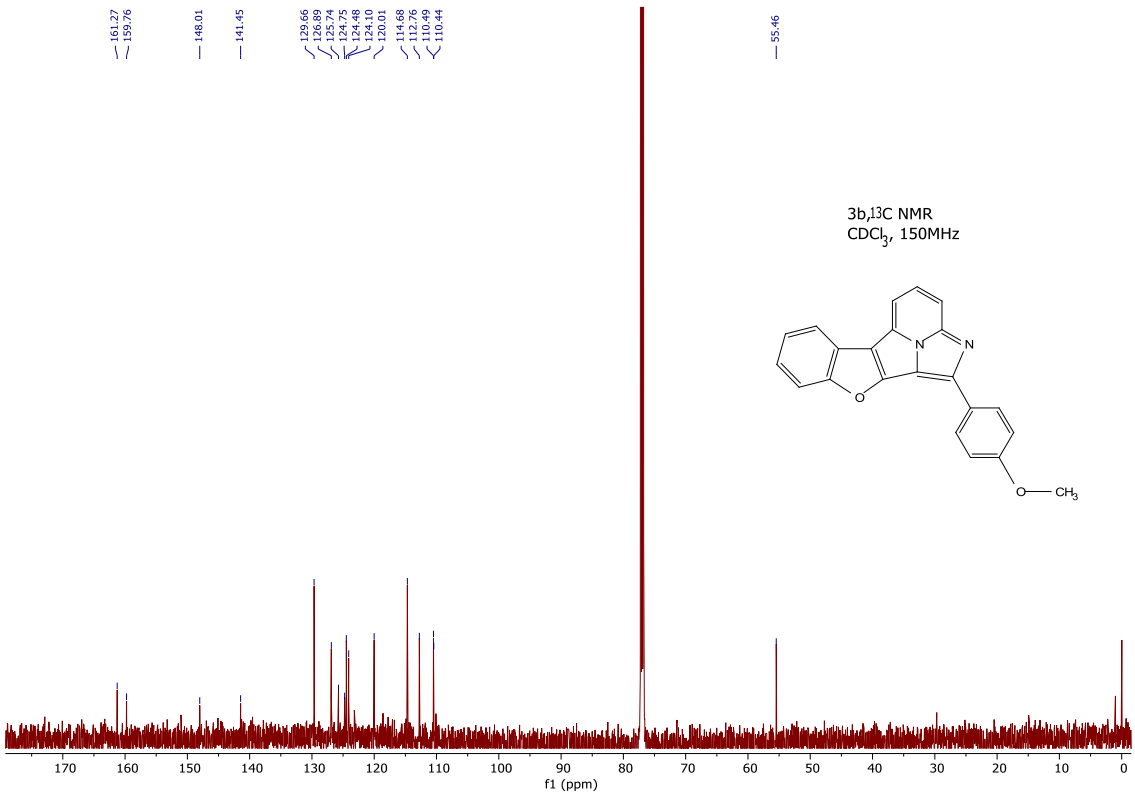
^{1}H NMR of **3a**



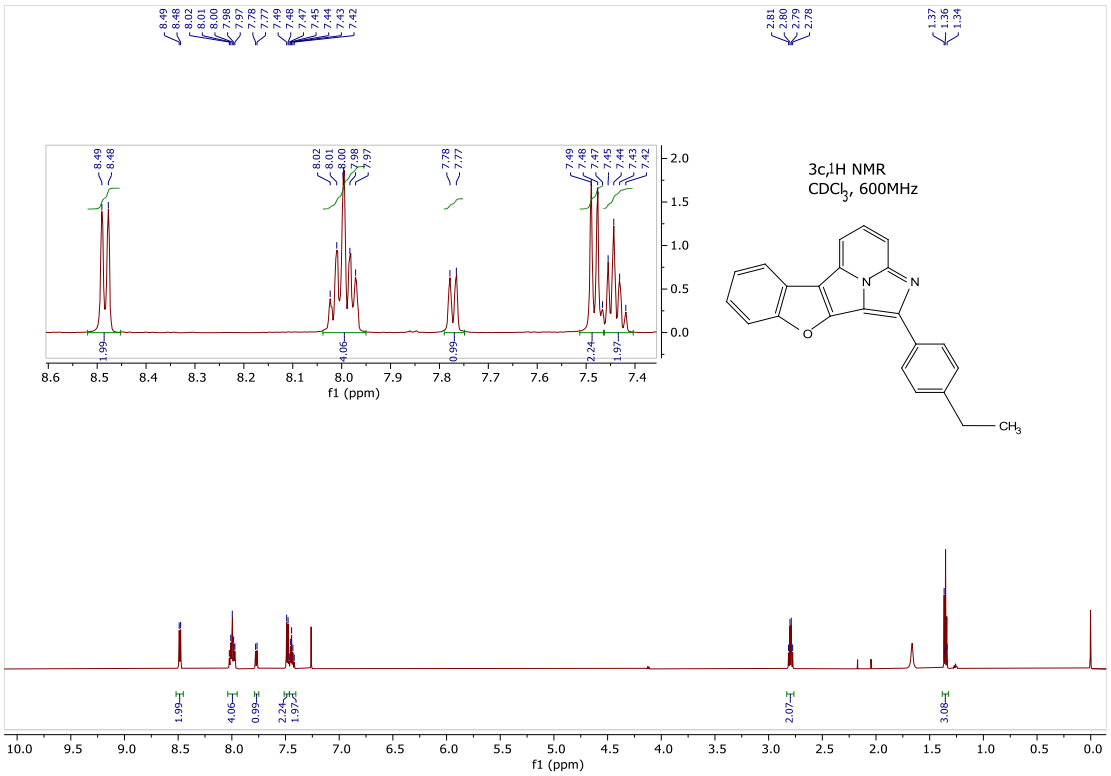
^{13}C NMR of **3a**



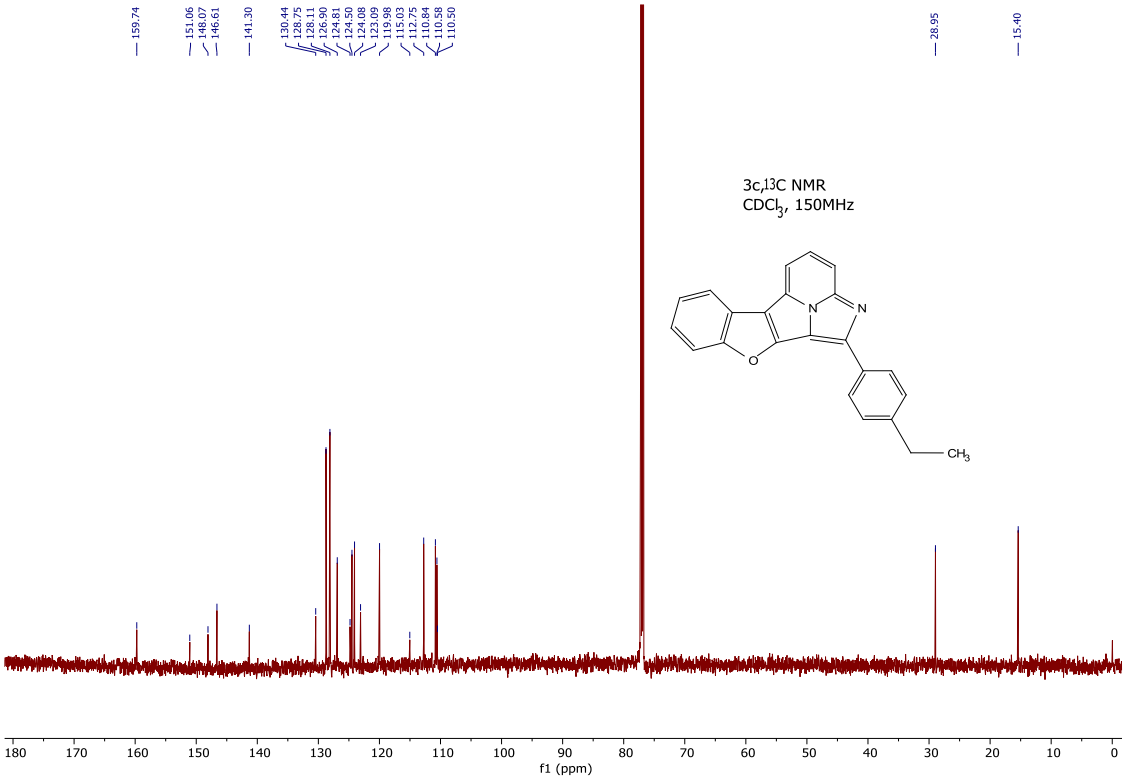
^{1}H NMR of **3b**



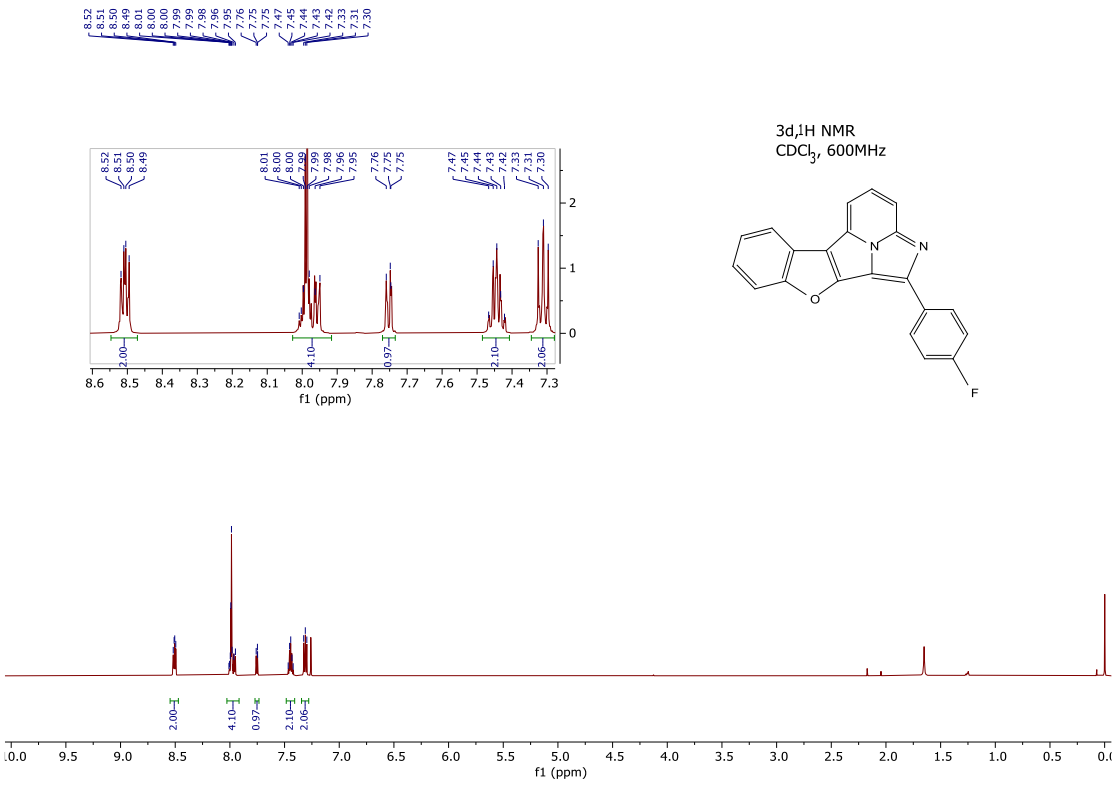
^{13}C NMR of **3b**



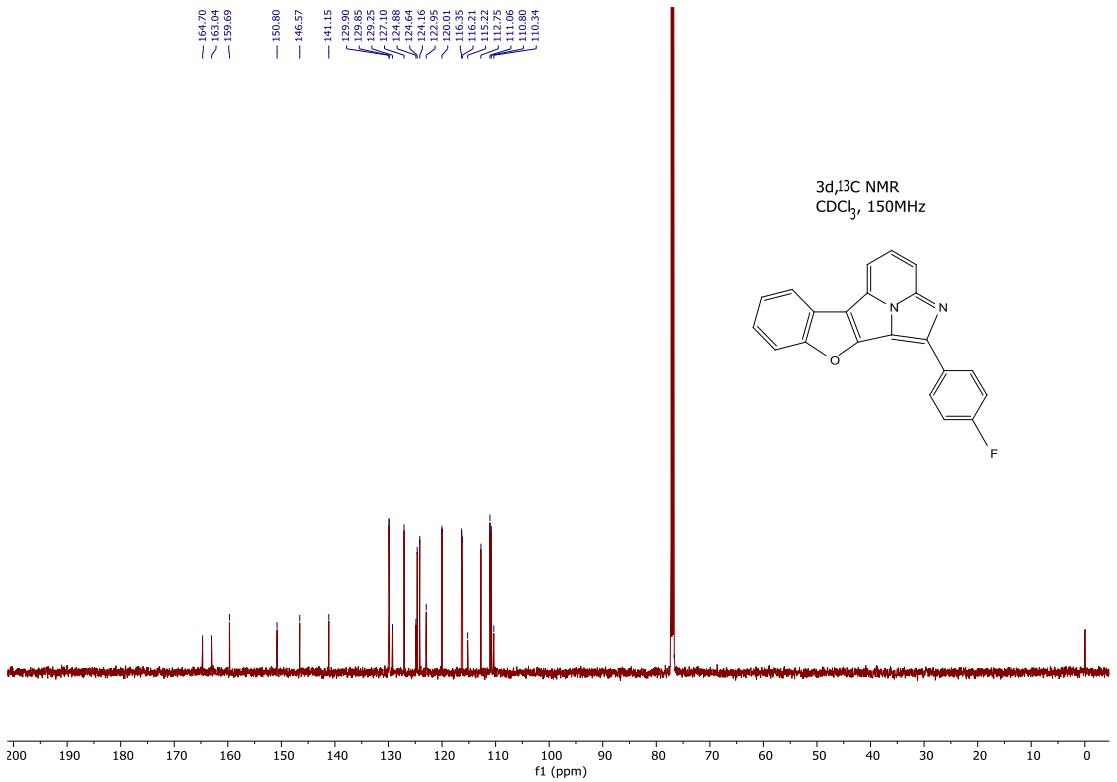
^{1}H NMR of **3c**



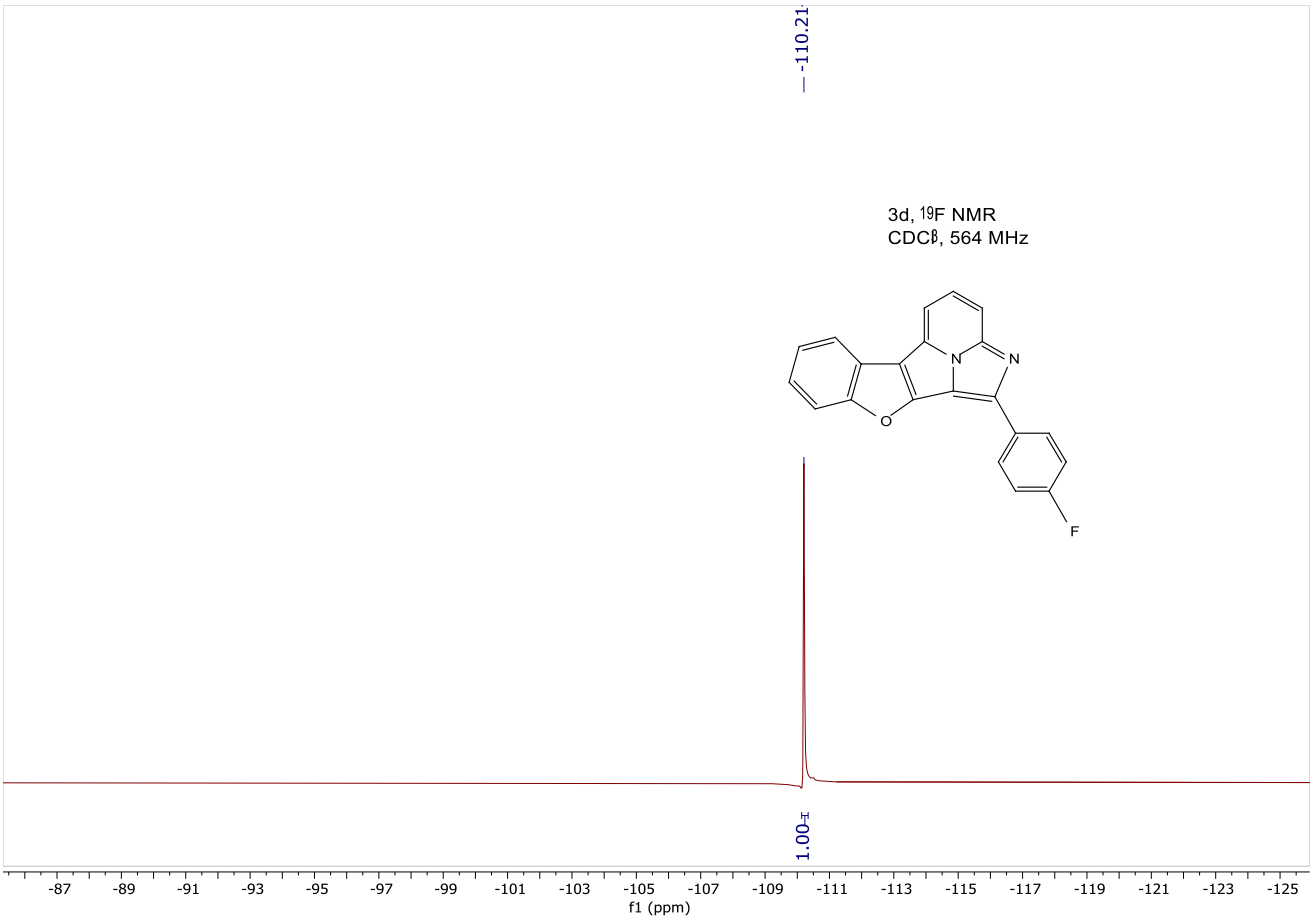
^{13}C NMR of **3c**



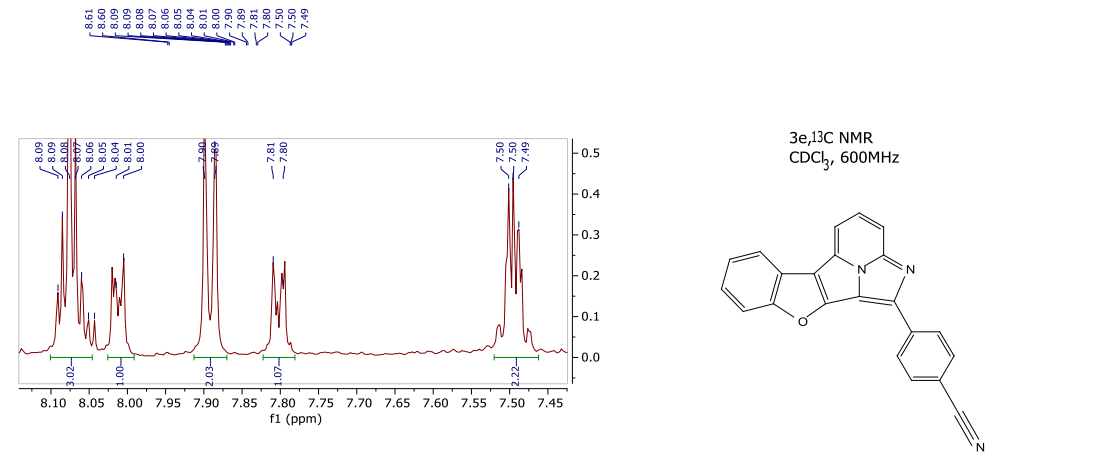
^{1}H NMR of **3d**

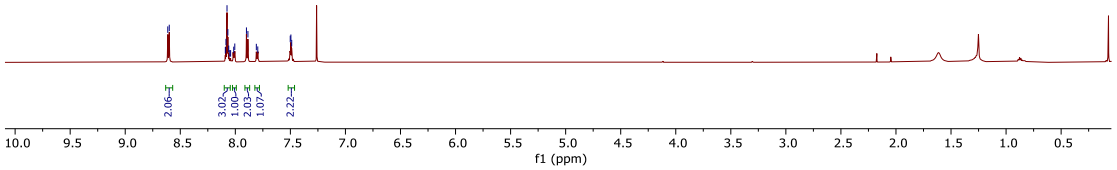


^{13}C NMR of **3d**

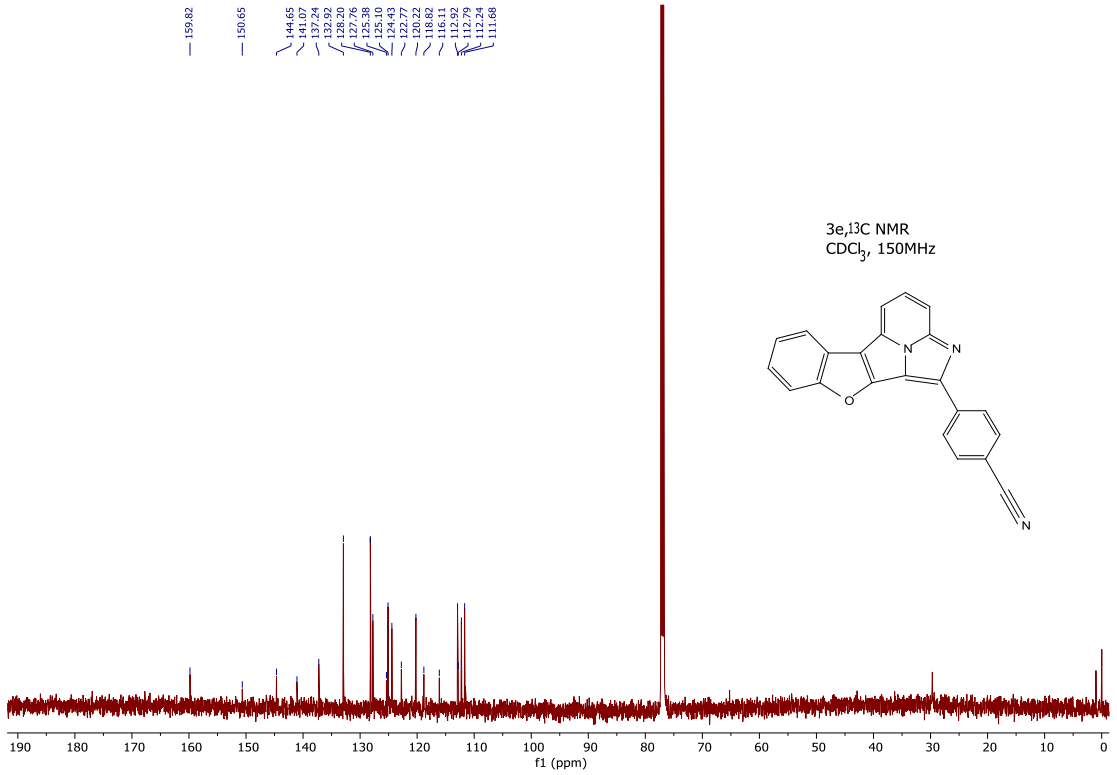

-110.21
3d, 19F NMR
CDCl3, 564 MHz
N
N
O
F
1.00
-87
-89
-91
-93
-95
-97
-99
-101
-103
-105
-107
-109
-111
-113
-115
-117
-119
-121
-123
-125
f1 (ppm)

^{19}F NMR of **3d**

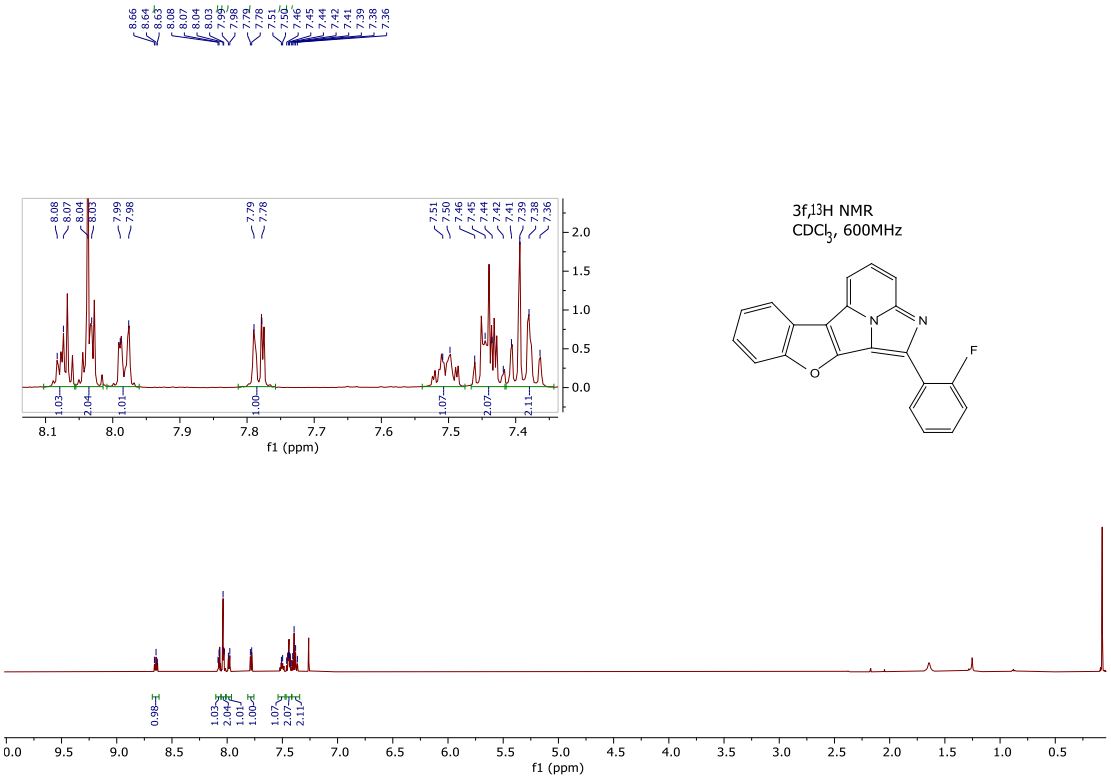




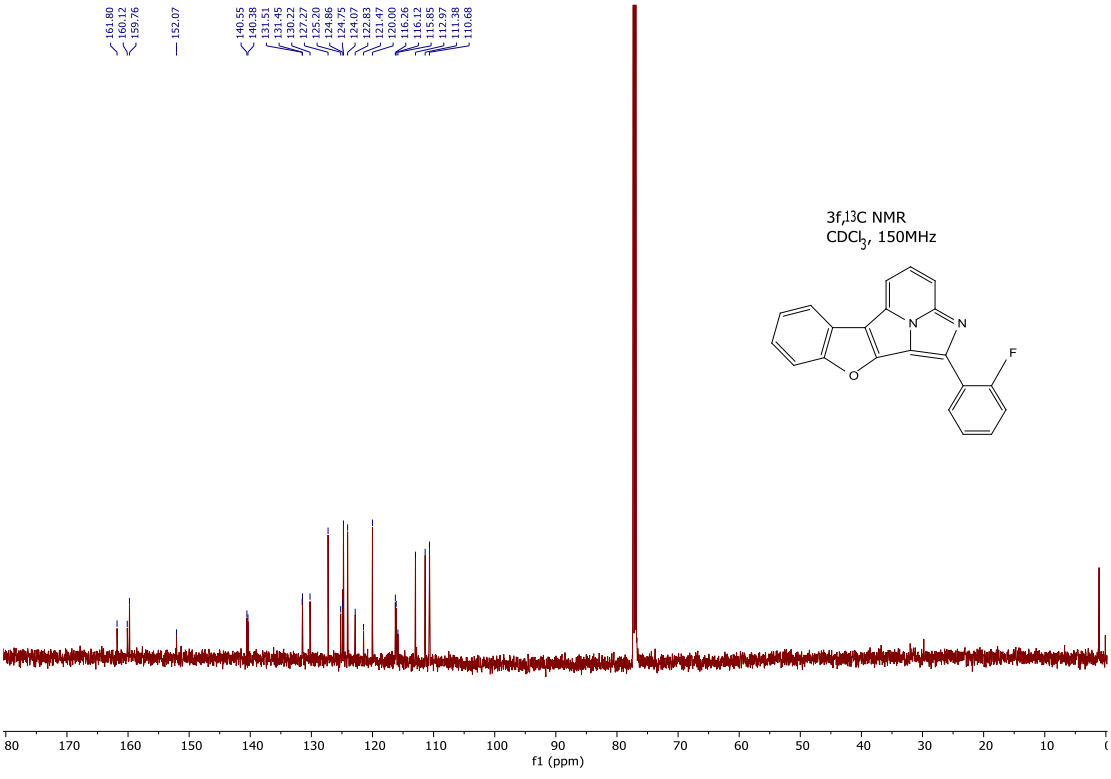
^{1}H NMR of **3e**



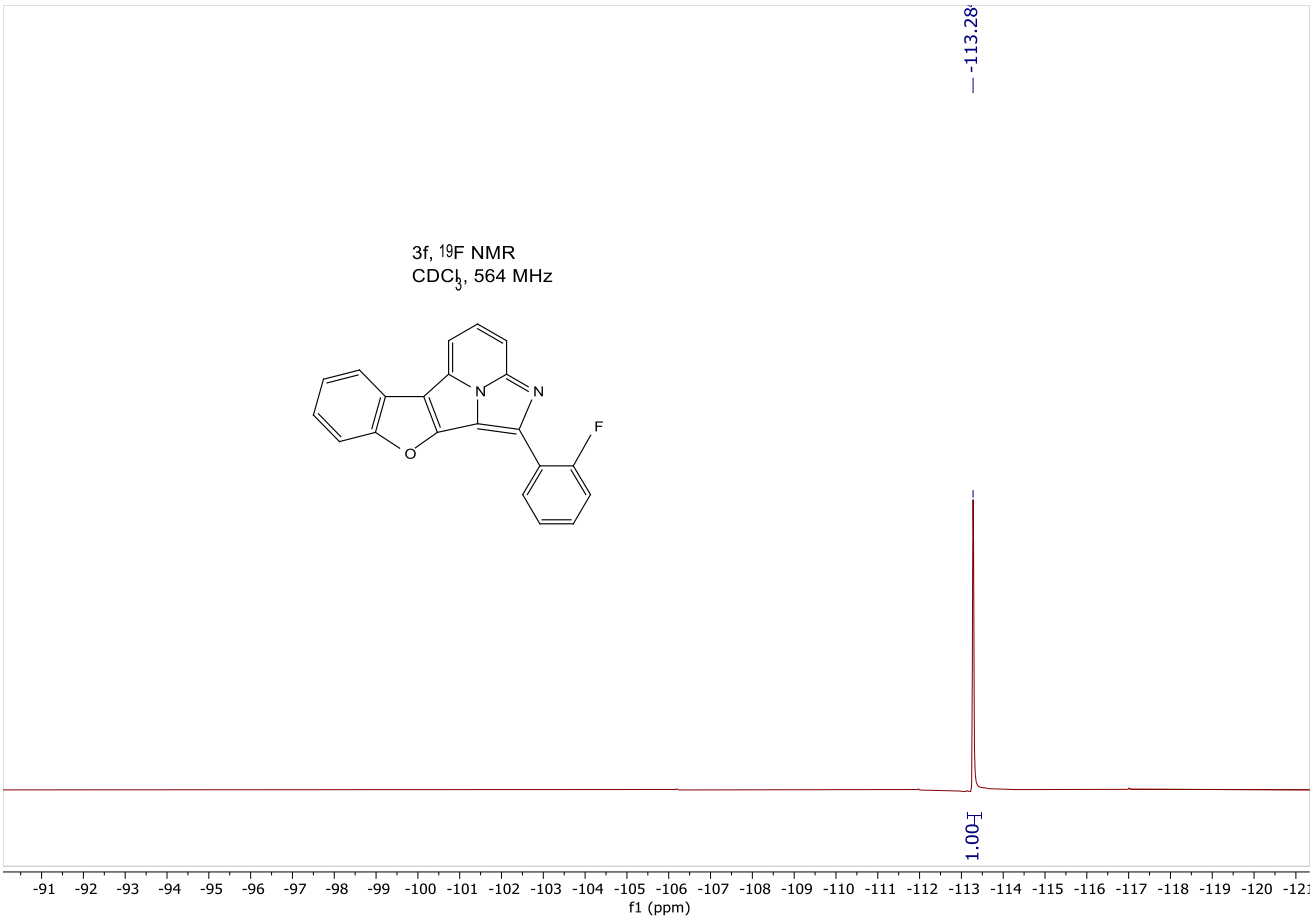
^{13}C NMR of **3e**



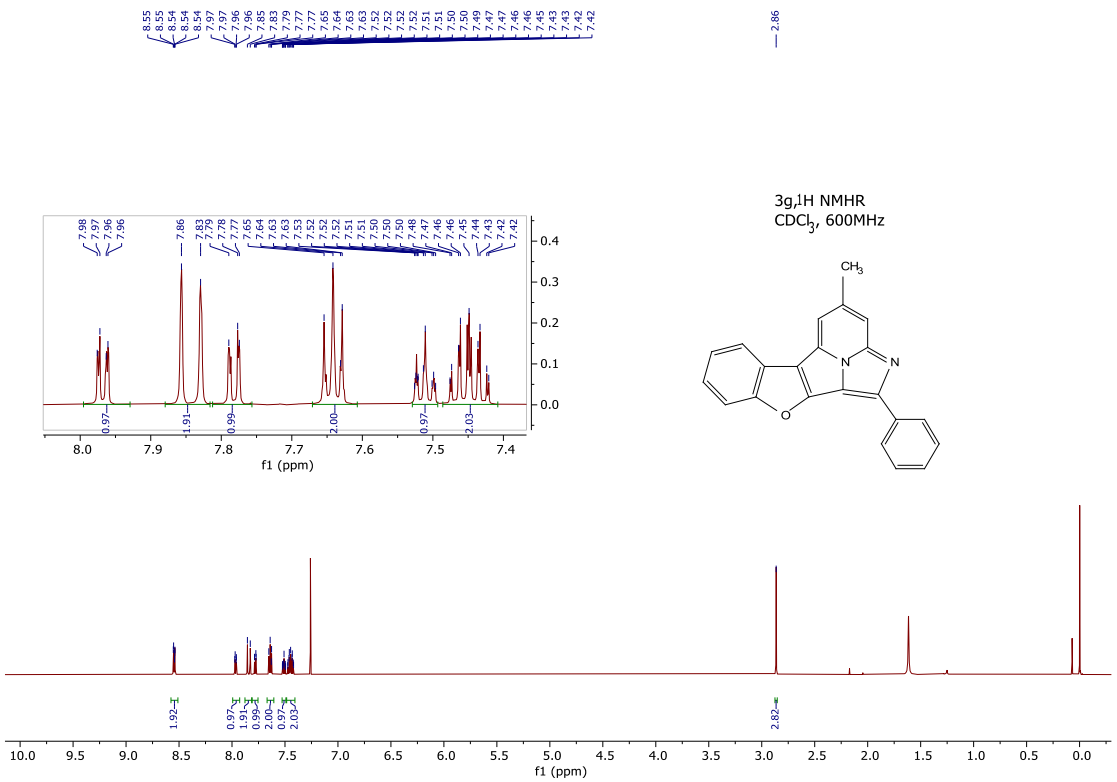
^{1}H NMR of **3f**



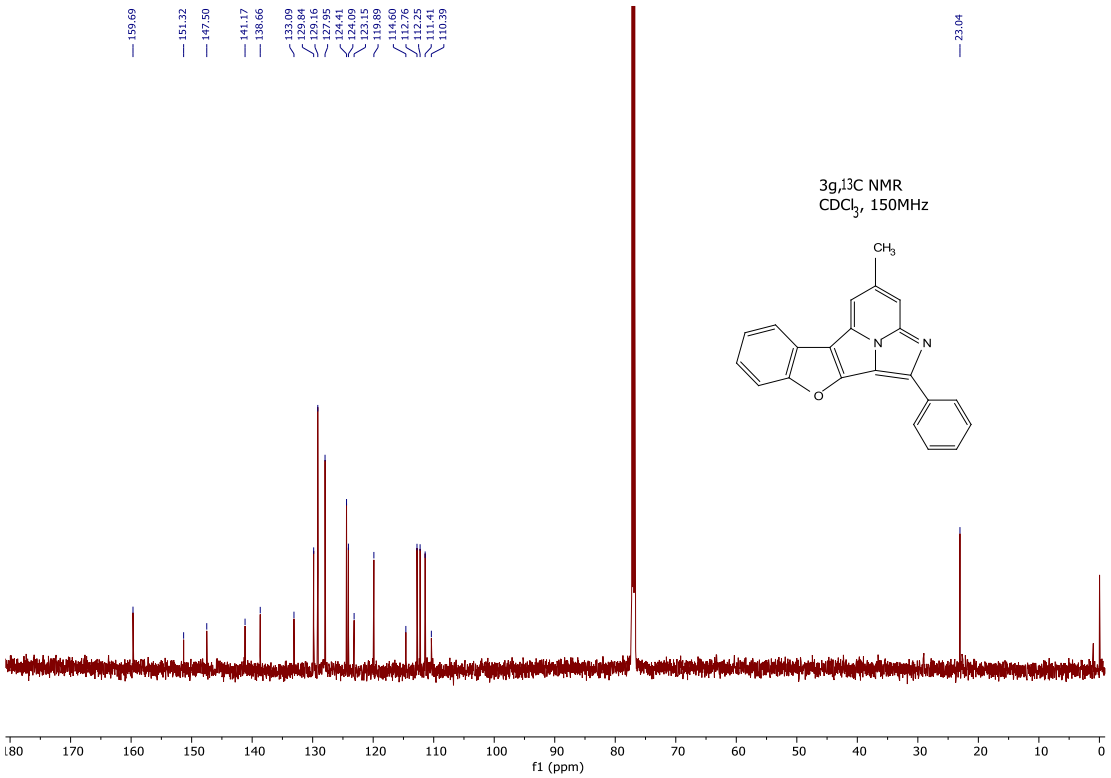
^{13}C NMR of **3f**


-113.28
3f, 19F NMR
CDCl3, 564 MHz
N
N
O
F
1.00
-91 -92 -93 -94 -95 -96 -97 -98 -99 -100 -101 -102 -103 -104 -105 -106 -107 -108 -109 -110 -111 -112 -113 -114 -115 -116 -117 -118 -119 -120
f1 (ppm)

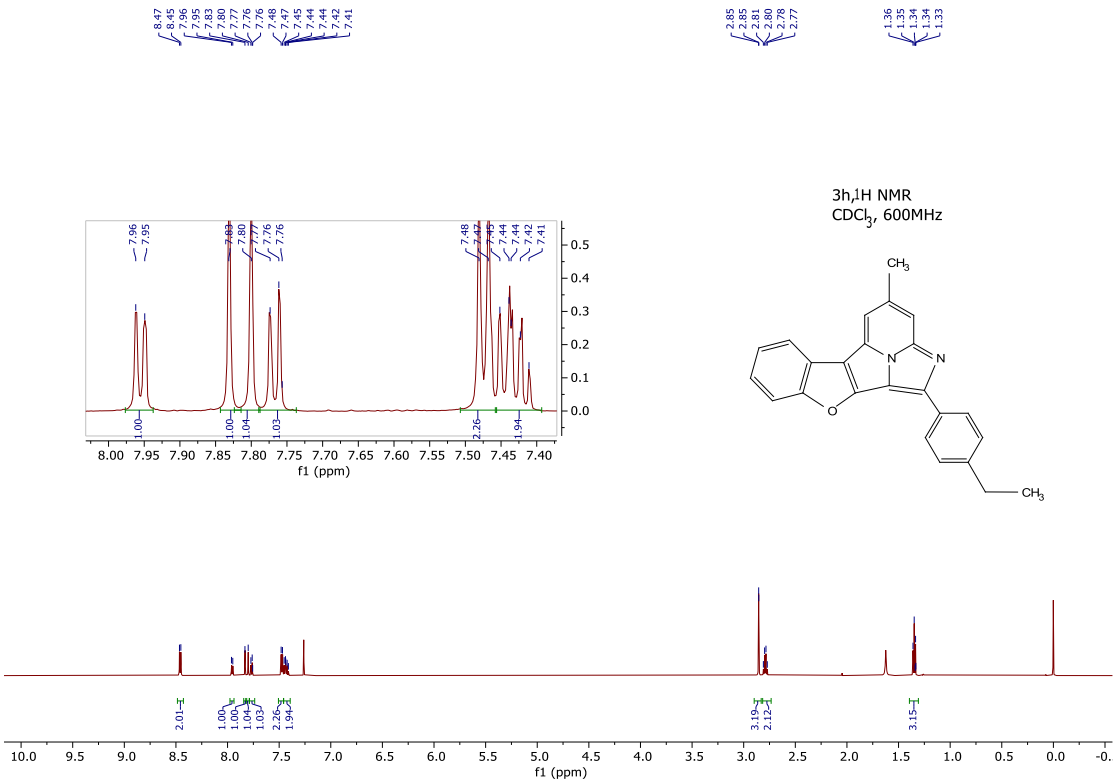
^{19}F NMR of **3f**



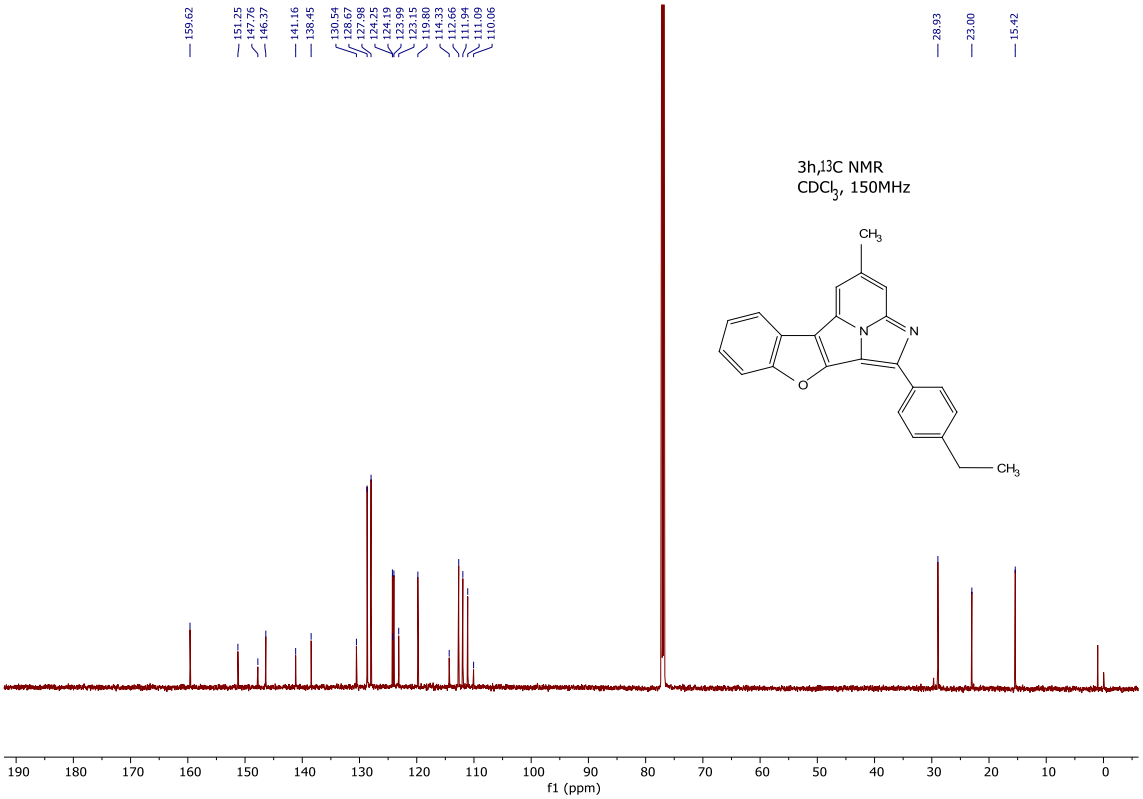
^{1}H NMR of **3g**



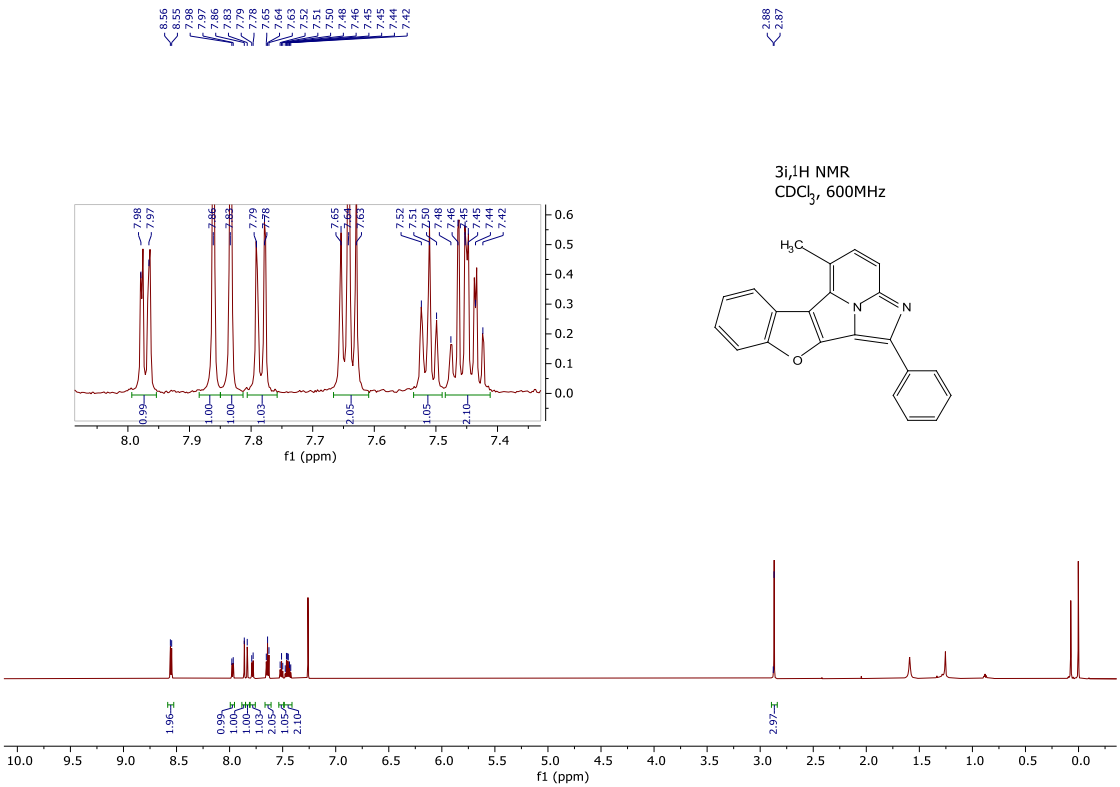
^{13}C NMR of **3g**



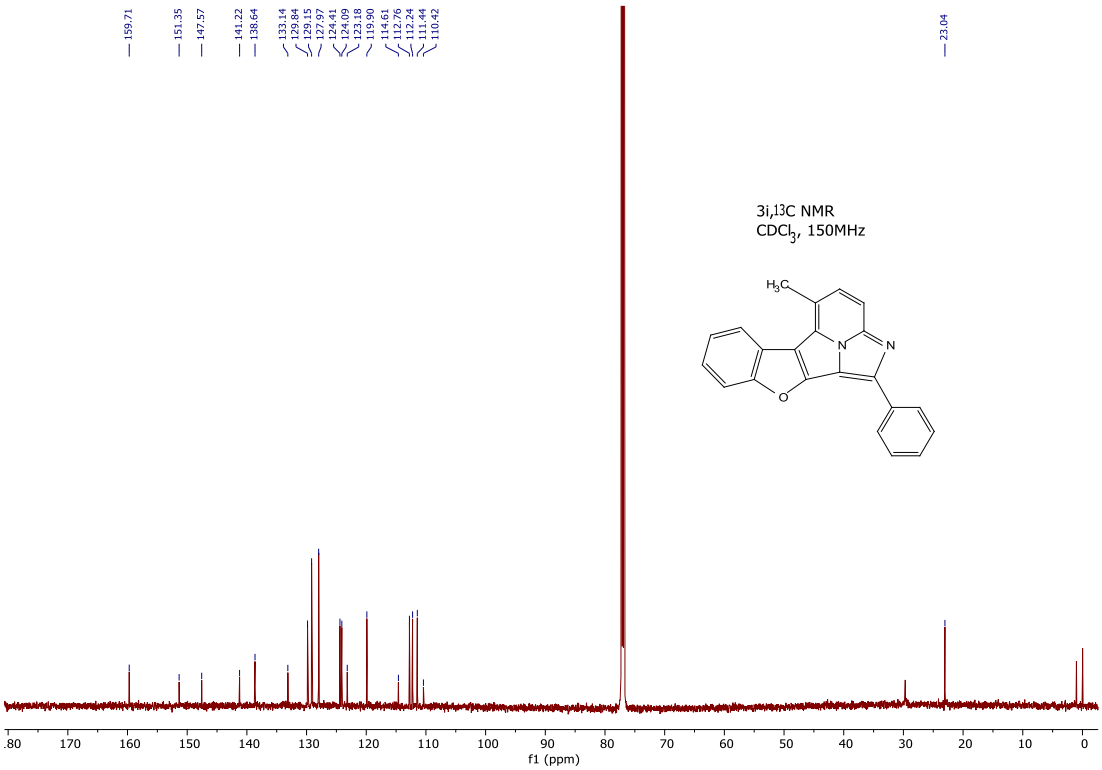
^{1}H NMR of **3h**



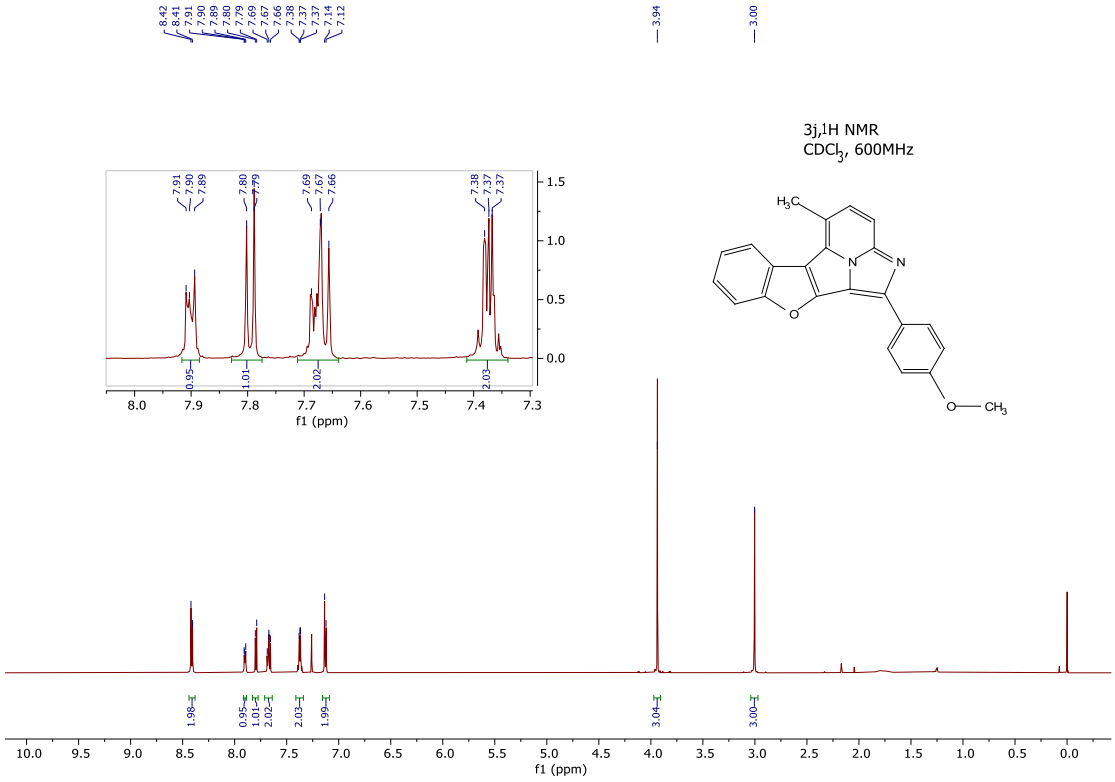
^{13}C NMR of **3h**



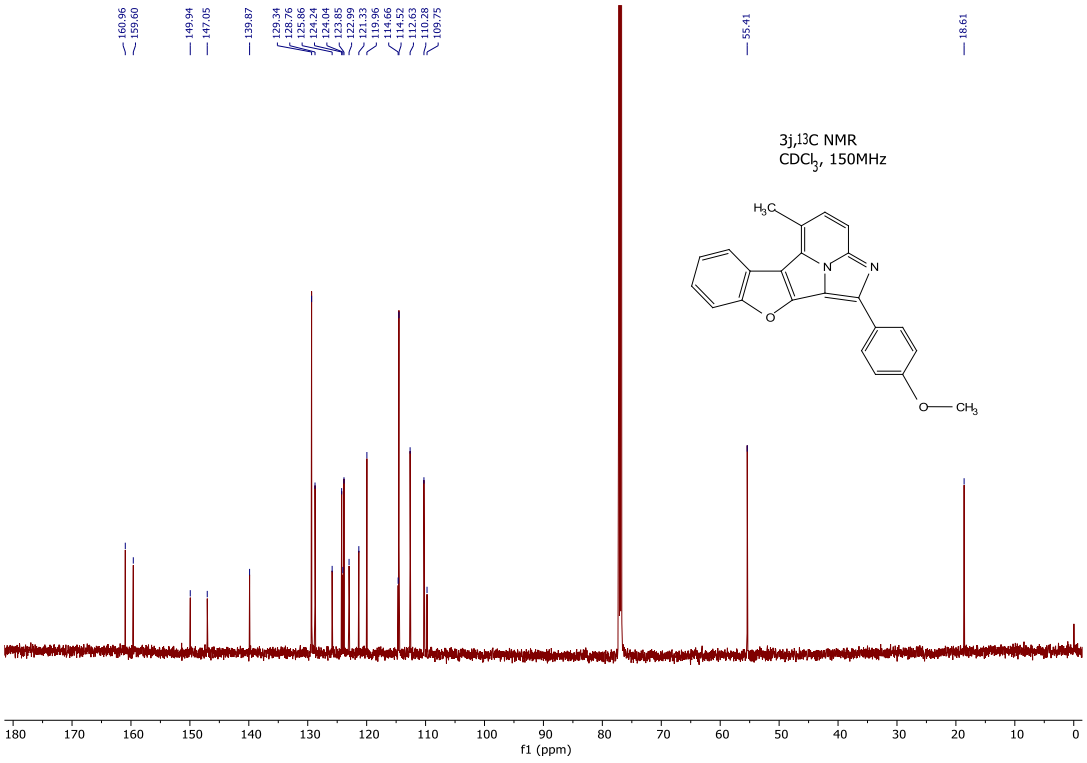
^{1}H NMR of **3i**



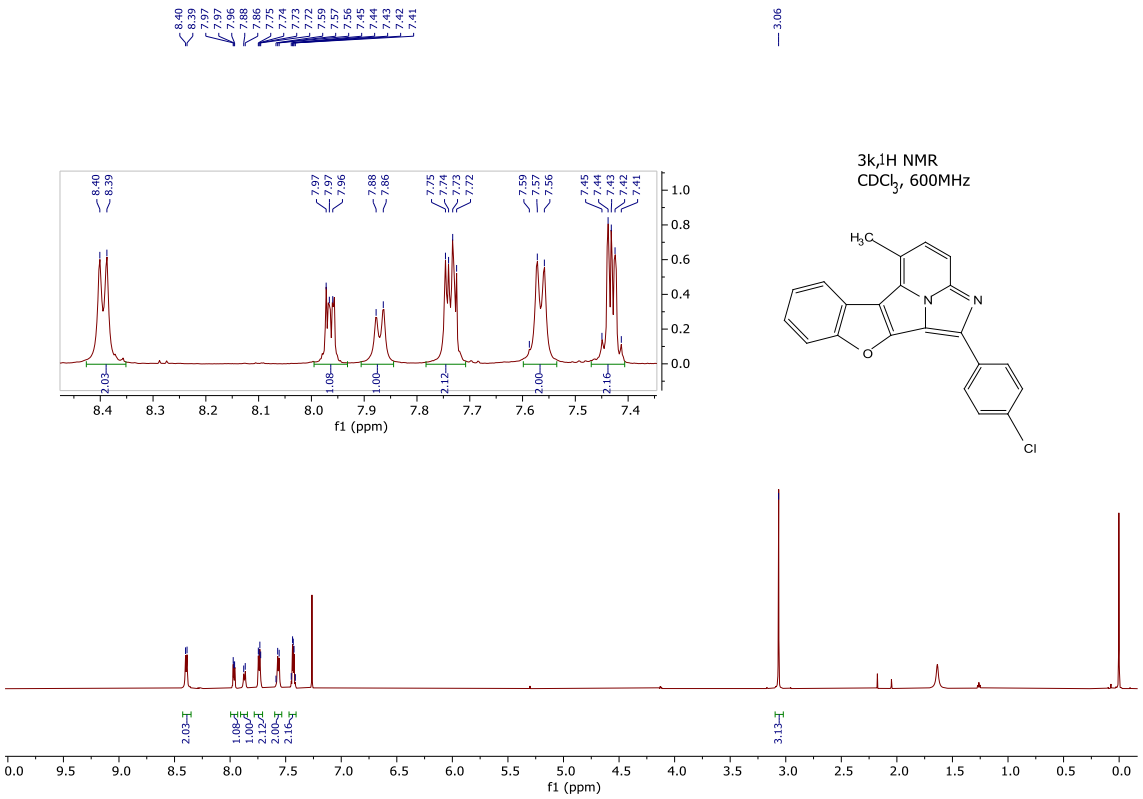
^{13}C NMR of **3i**



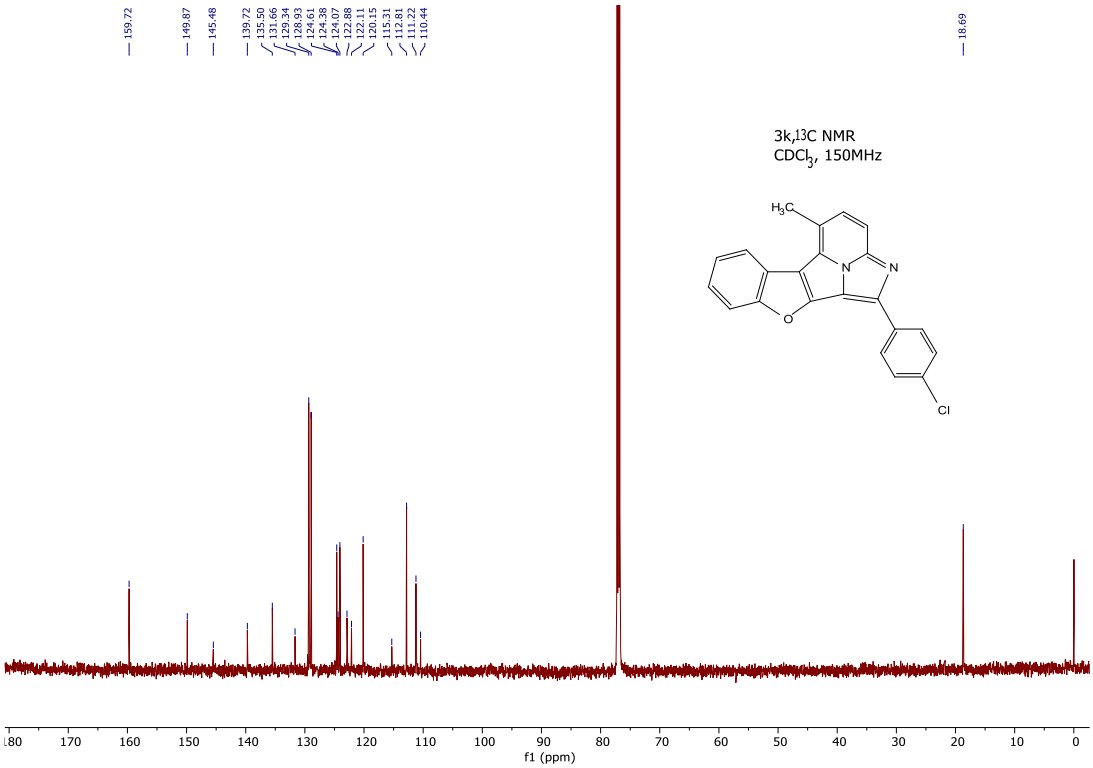
^{1}H NMR of **3j**



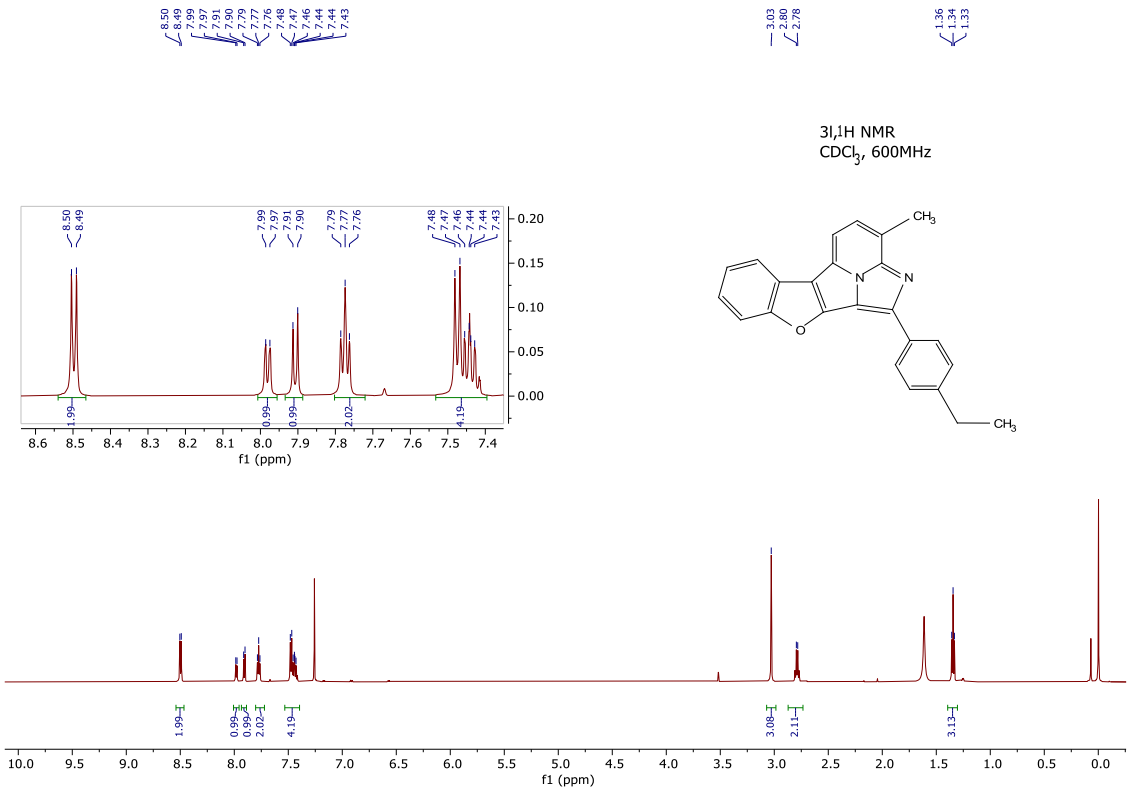
^{13}C NMR of **3j**



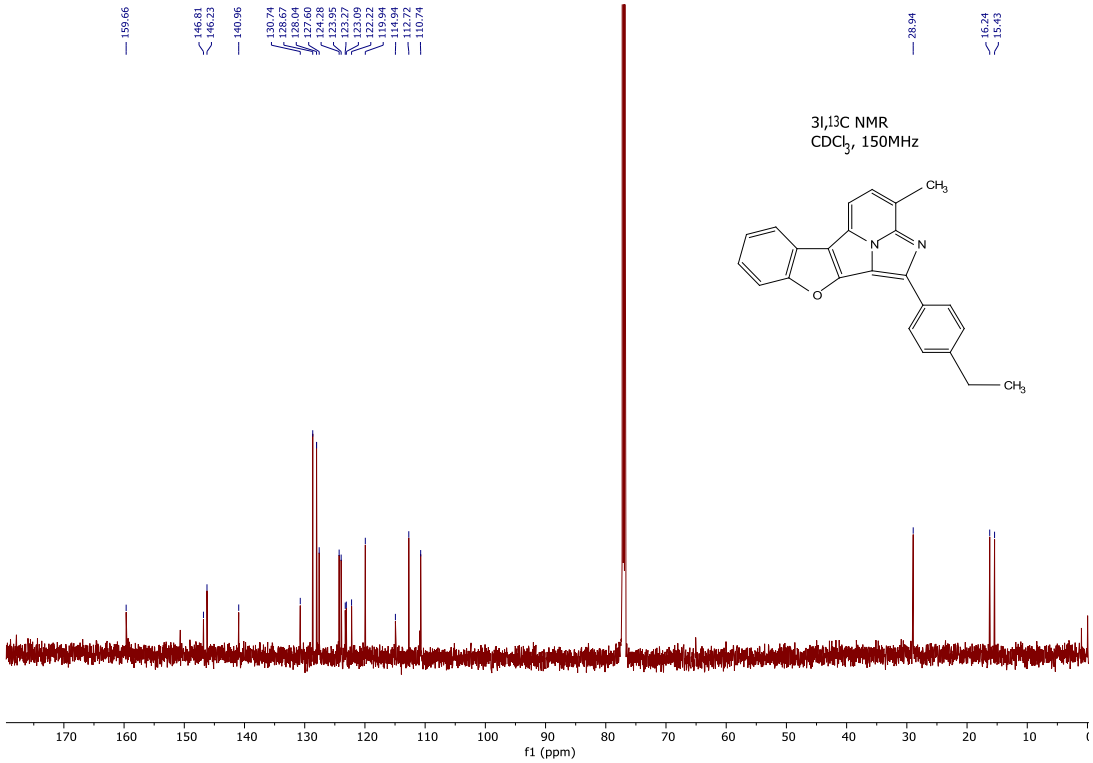
^{1}H NMR of **3k**



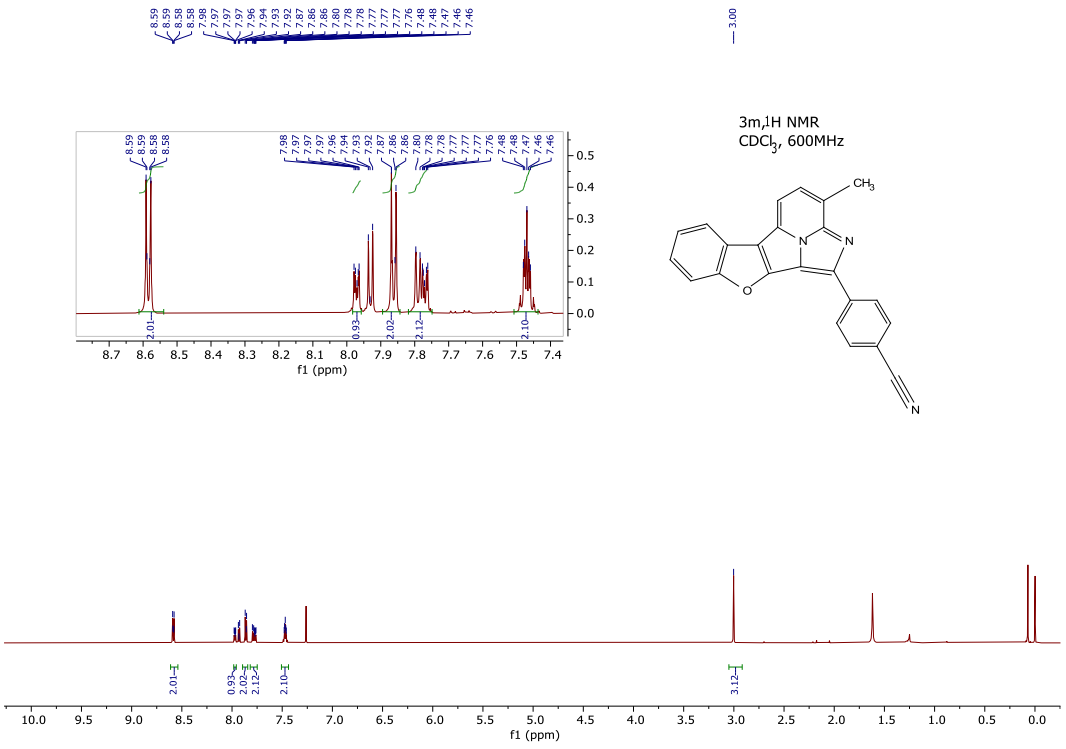
^{13}C NMR of **3k**



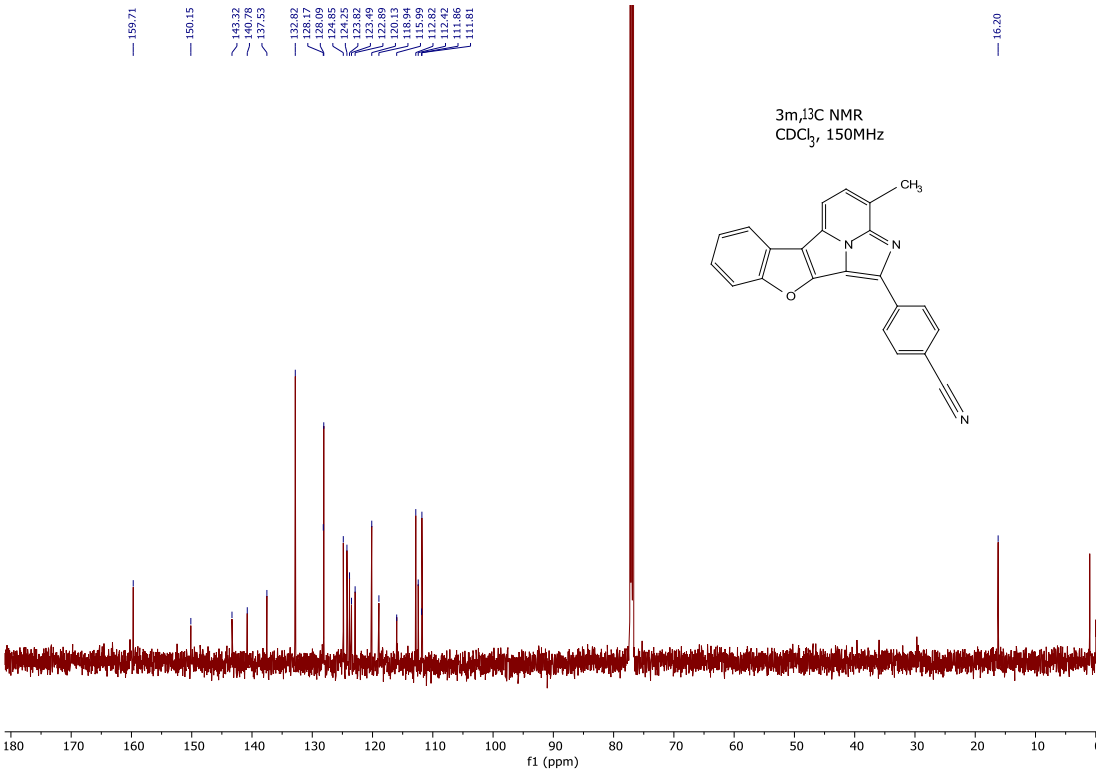
^{1}H NMR of **3l**



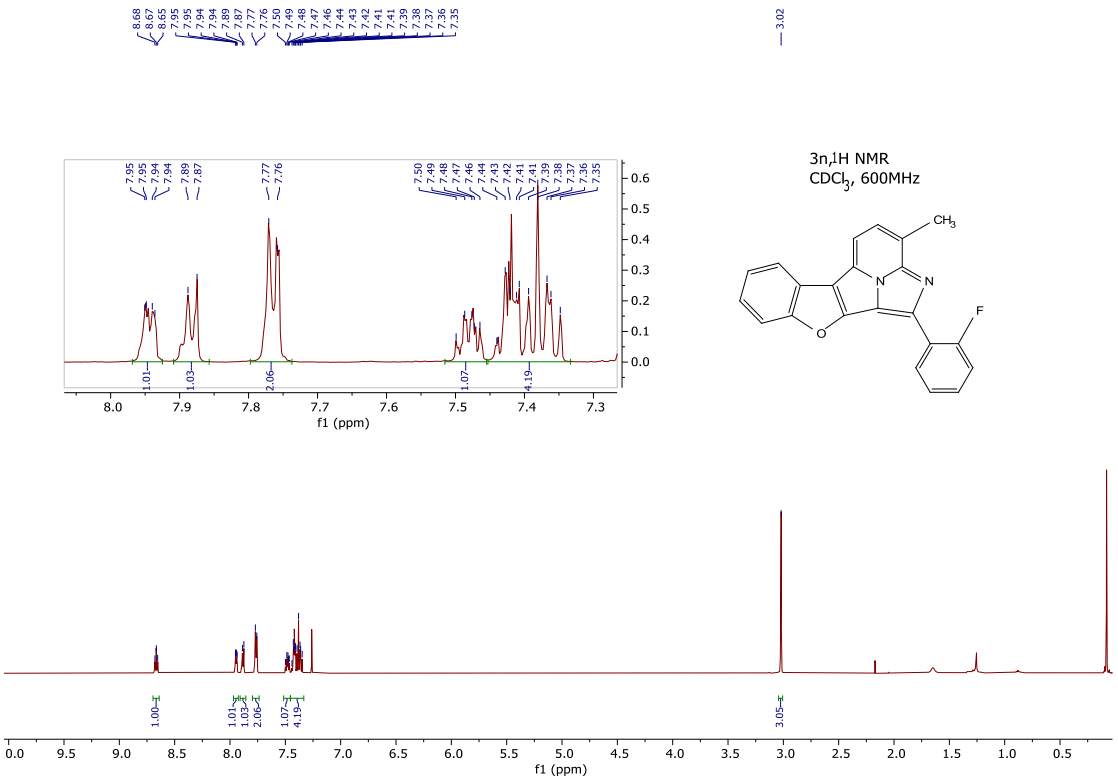
^{13}C NMR of **3l**



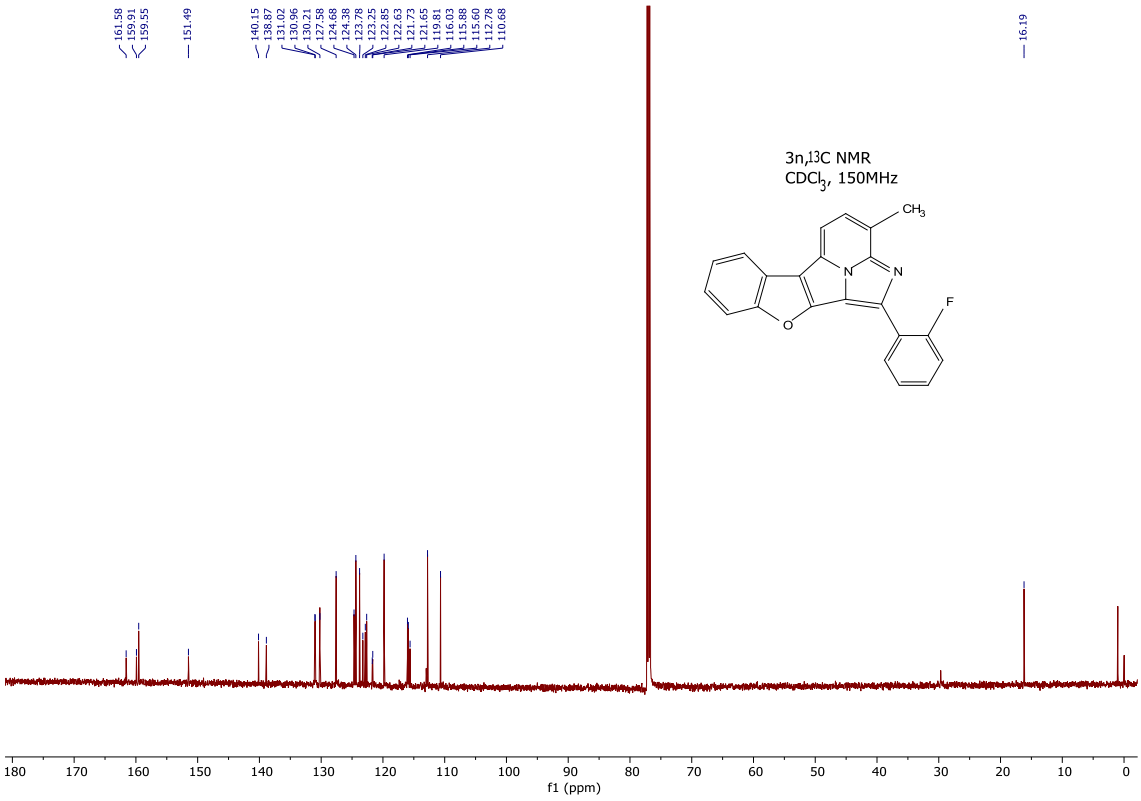
^{1}H NMR of **3m**



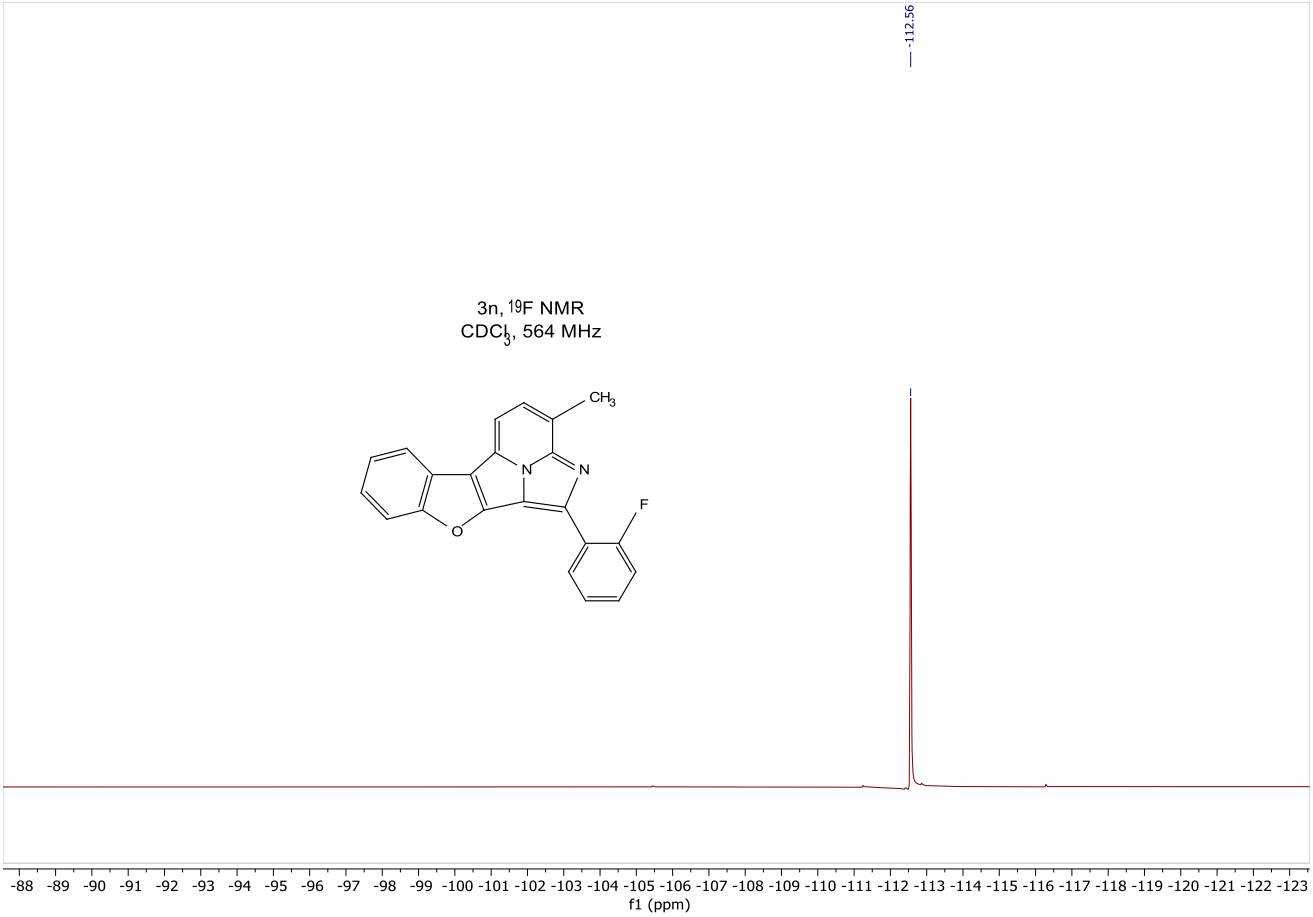
^{13}C NMR of **3m**



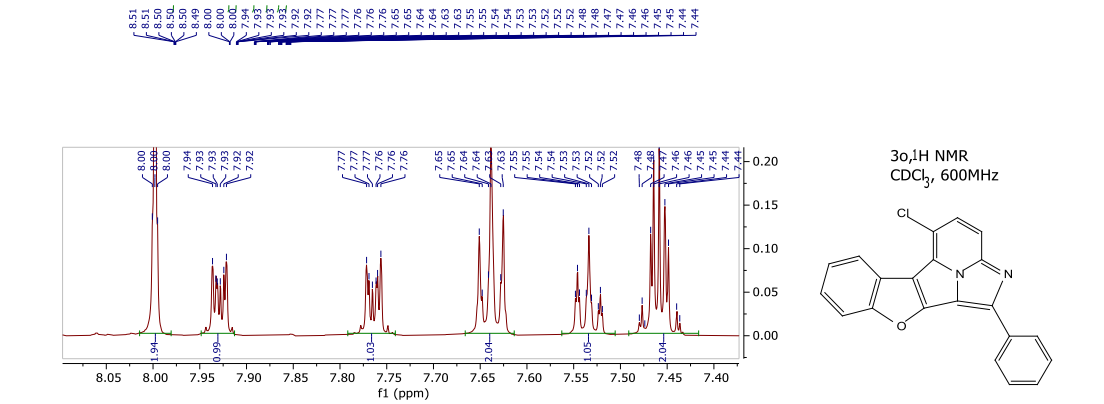
^{1}H NMR of **3n**



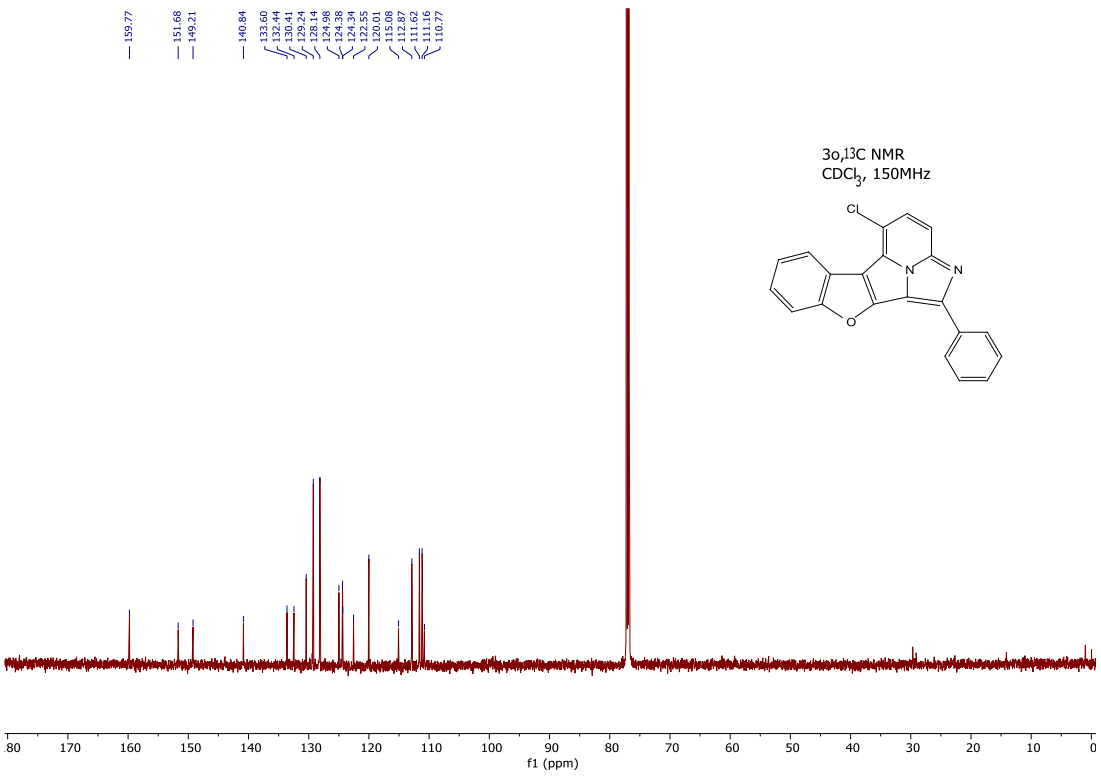
^{13}C NMR of **3n**


-112.56
3n, 19F NMR
CDCl3, 564 MHz
CH3
N
N
O
F
-88 -89 -90 -91 -92 -93 -94 -95 -96 -97 -98 -99 -100 -101 -102 -103 -104 -105 -106 -107 -108 -109 -110 -111 -112 -113 -114 -115 -116 -117 -118 -119 -120 -121 -122 -123
f1 (ppm)

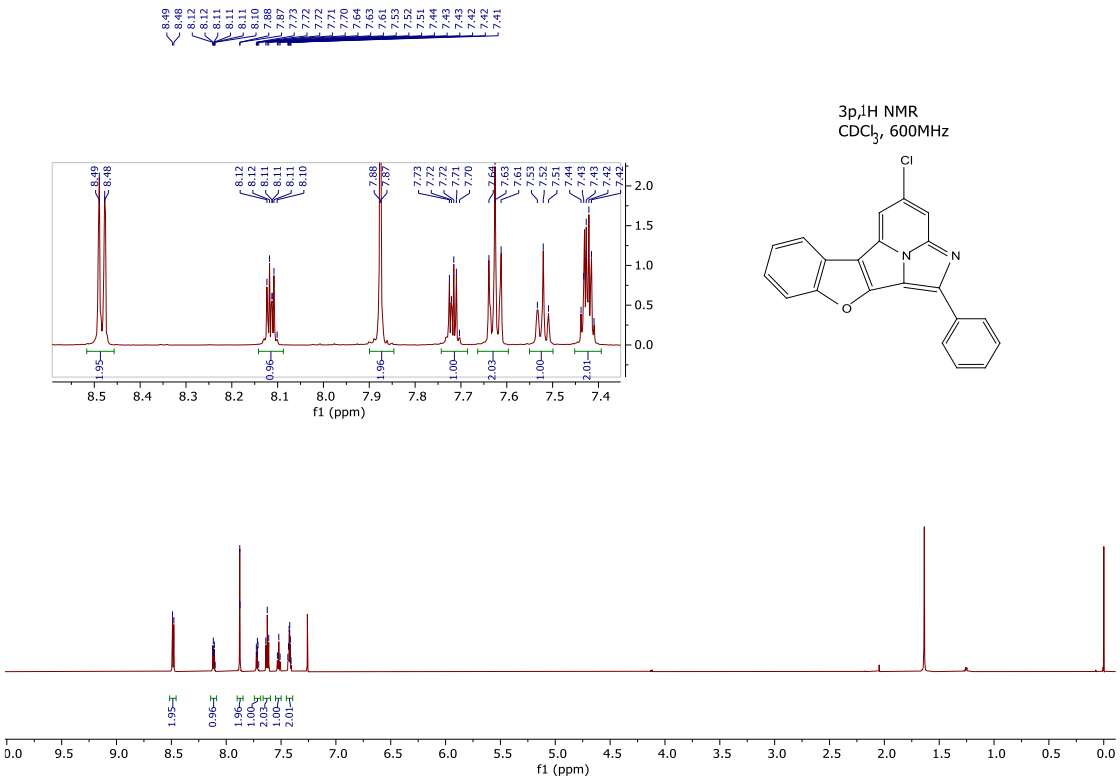
^{19}F NMR of **3n**



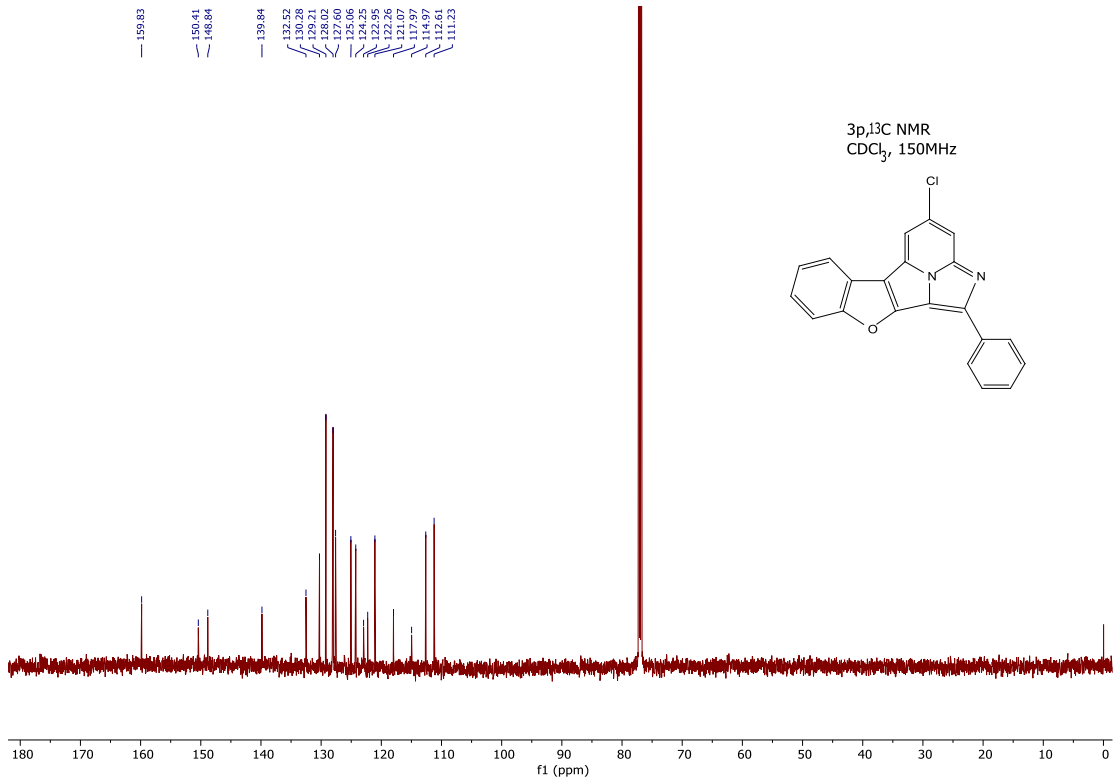
^{1}H NMR of **3o**



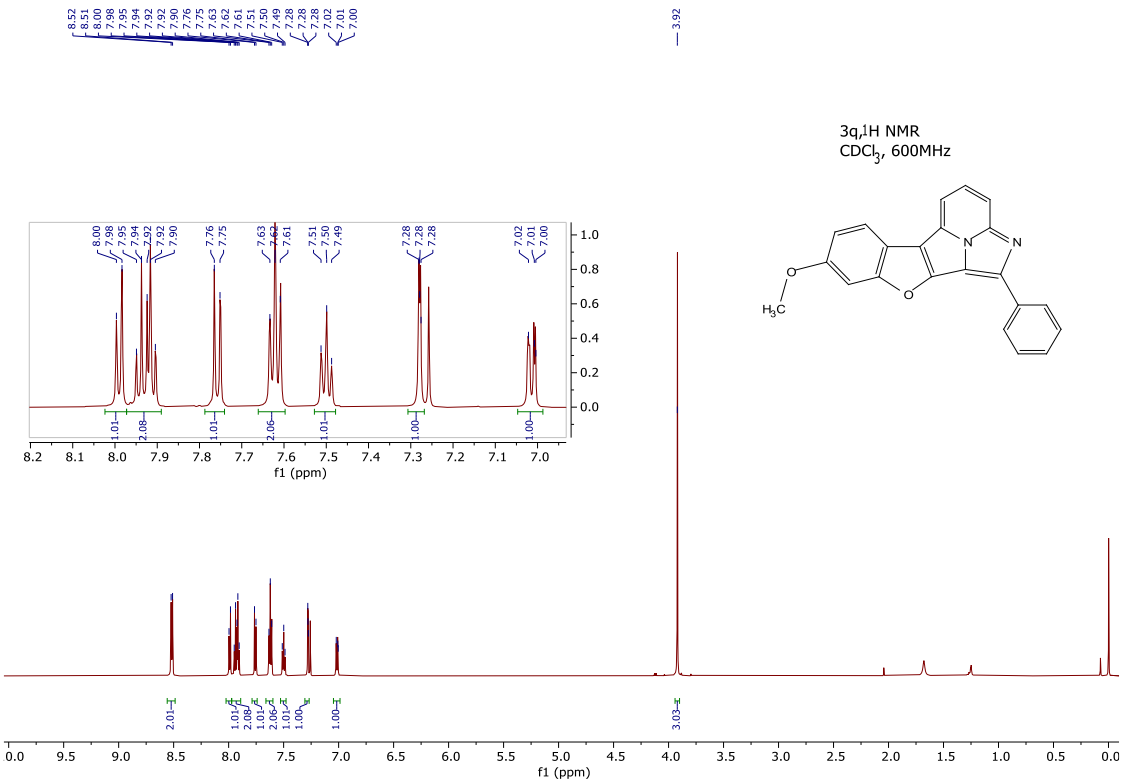
^{13}C NMR of **3o**



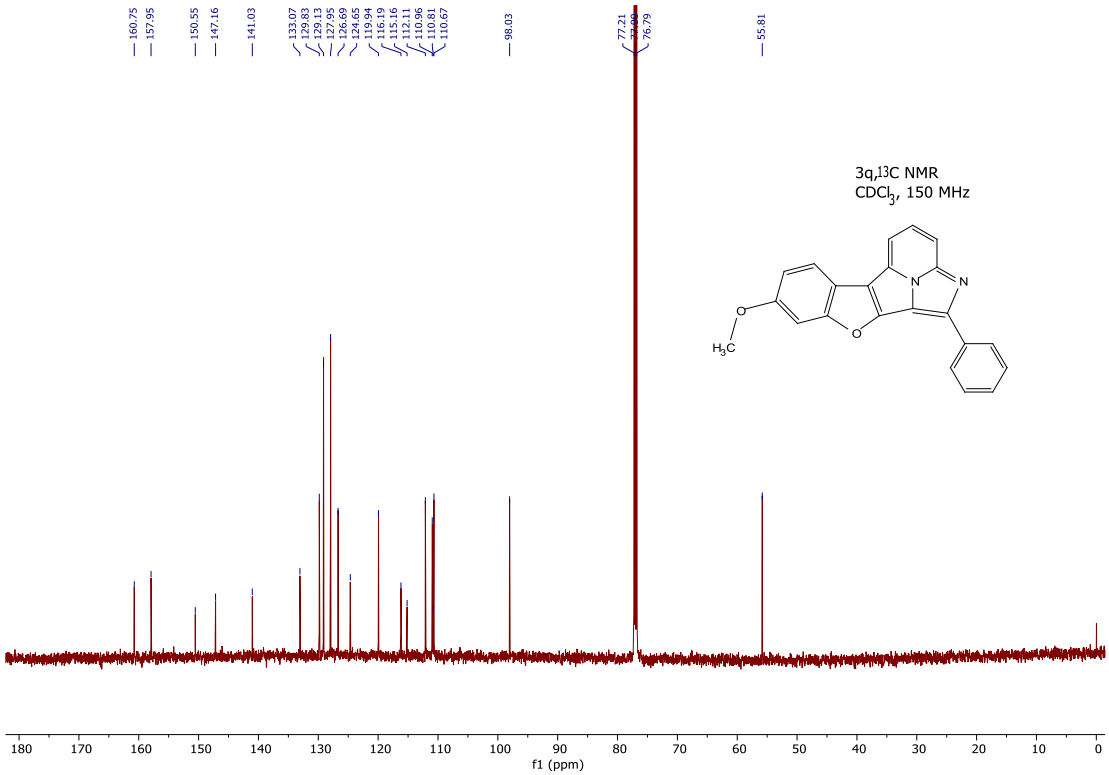
^{1}H NMR of **3p**



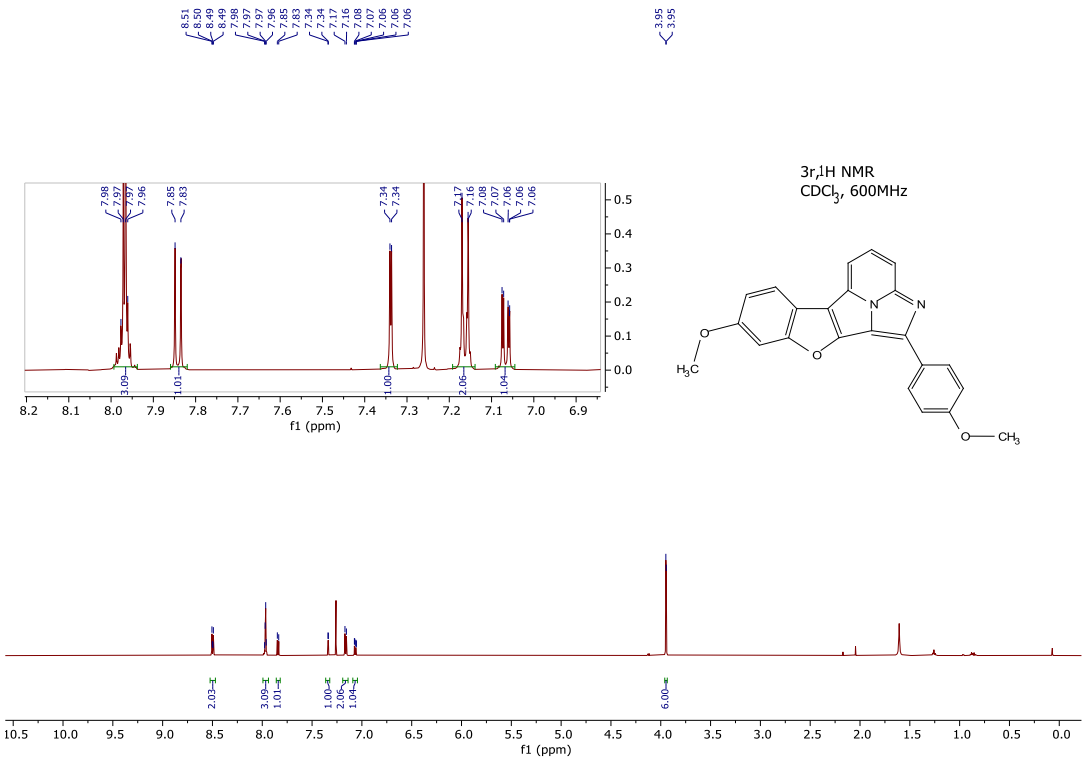
^{13}C NMR of **3p**



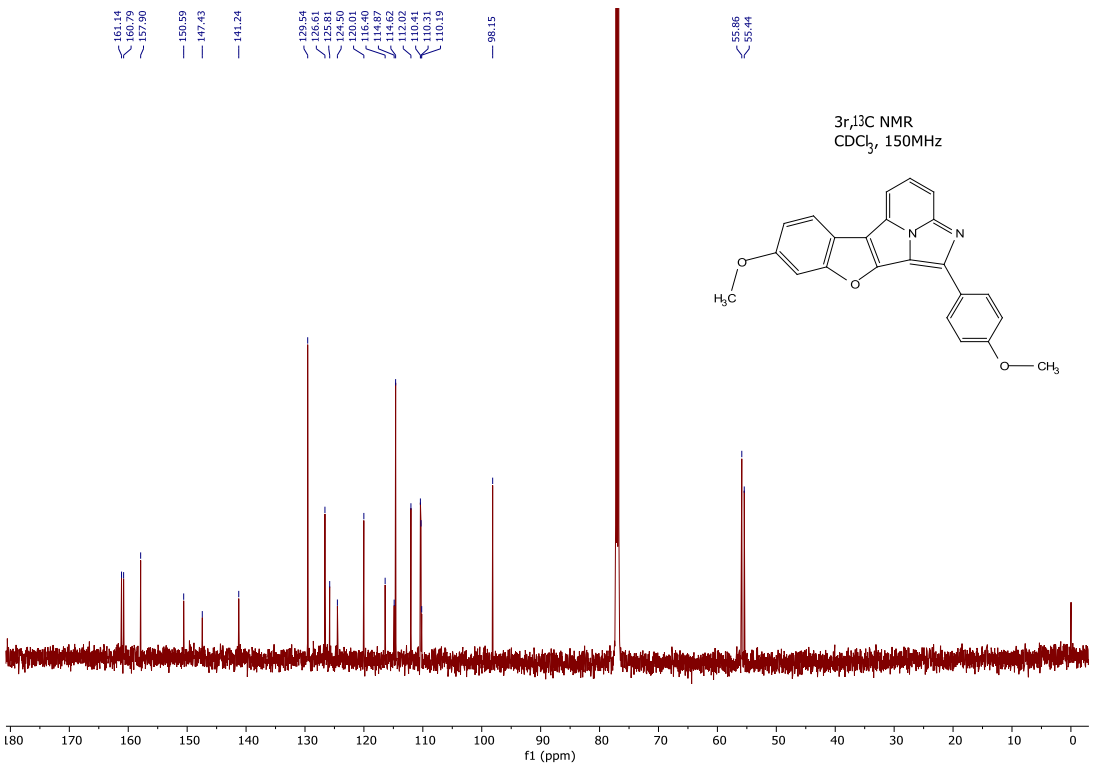
^{1}H NMR of **3q**



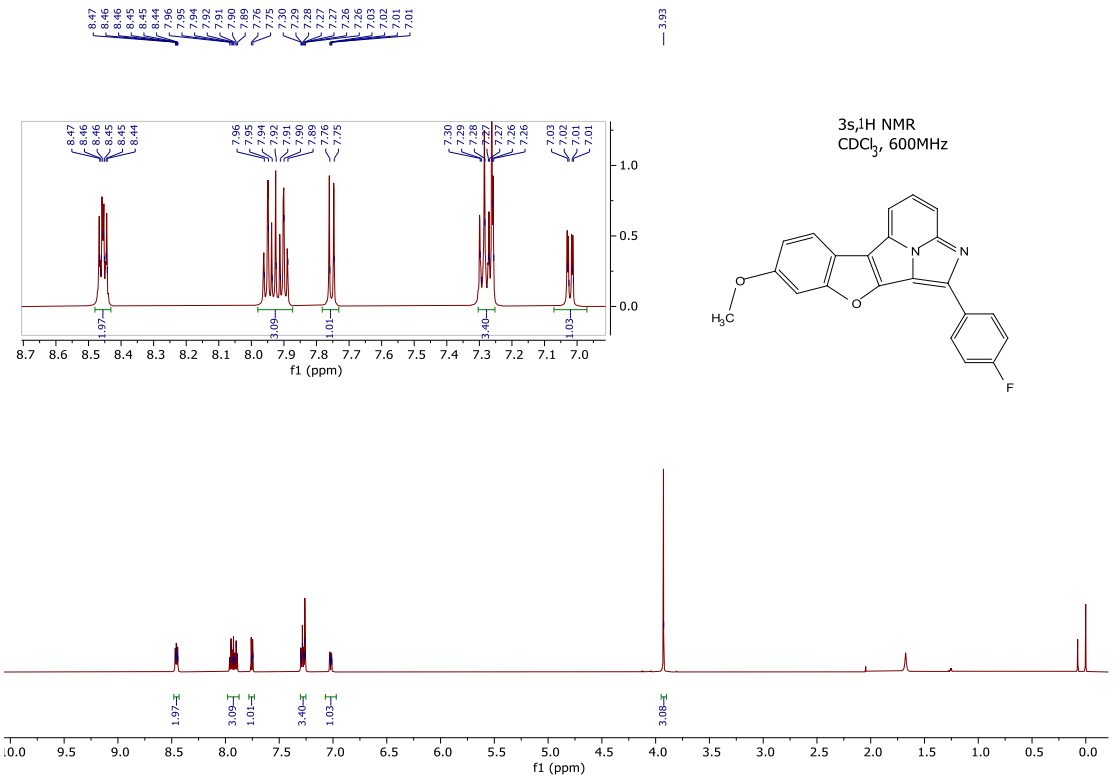
^{13}C NMR of **3q**



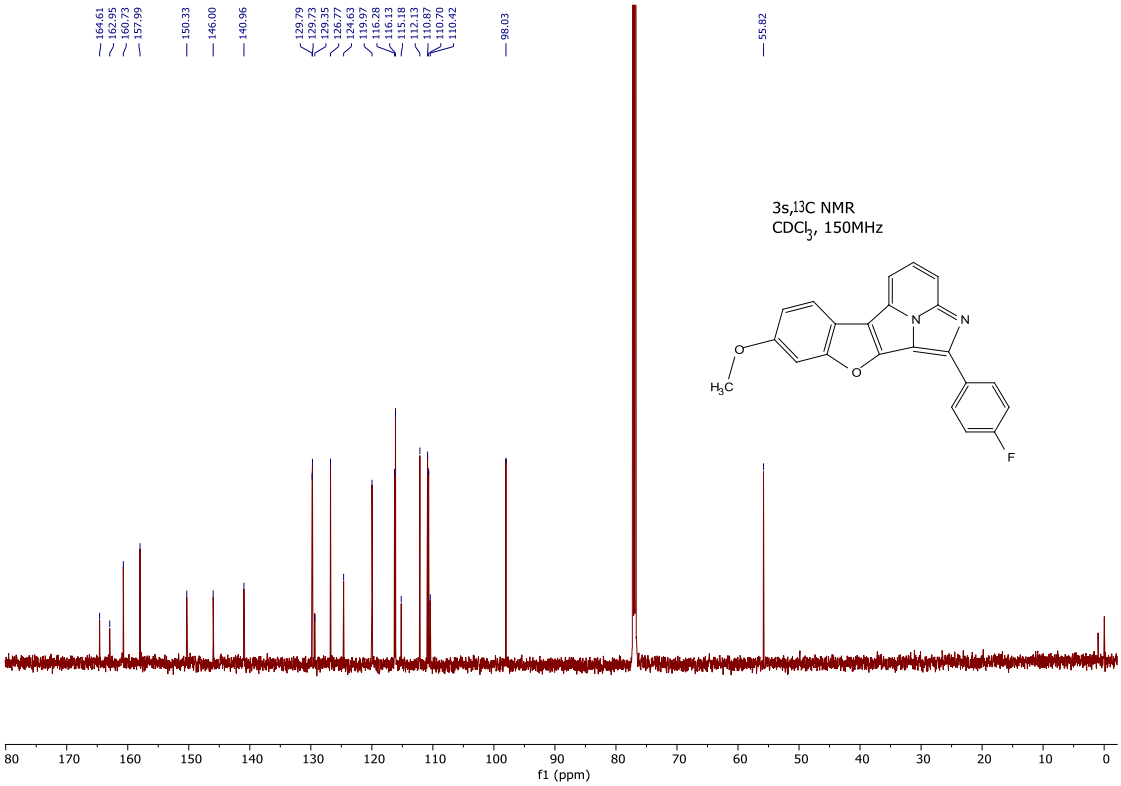
^{1}H NMR of **3r**



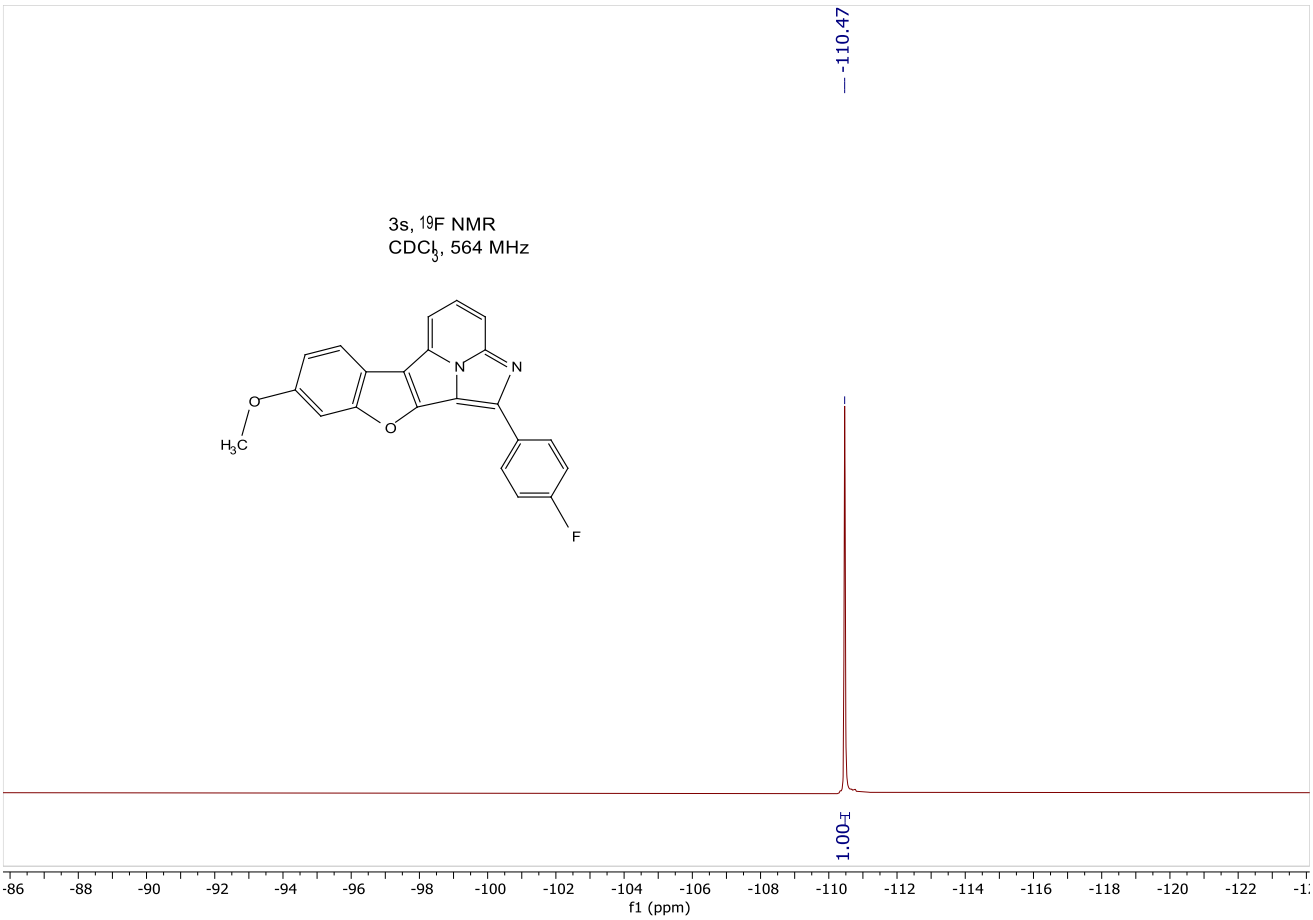
^{13}C NMR of **3r**



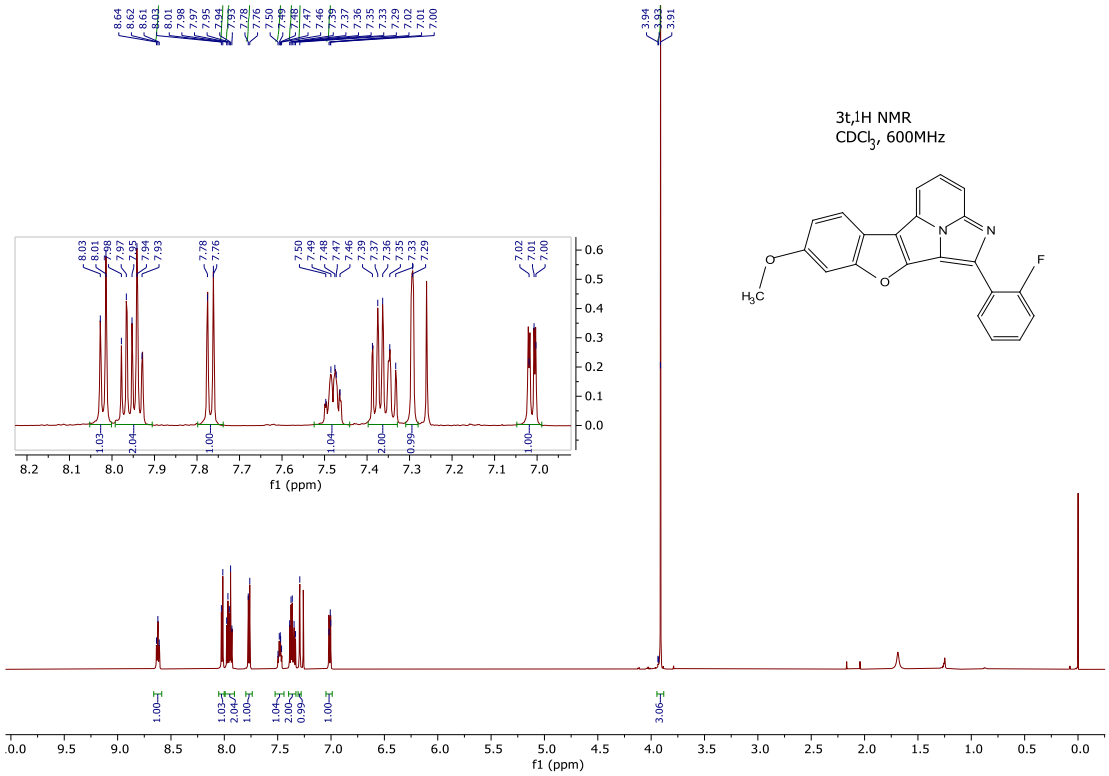
^{1}H NMR of **3s**



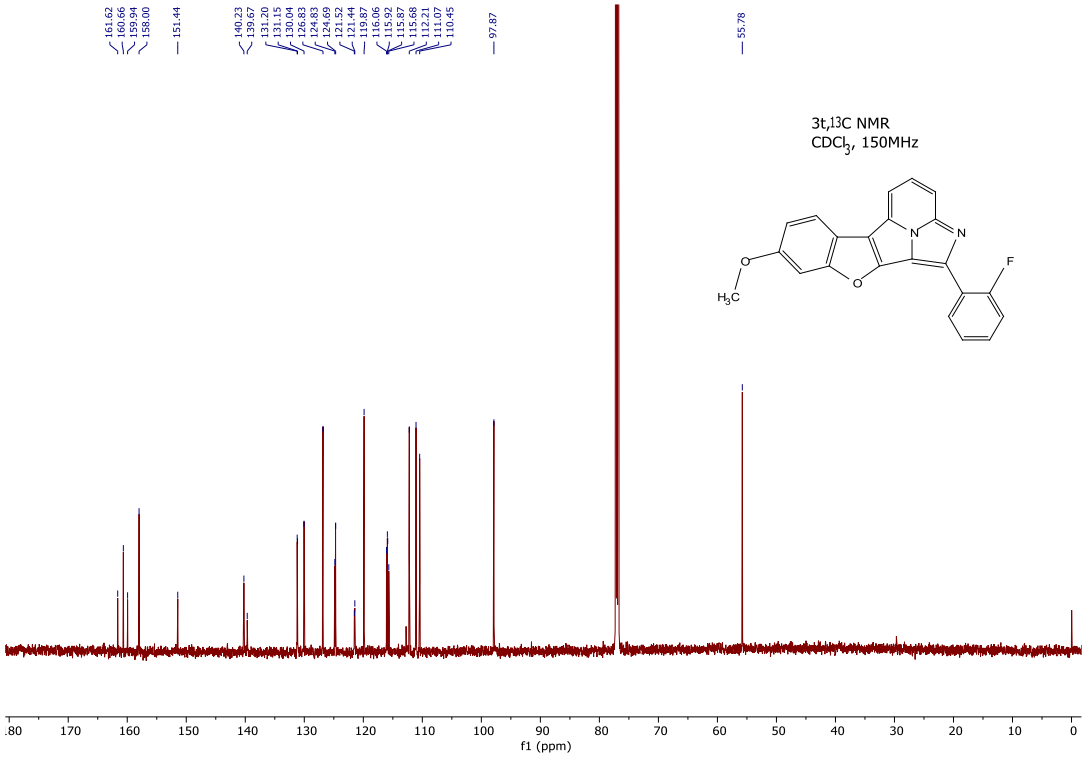
^{13}C NMR of **3s**


-110.47
3s, 19F NMR
CDCl3, 564 MHz
O
H3C
O
N
N
F
1.00
-86
-88
-90
-92
-94
-96
-98
-100
-102
-104
-106
-108
-110
-112
-114
-116
-118
-120
-122
f1 (ppm)

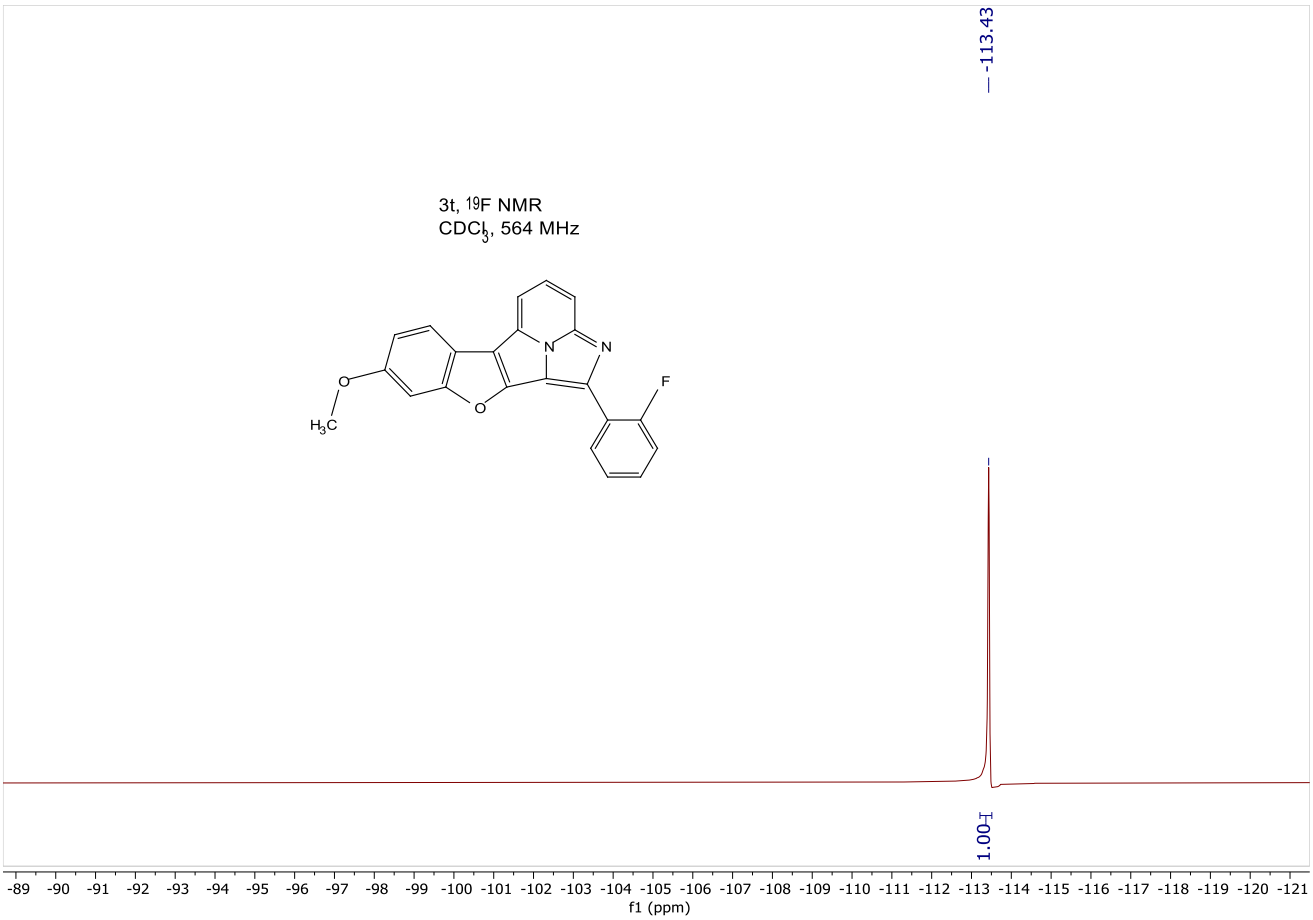
^{19}F NMR of **3s**



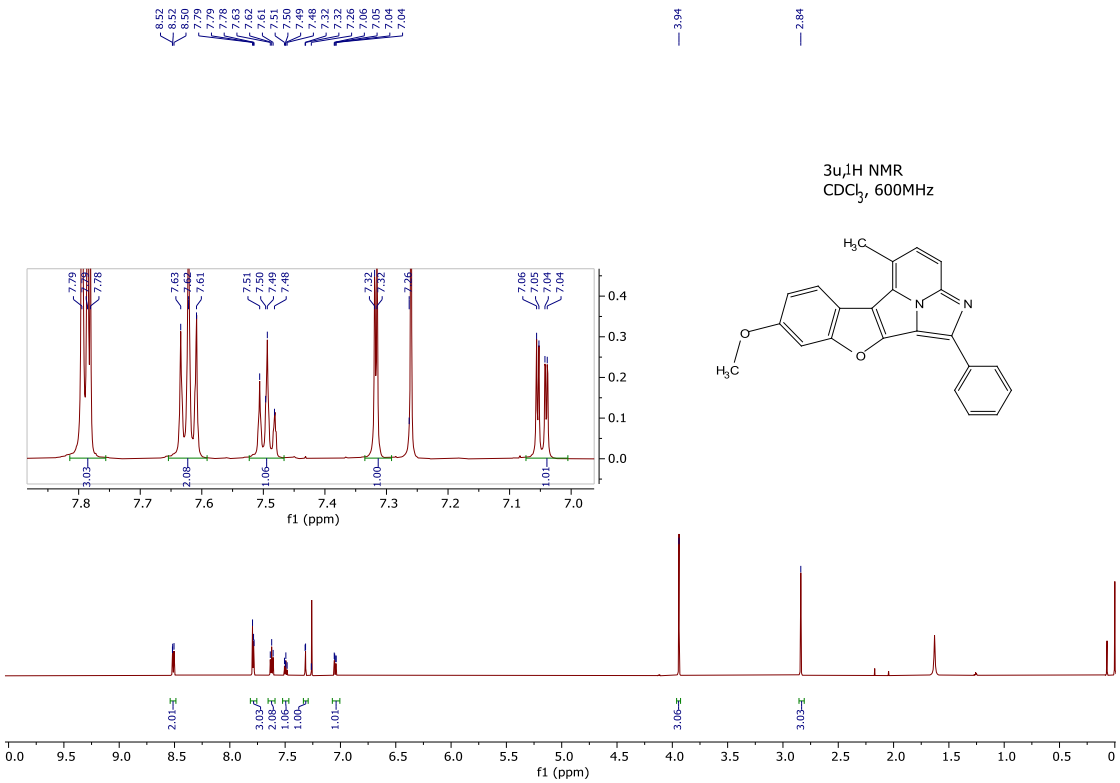
^{1}H NMR of **3t**



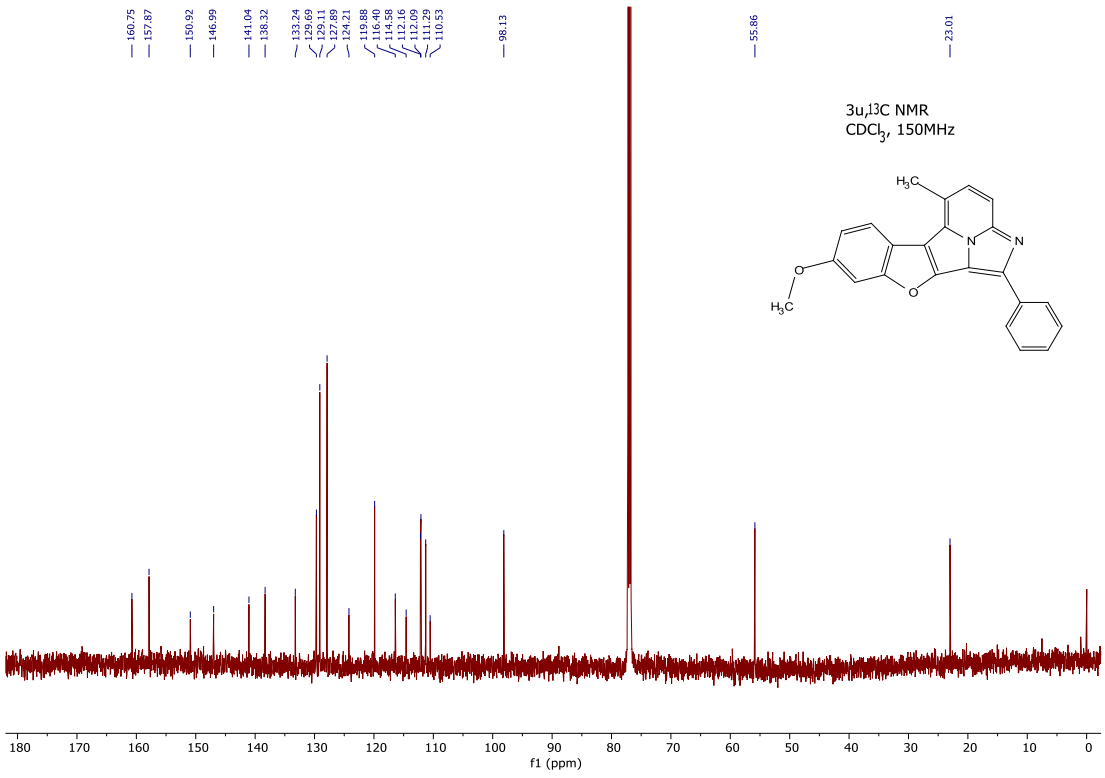
^{13}C NMR of **3t**


-113.43
3t, 19F NMR
CDCl3, 564 MHz
O
H3C
O
N
N
F
1.00
-89 -90 -91 -92 -93 -94 -95 -96 -97 -98 -99 -100 -101 -102 -103 -104 -105 -106 -107 -108 -109 -110 -111 -112 -113 -114 -115 -116 -117 -118 -119 -120 -121
f1 (ppm)

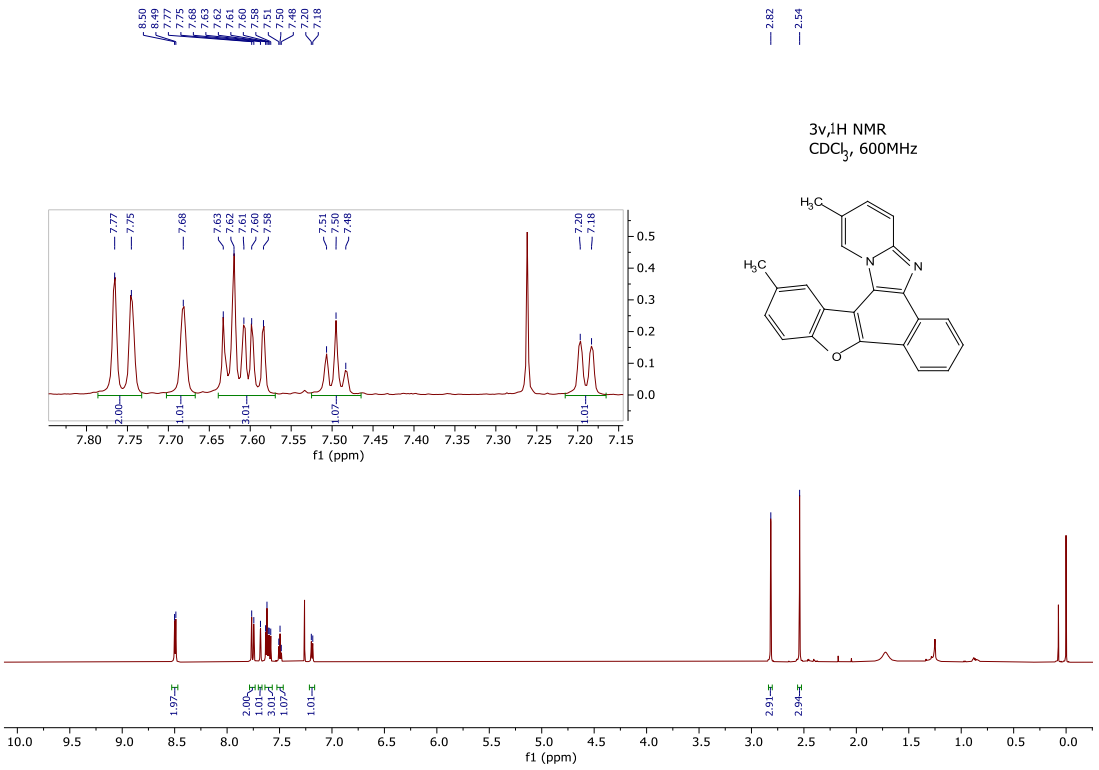
^{19}F NMR of **3t**



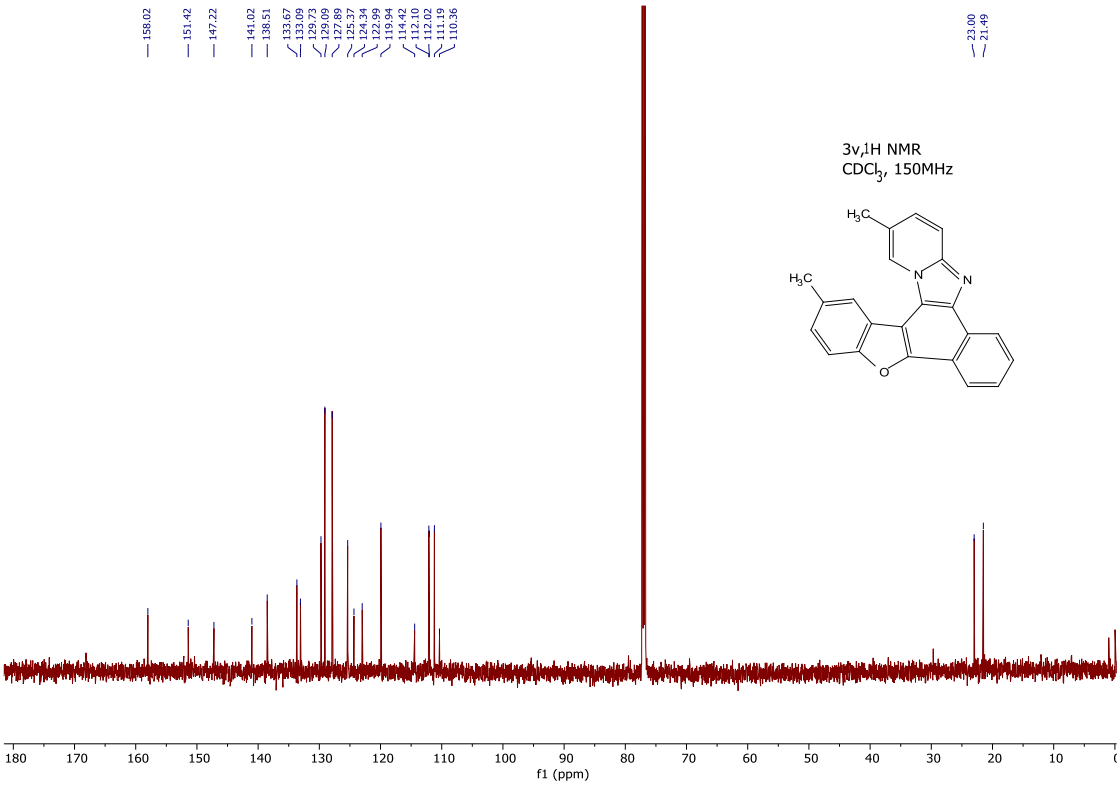
^{1}H NMR of **3u**



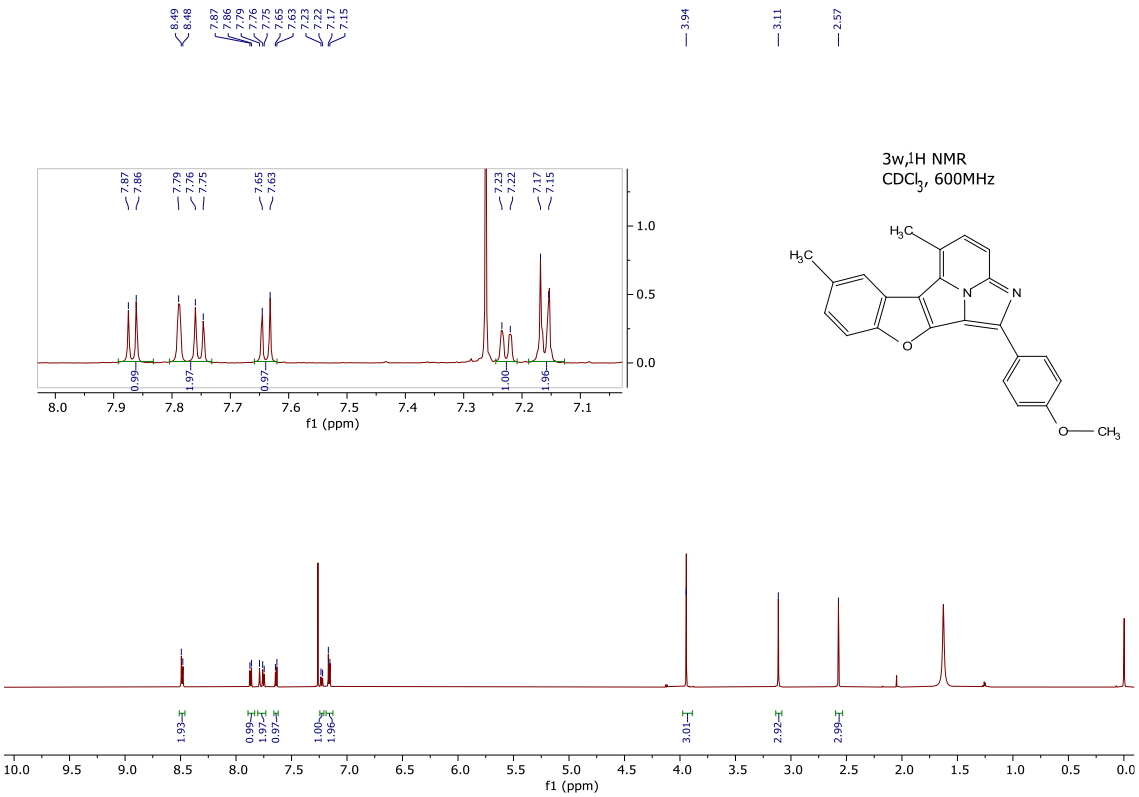
^{13}C NMR of **3u**



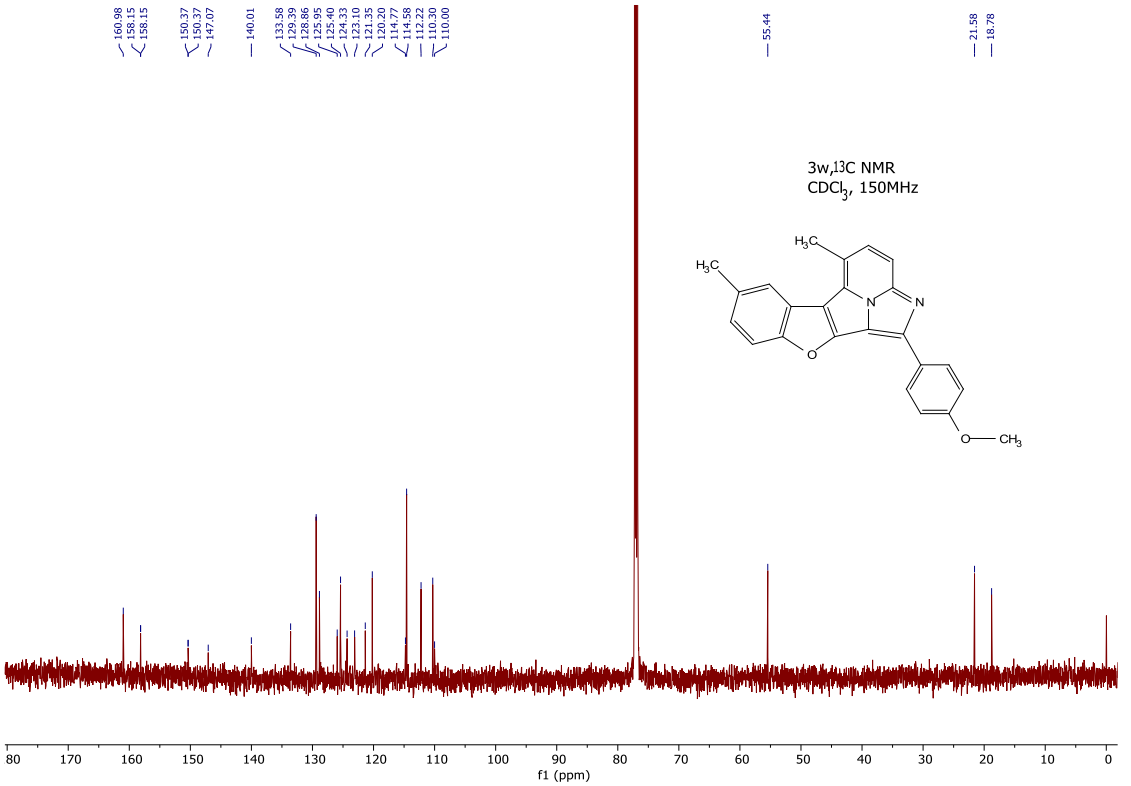
^{1}H NMR of **3v**



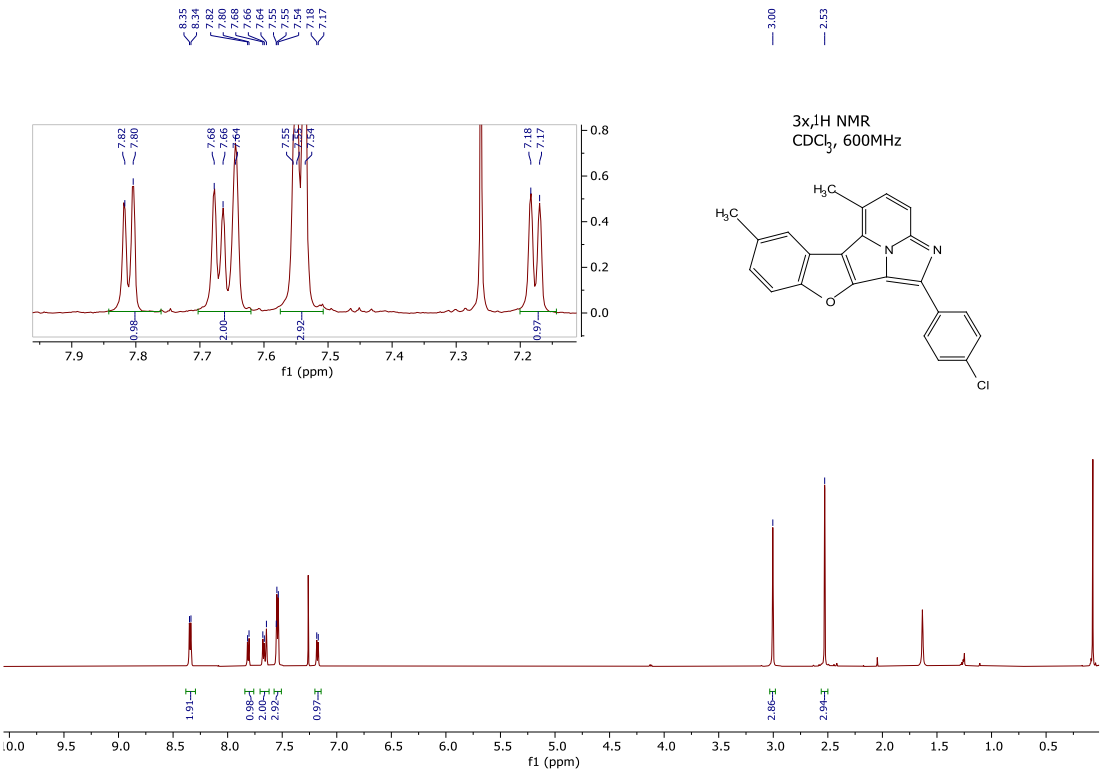
^{13}C NMR of **3v**



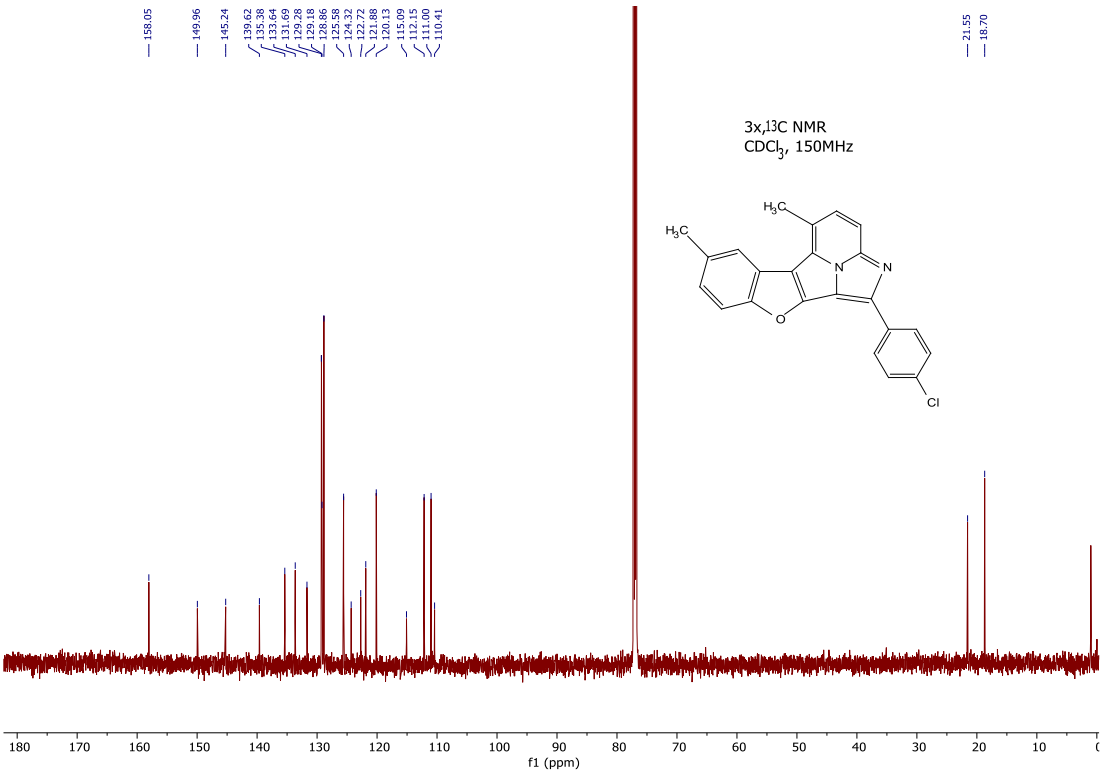
^{1}H NMR of **3w**



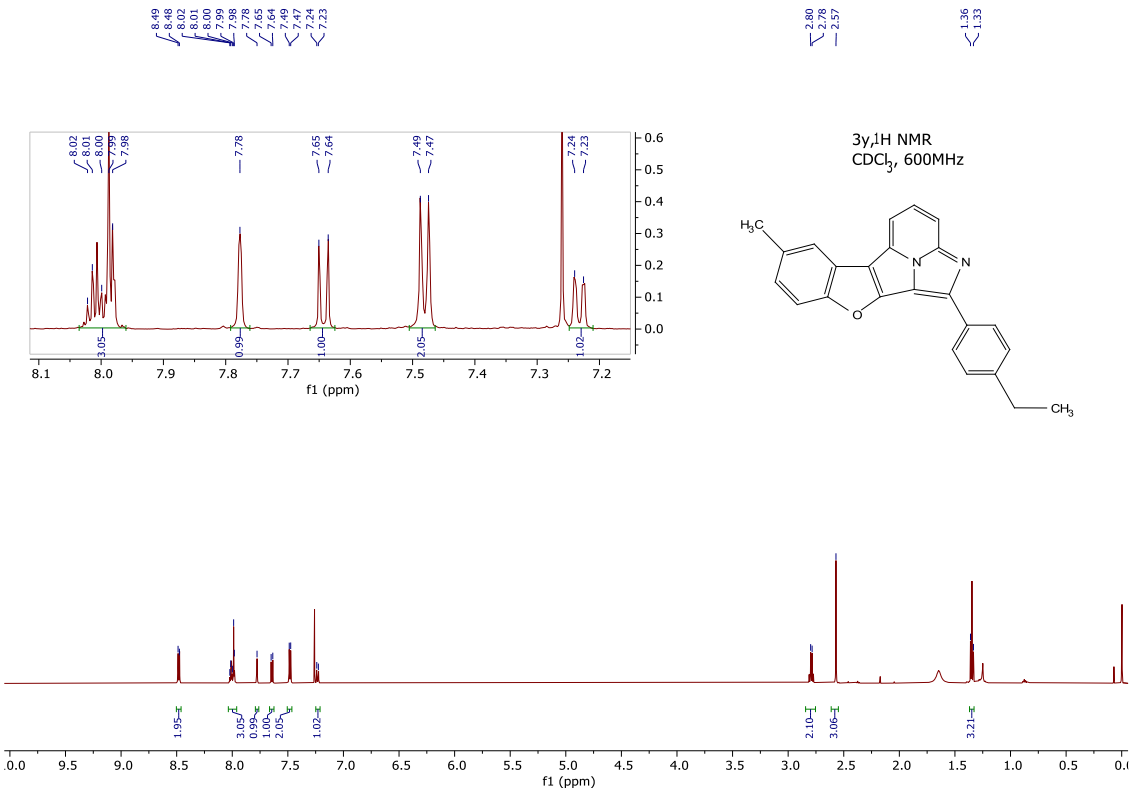
^{13}C NMR of **3w**



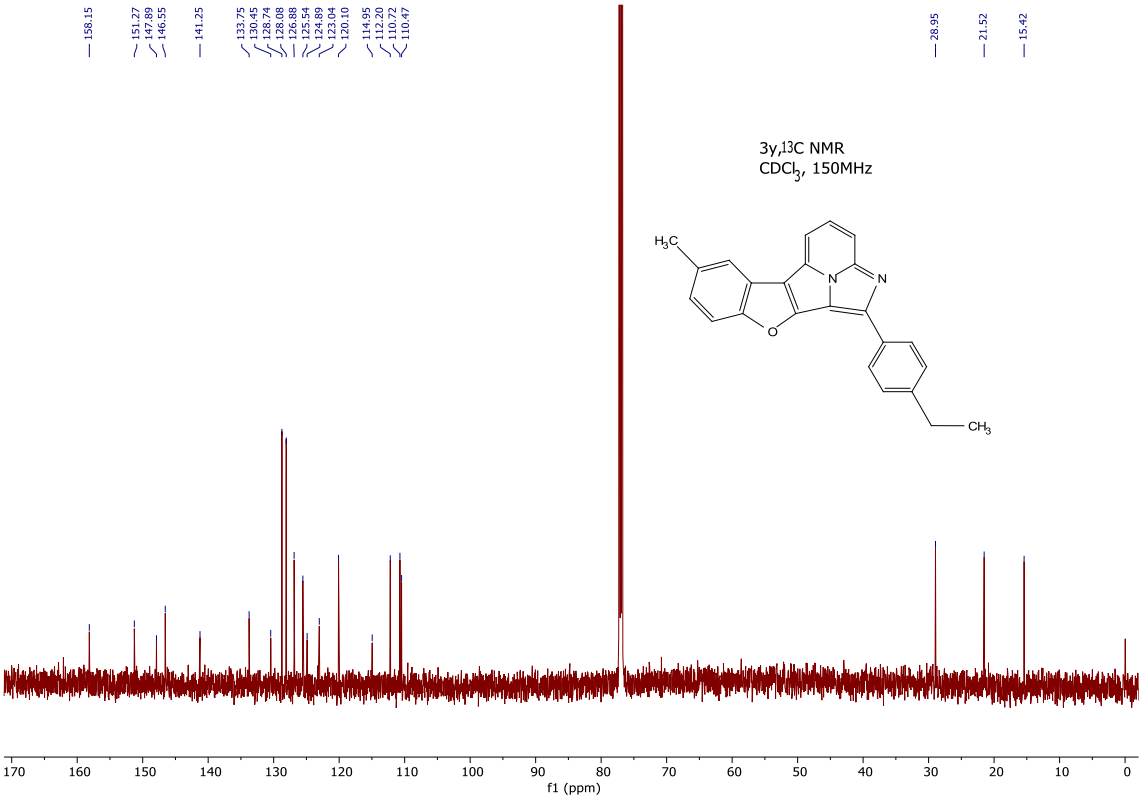
^{1}H NMR of **3x**



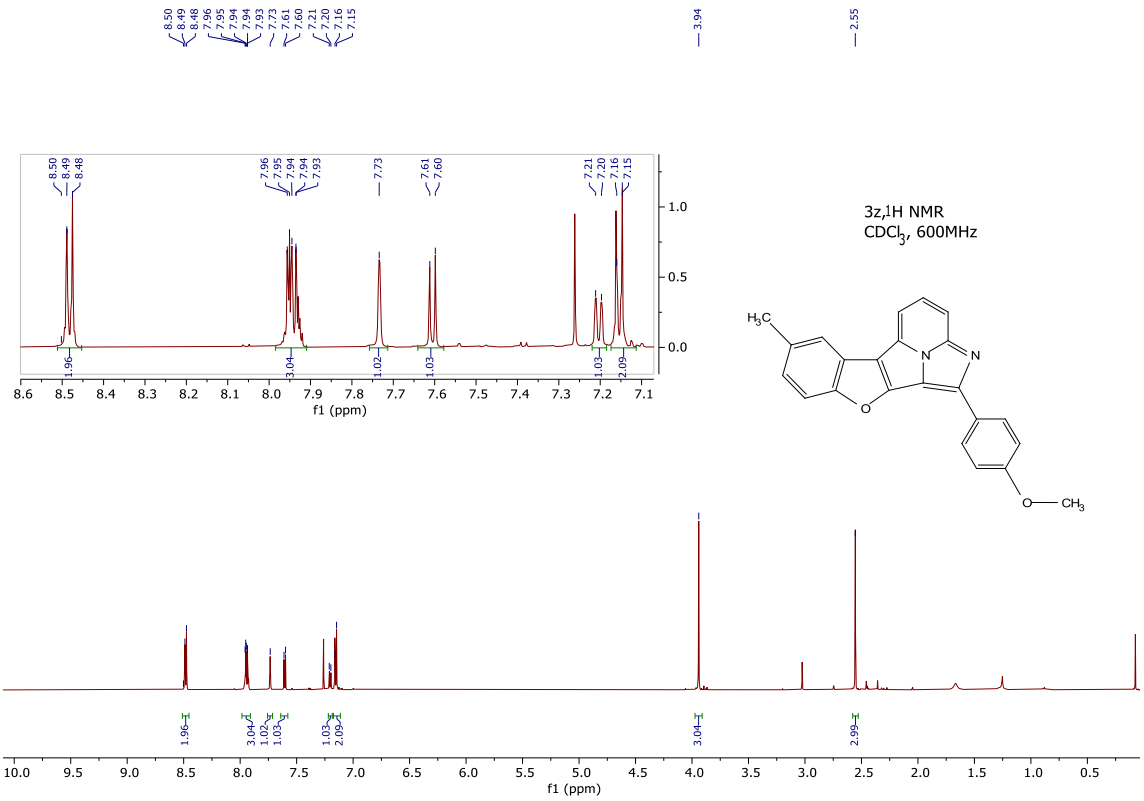
^{13}C NMR of **3x**



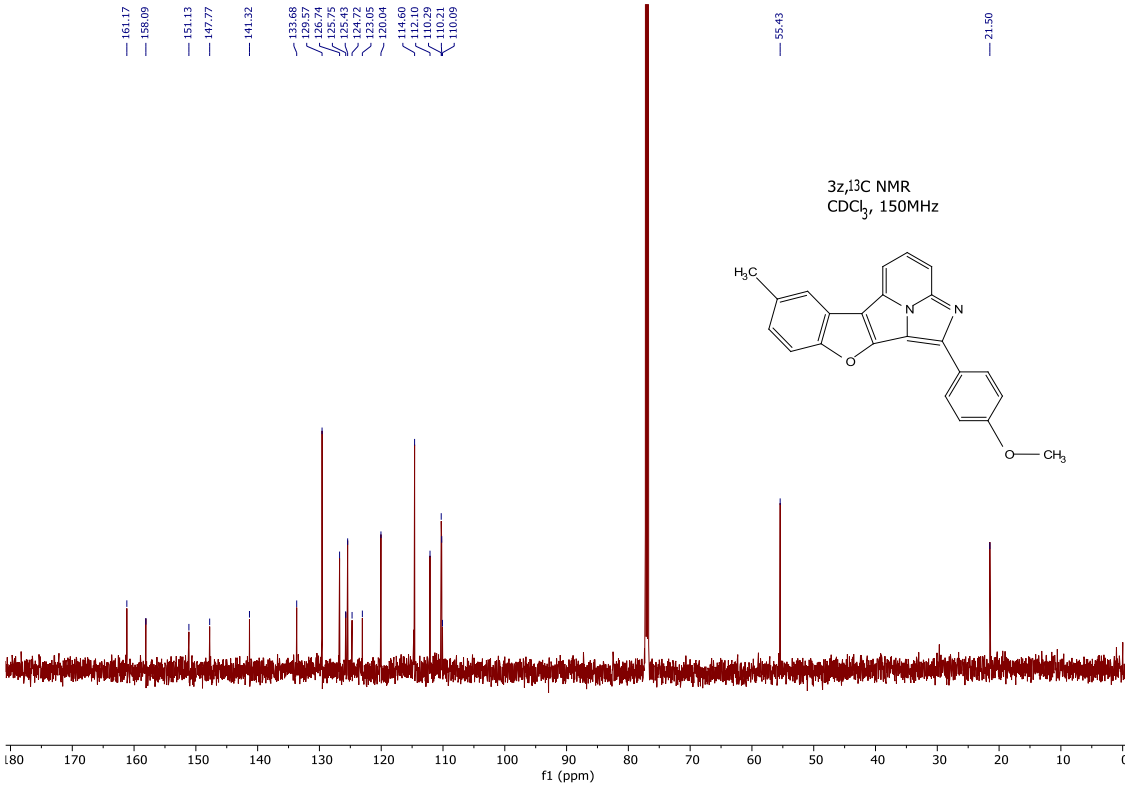
^{1}H NMR of **3y**



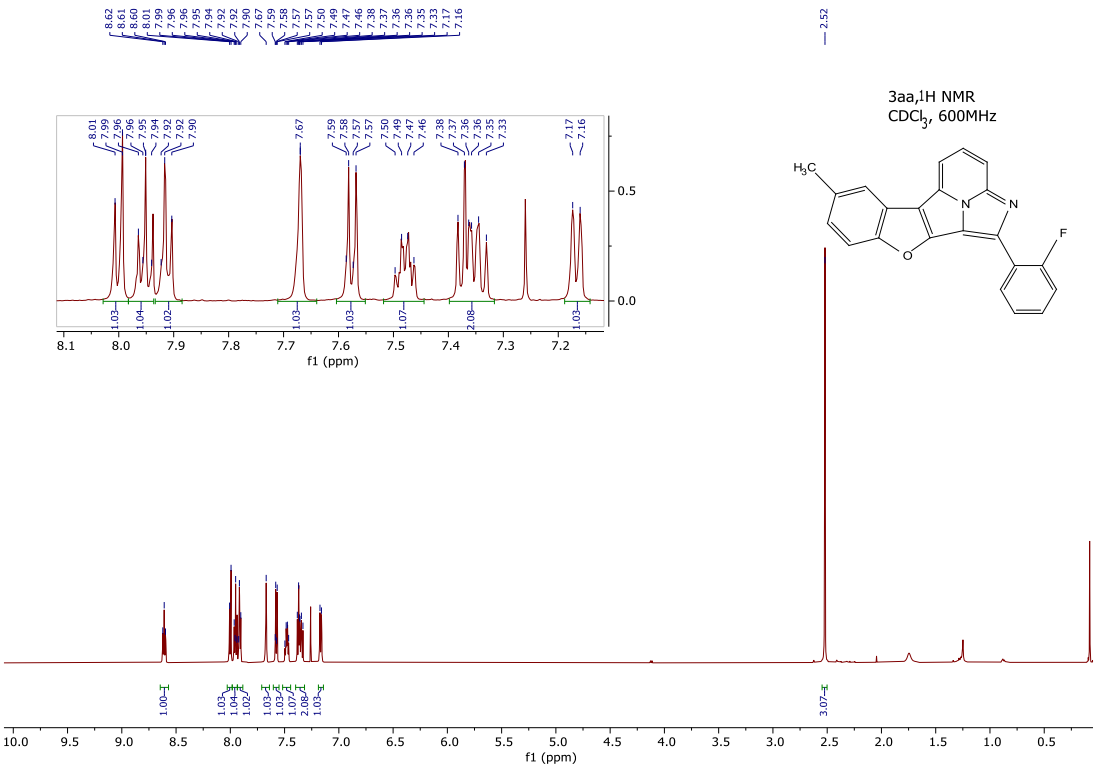
^{13}C NMR of **3y**



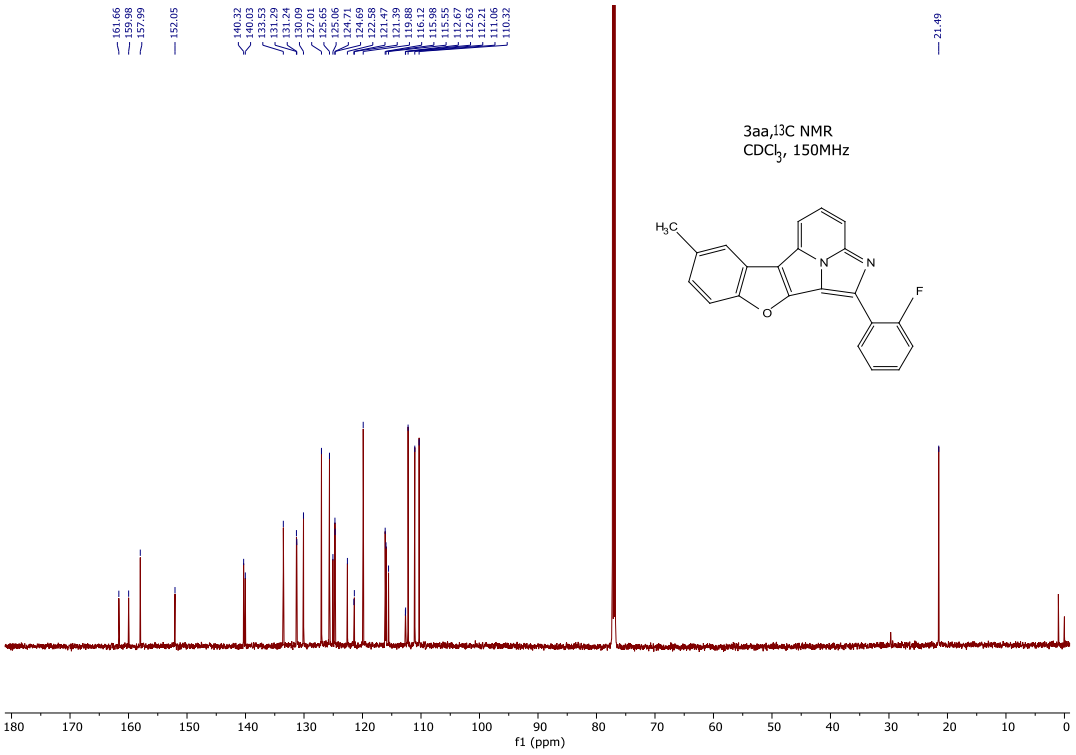
^{1}H NMR of **3z**



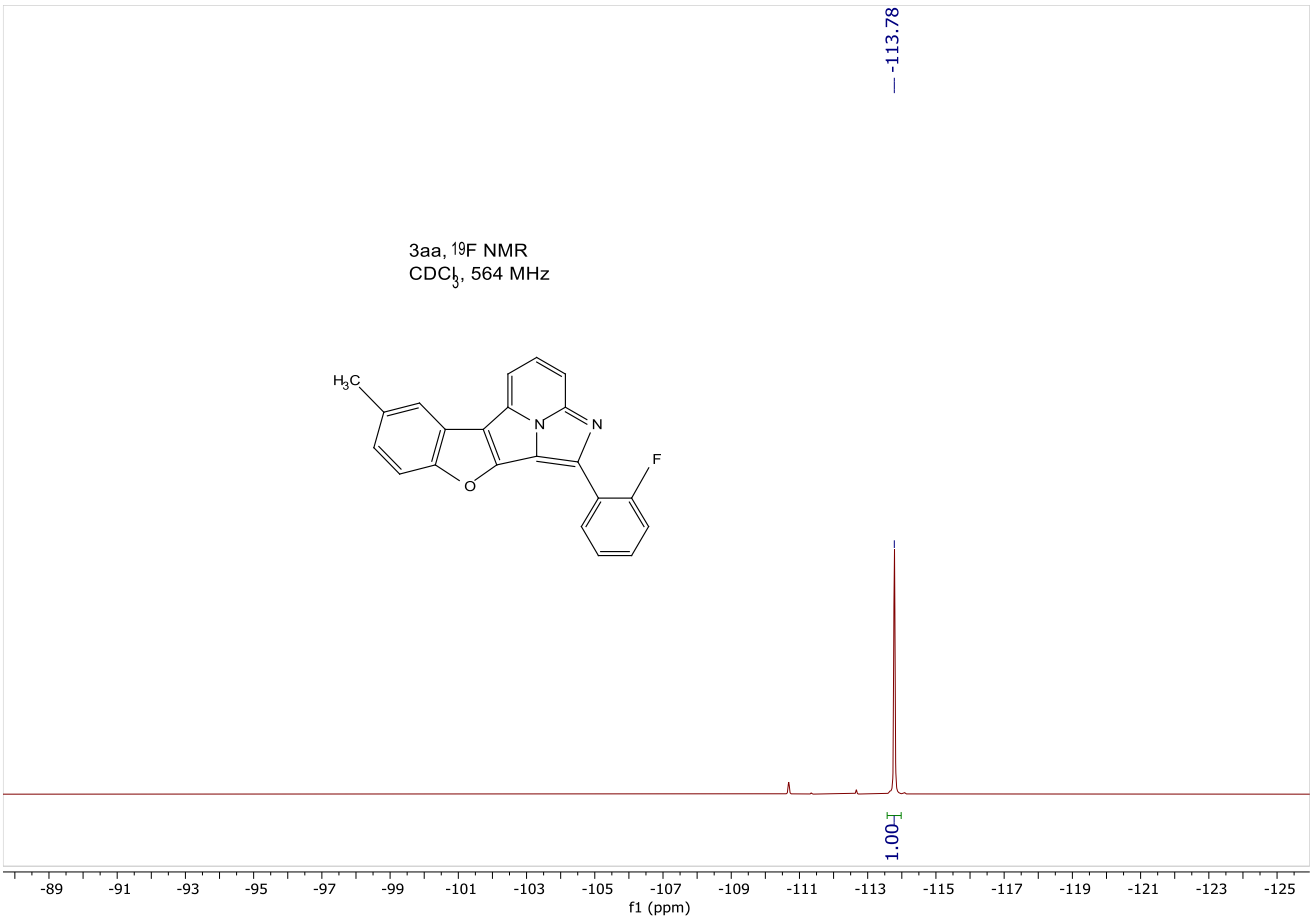
^{13}C NMR of **3z**



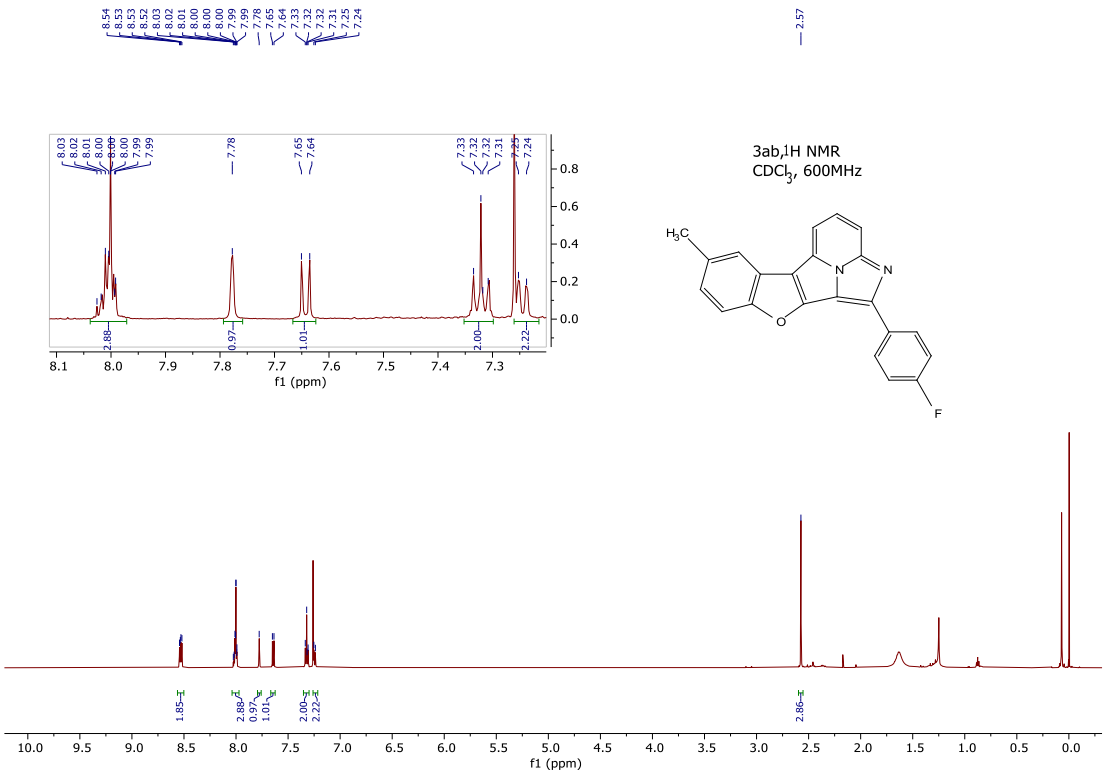
^{1}H NMR of **3aa**



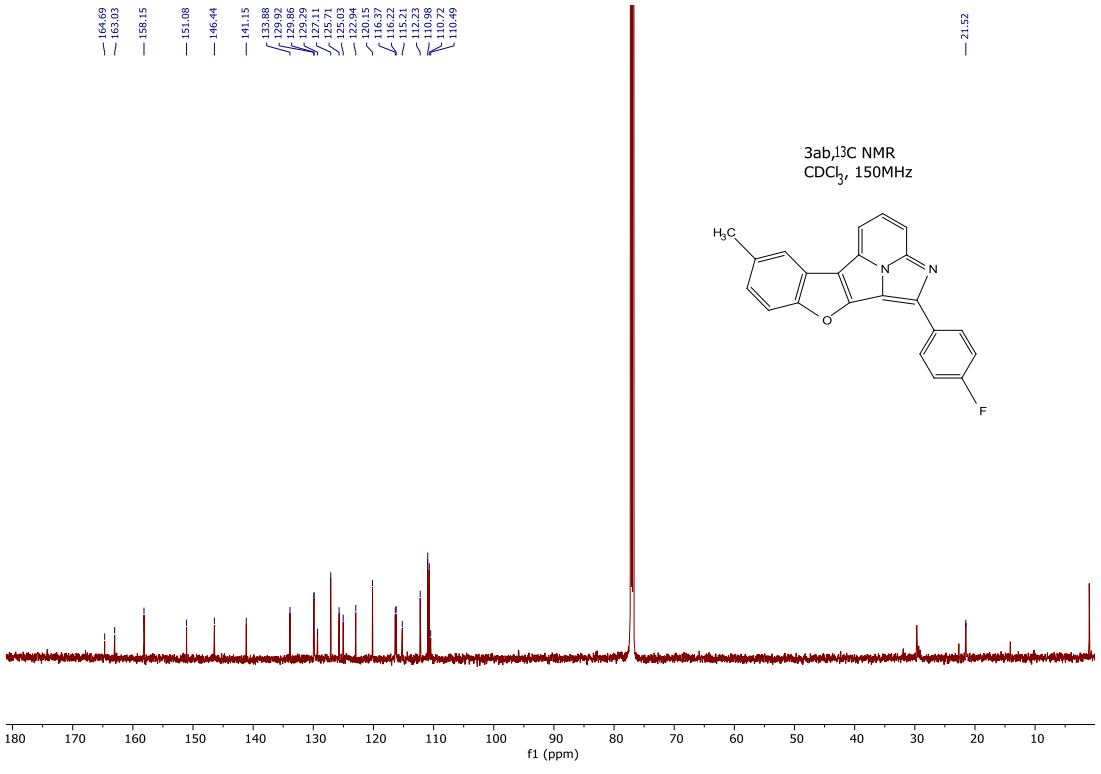
^{13}C NMR of **3aa**



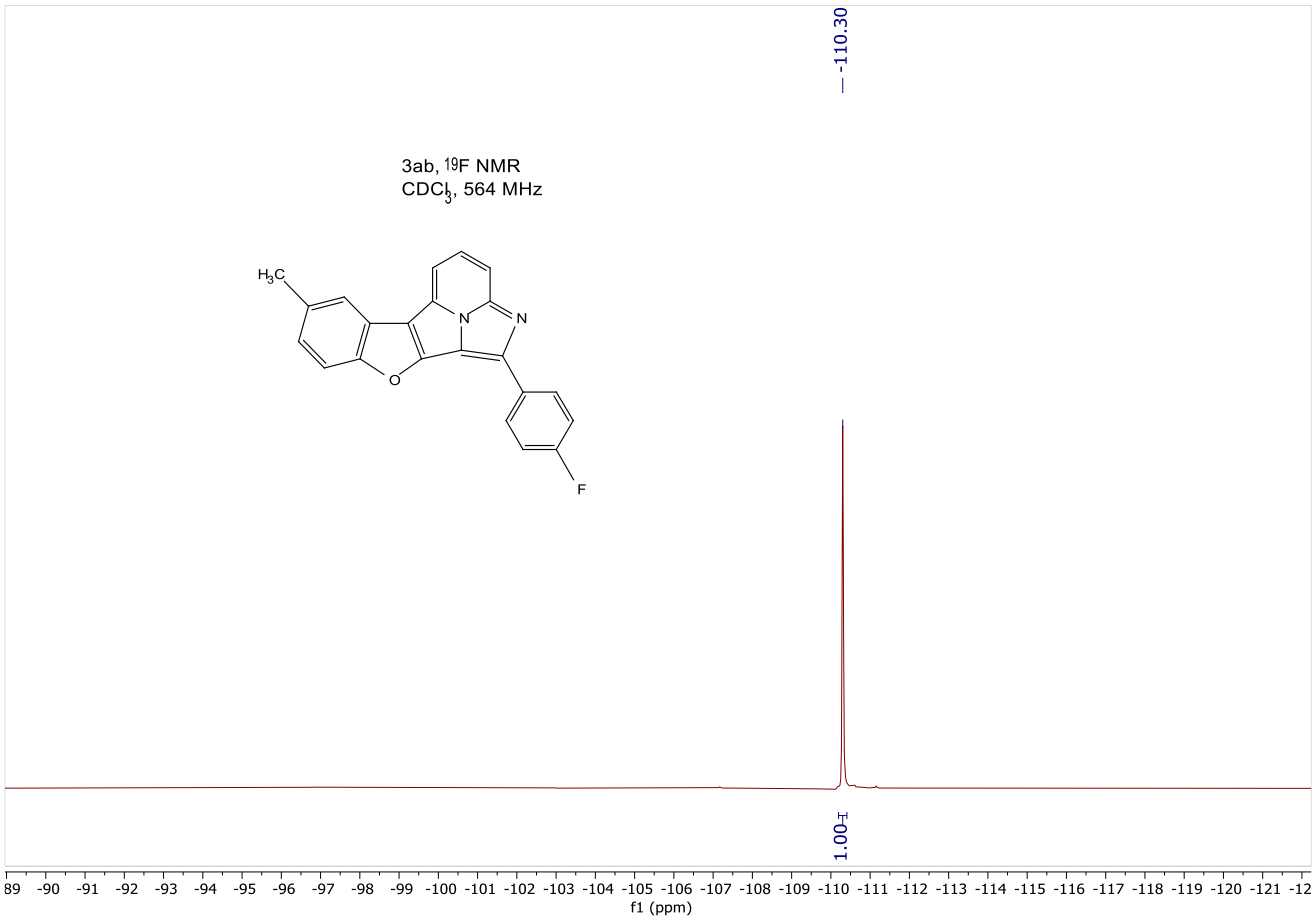
^{19}F NMR of **3aa**



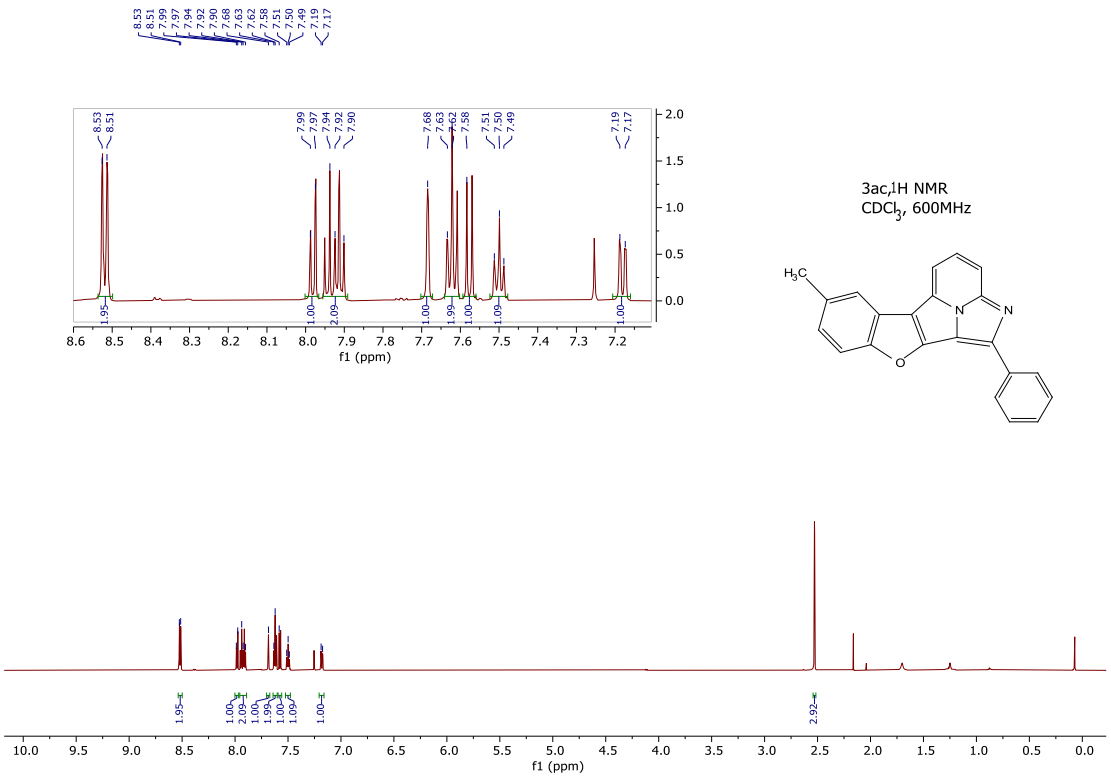
^{1}H NMR of **3ab**



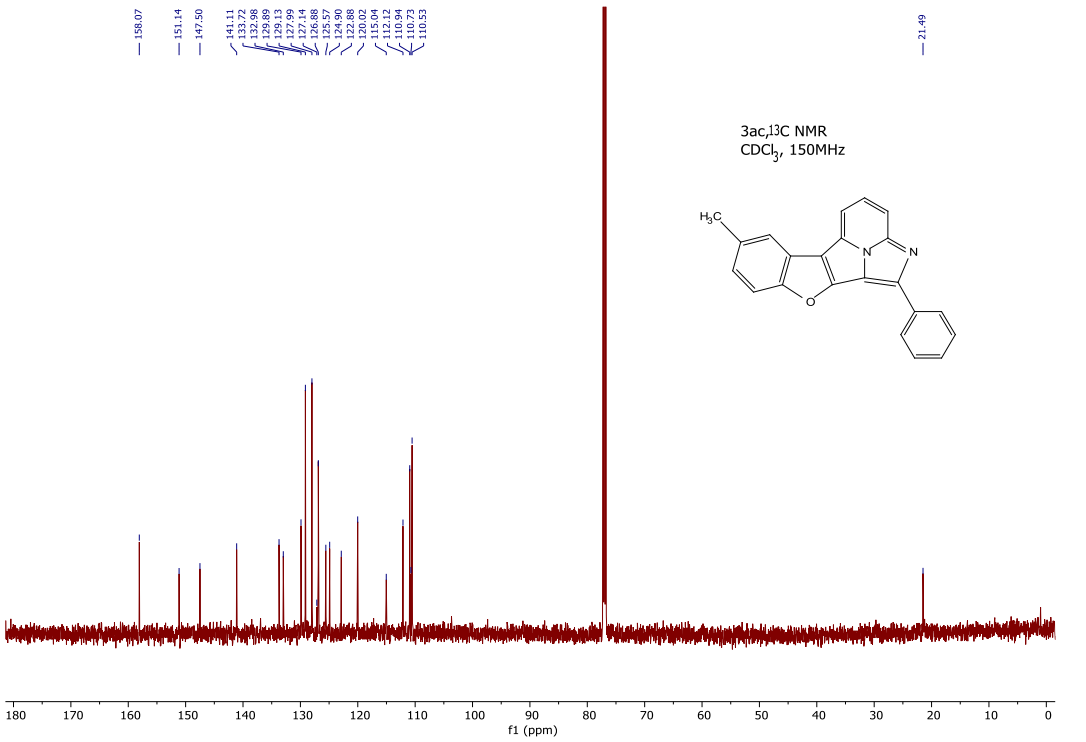
^{13}C NMR of **3ab**



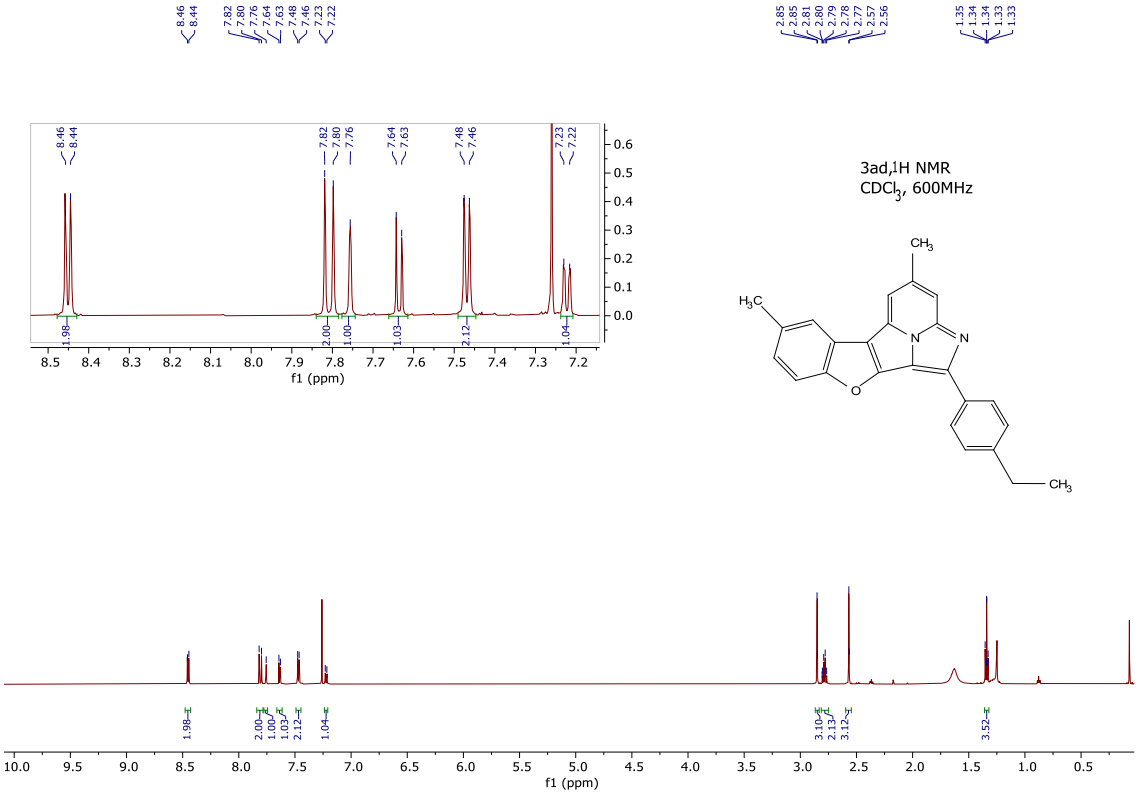
19F NMR of **3ab**



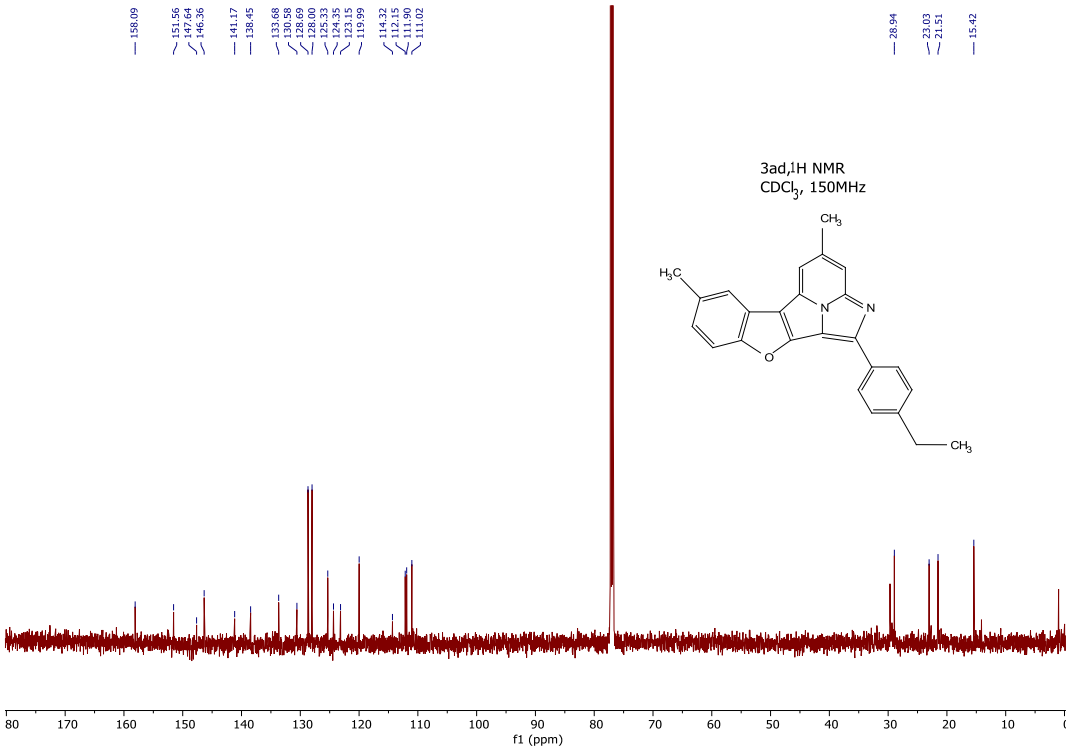
^{1}H NMR of **3ac**



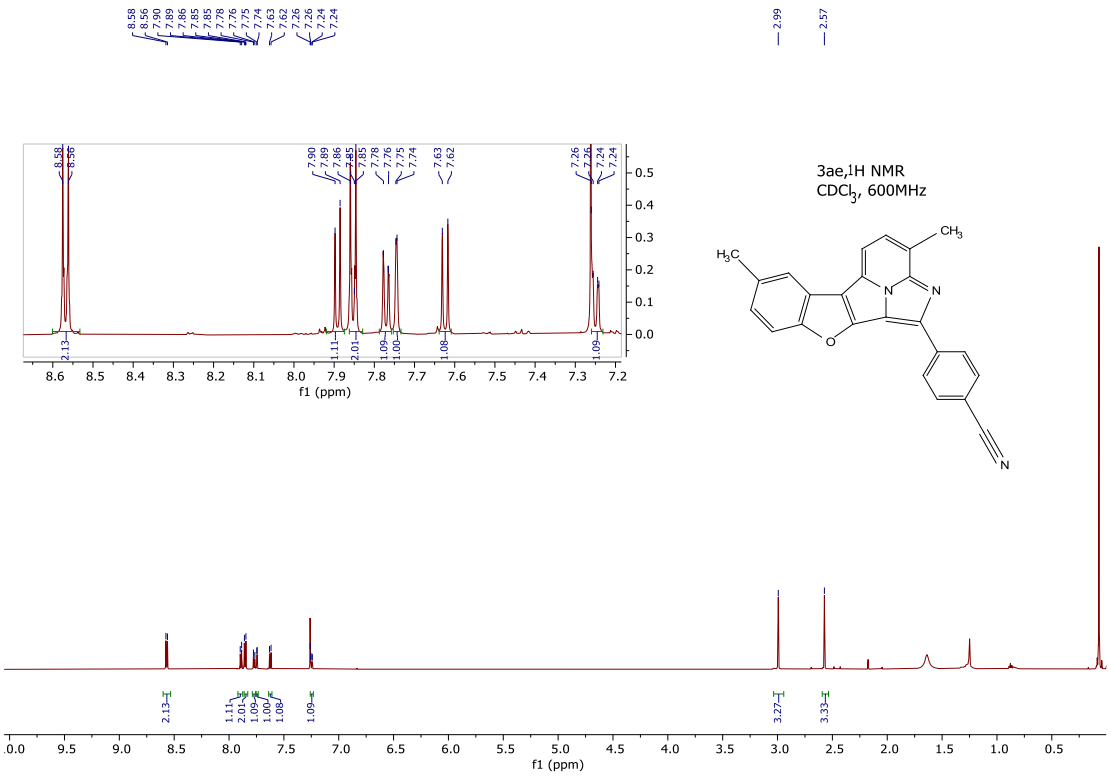
^{13}C NMR of **3ac**



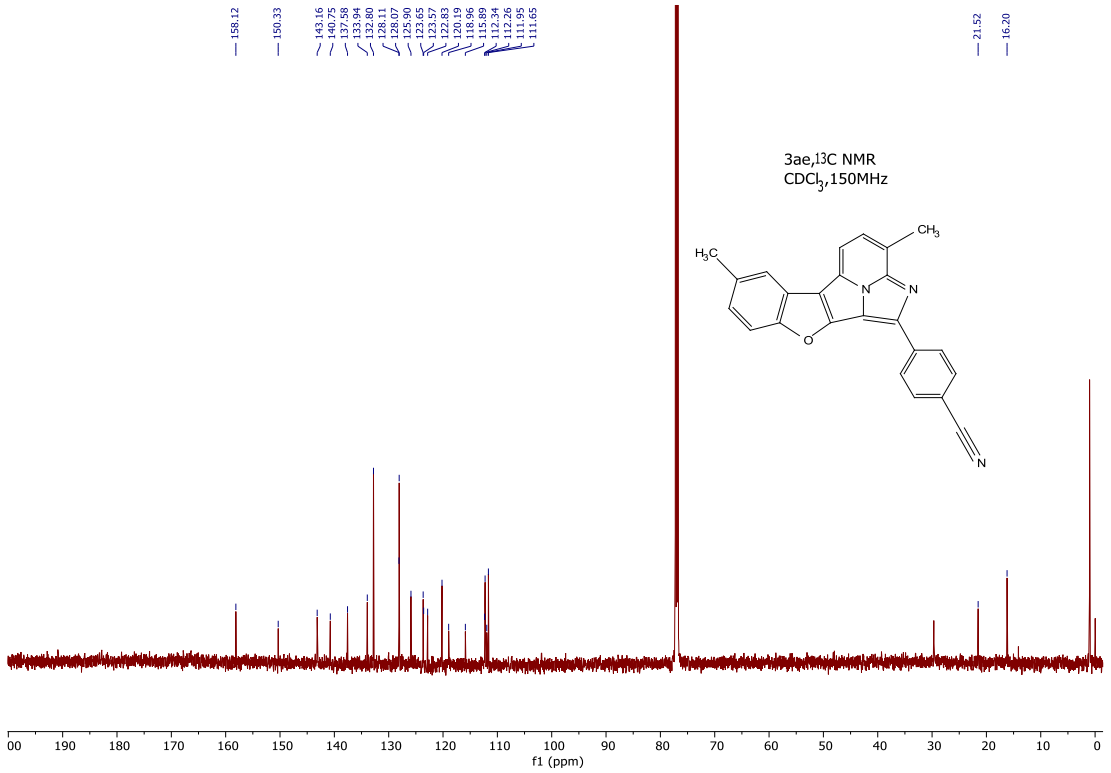
^{1}H NMR of **3ad**



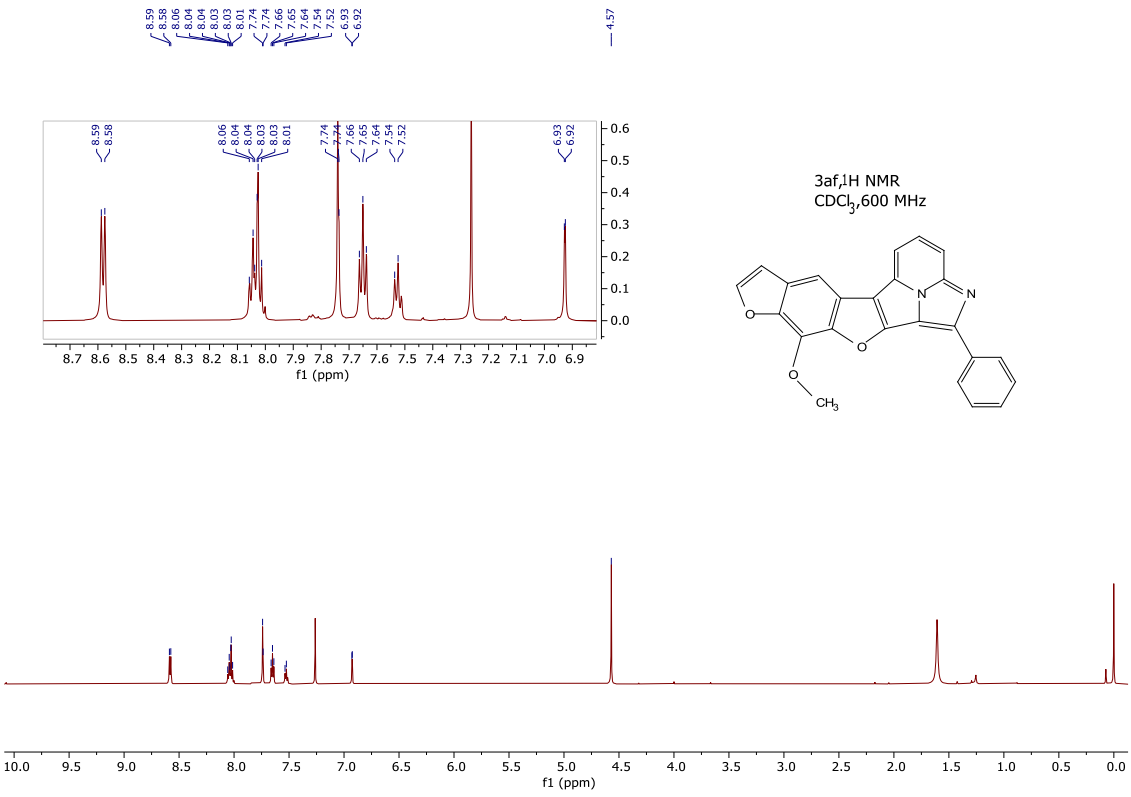
^{13}C NMR of **3ad**



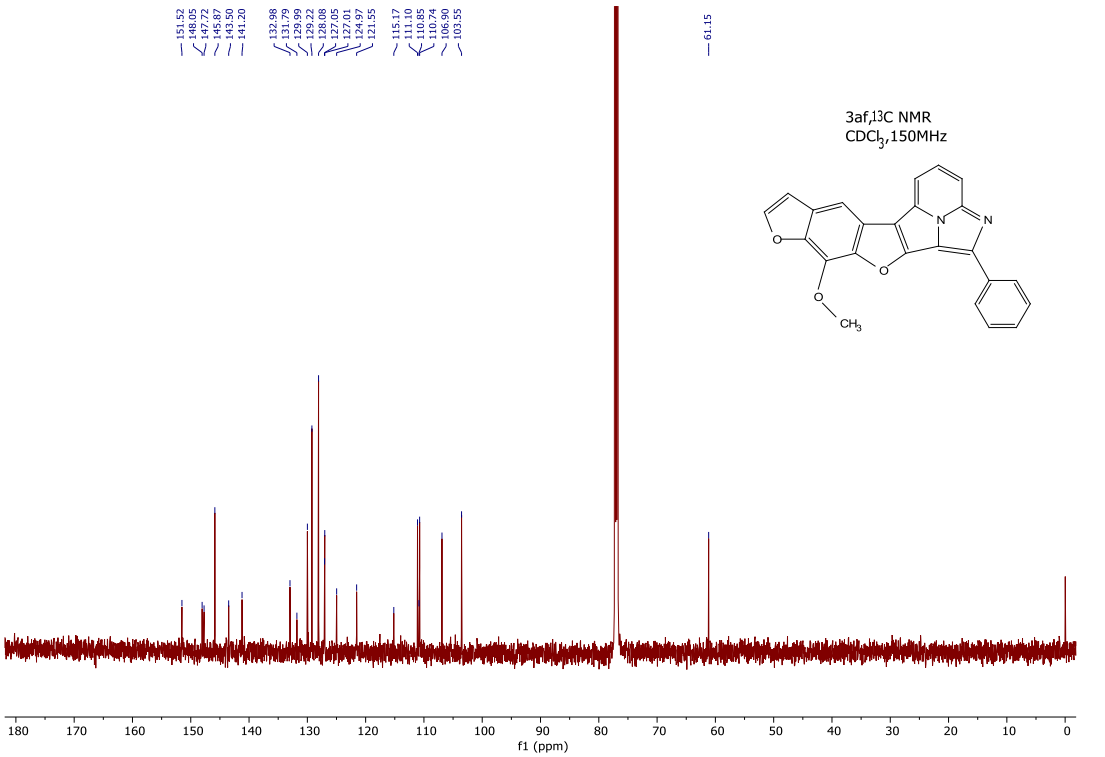
^{1}H NMR of **3ae**



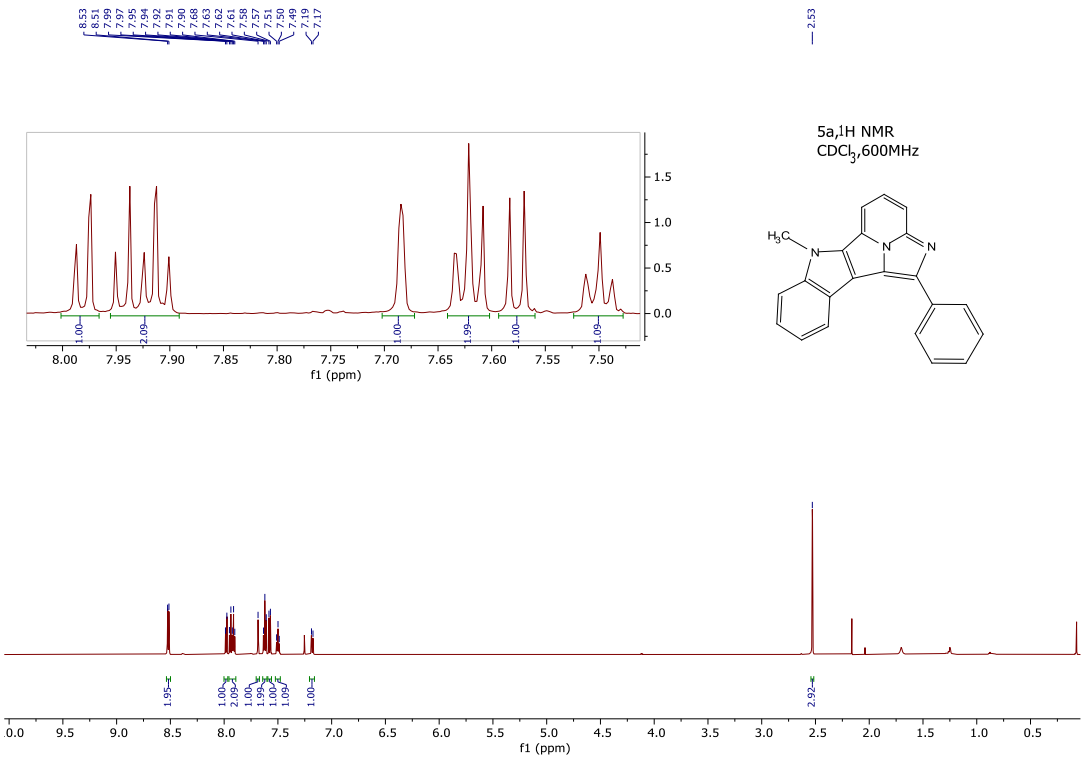
^{13}C NMR of **3ae**



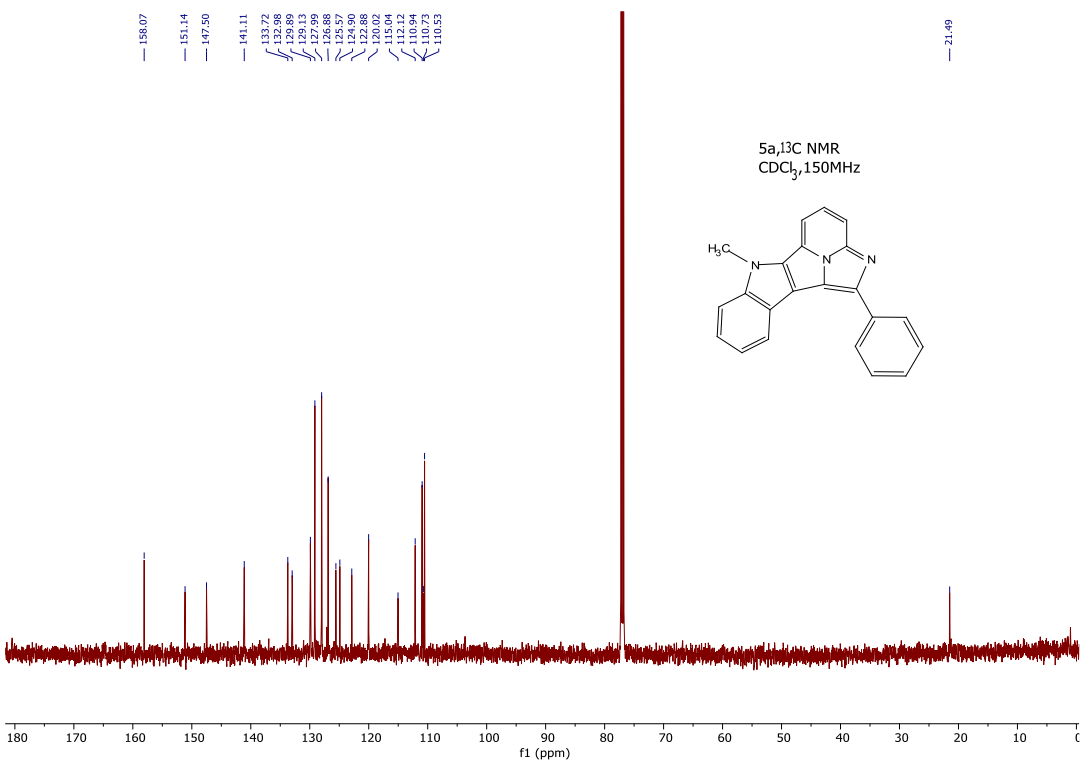
^{1}H NMR of **3af**



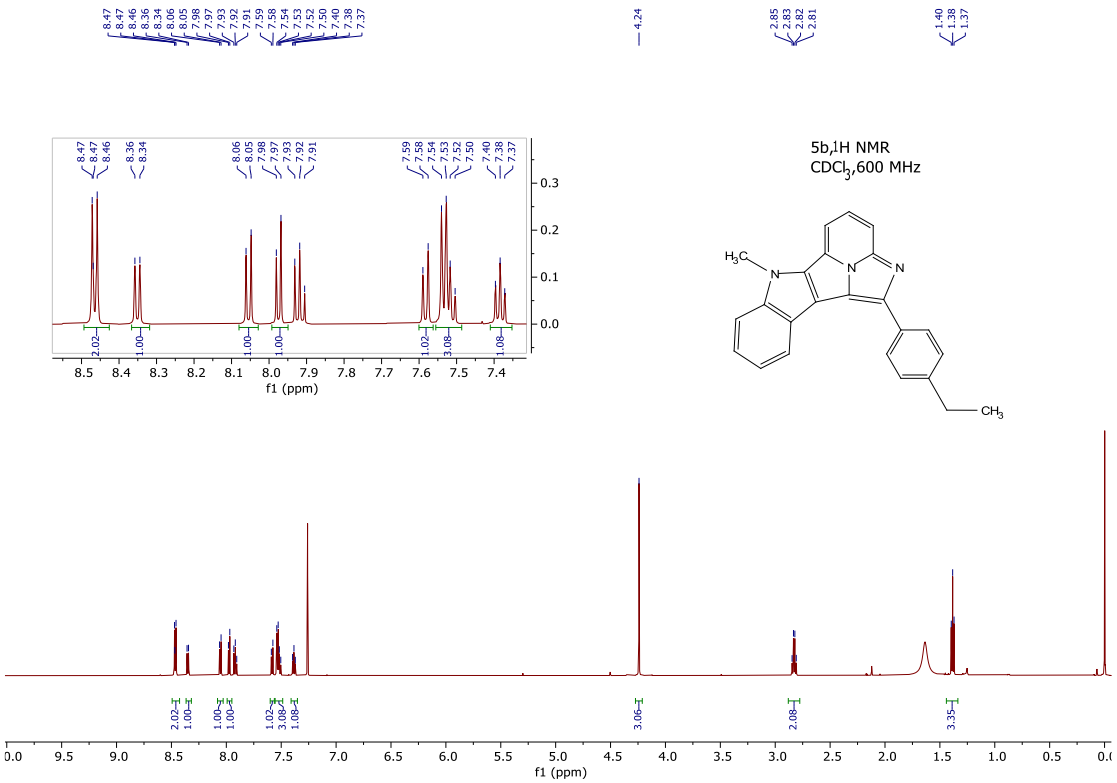
^{13}C NMR of **3af**



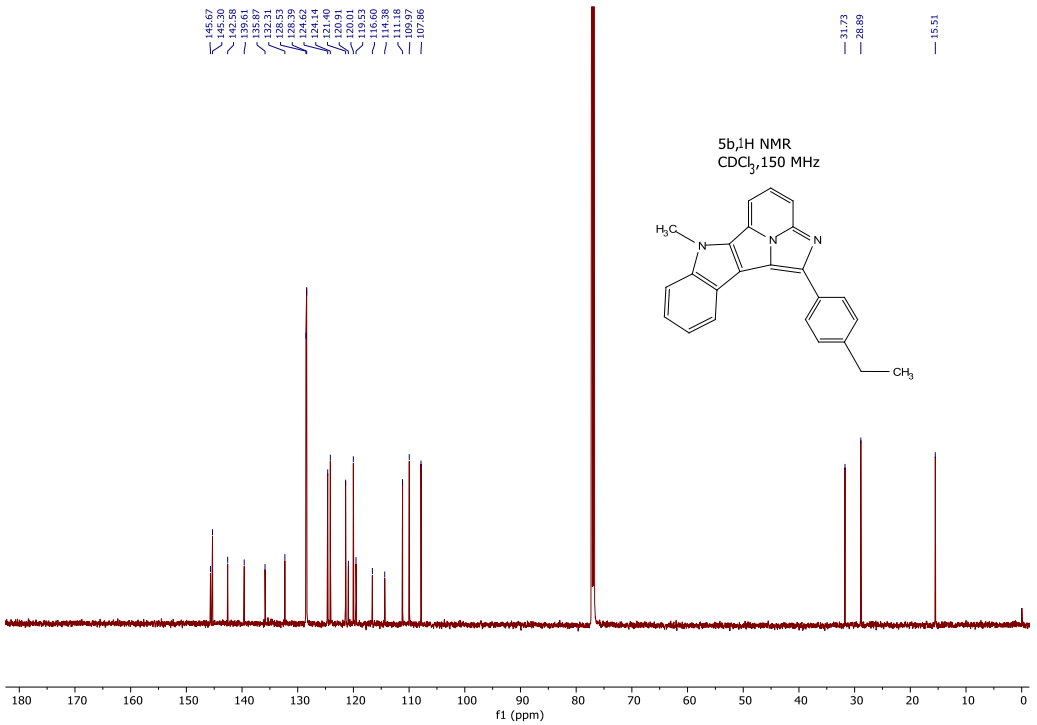
^{1}H NMR of **5a**



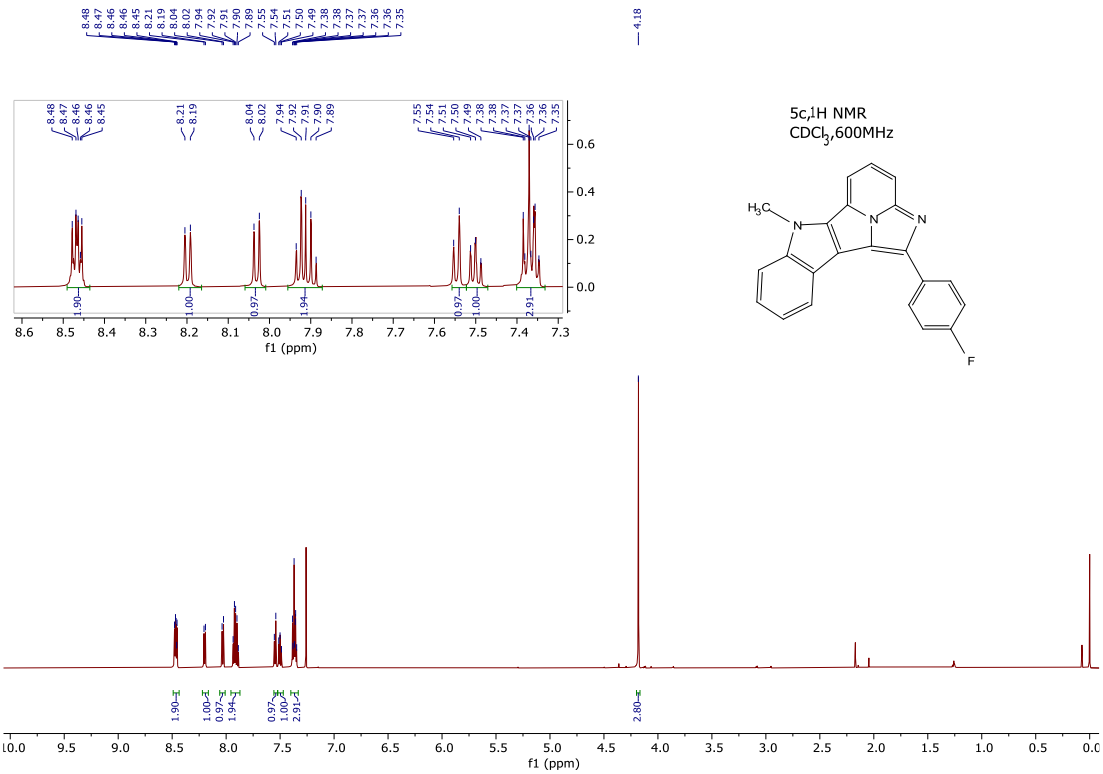
^{13}C NMR of **5a**



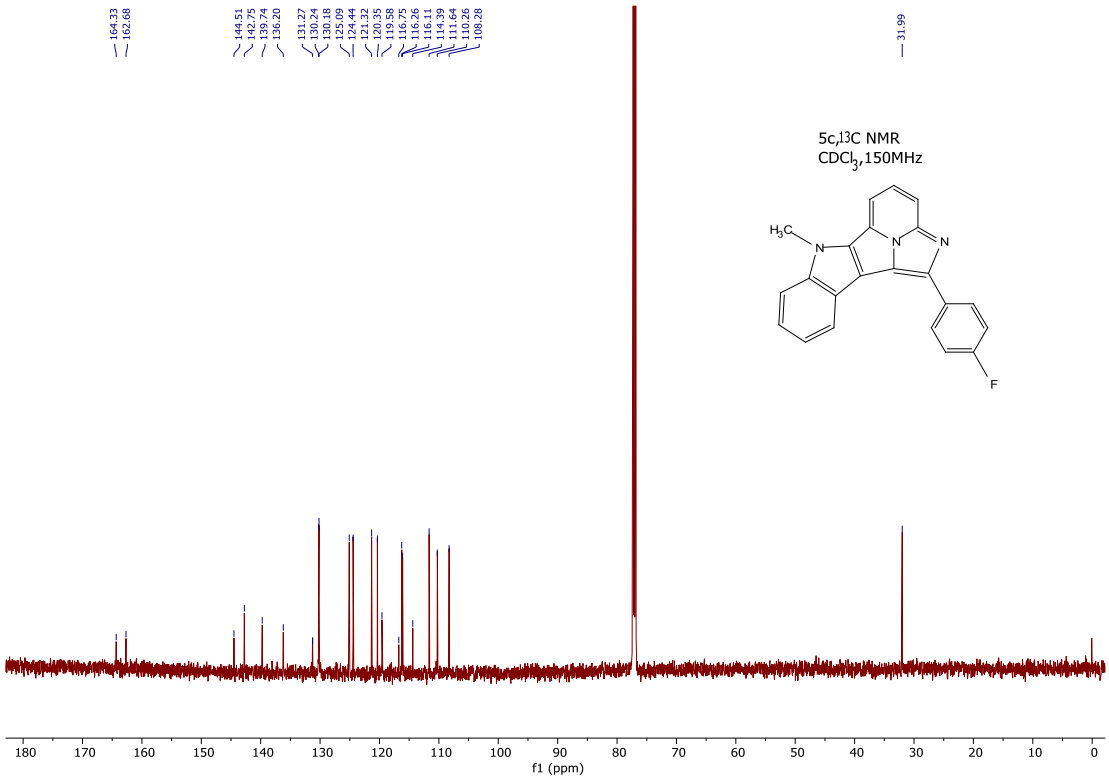
^{1}H NMR of **5b**



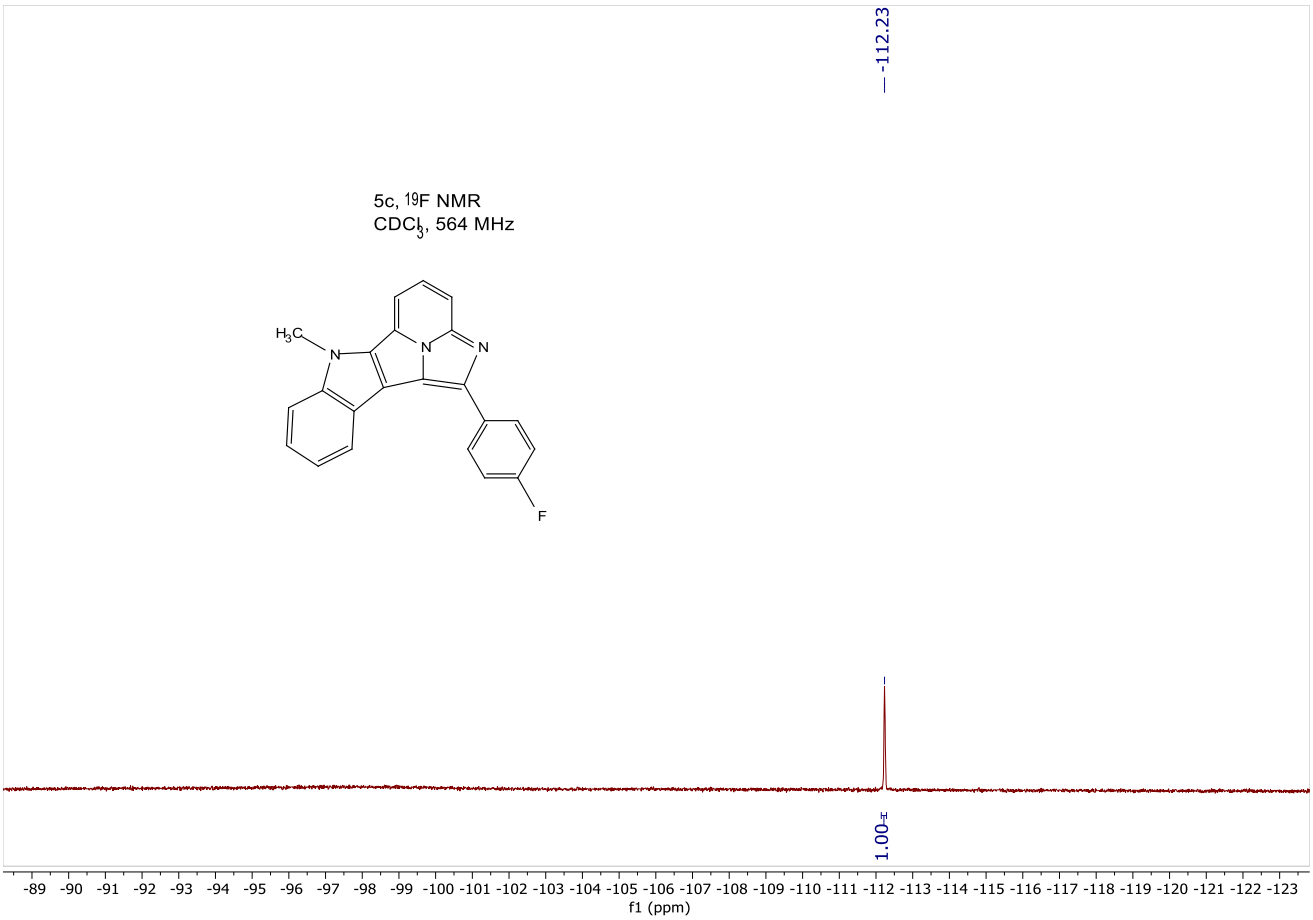
^{13}C NMR of **5b**



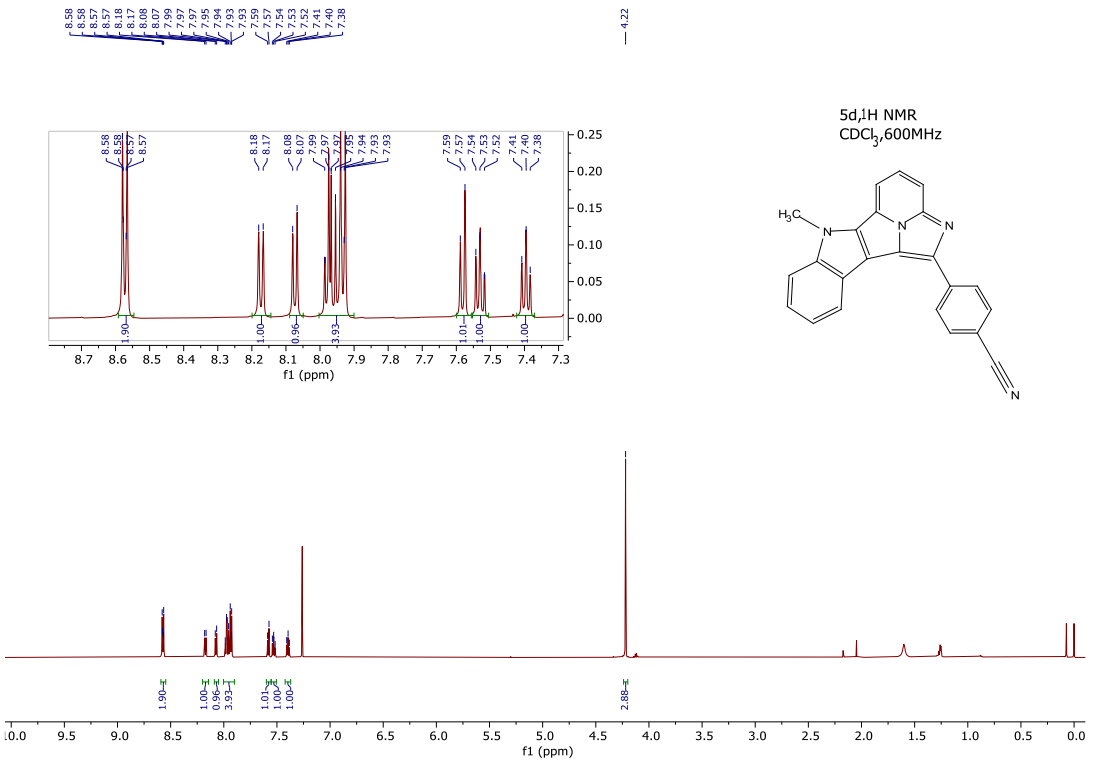
^{1}H NMR of **5c**



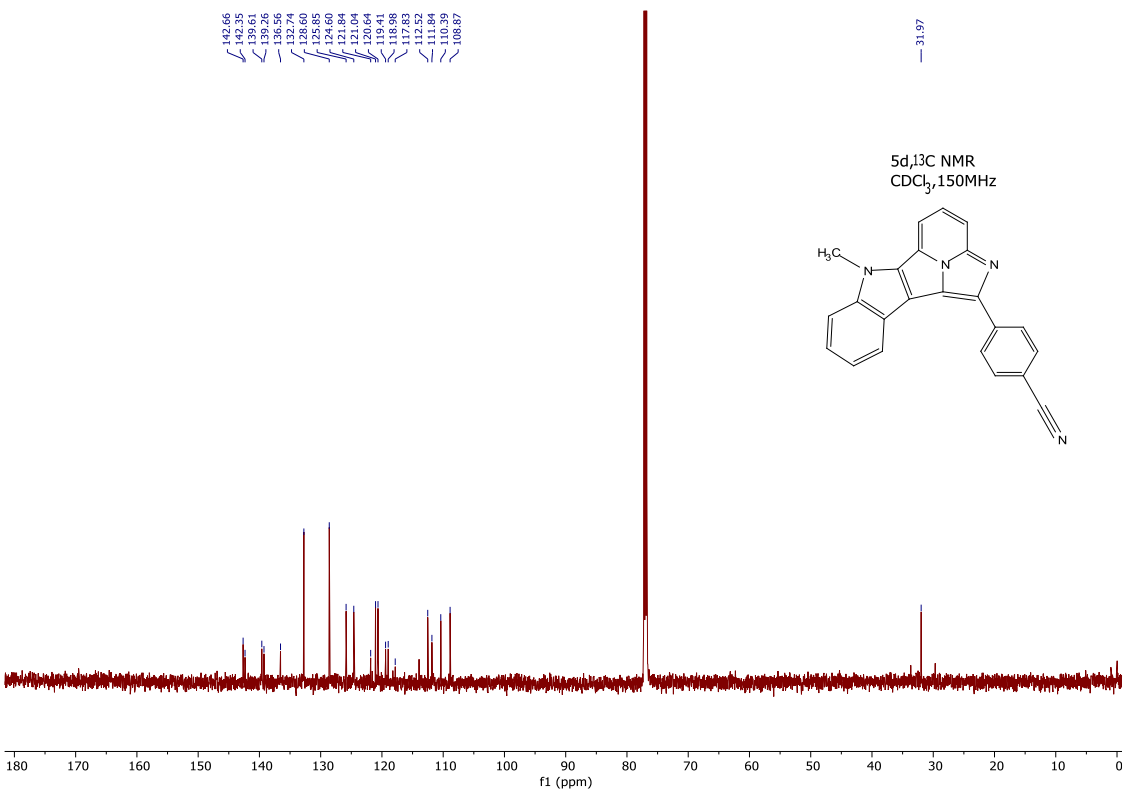
^{13}C NMR of **5c**


-112.23
5c, 19F NMR
CDCl3, 564 MHz
H3C
N
N
N
F
1.00
-89 -90 -91 -92 -93 -94 -95 -96 -97 -98 -99 -100 -101 -102 -103 -104 -105 -106 -107 -108 -109 -110 -111 -112 -113 -114 -115 -116 -117 -118 -119 -120 -121 -122 -123
f1 (ppm)

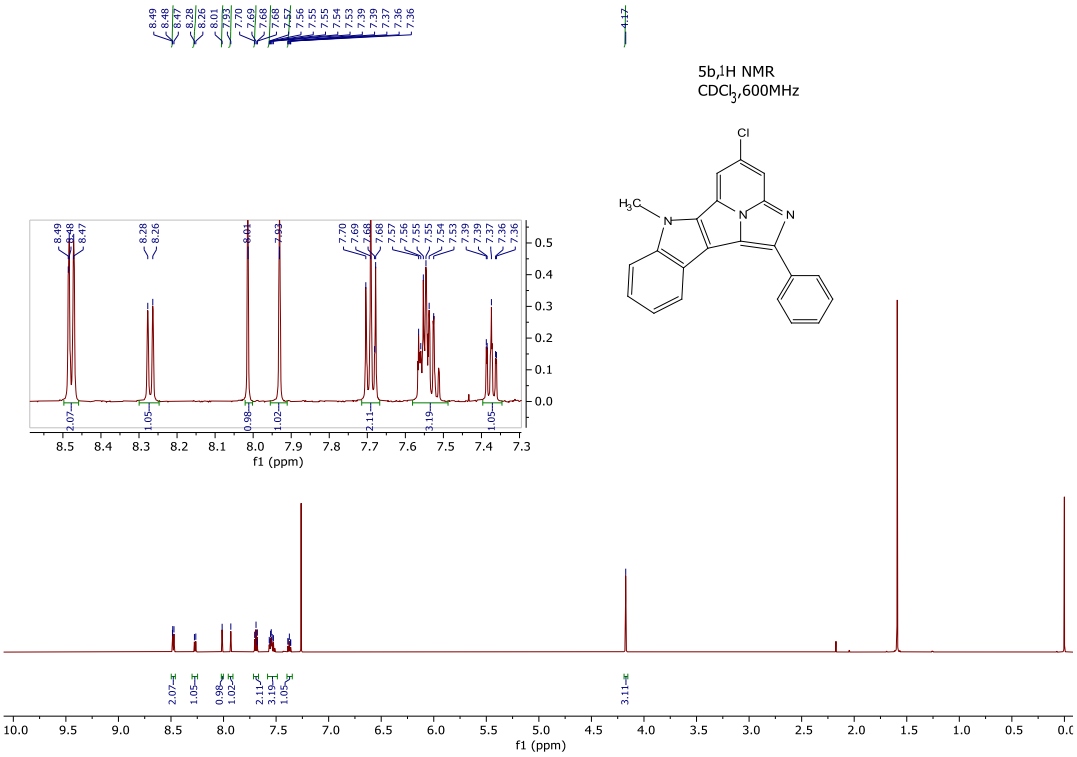
^{19}F NMR of **5c**



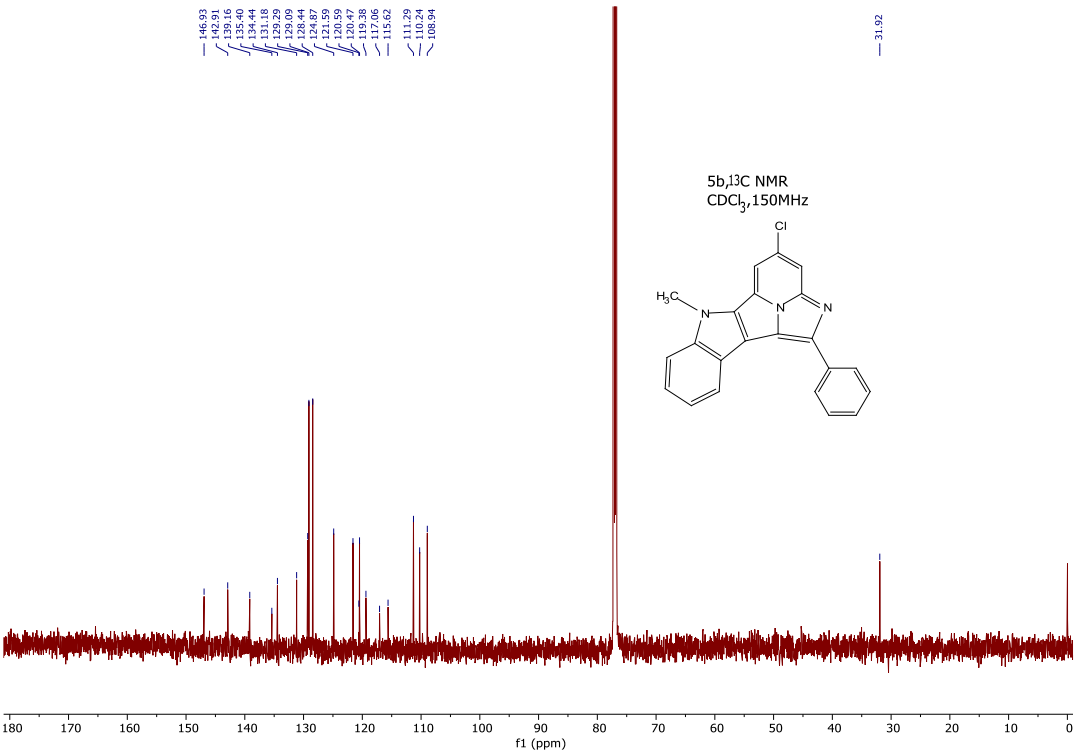
^{1}H NMR of **5d**



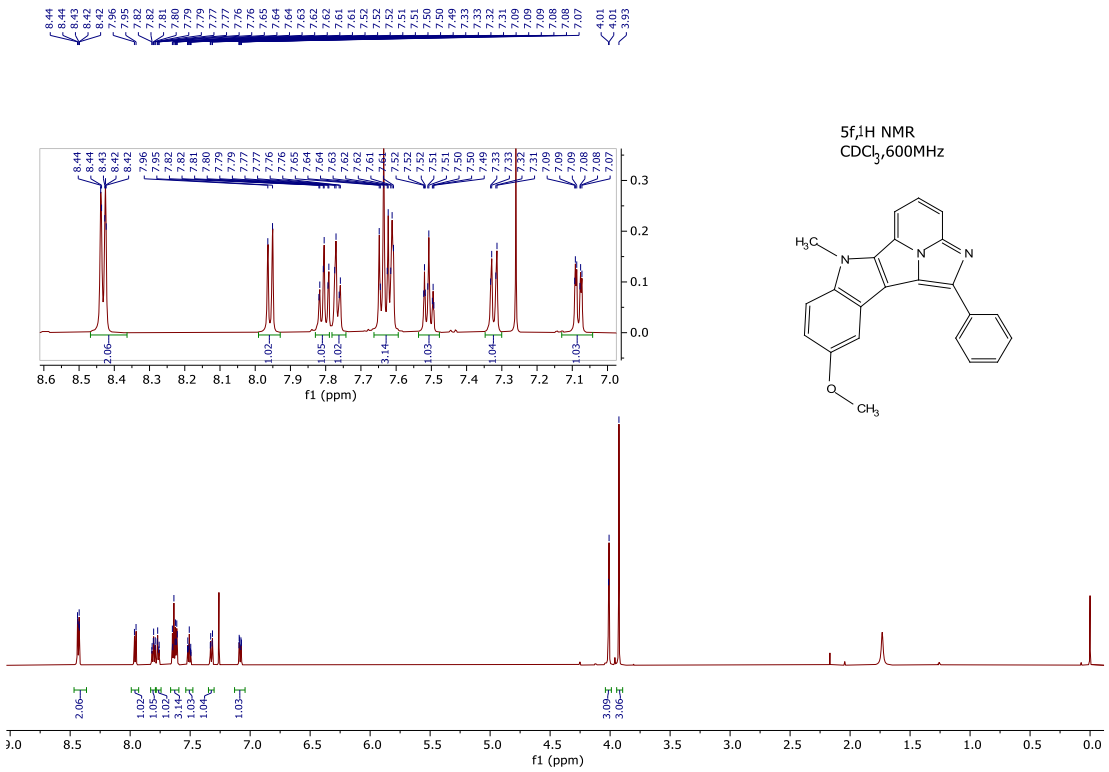
^{13}C NMR of **5d**



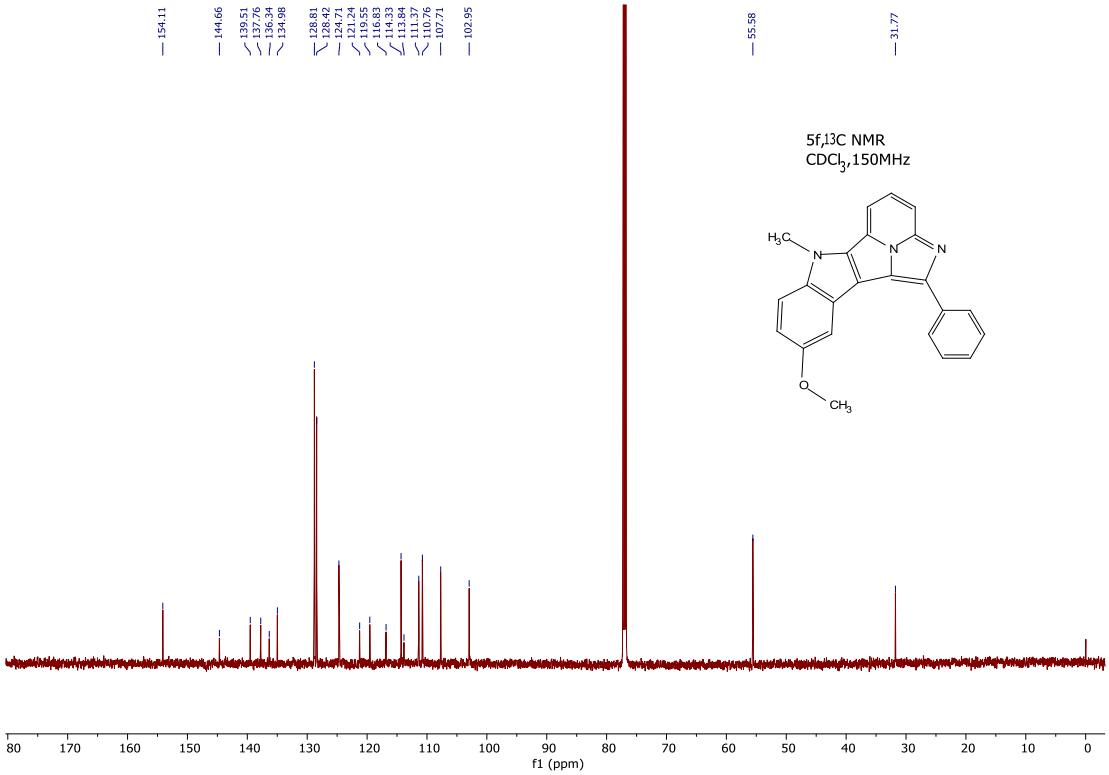
^{1}H NMR of **5e**



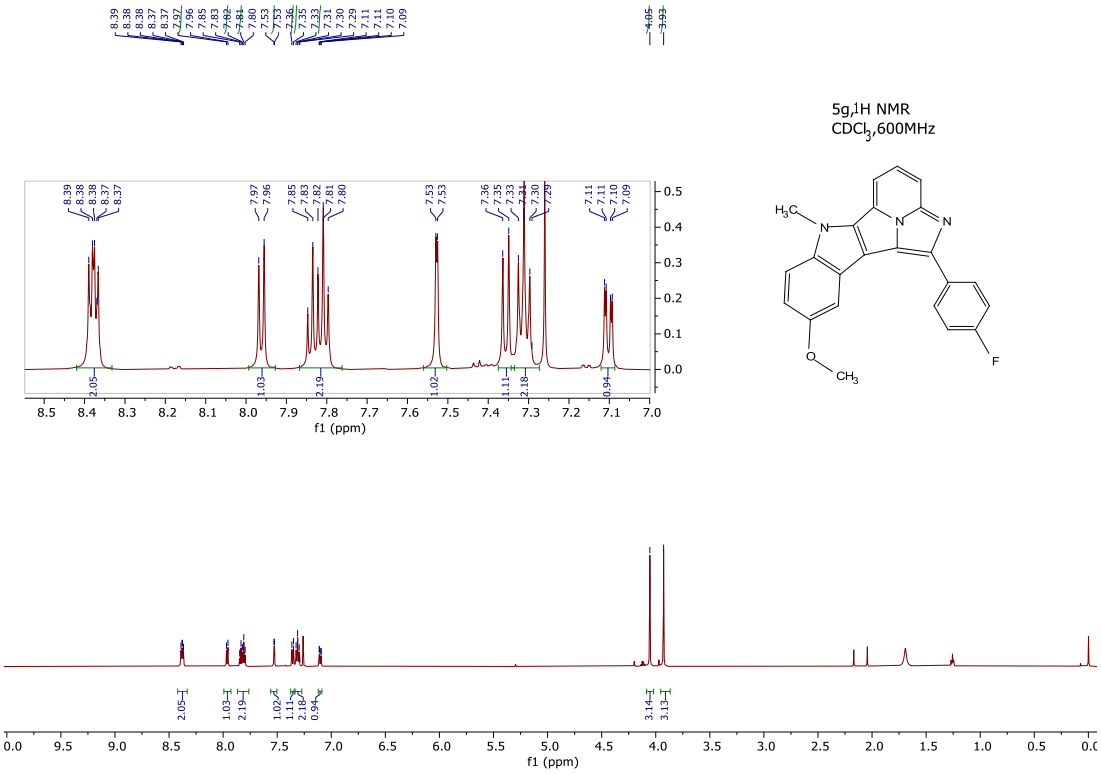
^{13}C NMR of **5e**



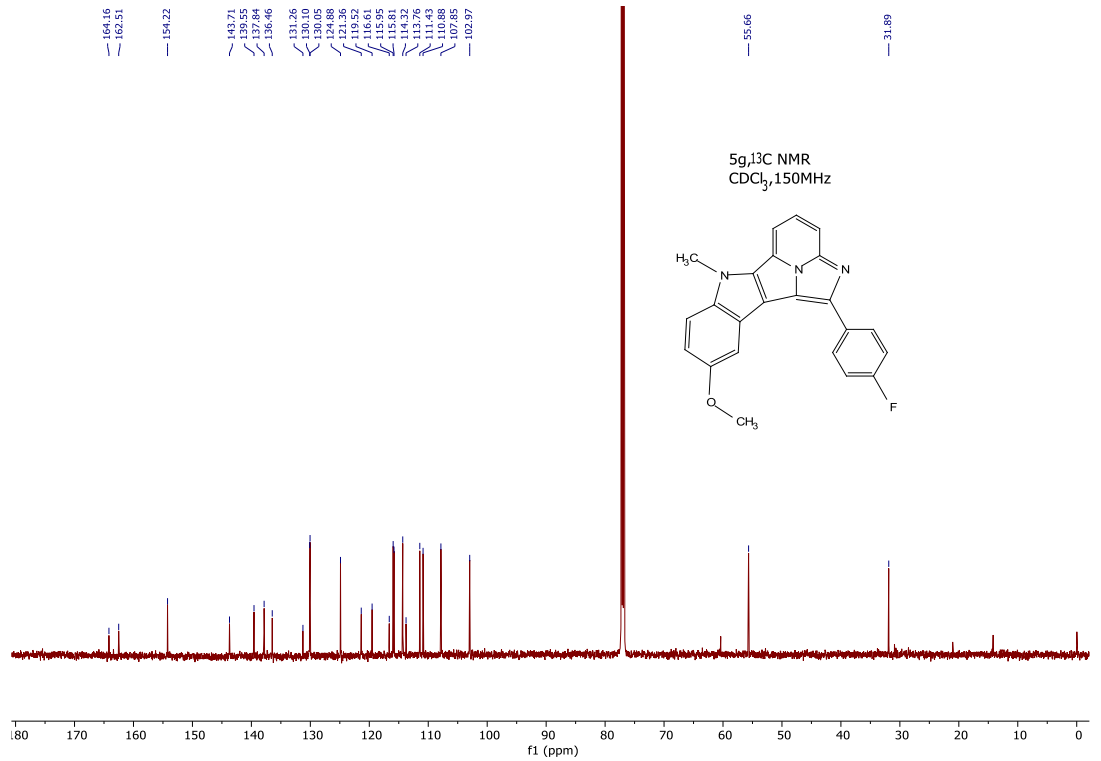
^{1}H NMR of **5f**



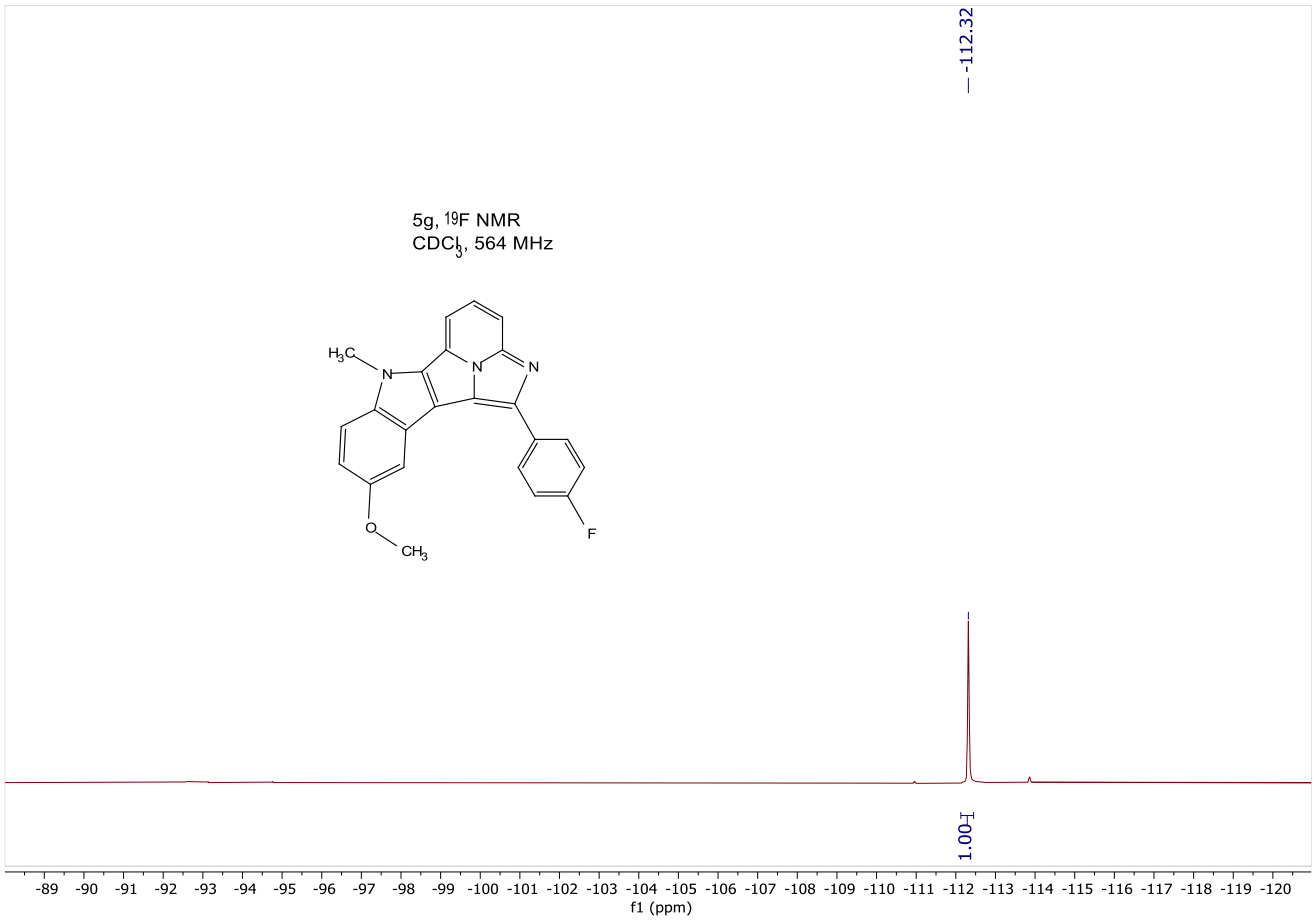
^{13}C NMR of **5f**



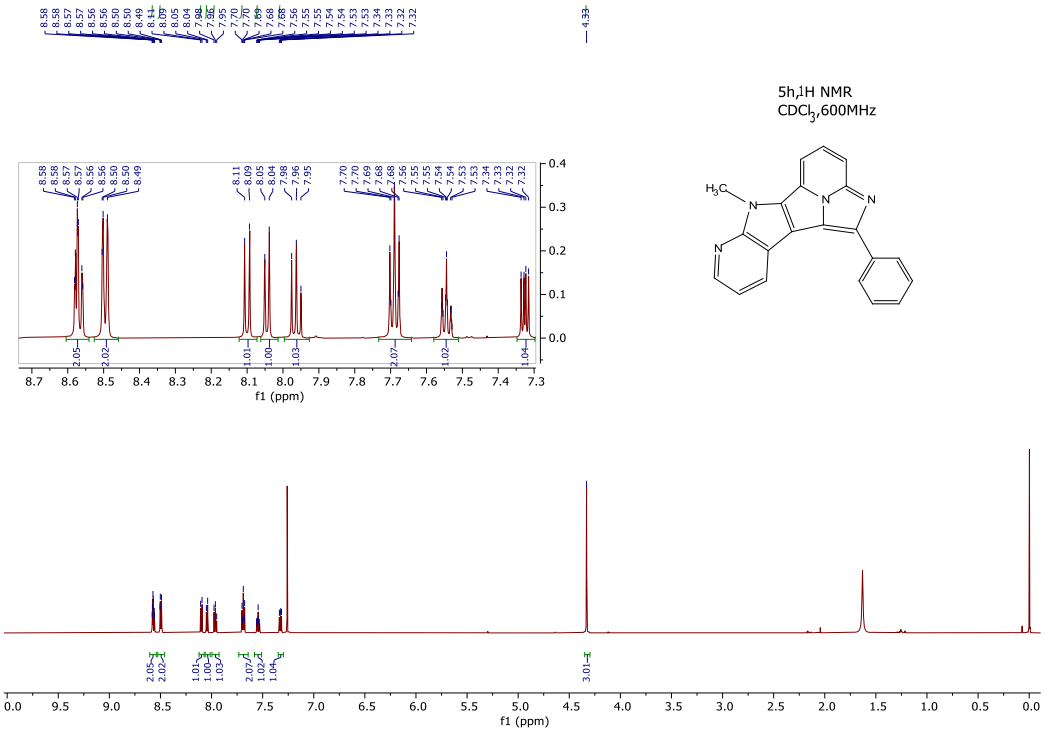
^{1}H NMR of **5g**



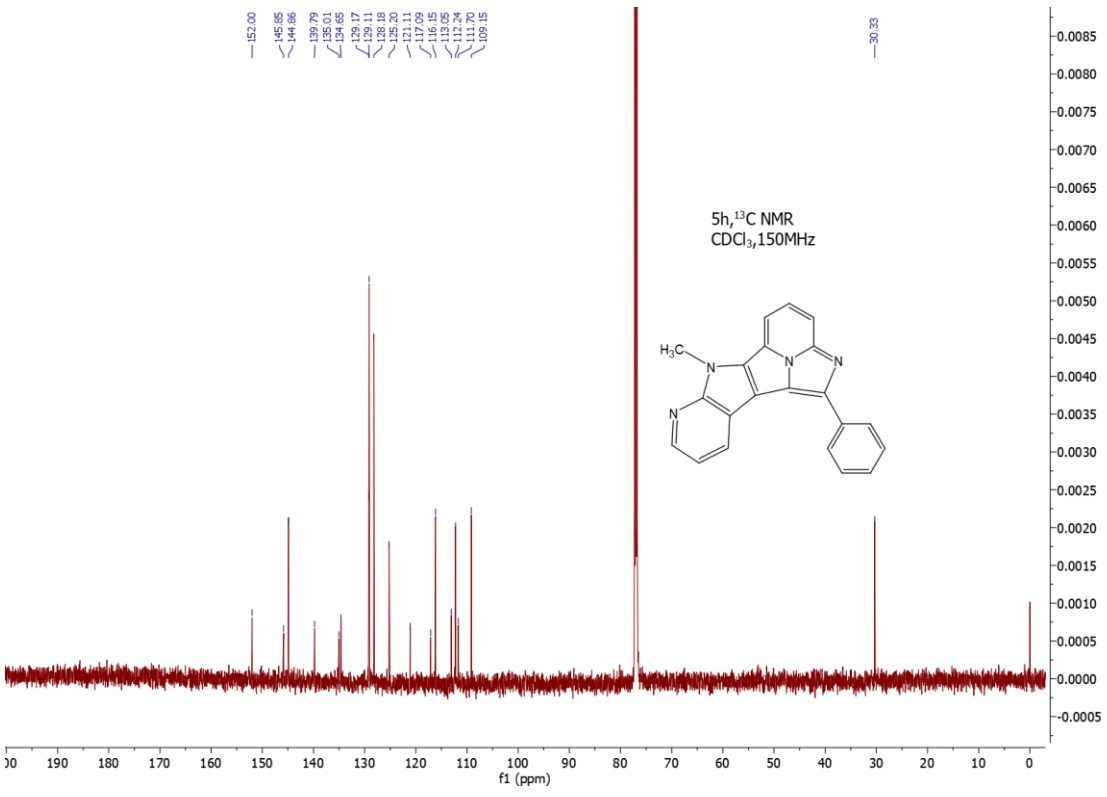
^{13}C NMR of **5g**


-112.32
5g, 19F NMR
CDCl3, 564 MHz
H3C
N
N
N
O
CH3
F
1.00
-89 -90 -91 -92 -93 -94 -95 -96 -97 -98 -99 -100 -101 -102 -103 -104 -105 -106 -107 -108 -109 -110 -111 -112 -113 -114 -115 -116 -117 -118 -119 -120
f1 (ppm)

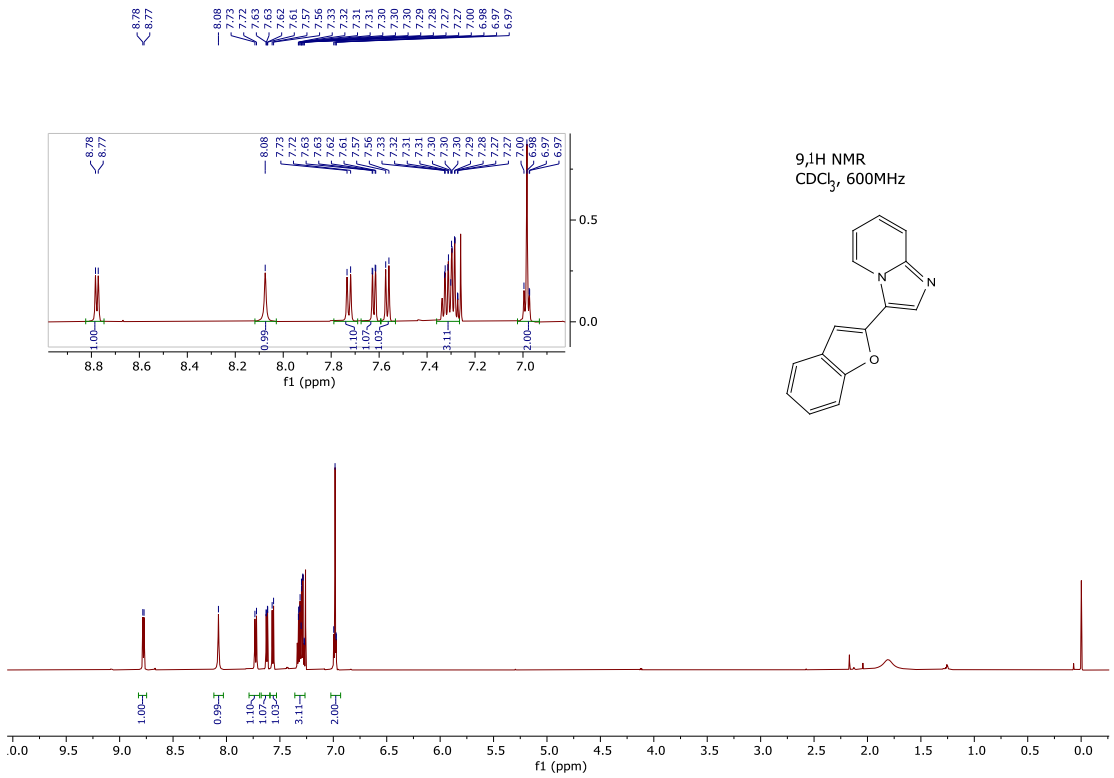
^{19}F NMR of **5g**



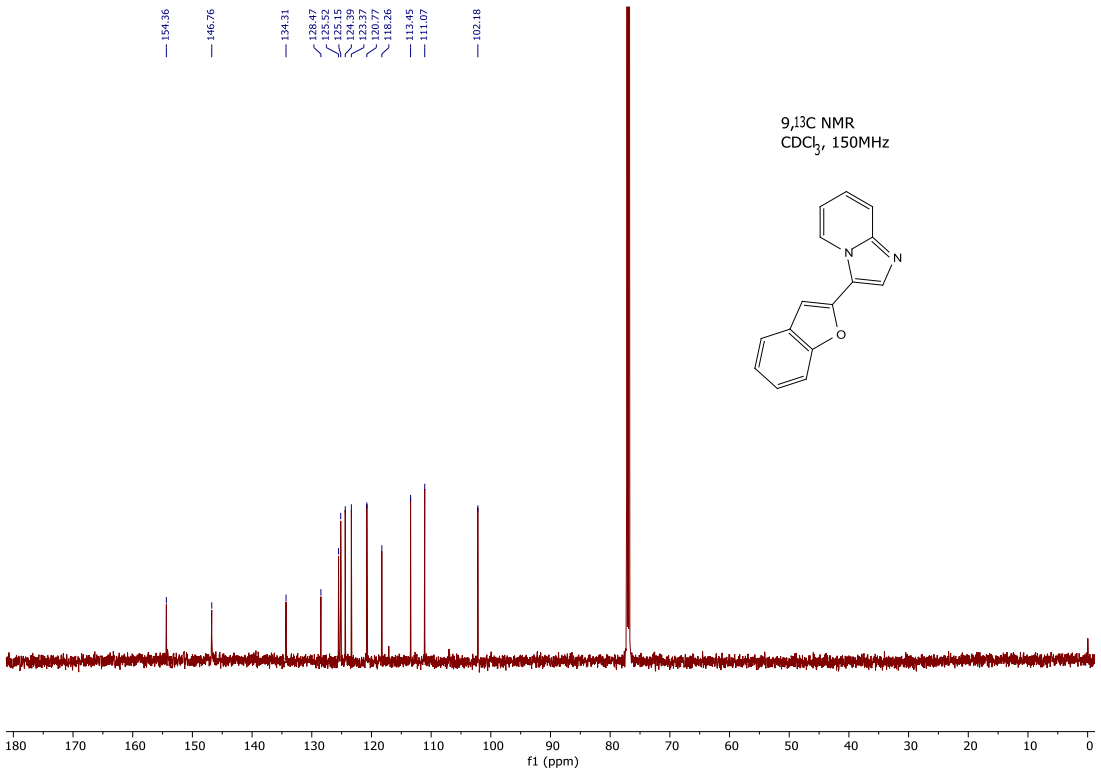
^{1}H NMR of **5h**



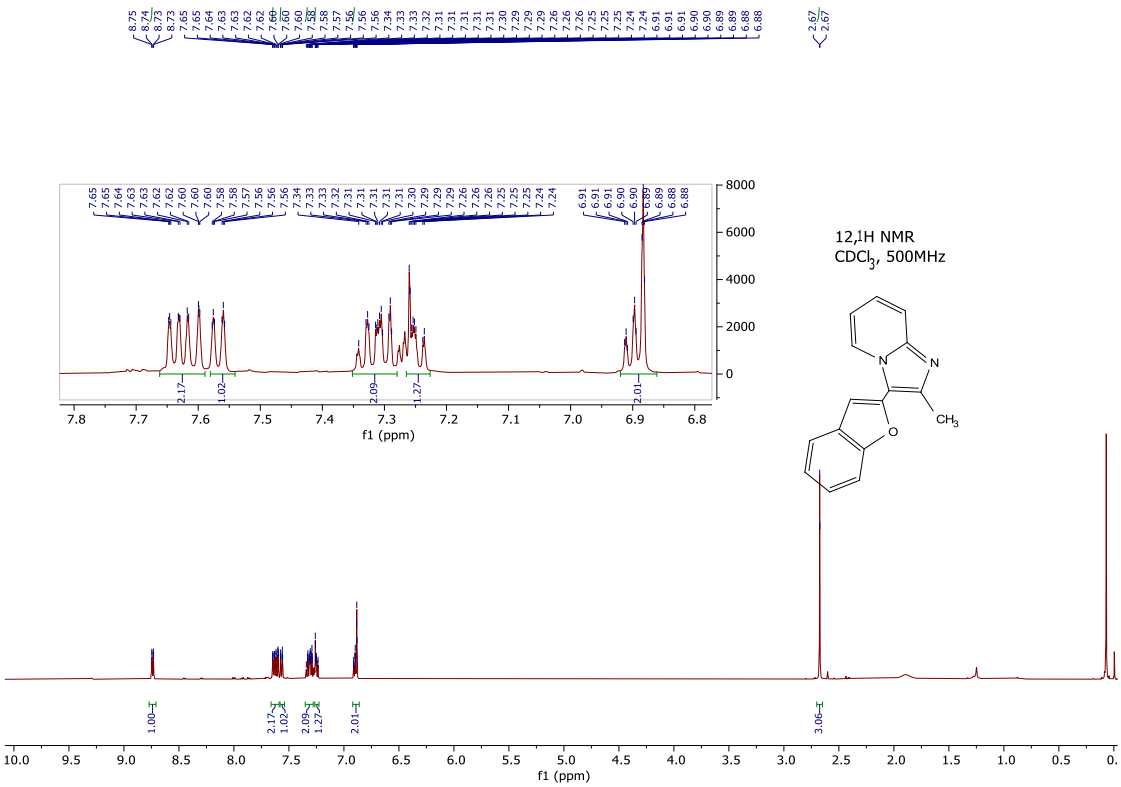
^{13}C NMR of **5h**



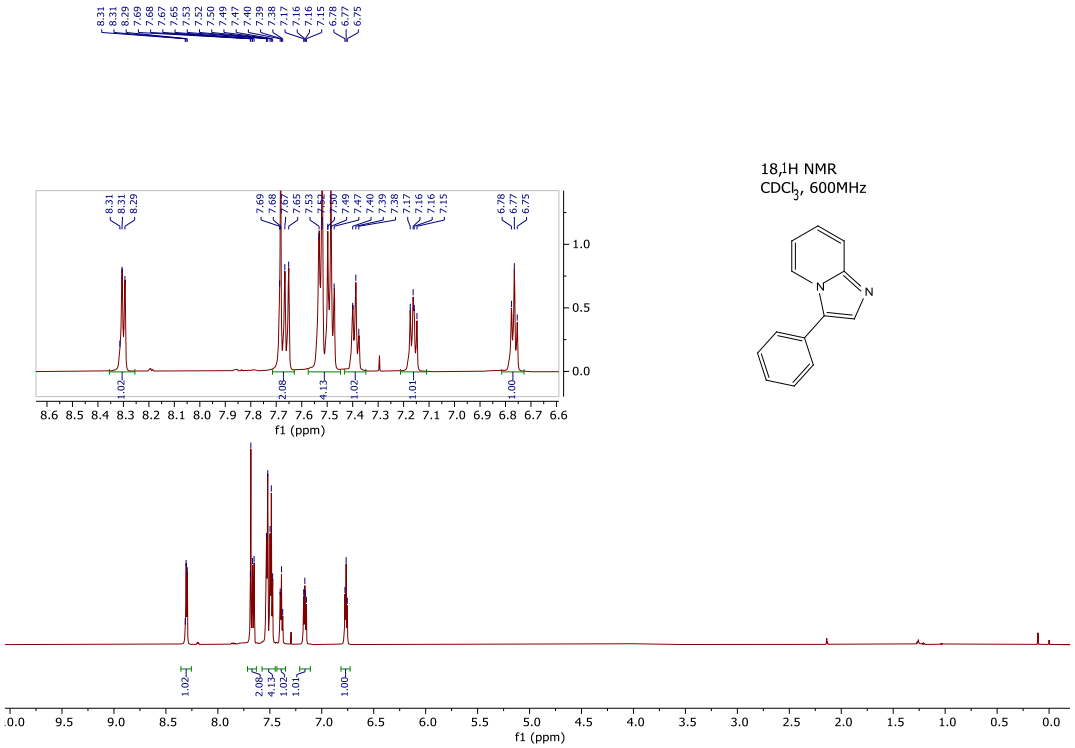
^{1}H NMR of **9**



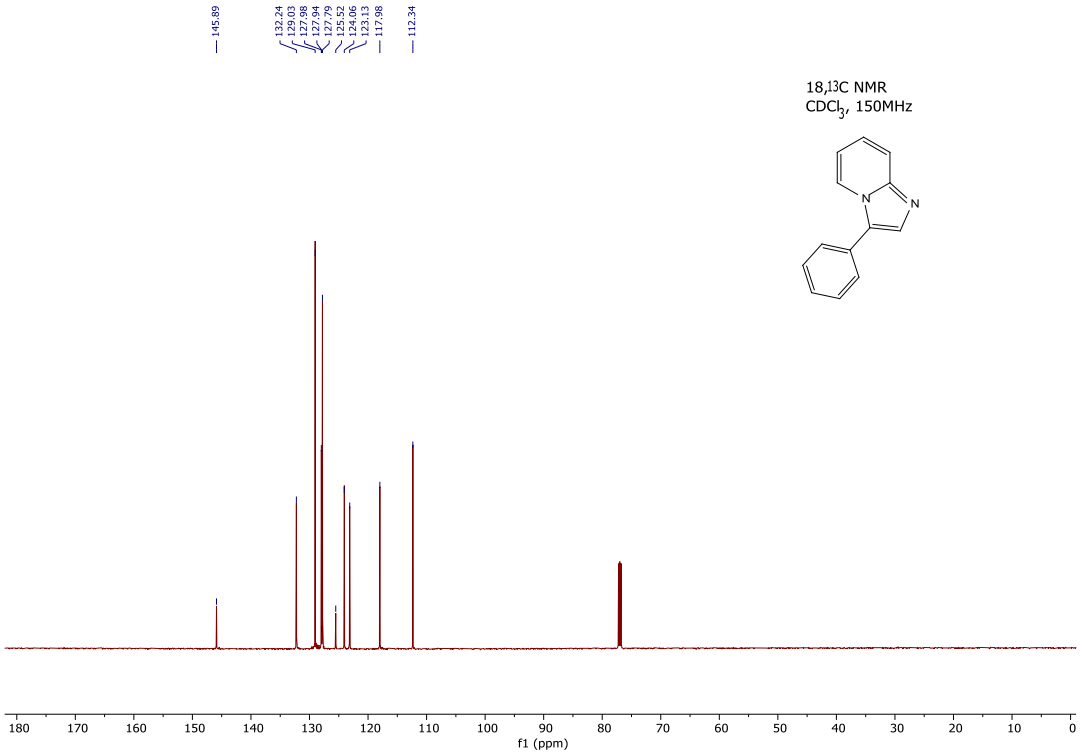
^{13}C NMR of **9**



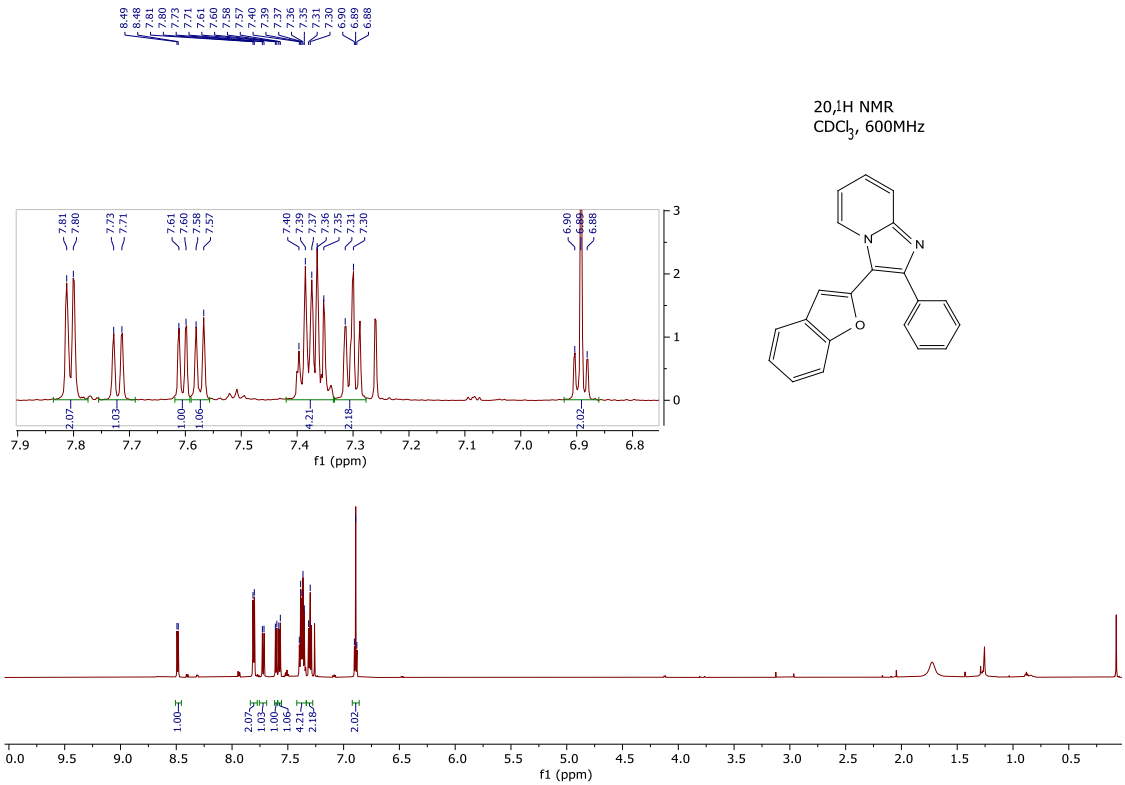
^{1}H NMR of **12**



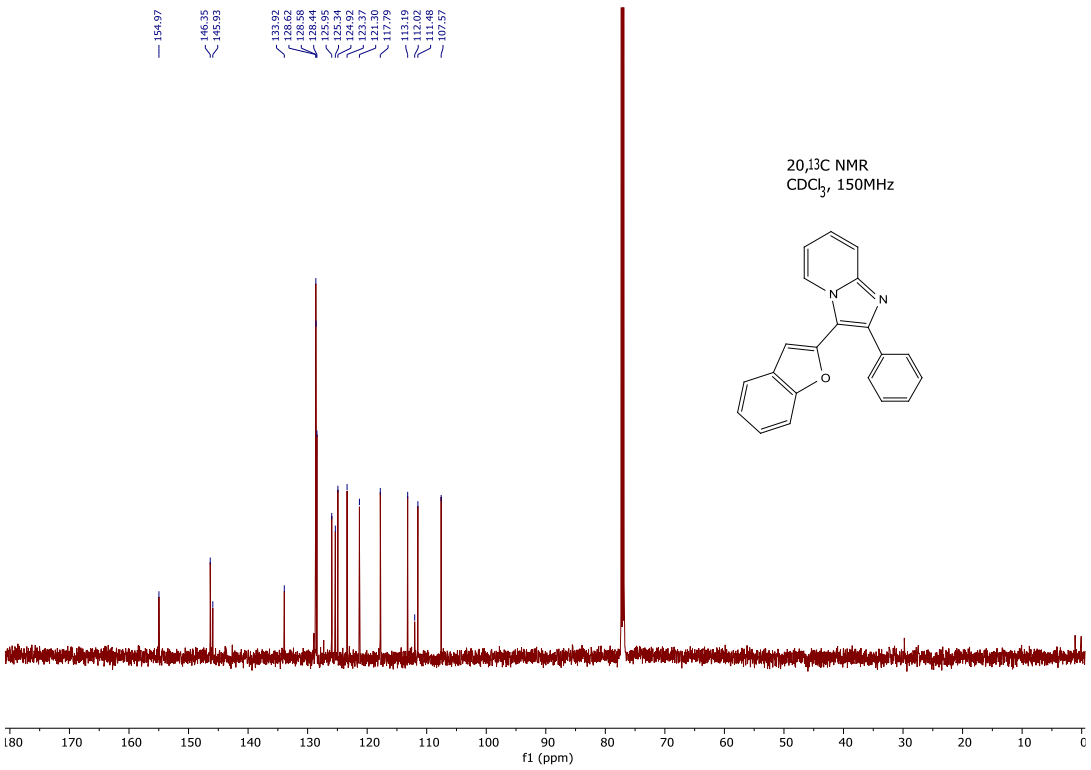
^{1}H NMR of **18**



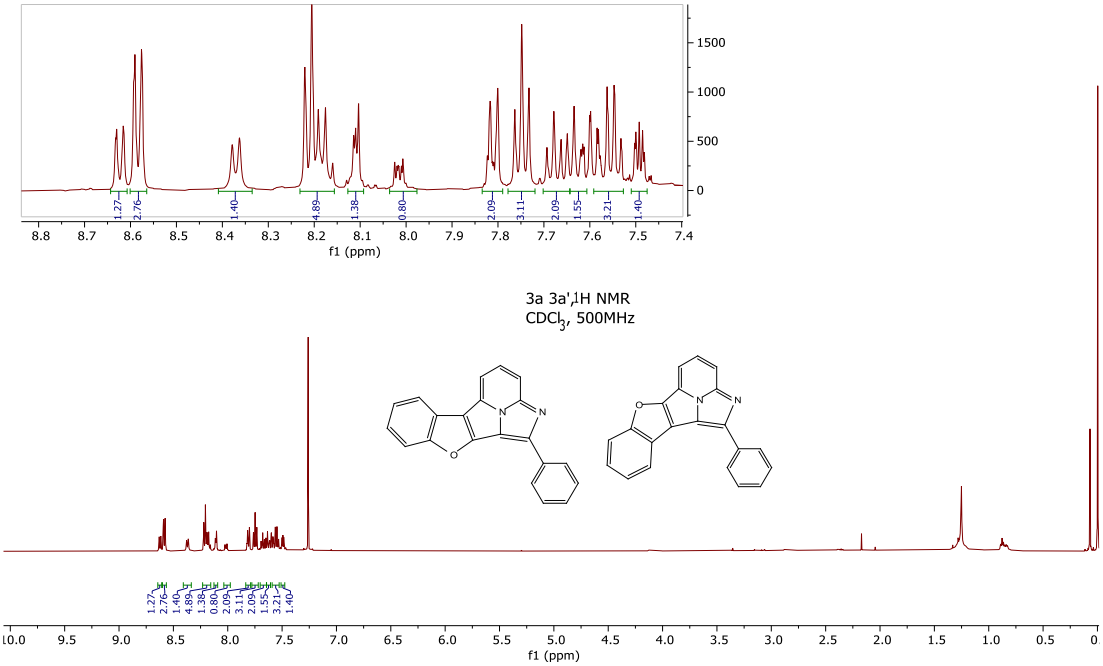
^{13}C NMR of **18**



^{1}H NMR of **20**



^{13}C NMR of **20**



^{1}H NMR of **3a** and **3a'** (inseparable mixture)