Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supplementary Information

The $B(C_6F_5)_3 \cdot H_2O$ Promoted Synthesis of Fluoroalkylated 3,3',3''-Trisindolylmethanes from Fluorocarboxylic Acids and Indoles

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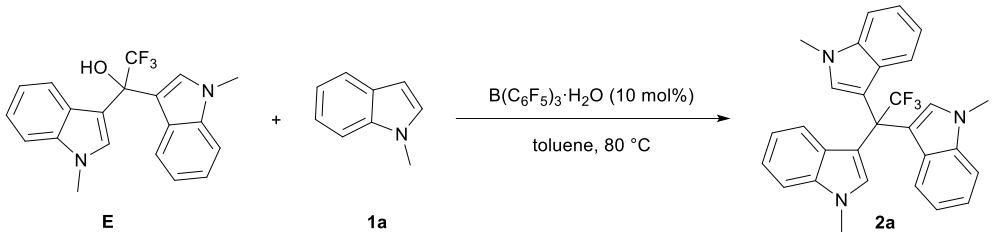
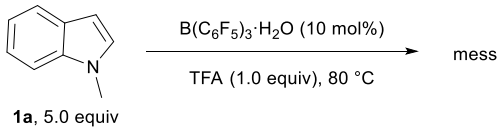
1. Control experiments

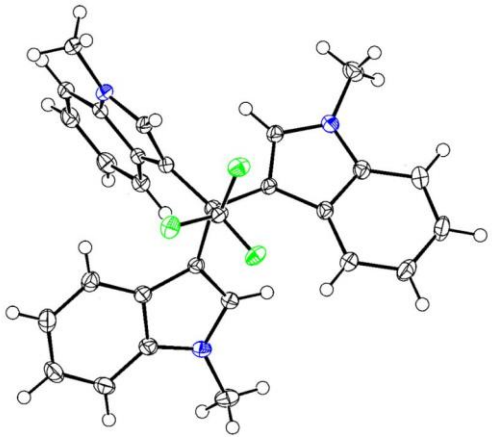


Compound **E** (prepared according to X.-T. Wu, F. Ma, E.-K. Xiao, J. Yin, F. Sun, Q. Wang, Y.-J. Jiang and P. Chen, *Org. Biomol. Chem.*, 2022, **20**, 7491–7498.) (36 mg, 0.1 mmol, 1.0 equiv), *N*-methyl indole **1a** (13 mg, 0.1 mmol, 1.0 equiv), $B(C_6F_5)_3 \cdot H_2O$ (5 mg, 0.01 mmol, 0.1 equiv, 10 mol%), and toluene (1.0 mL) were mixed in a 5-mL vial equipped with a stir bar. The resulting mixture was stirred at 80 ℃ (heating mantle). The reaction was monitored by TLC. The compound **E** mainly converted to the product **2a** in 8 hours.



Solvent-free reaction: *N*-methyl indole **1a** (131 mg, 1.0 mmol, 5.0 equiv), trifluoroacetic acid (23 mg, TFA, 0.2 mmol, 1.0 equiv), and $B(C_6F_5)_3 \cdot H_2O$ (10 mg, 0.02 mmol, 0.1 equiv, 10 mol%) were mixed in a 5-mL vial equipped with a stir bar. The resulting mixture was stirred at 80 ℃ (heating mantle) for 36 h. The reaction was monitored by TLC, and a messy mixture was obtained.

2. X-ray crystal structure and crystallographic data of compound 2a



Thermal ellipsoids are at the 50% probability level. (CCDC 2121801) Crystals suitable for X-ray analysis were obtained by the diffusion of hexane to the dichloromethane solution of compound **2a**. Clear colourless bulk; XtaLAB PRO MM007HF Cu; Rigaku, Japan.

Bond precision: C-C = 0.0017 A Wavelength=1.54184

Cell: a=8.86737(3) b=15.02535(6) c=17.36072(7)
alpha=90 beta=91.6634(3) gamma=90

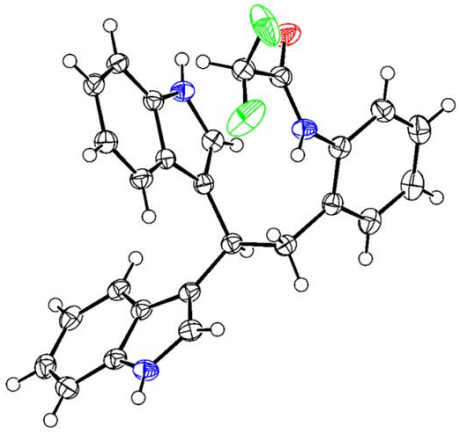
Temperature: 100 K

	Calculated	Reported
Volume	2312.087(15)	2312.087(16)
Space group	P 21/n	P 1 21/n 1
Hall group	-P 2yn	-P 2yn
Moiety formula	C29 H24 F3 N3	C29 H24 F3 N3
Sum formula	C29 H24 F3 N3	C29 H24 F3 N3
Mr	471.51	471.51
Dx,g cm-3	1.355	1.355
Z	4	4
Mu (mm-1)	0.802	0.802
F000	984.0	984.0
F000'	987.18	
h,k,lmax	11,18,21	11,18,21
Nref	4690	4647
Tmin,Tmax	0.786,0.852	0.771,1.000
Tmin'	0.755	

R(reflections)= 0.0377(4570) wR2(reflections)= 0.0928(4647)

S = 1.073 Npar= 319

3. X-ray crystal structure and crystallographic data of compound 4



Thermal ellipsoids are at the 50% probability level. (CCDC 2213382) Crystals suitable for X-ray analysis were obtained by the diffusion of hexane to the dichloromethane solution of compound **4**. Clear colourless bulk; XtaLAB PRO MM007HF Cu; Rigaku, Japan.

Bond precision: C-C = 0.0018 A Wavelength=1.54184

Cell: a=9.3177(1) b=11.8518(1) c=19.9301(2)
alpha=96.903(1) beta=93.425(1) gamma=106.005(1)

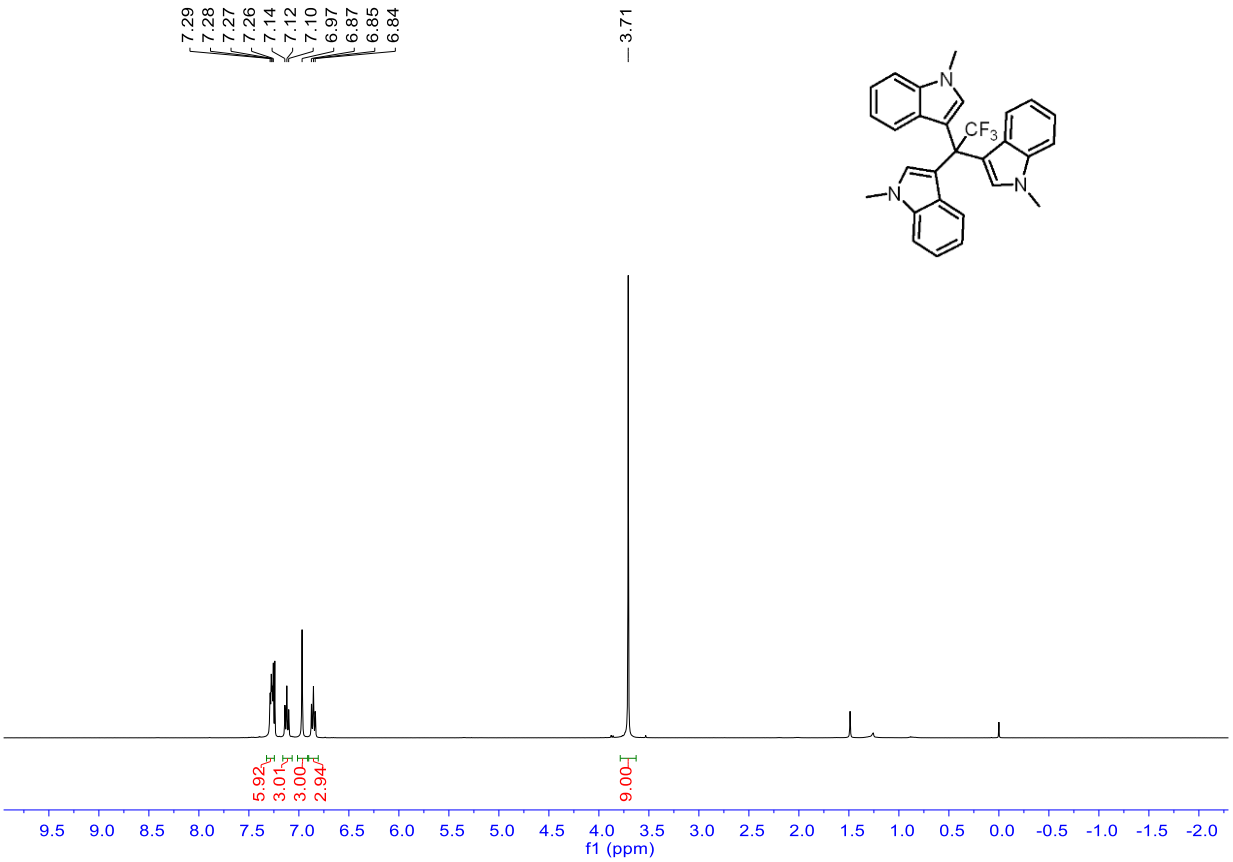
Temperature: 100 K

	Calculated	Reported
Volume	2090.29(4)	2090.29(4)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C26 H21 F2 N3 O	C26 H21 F2 N3 O
Sum formula	C26 H21 F2 N3 O	C26 H21 F2 N3 O
Mr	429.46	429.46
Dx,g cm-3	1.365	1.365
Z	4	4
Mu (mm-1)	0.798	0.798
F000	896.0	896.0
F000'	898.88	
h,k,lmax	11,14,24	11,14,24
Nref	8492	8275
Tmin,Tmax	0.839,0.923	0.756,1.000
Tmin'	0.839	

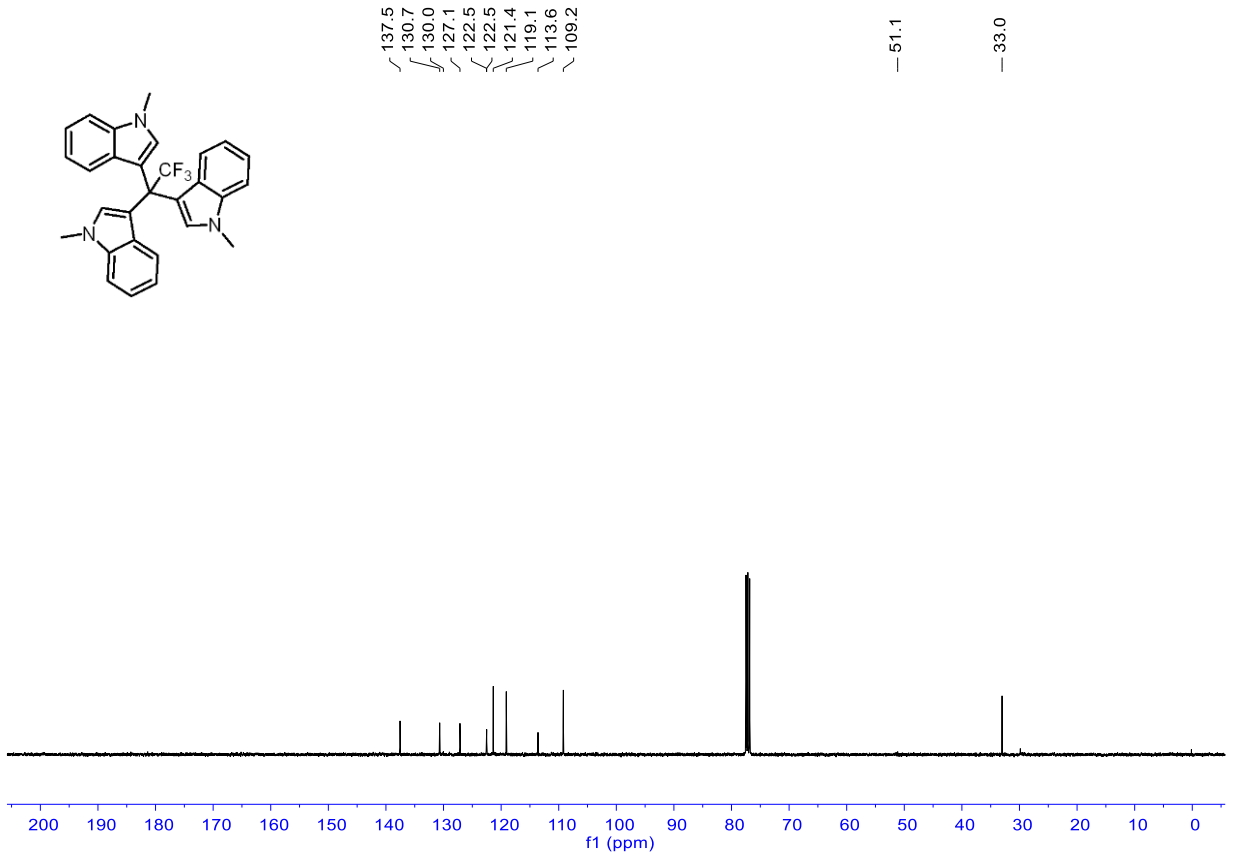
R(reflections)= 0.0376(7882) wR2(reflections)= 0.0918(8275)

S = 1.009 Npar= 578

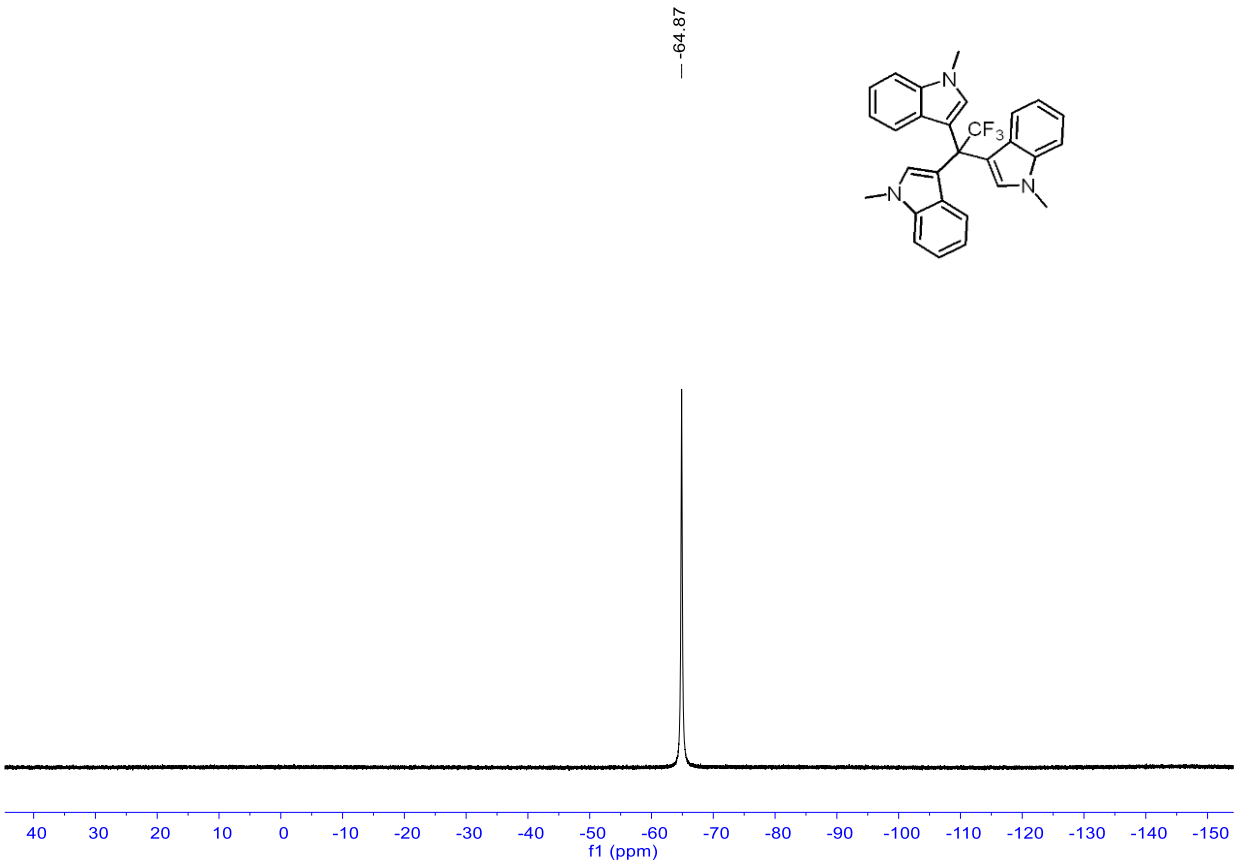
4. NMR Spectra of all compounds



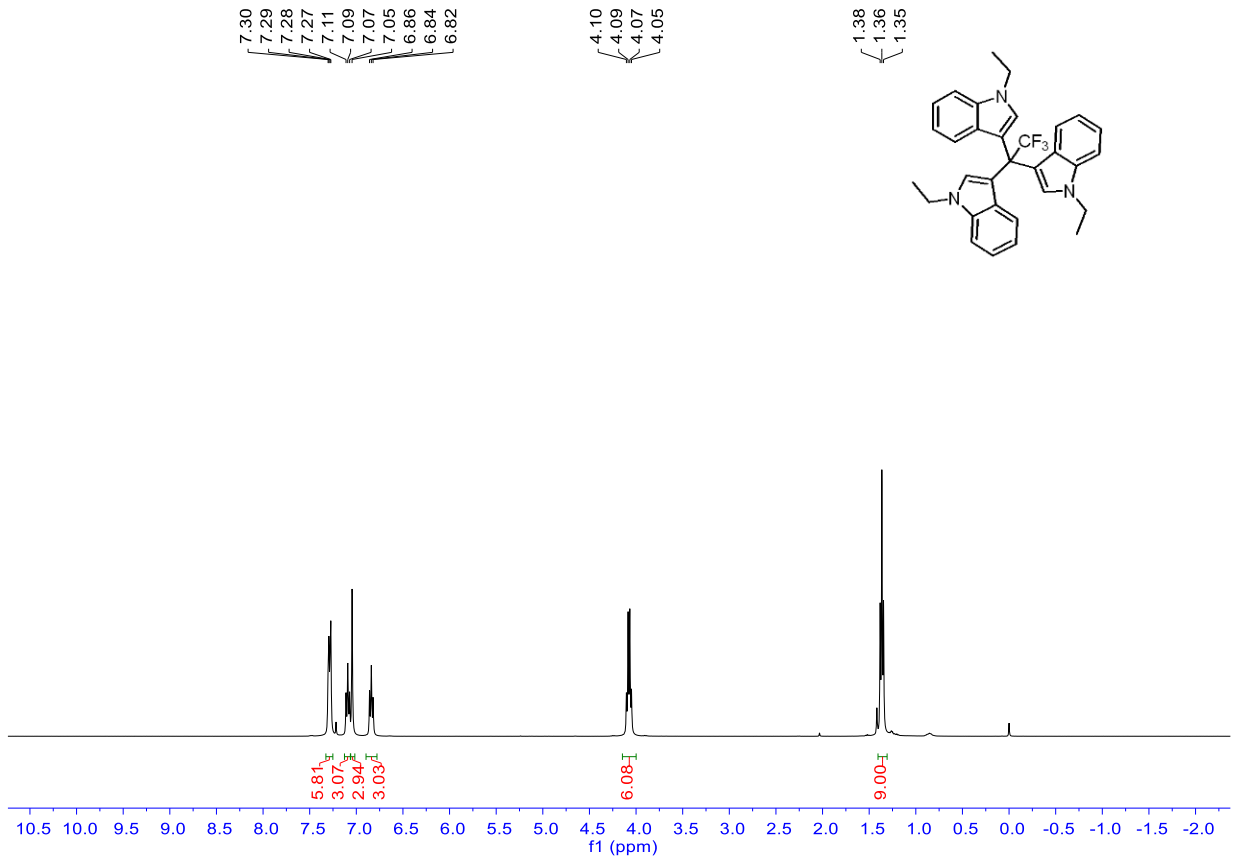
^{1}H NMR spectrum of **2a**



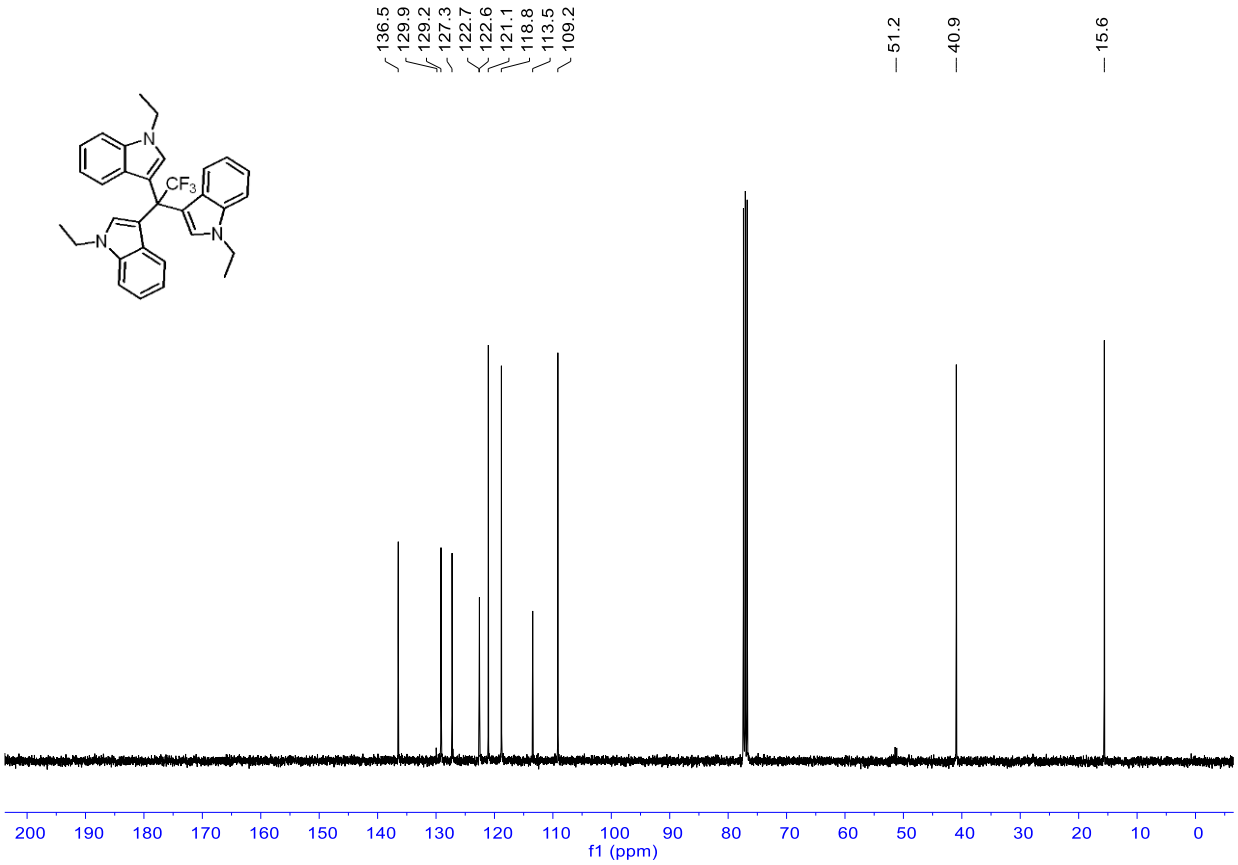
^{13}C{^{1}H} NMR spectrum of **2a**



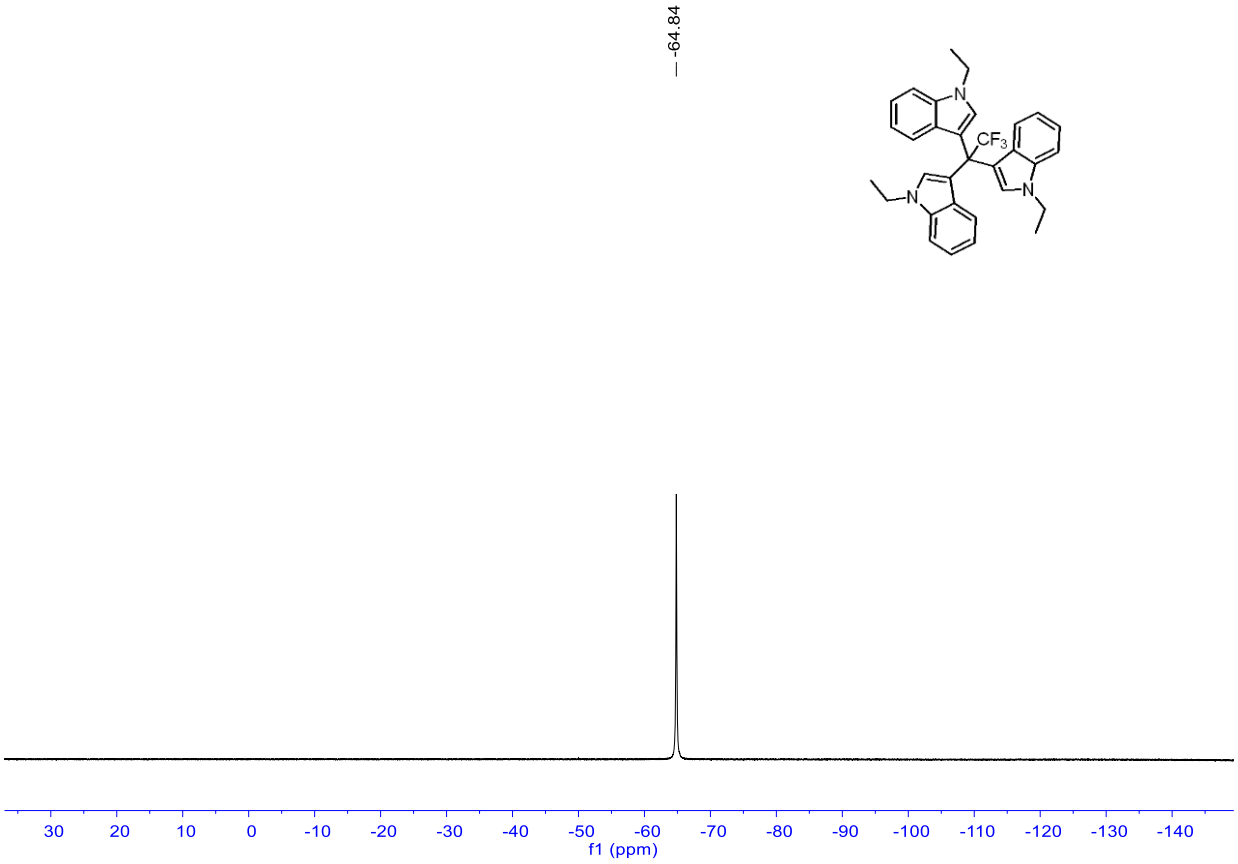
^{19}F NMR spectrum of **2a**



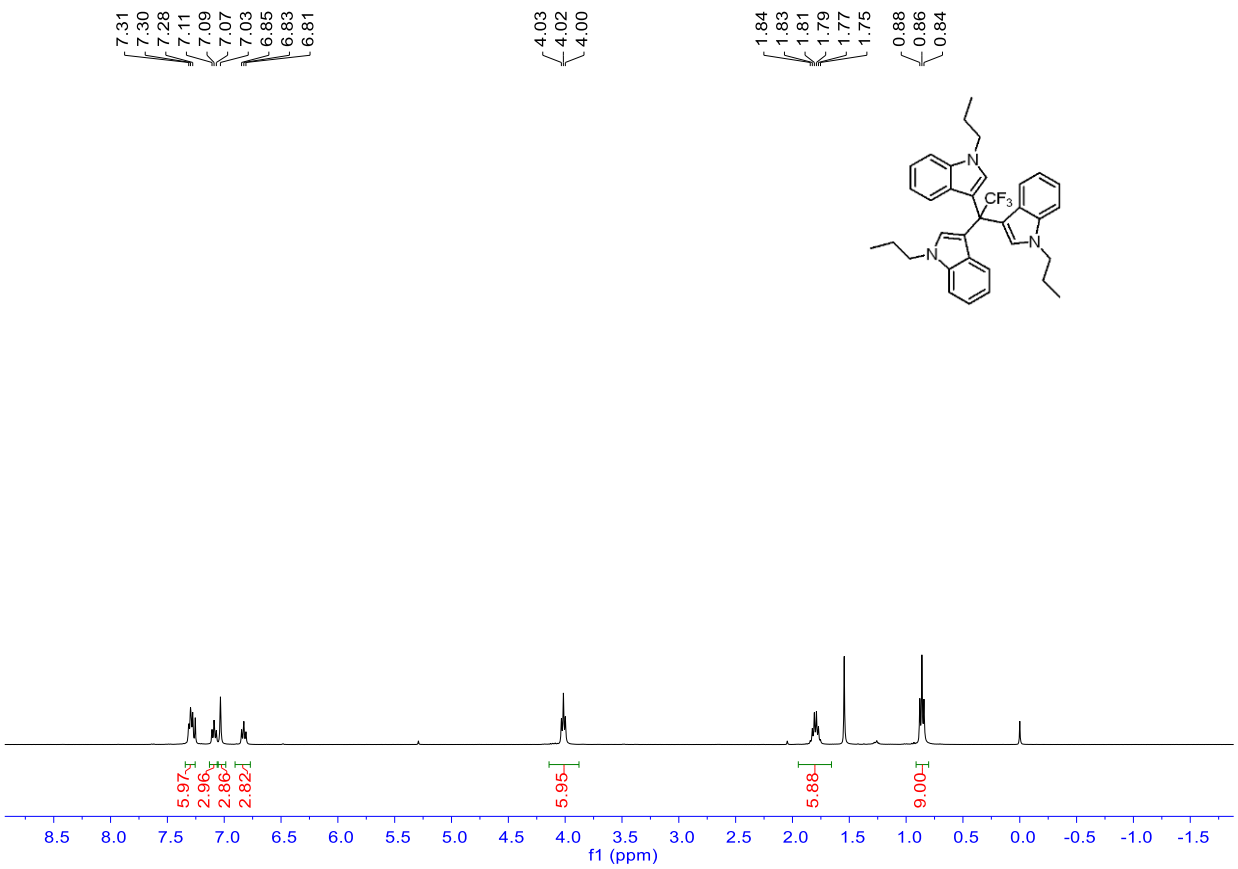
^{1}H NMR spectrum of **2b**



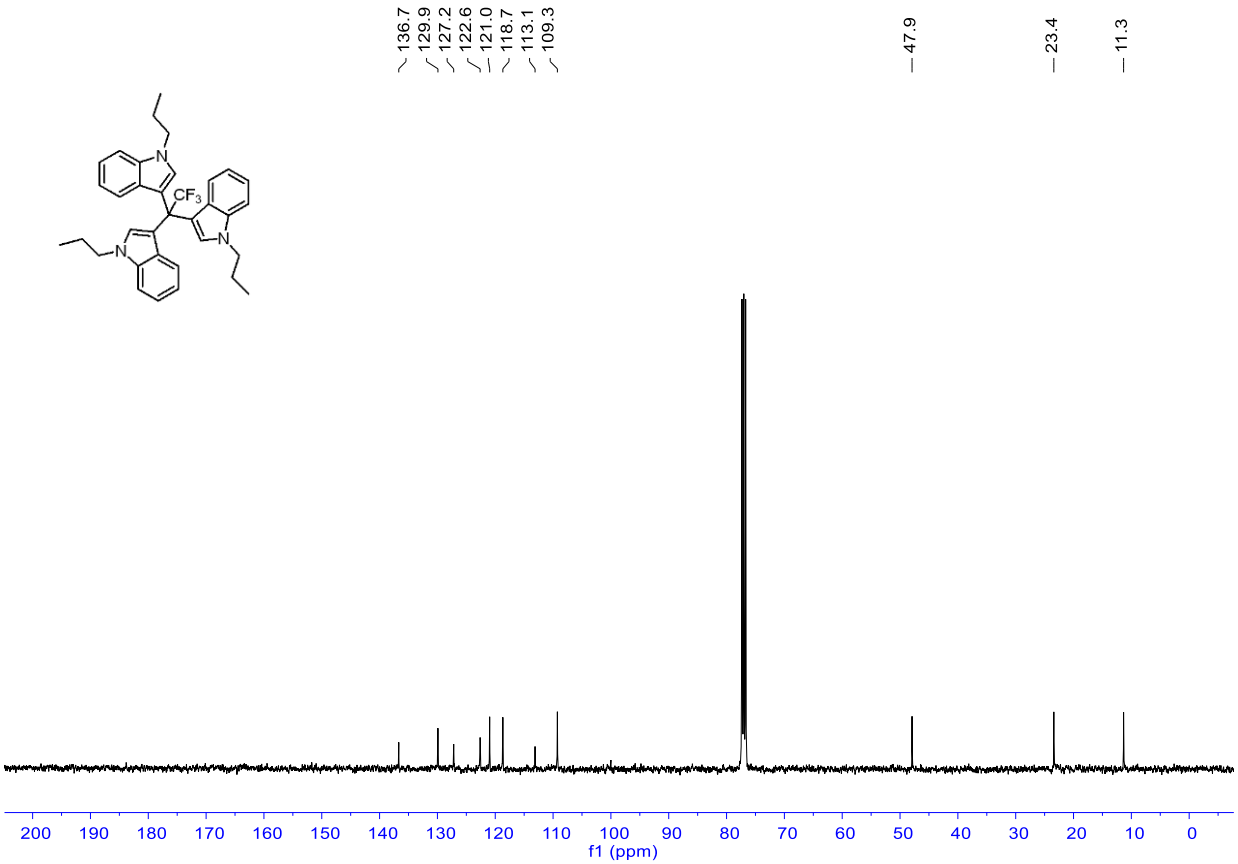
$^{13}C\{^{1}H\}$ NMR spectrum of **2b**



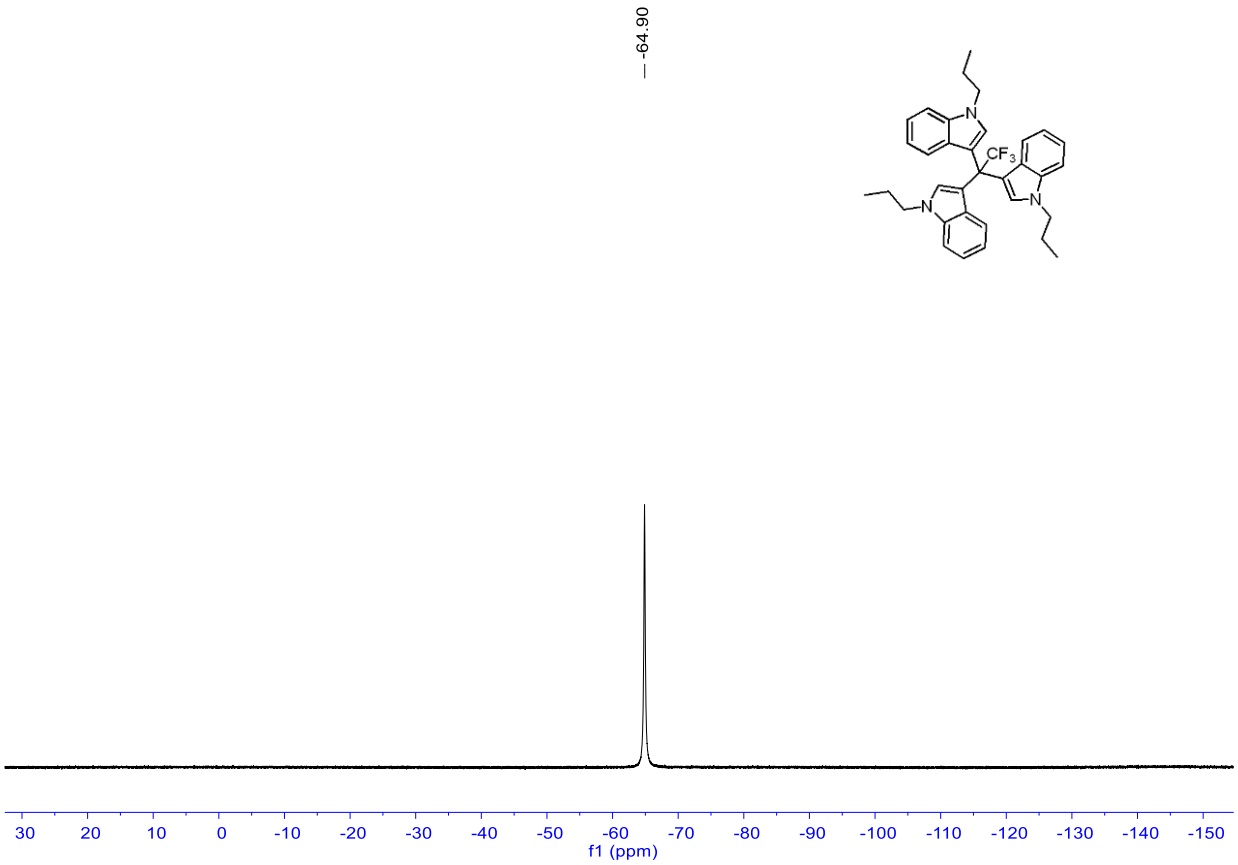
^{19}F NMR spectrum of **2b**



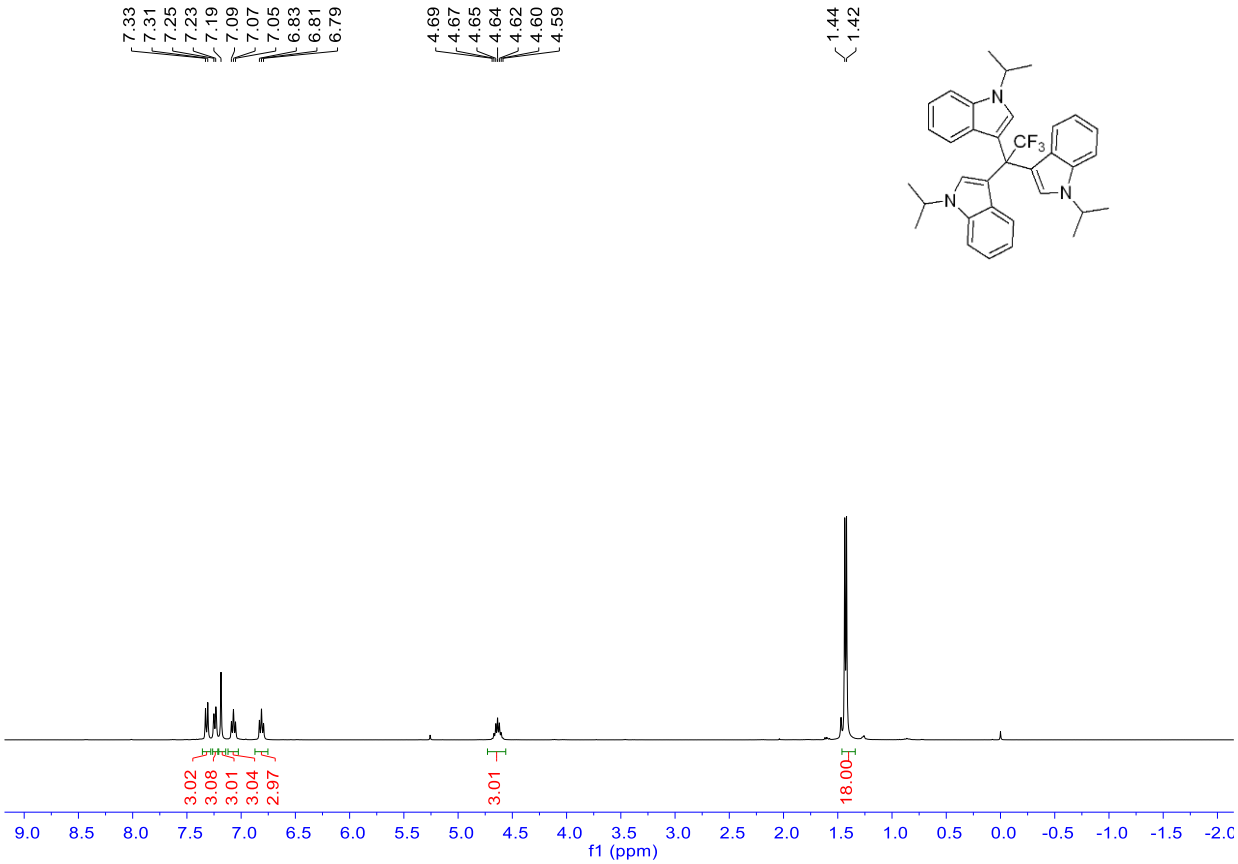
^{1}H NMR spectrum of **2c**



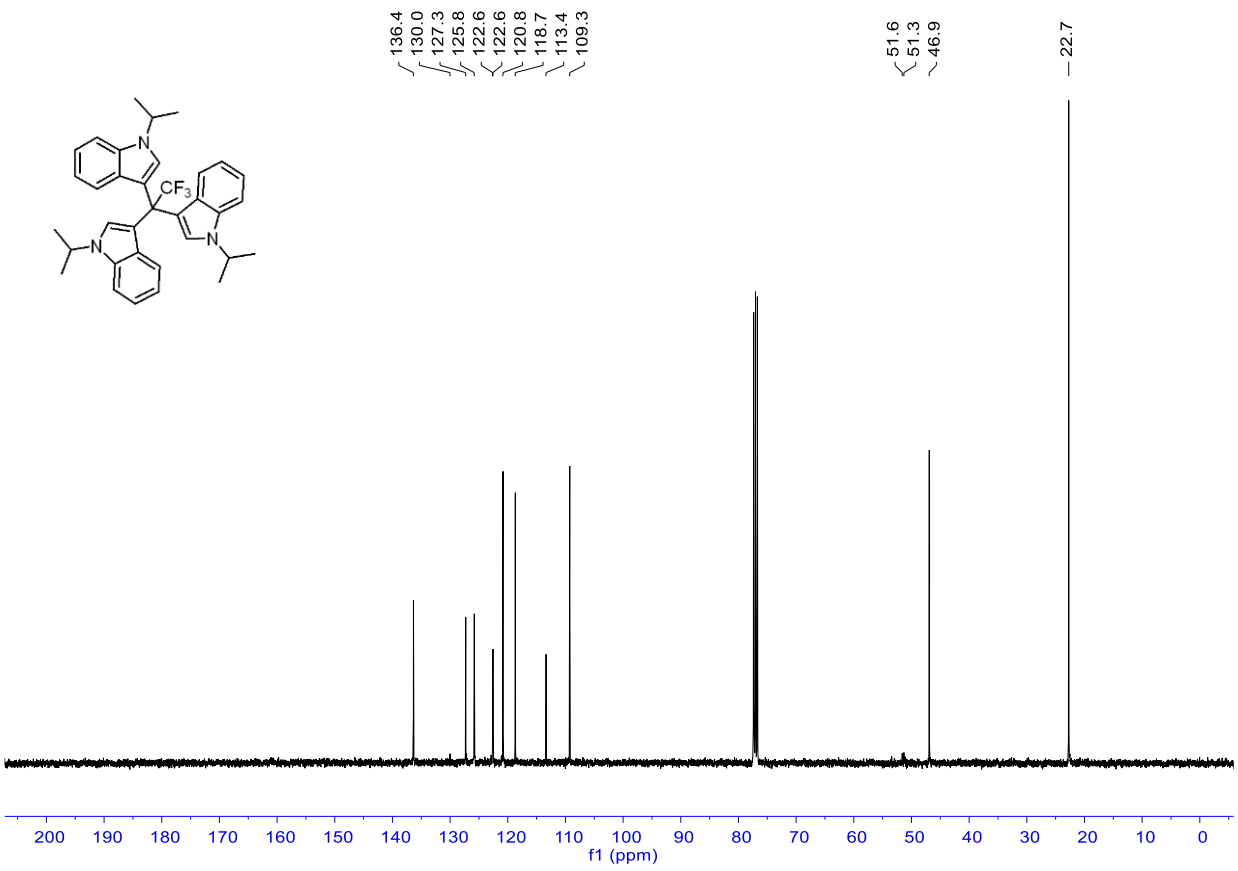
^{13}C{^{1}H} NMR spectrum of **2c**



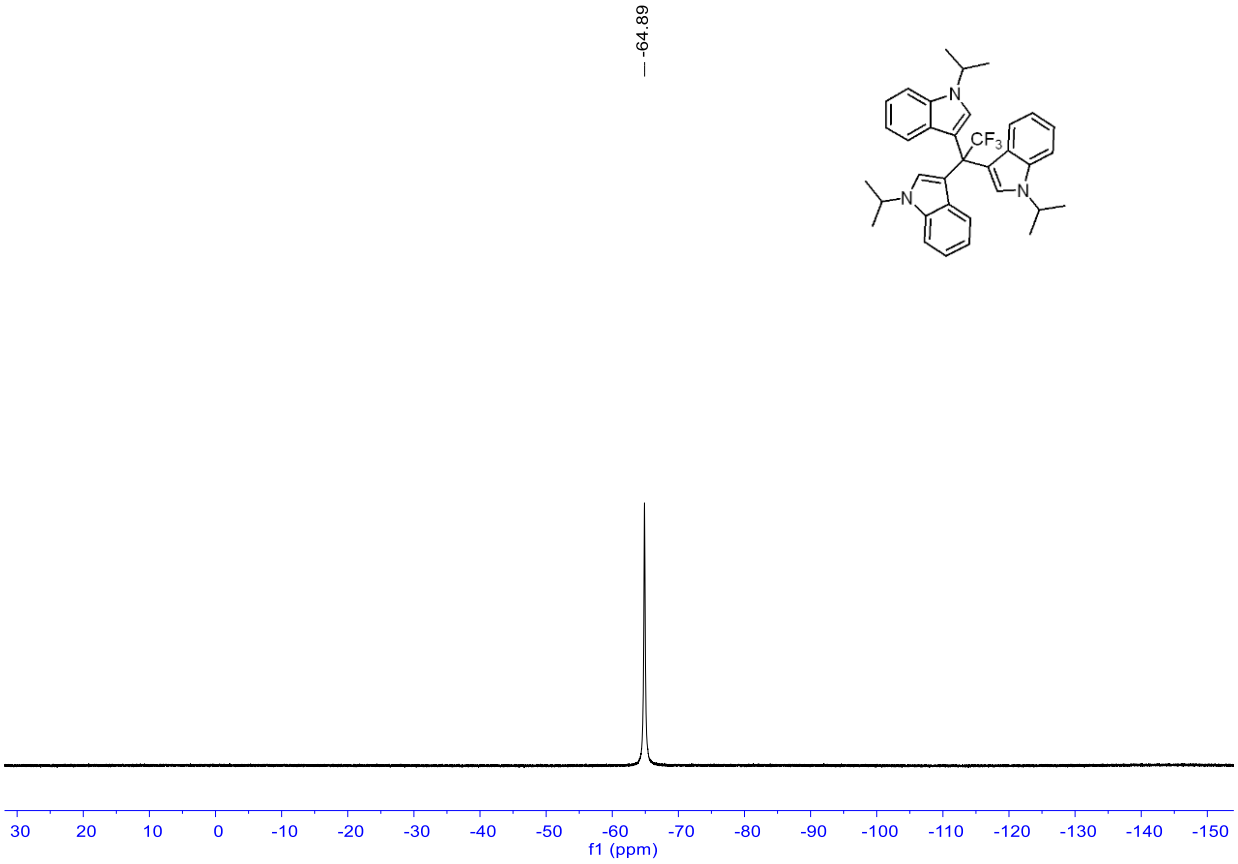
^{19}F NMR spectrum of **2c**



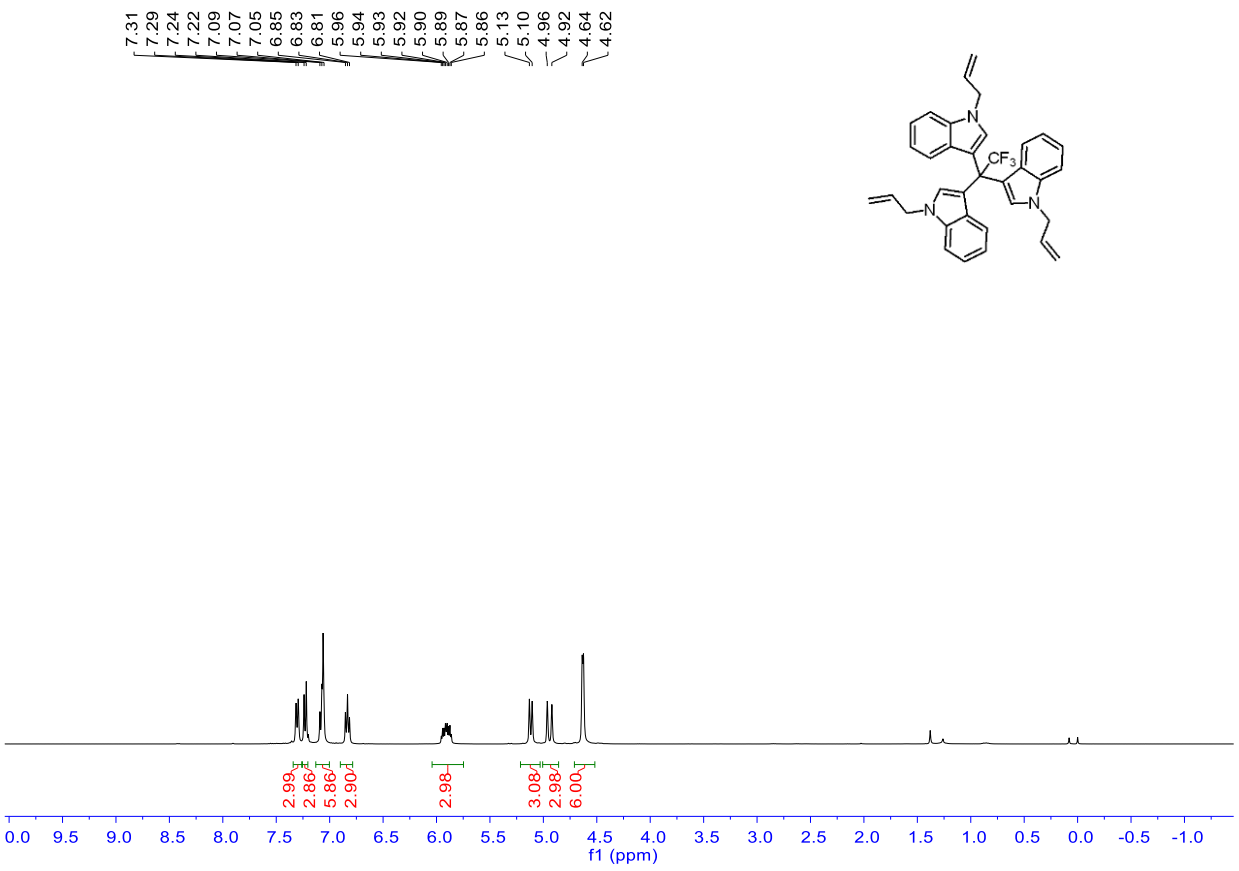
^{1}H NMR spectrum of **2d**



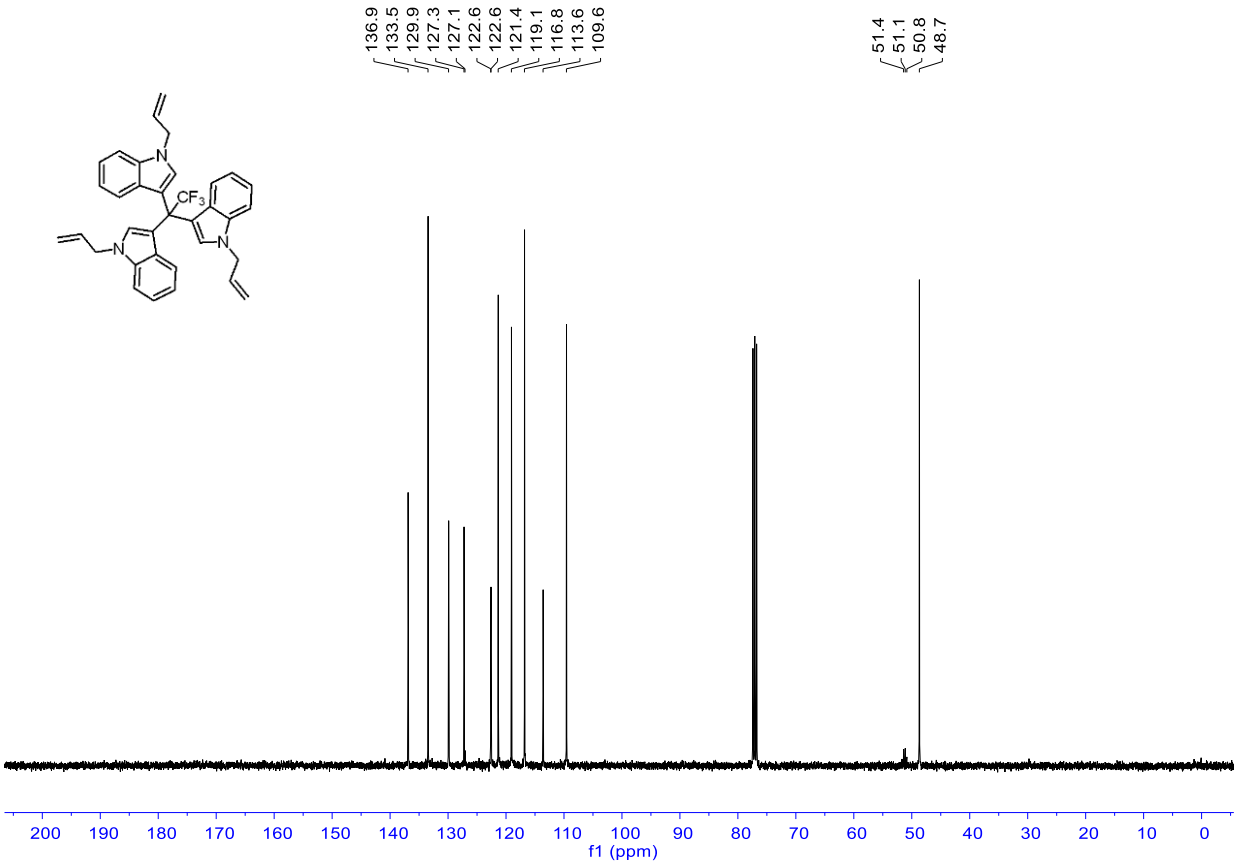
$^{13}C\{^{1}H\}$ NMR spectrum of **2d**



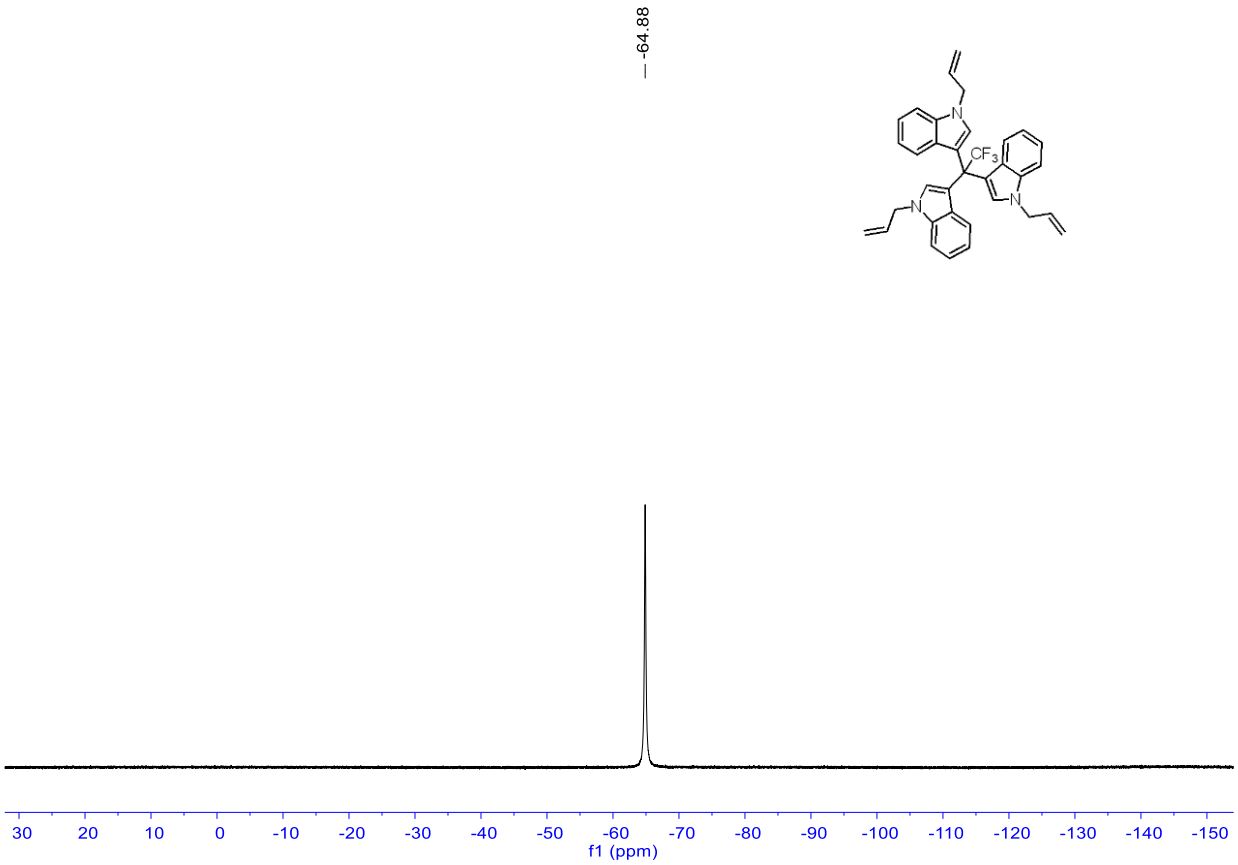
^{19}F NMR spectrum of **2d**



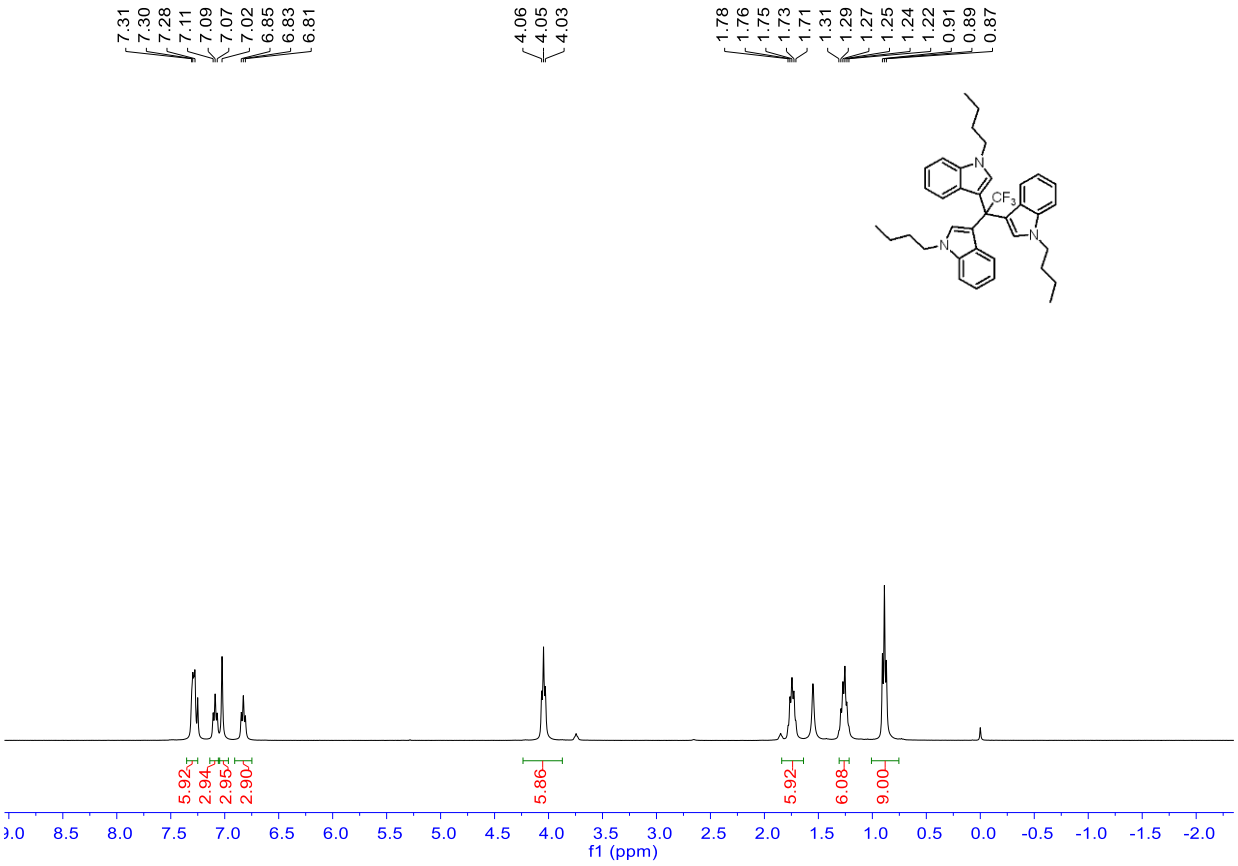
^{1}H NMR spectrum of **2e**



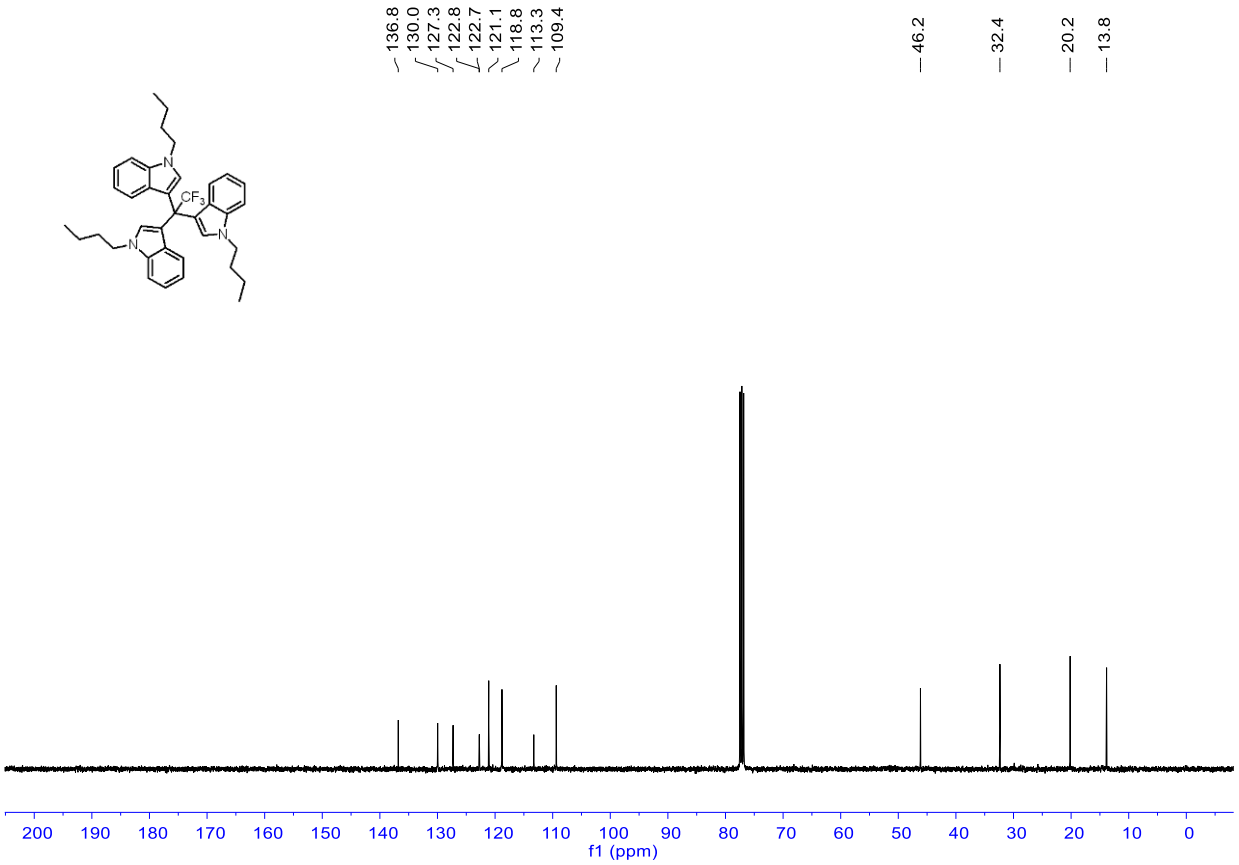
^{13}C{^{1}H} NMR spectrum of **2e**



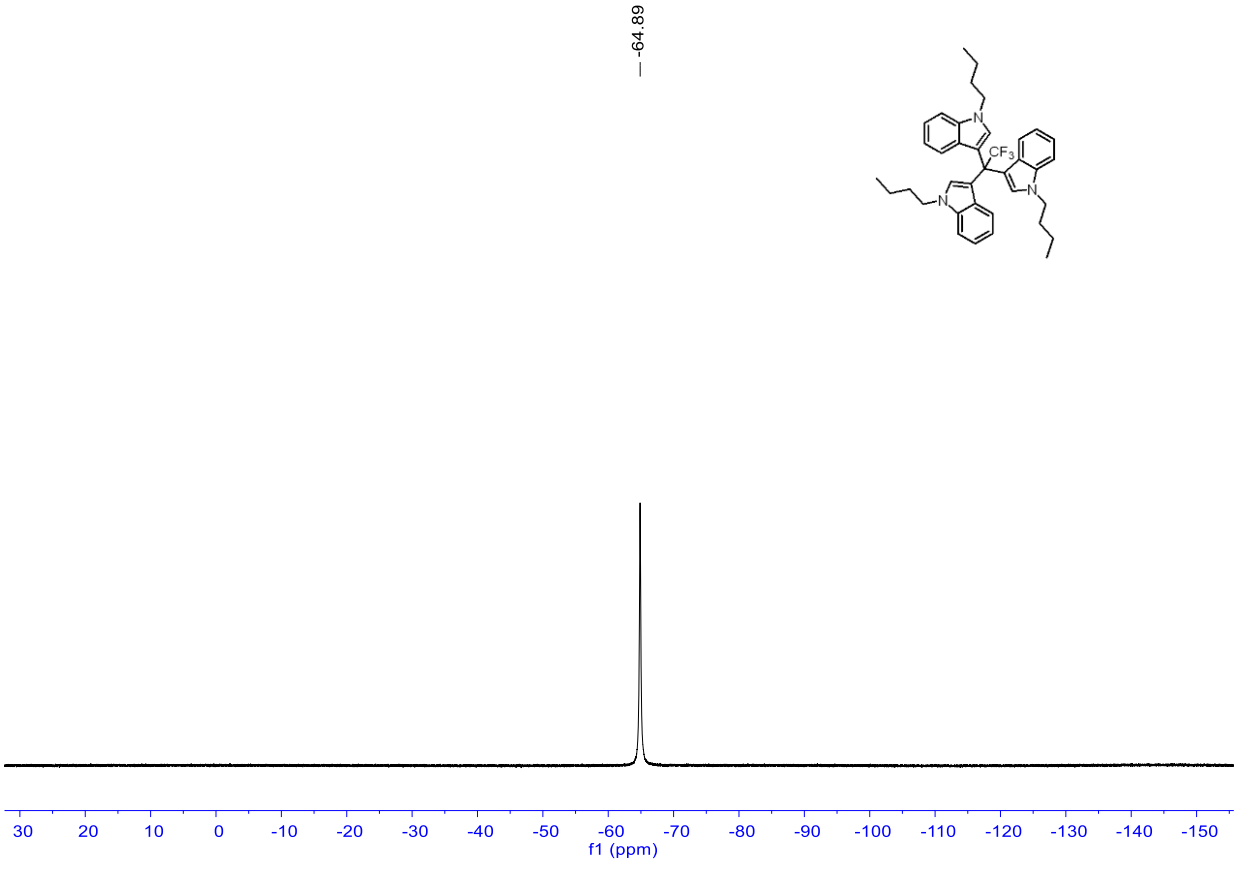
^{19}F NMR spectrum of **2e**



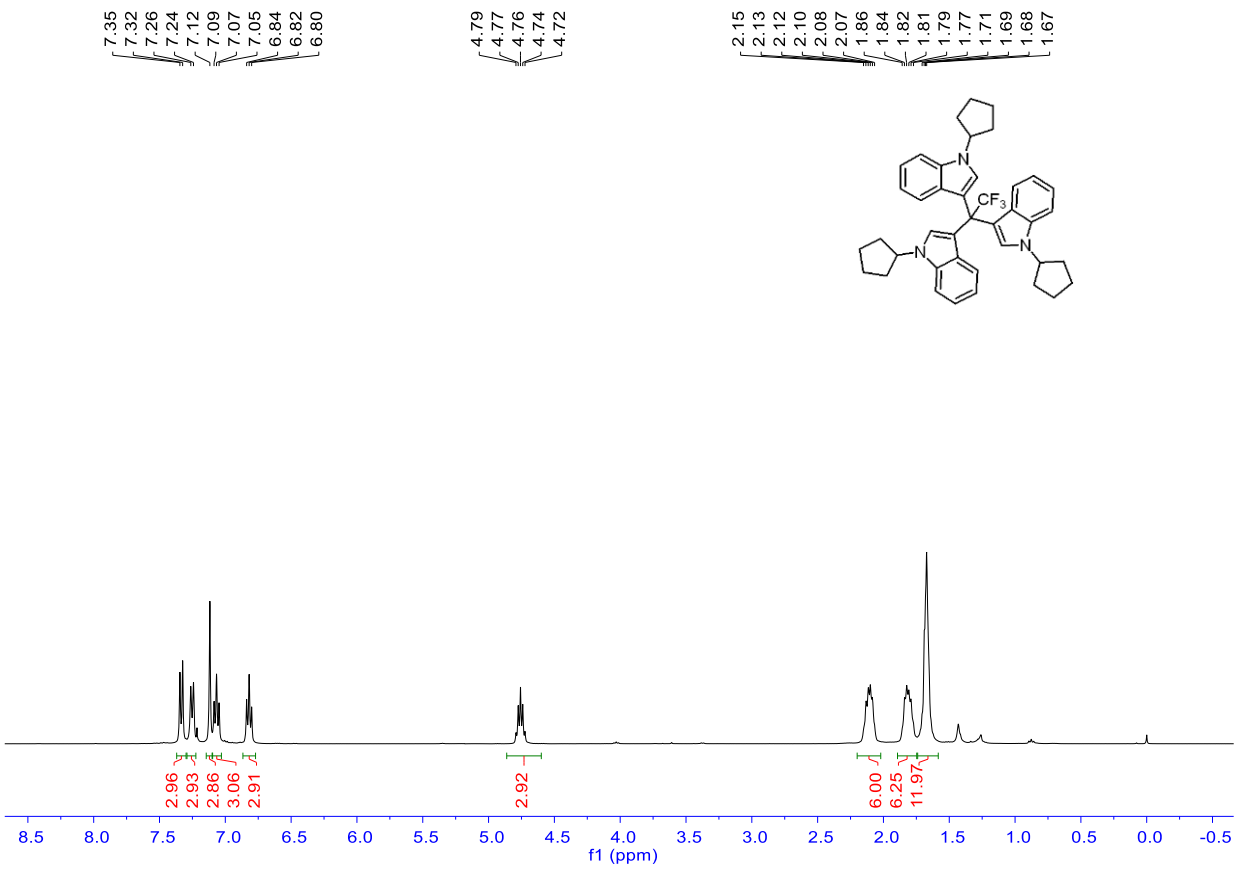
^{1}H NMR spectrum of **2f**



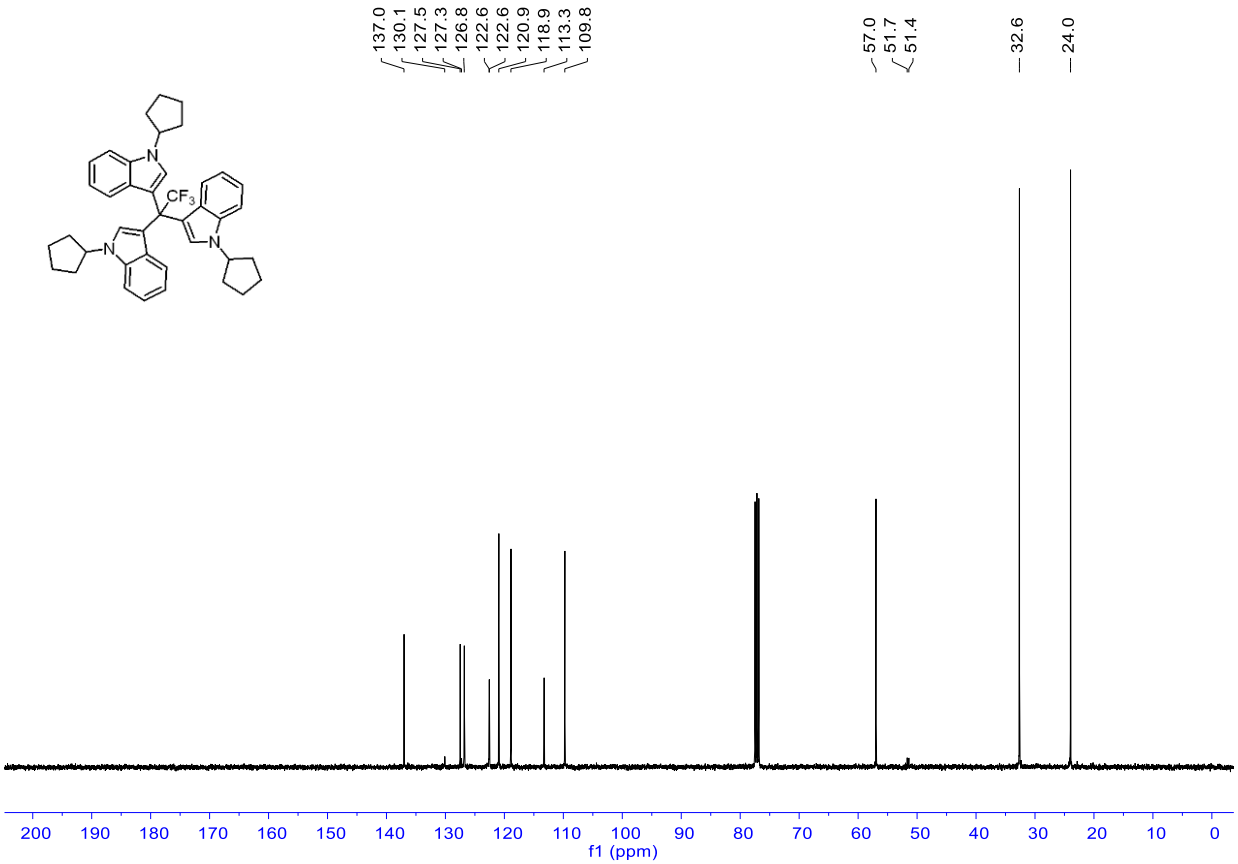
$^{13}C\{^{1}H\}$ NMR spectrum of **2f**



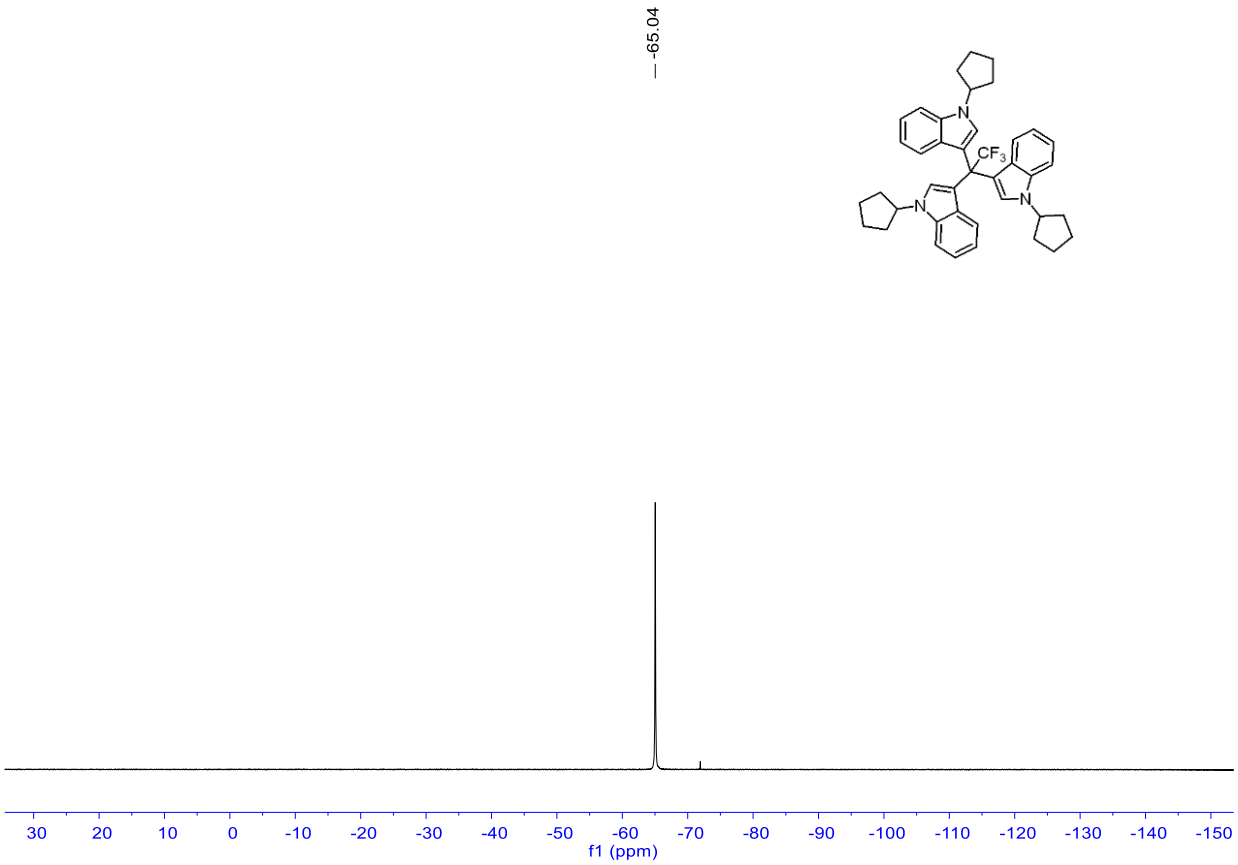
^{19}F NMR spectrum of **2f**



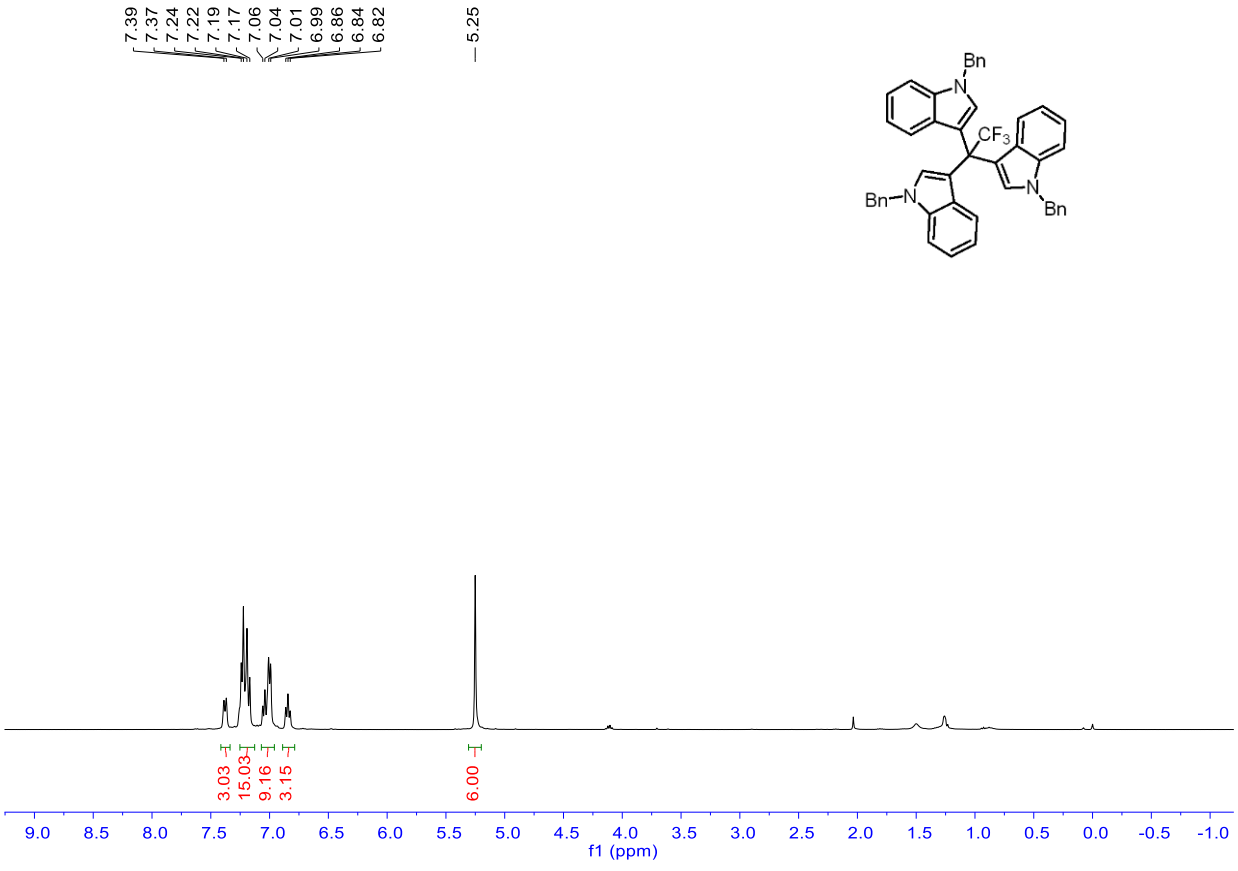
^{1}H NMR spectrum of **2g**



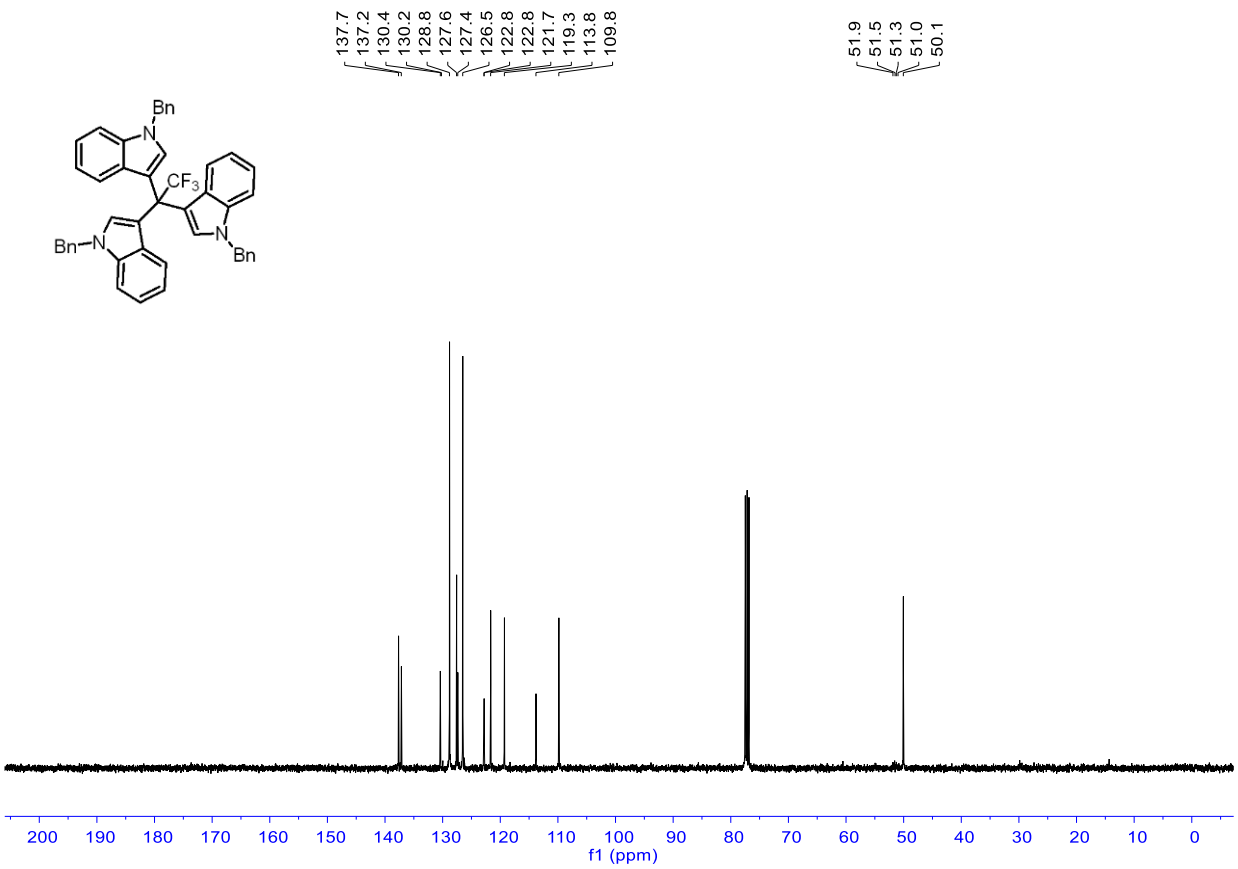
^{13}C{^{1}H} NMR spectrum of **2g**



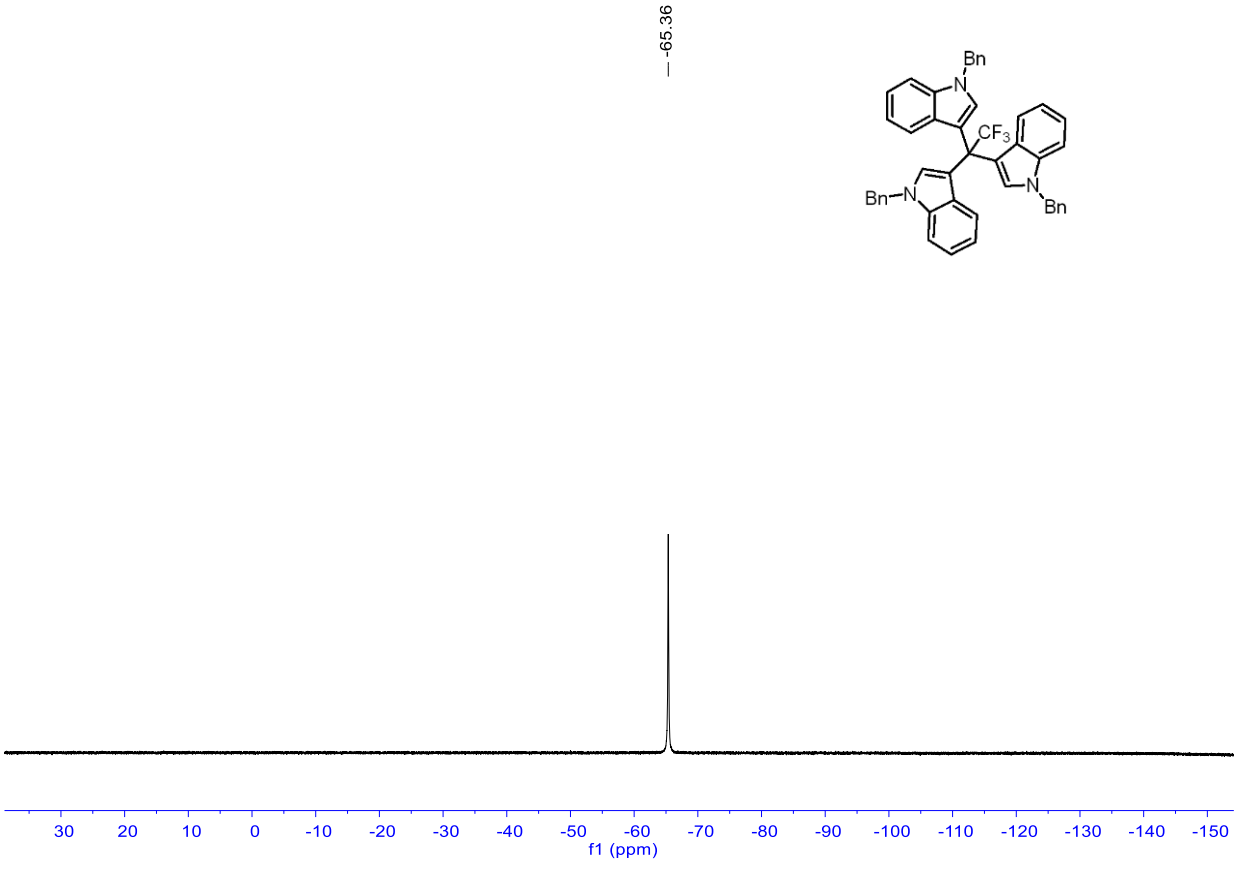
^{19}F NMR spectrum of **2g**



^{1}H NMR spectrum of **2h**



$^{13}C\{^{1}H\}$ NMR spectrum of **2h**



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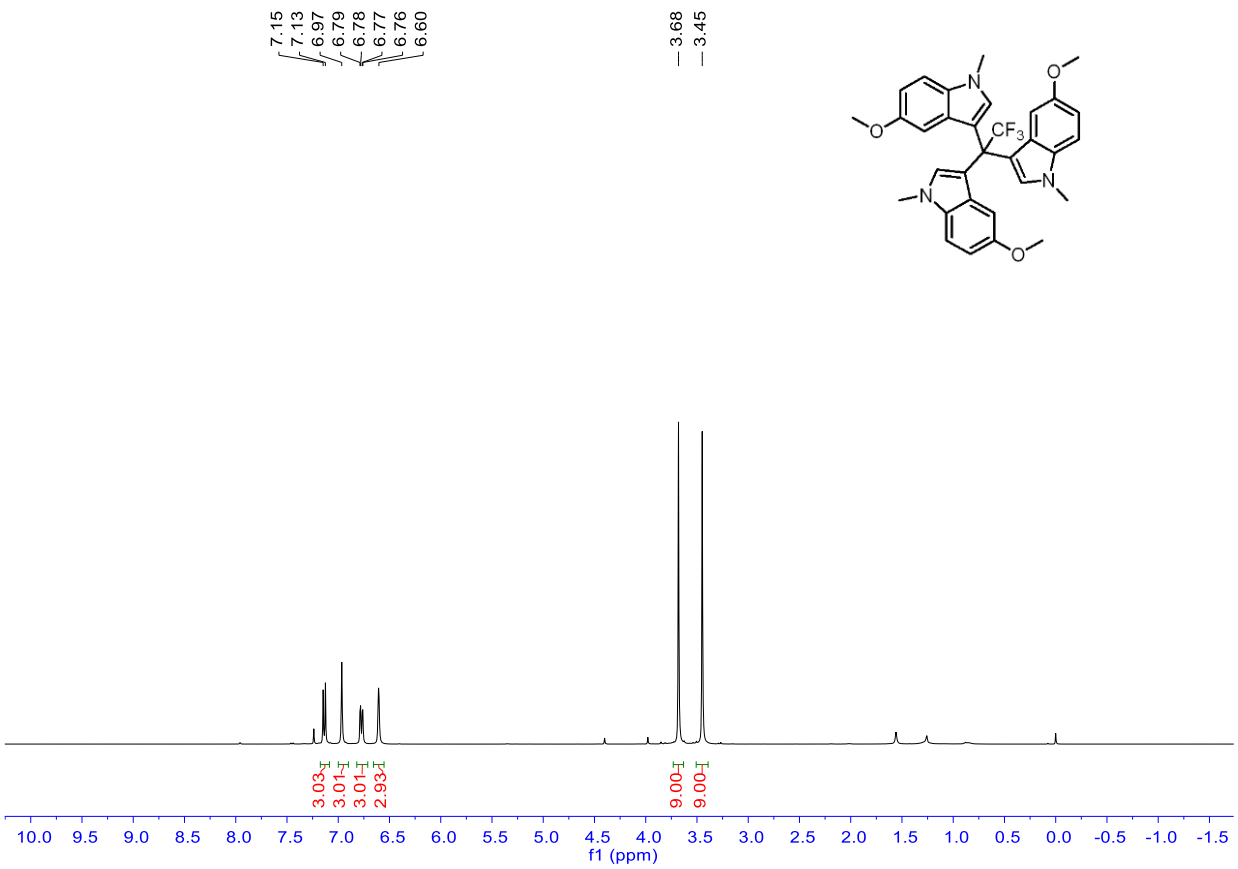
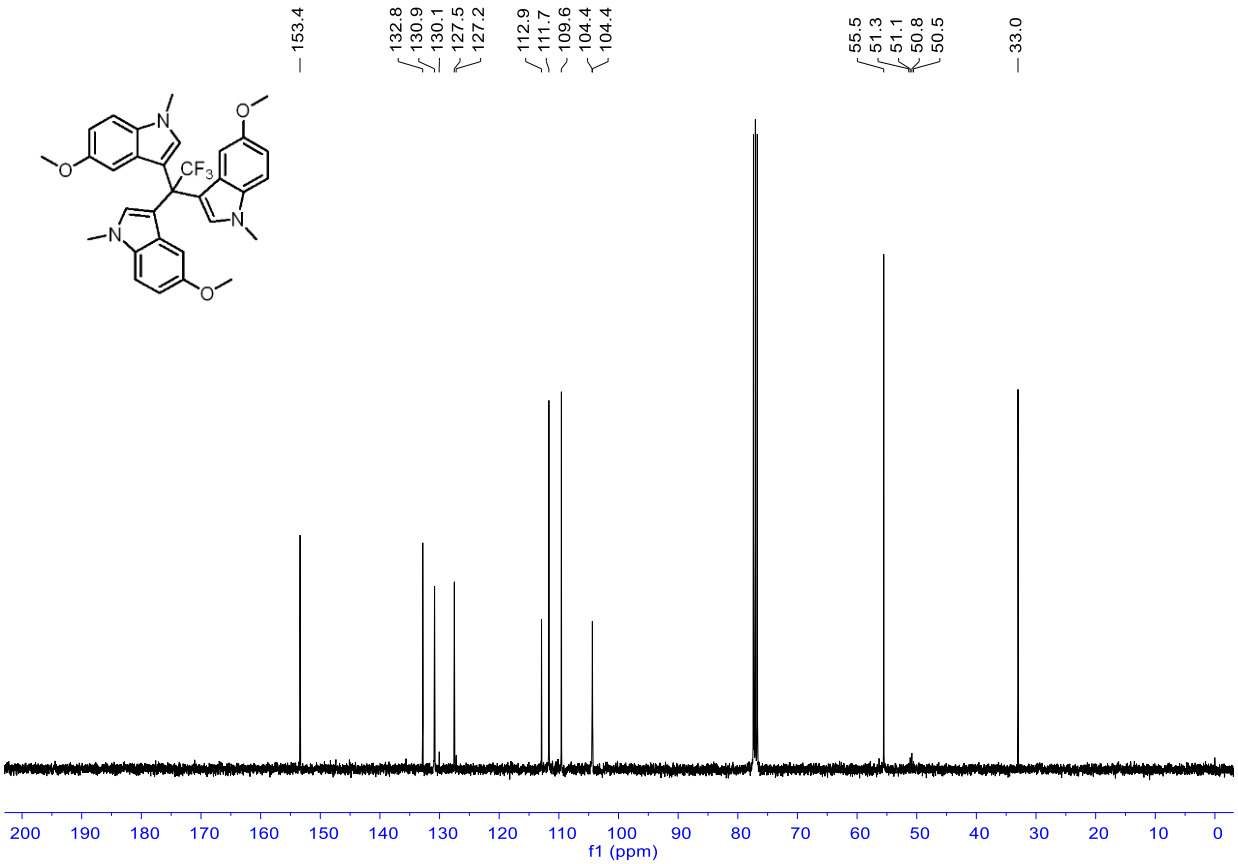
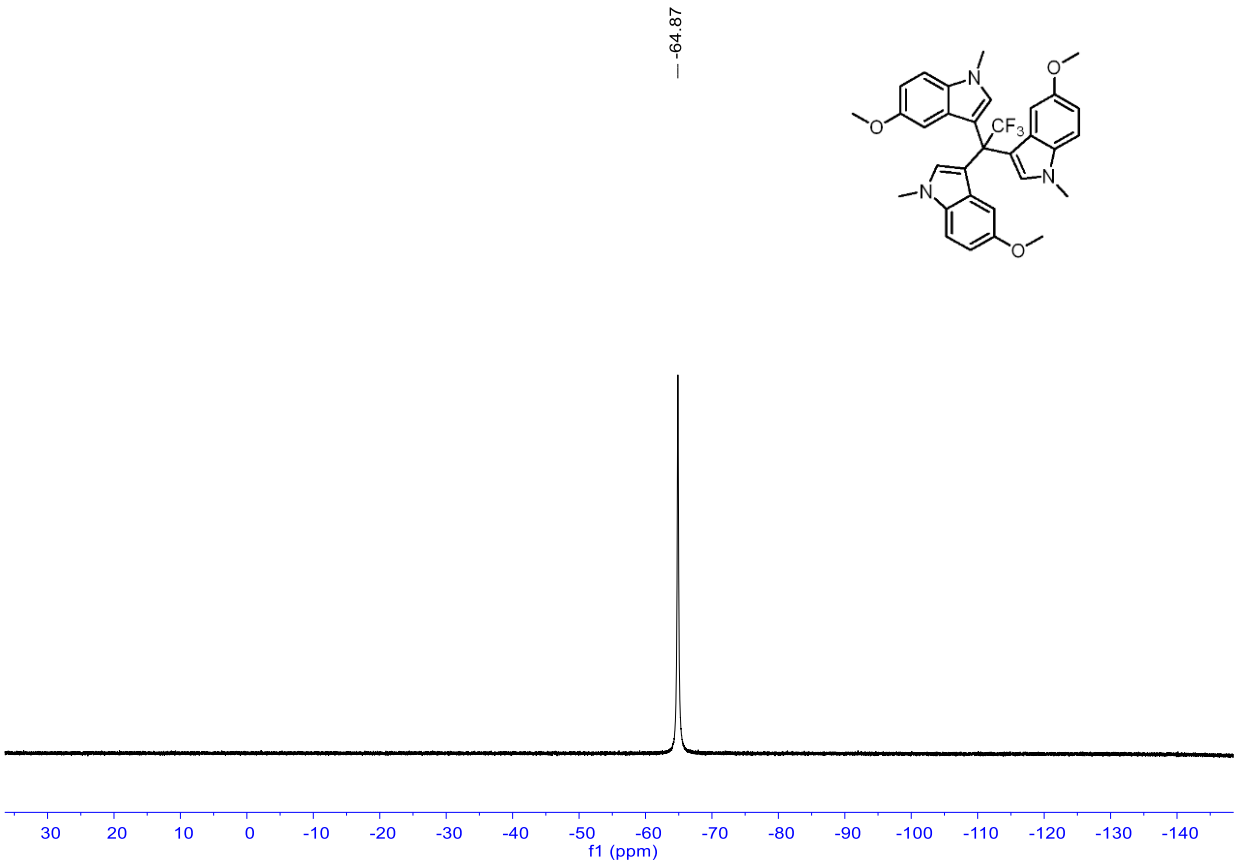


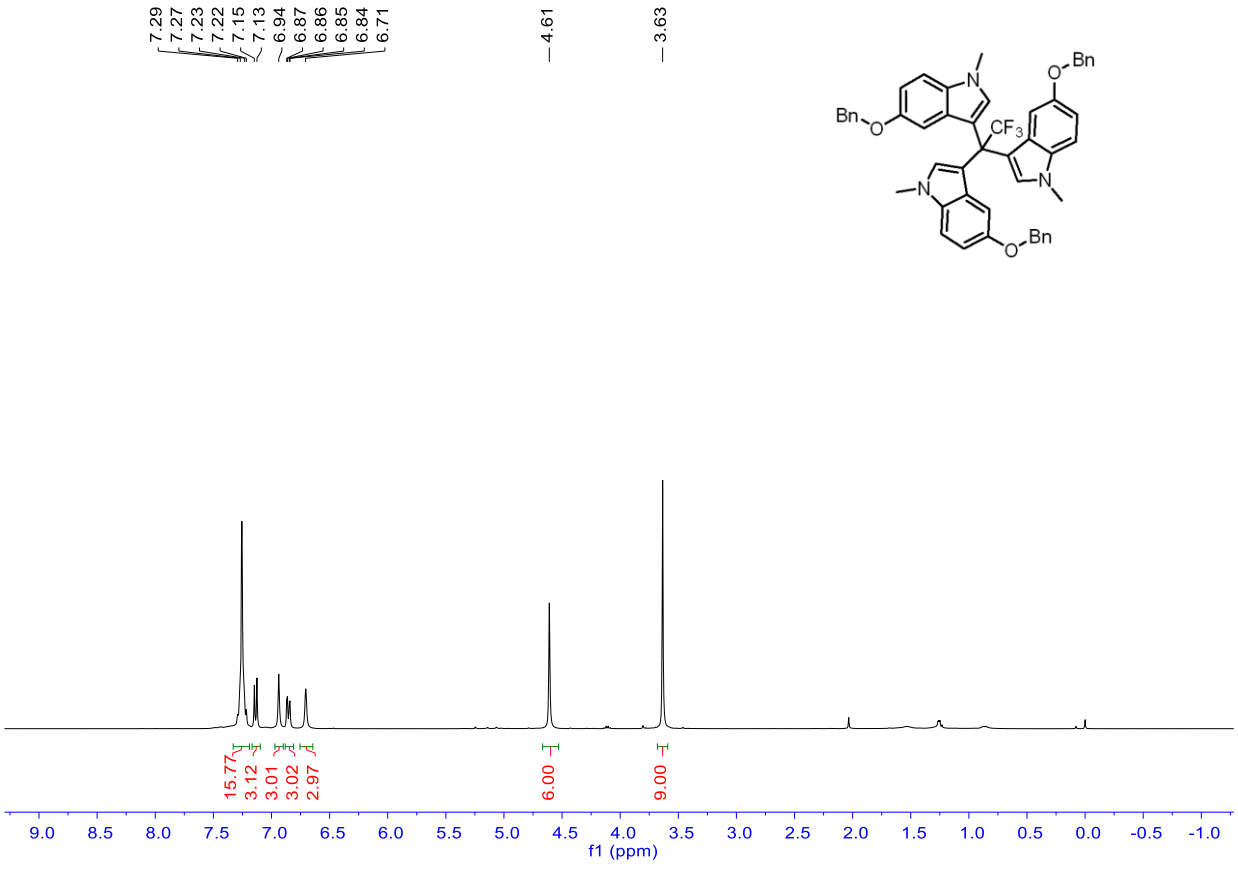
^{1}H NMR spectrum of **2i**



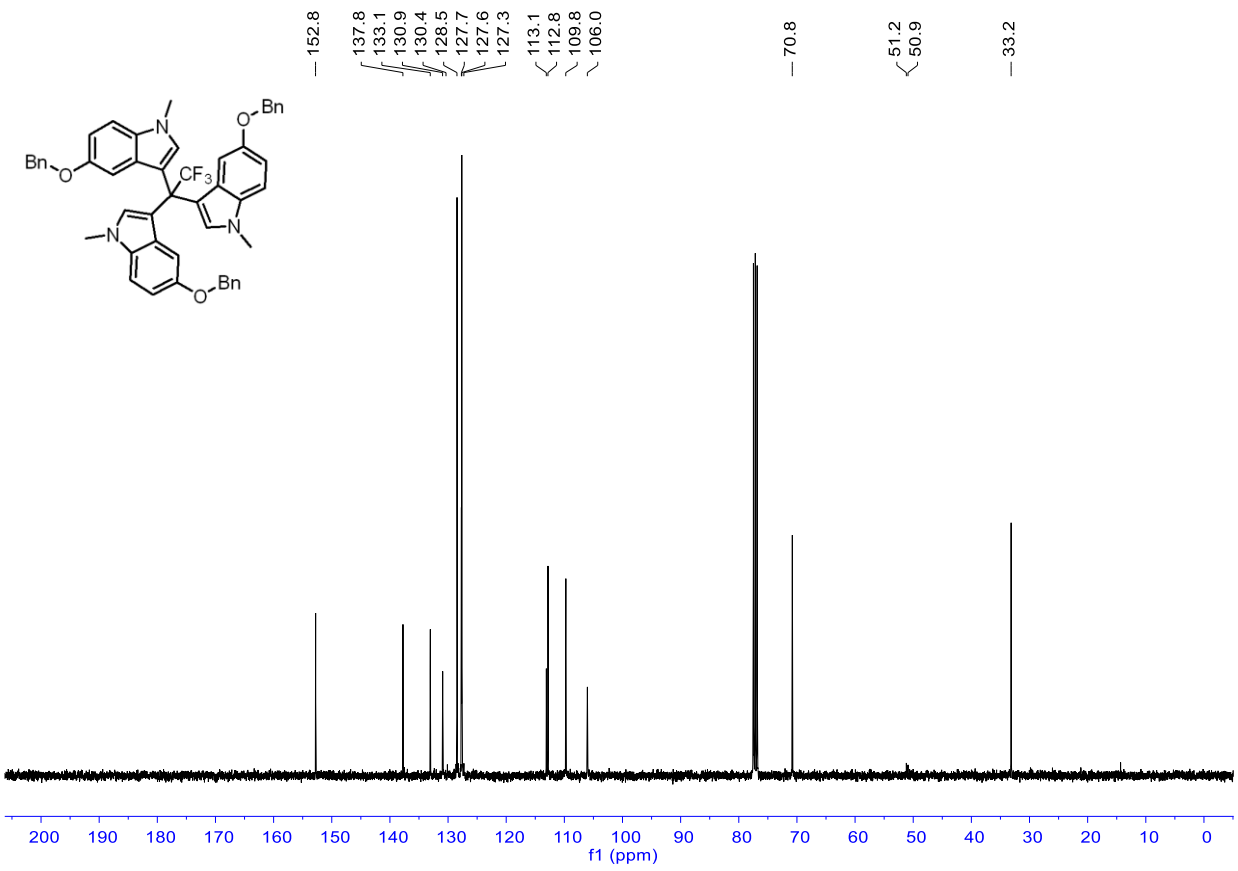
^{13}C{^{1}H} NMR spectrum of **2i**



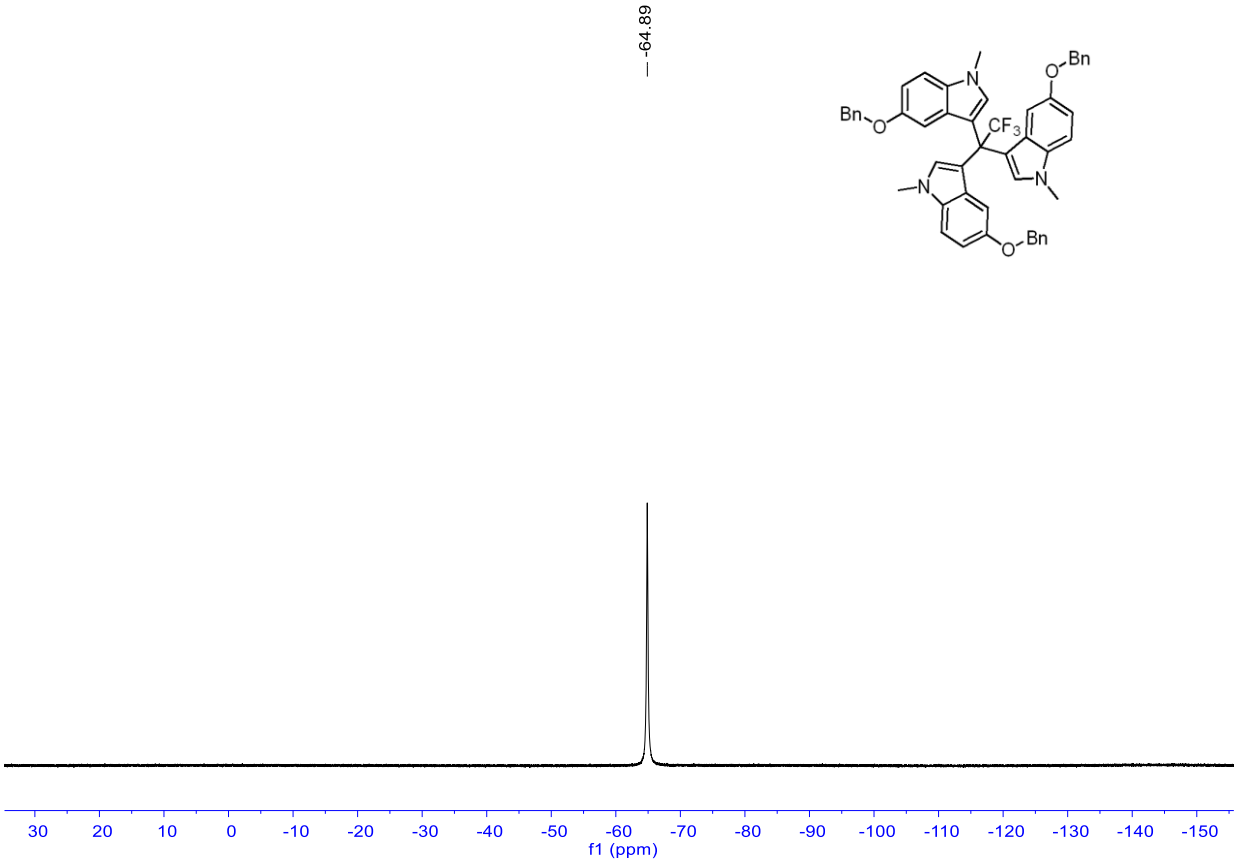
^{19}F NMR spectrum of **2i**



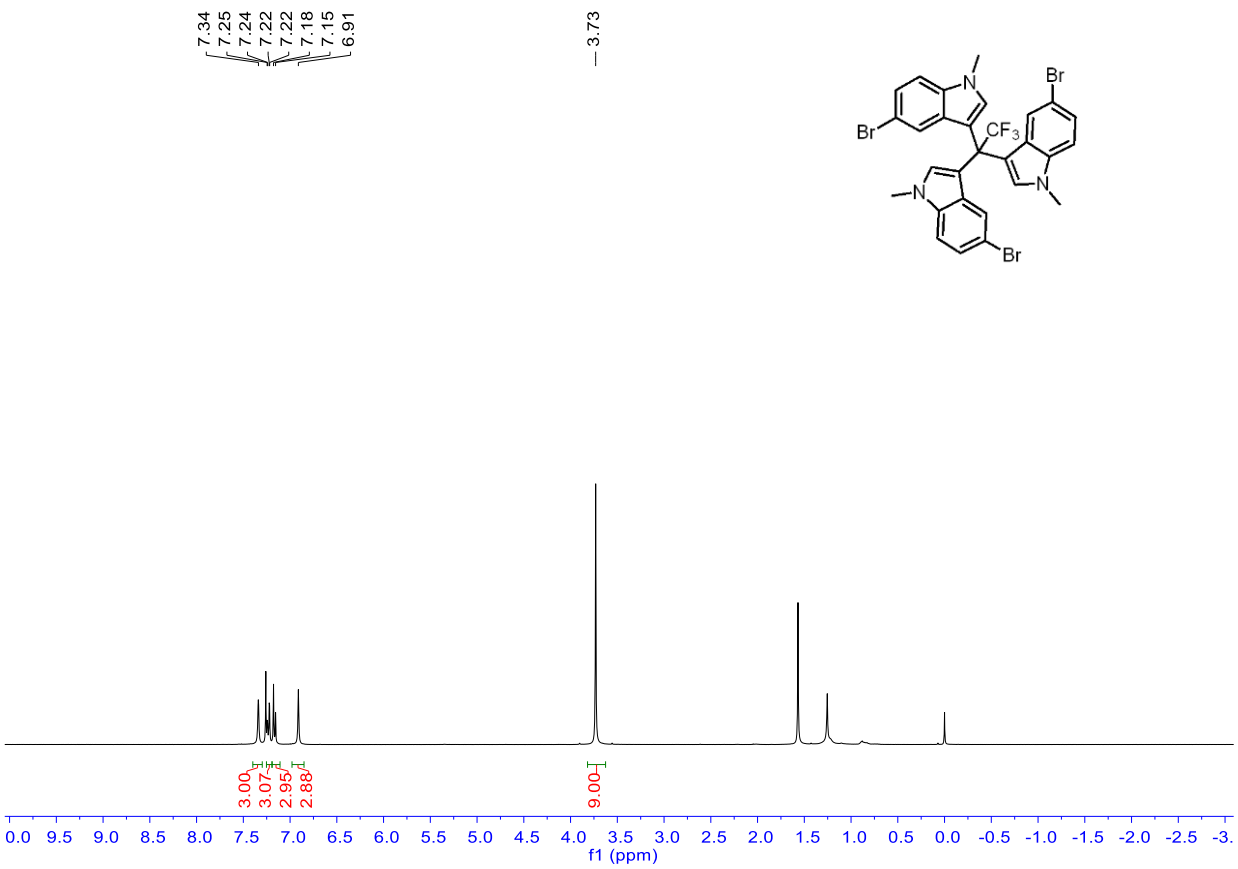
^{1}H NMR spectrum of **2j**



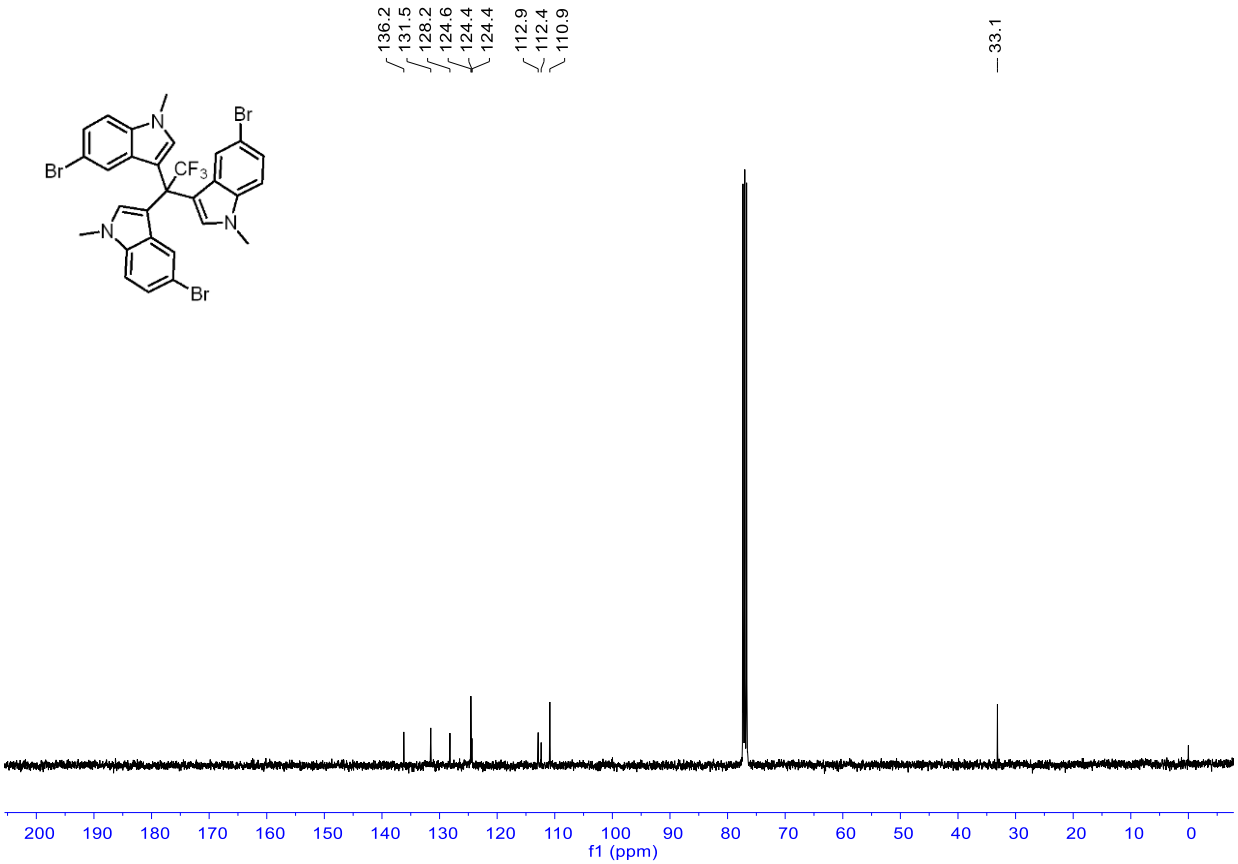
$^{13}C\{^{1}H\}$ NMR spectrum of **2j**



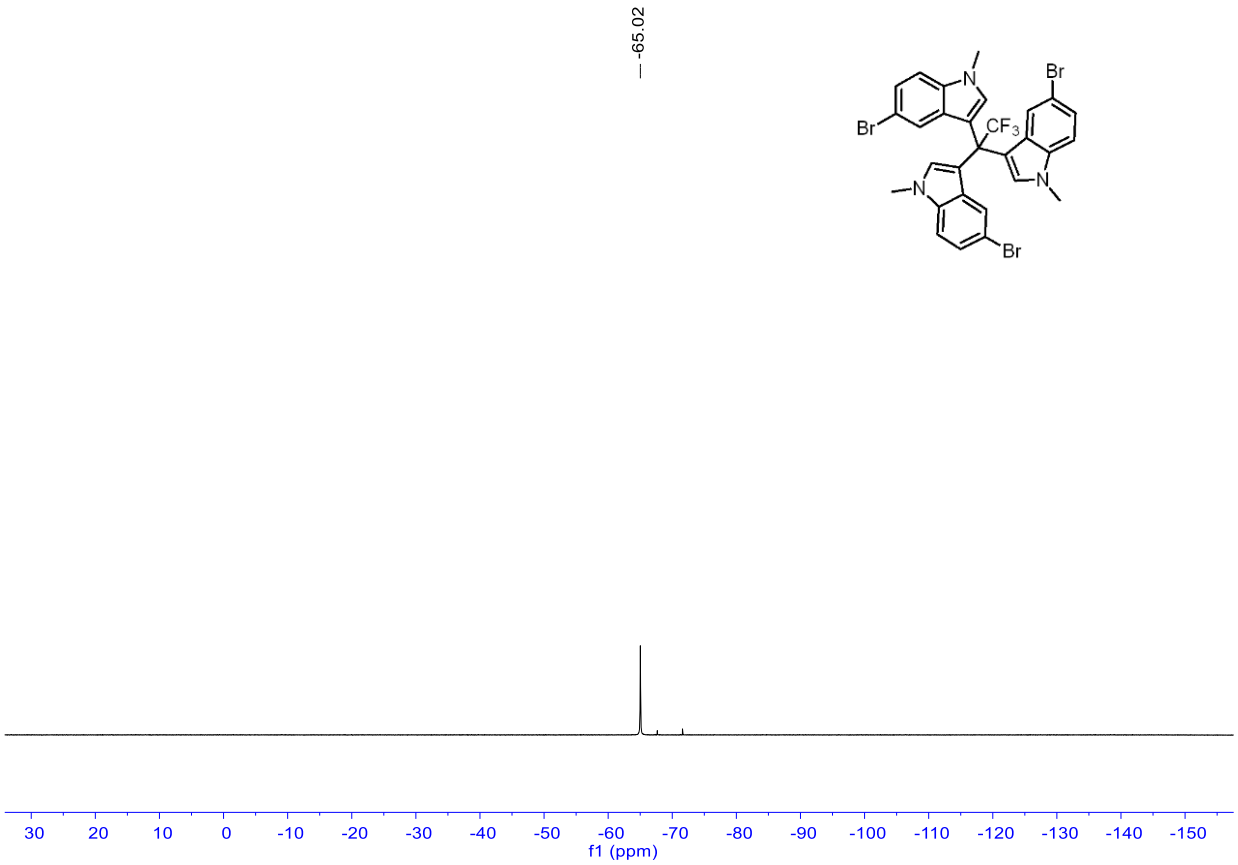
^{19}F NMR spectrum of **2j**



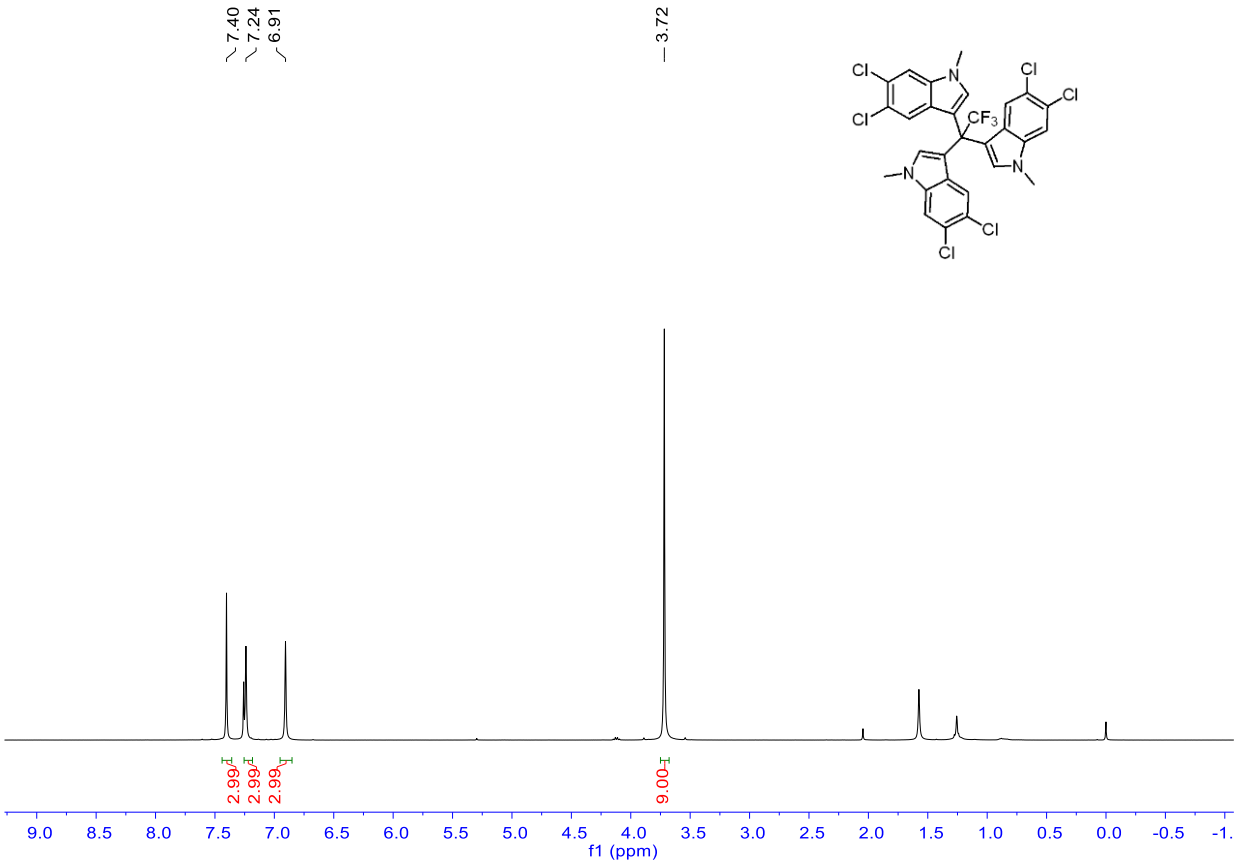
^{1}H NMR spectrum of **2k**



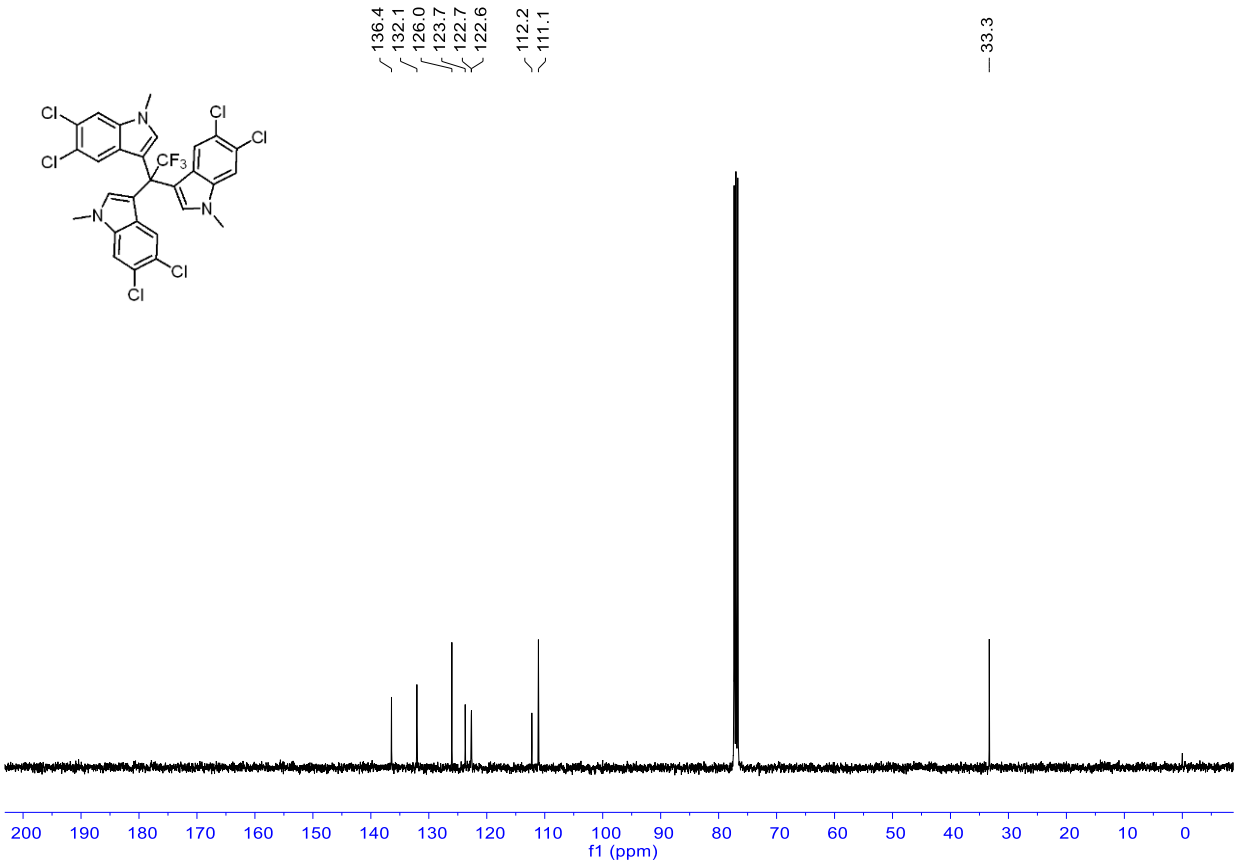
^{13}C{^{1}H} NMR spectrum of **2k**



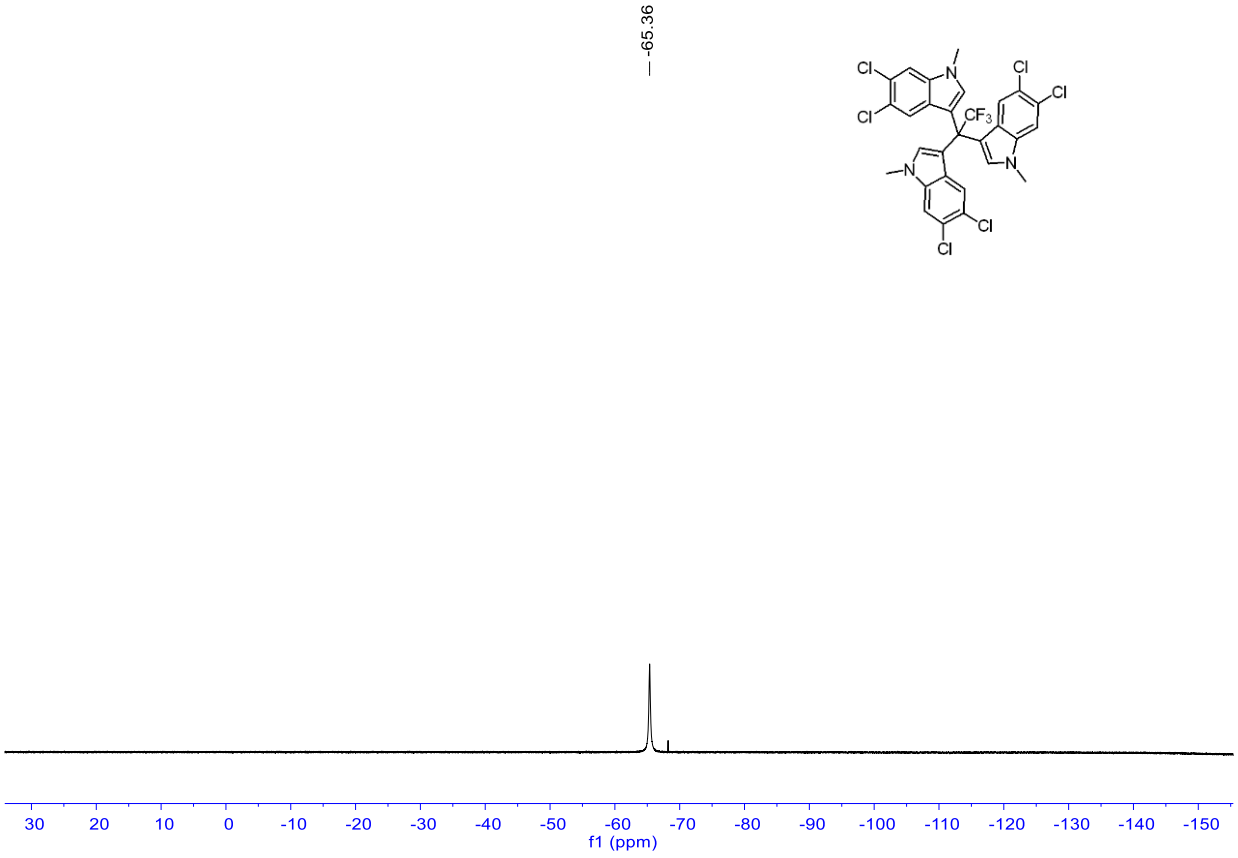
^{19}F NMR spectrum of **2k**



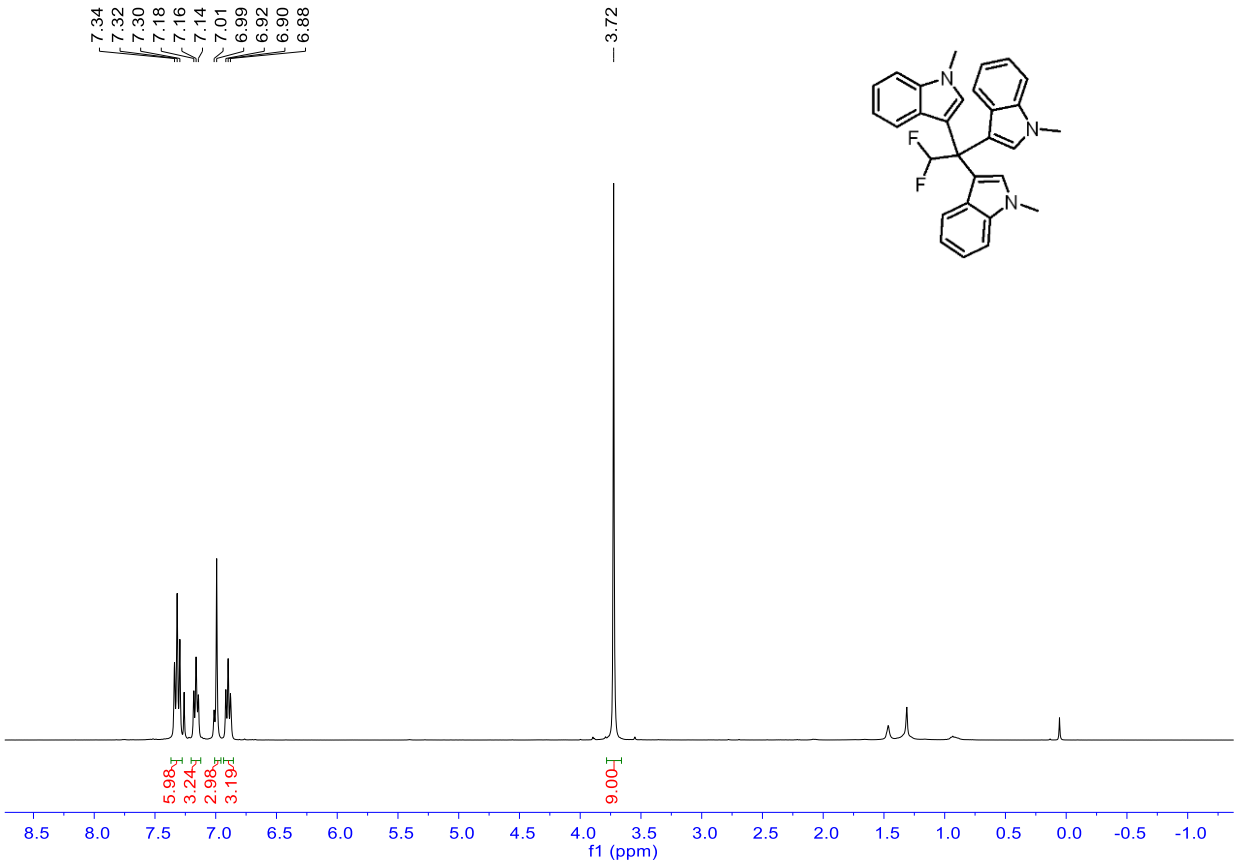
^{1}H NMR spectrum of **2l**



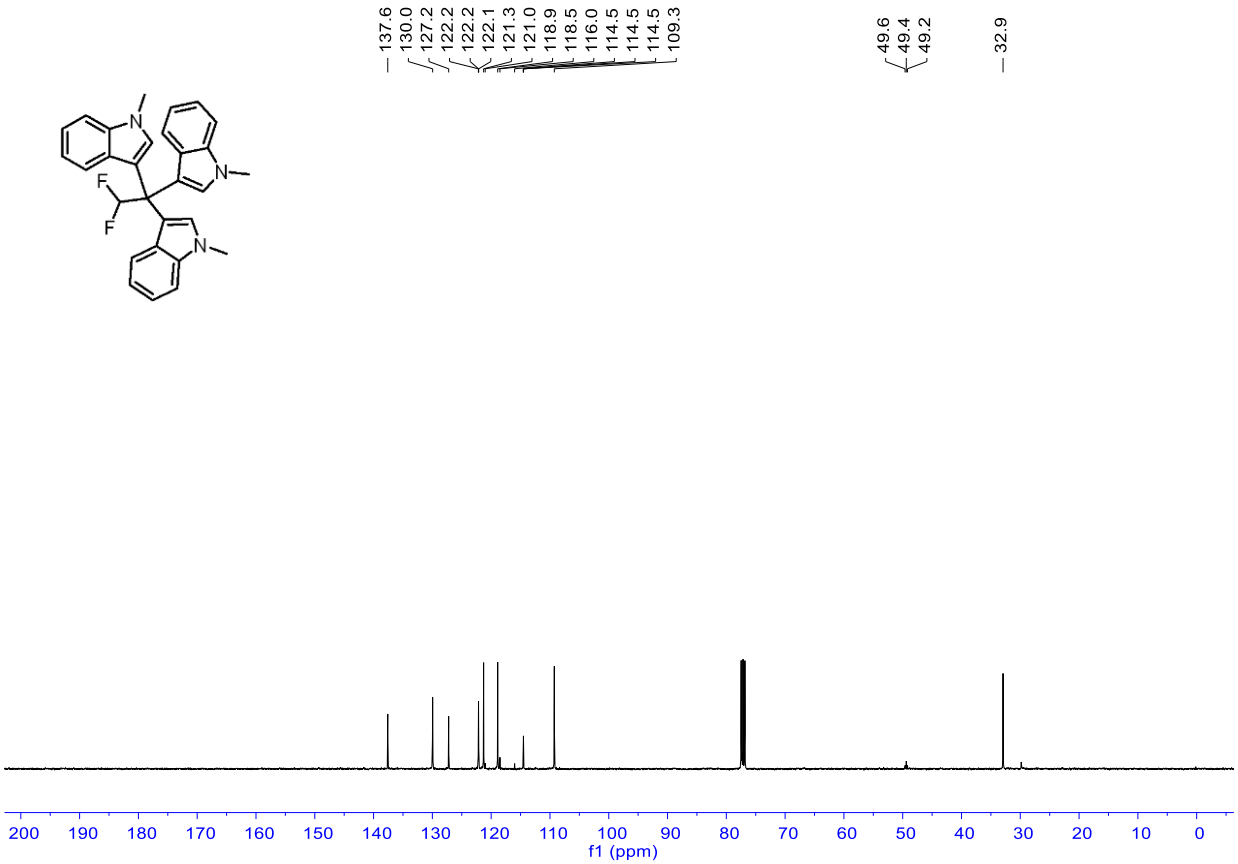
$^{13}C\{^{1}H\}$ NMR spectrum of **2l**



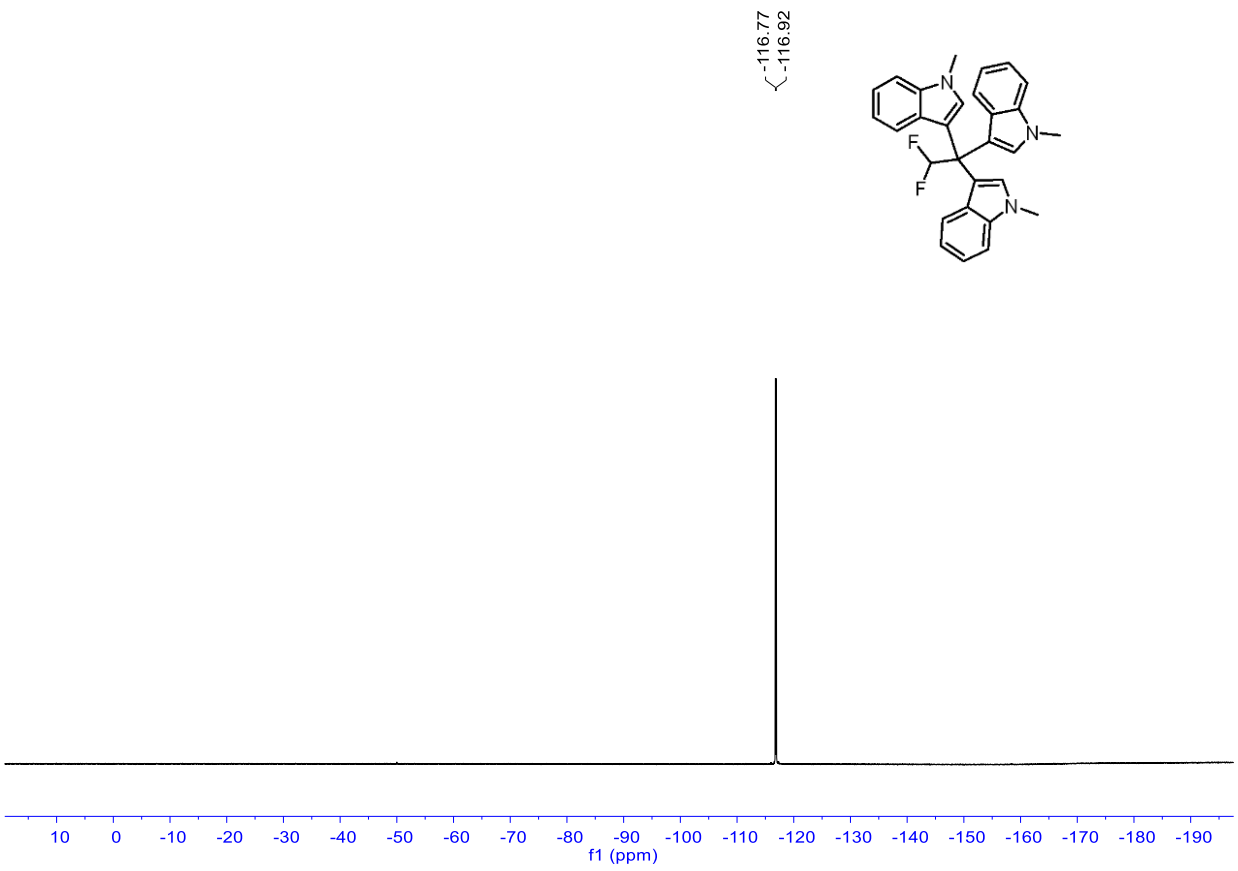
^{19}F NMR spectrum of **2l**



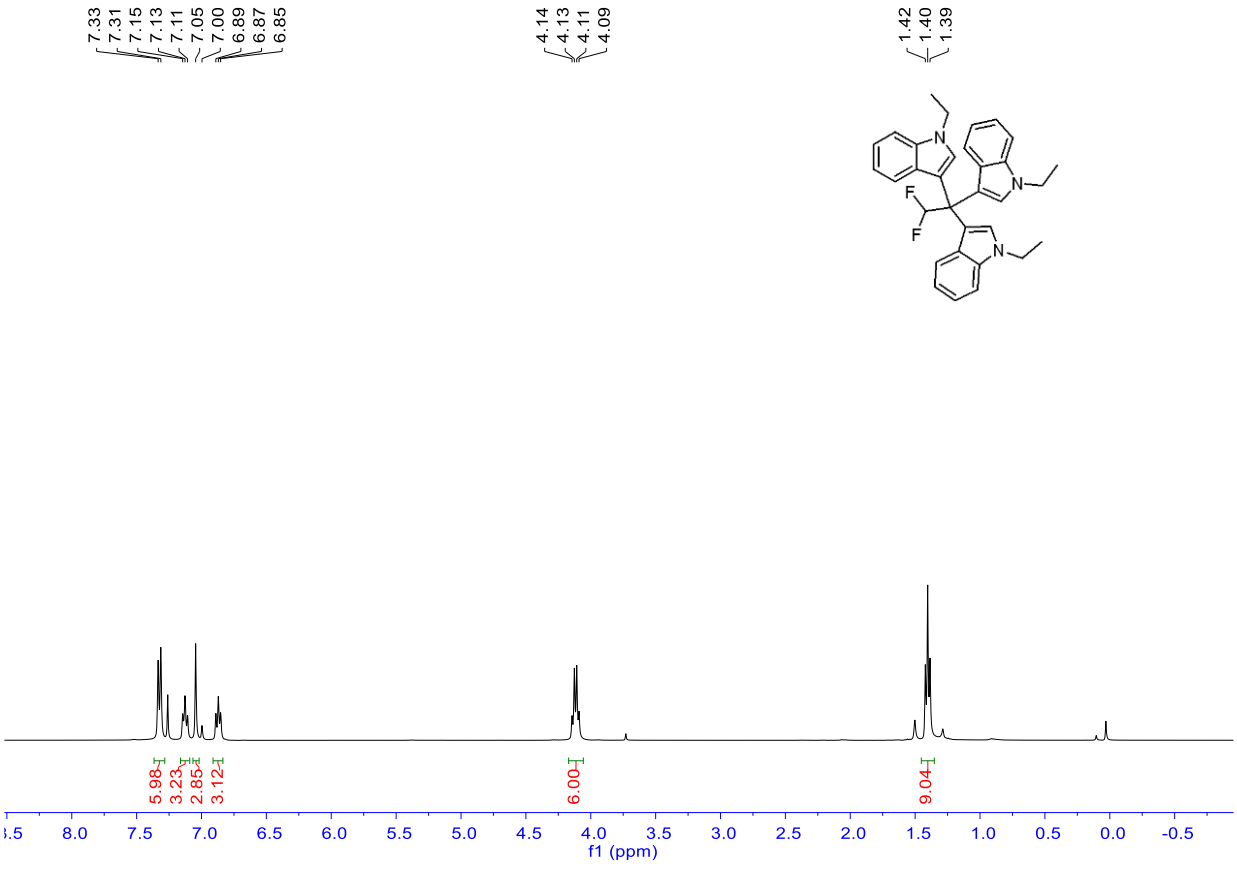
^{1}H NMR spectrum of **3a**



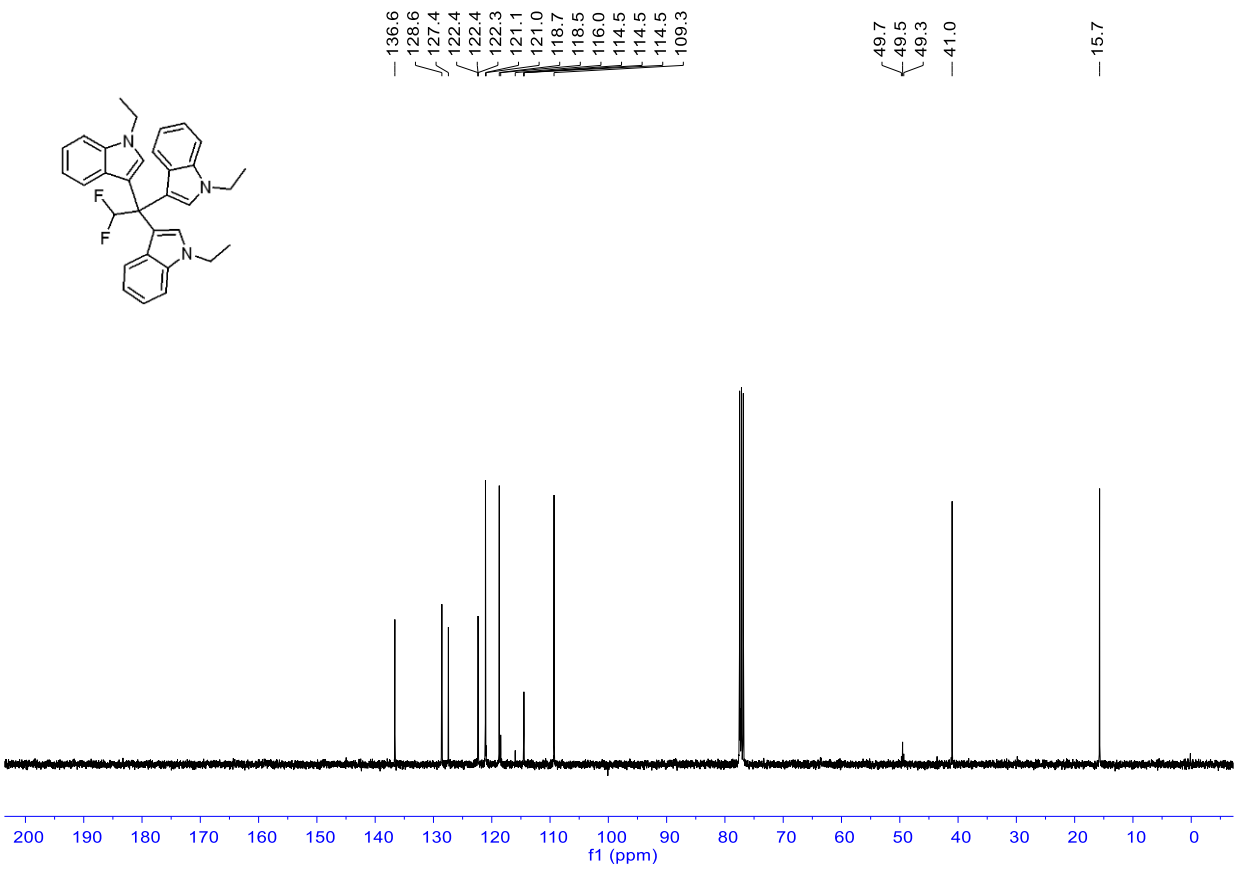
^{13}C{^{1}H} NMR spectrum of **3a**



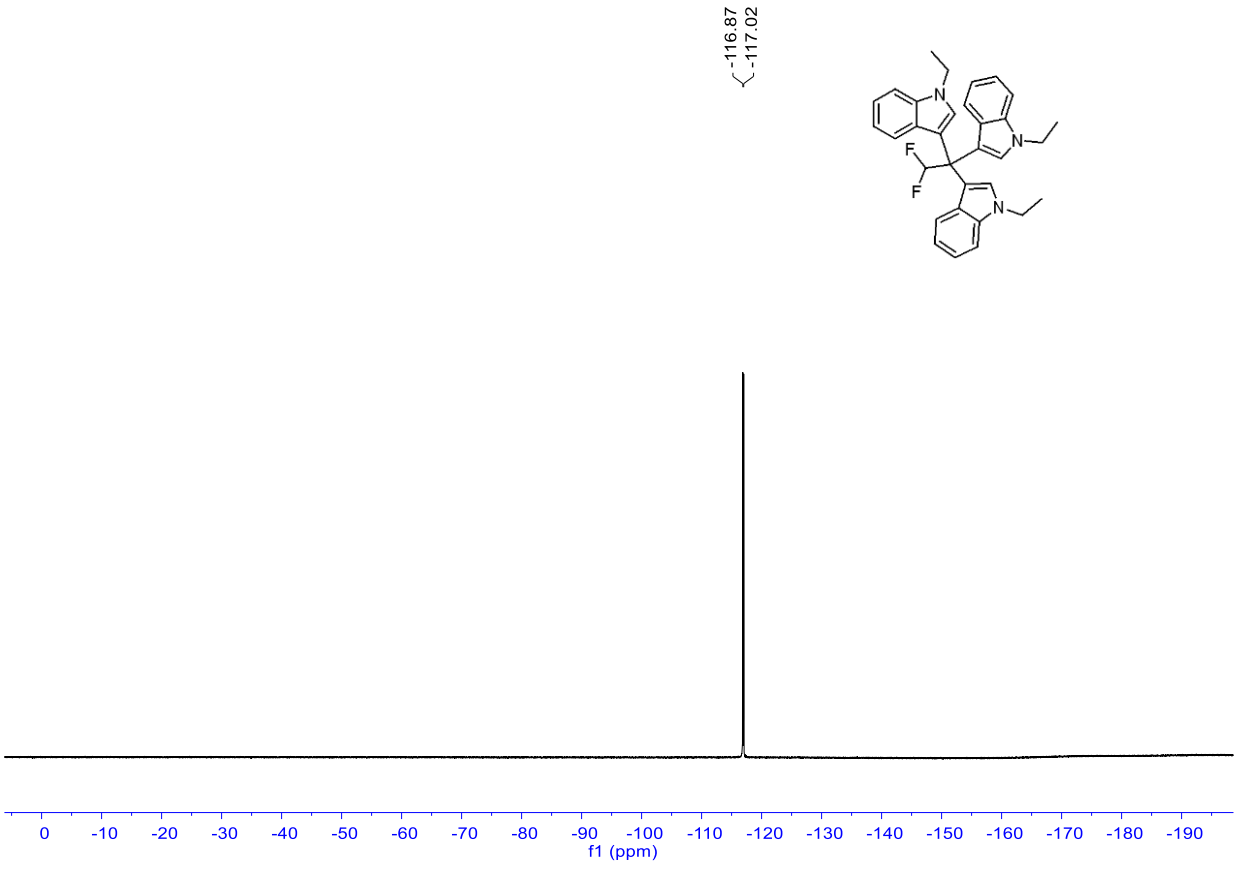
^{19}F NMR spectrum of **3a**



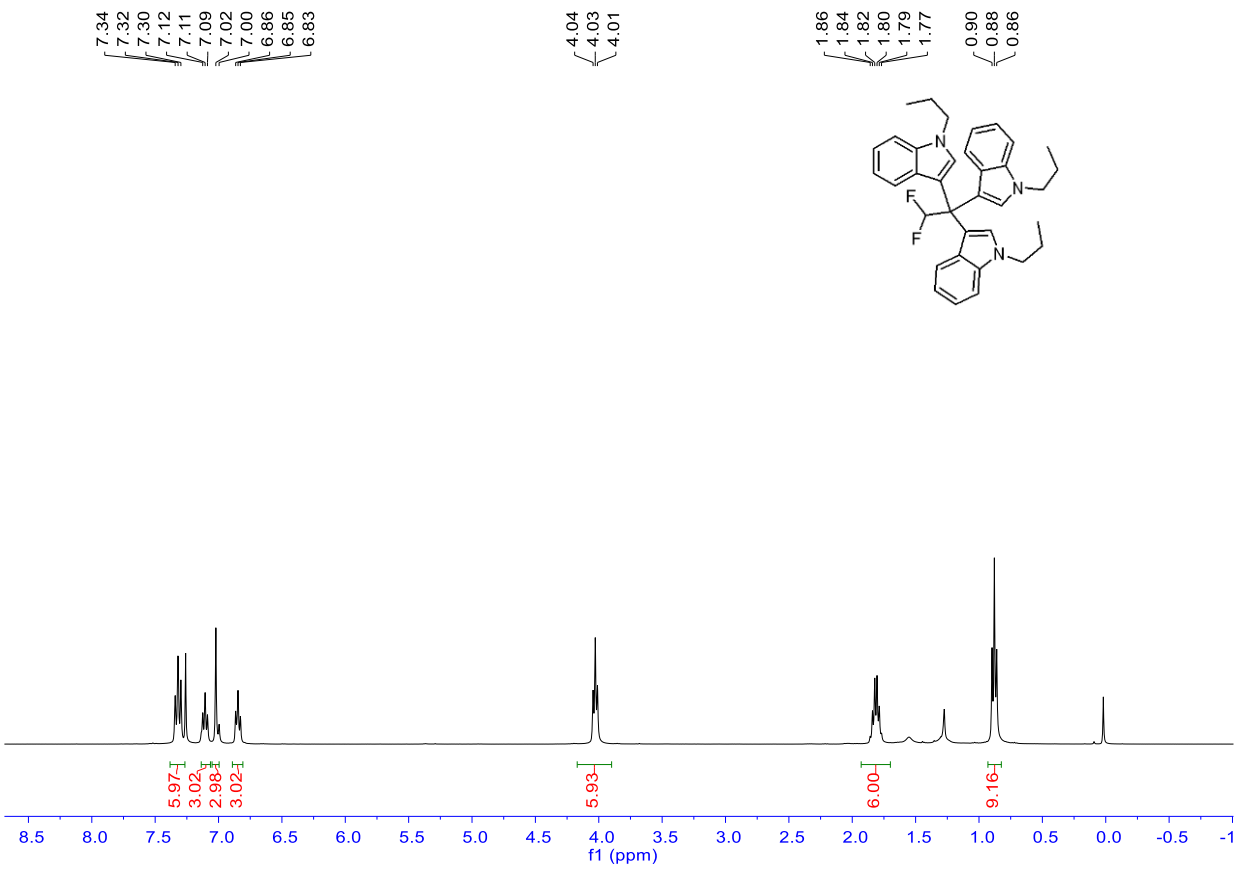
^{1}H NMR spectrum of **3b**



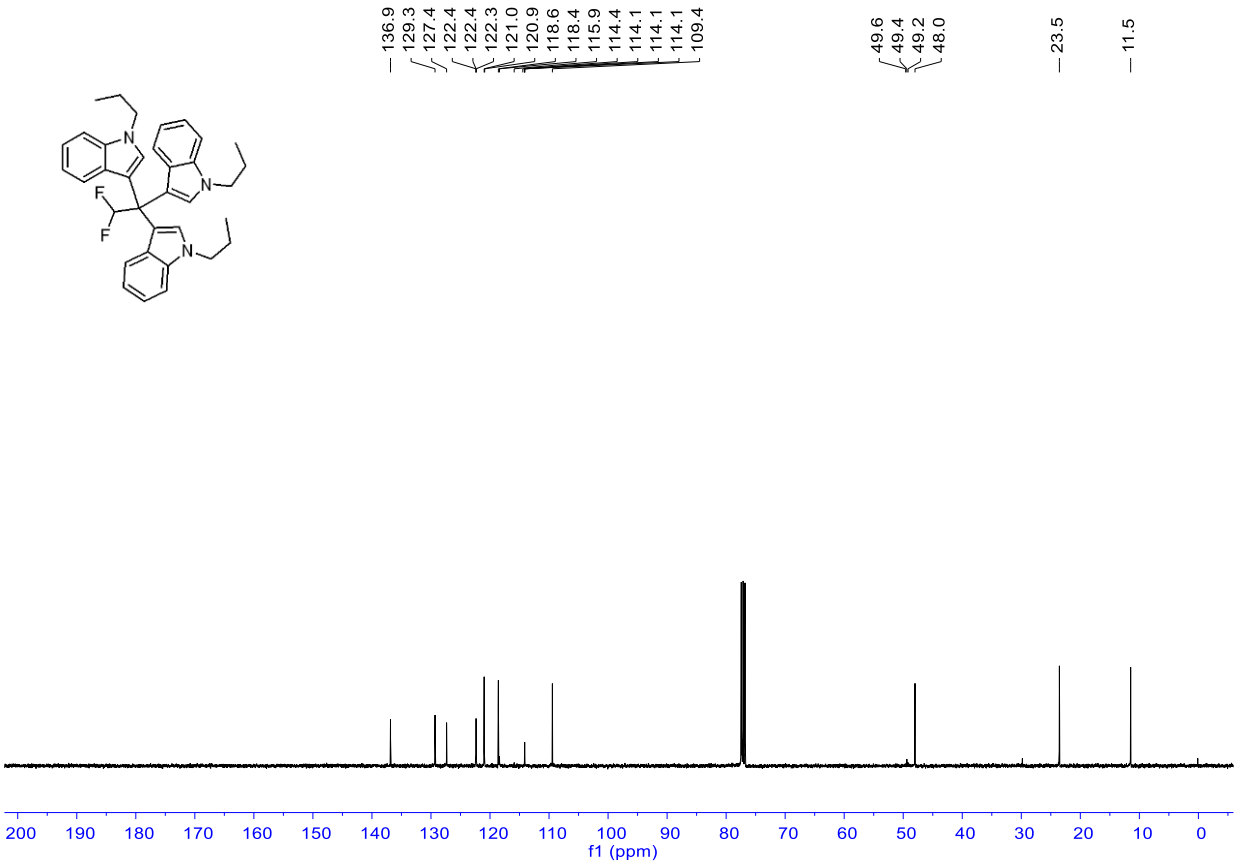
$^{13}C\{^{1}H\}$ NMR spectrum of **3b**



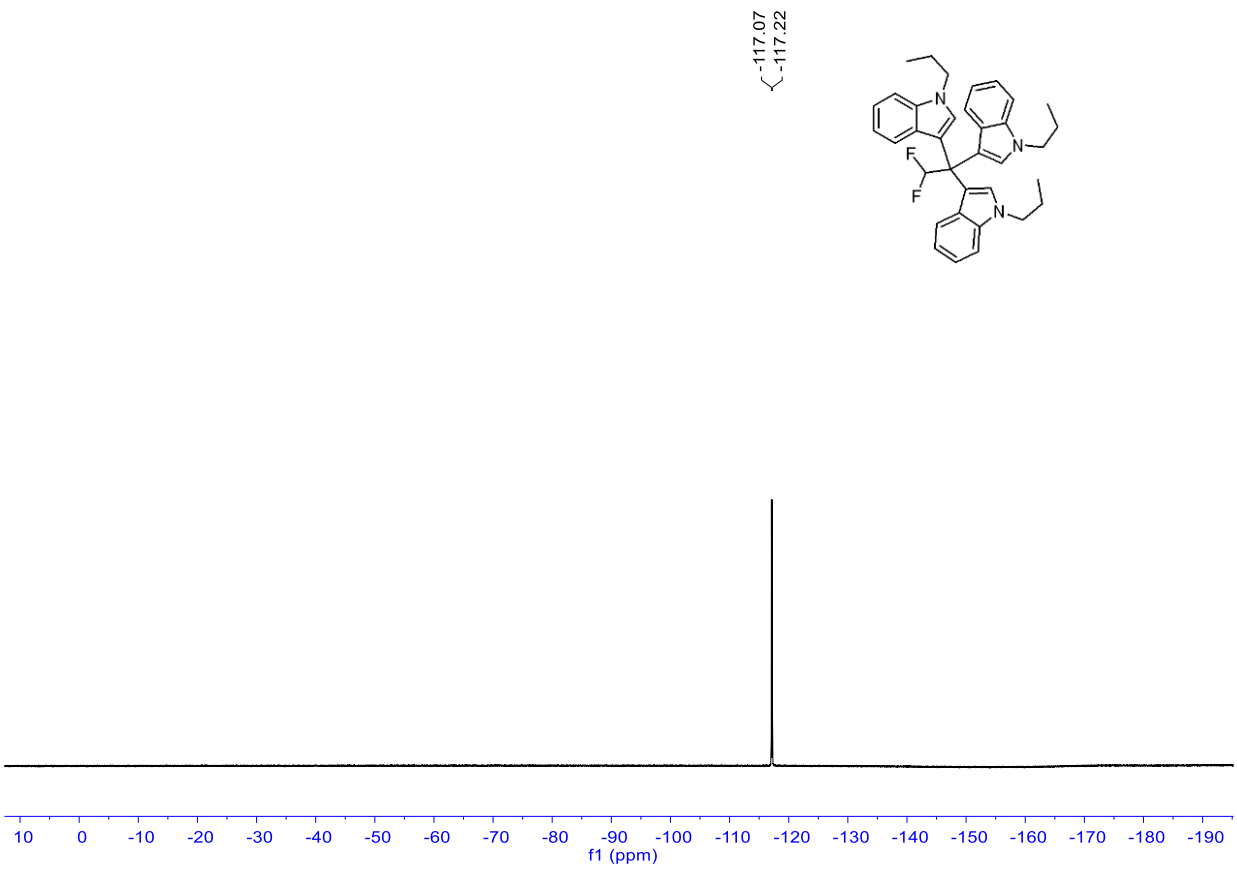
^{19}F NMR spectrum of **3b**



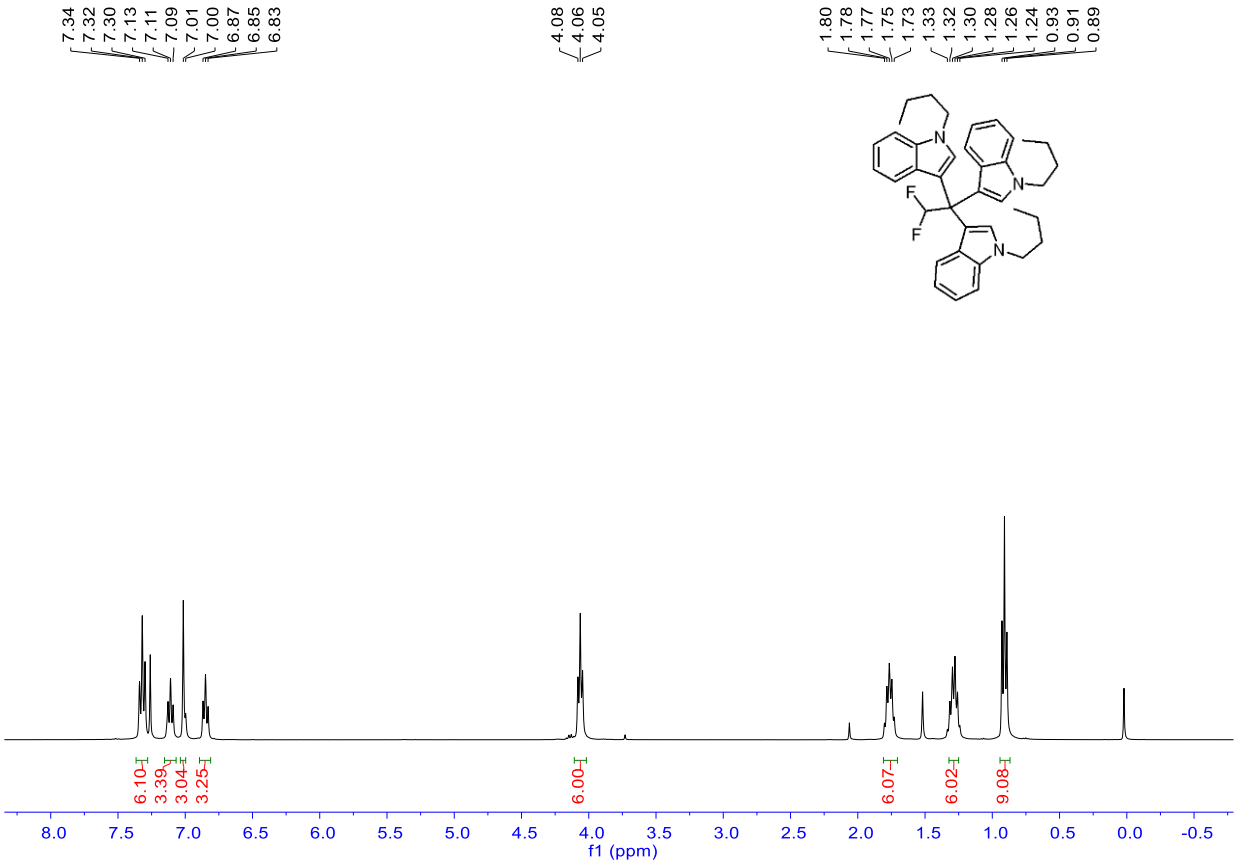
^{1}H NMR spectrum of **3c**



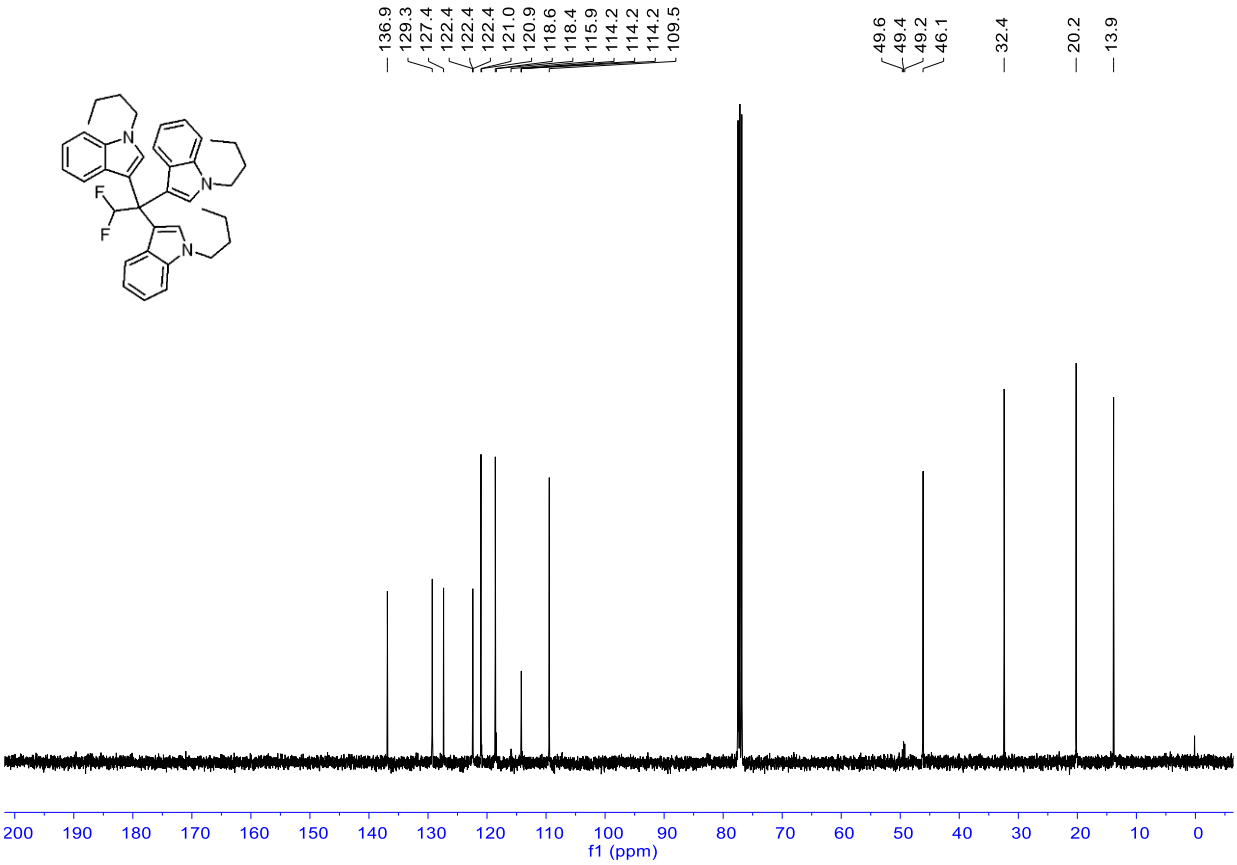
^{13}C{^{1}H} NMR spectrum of **3c**



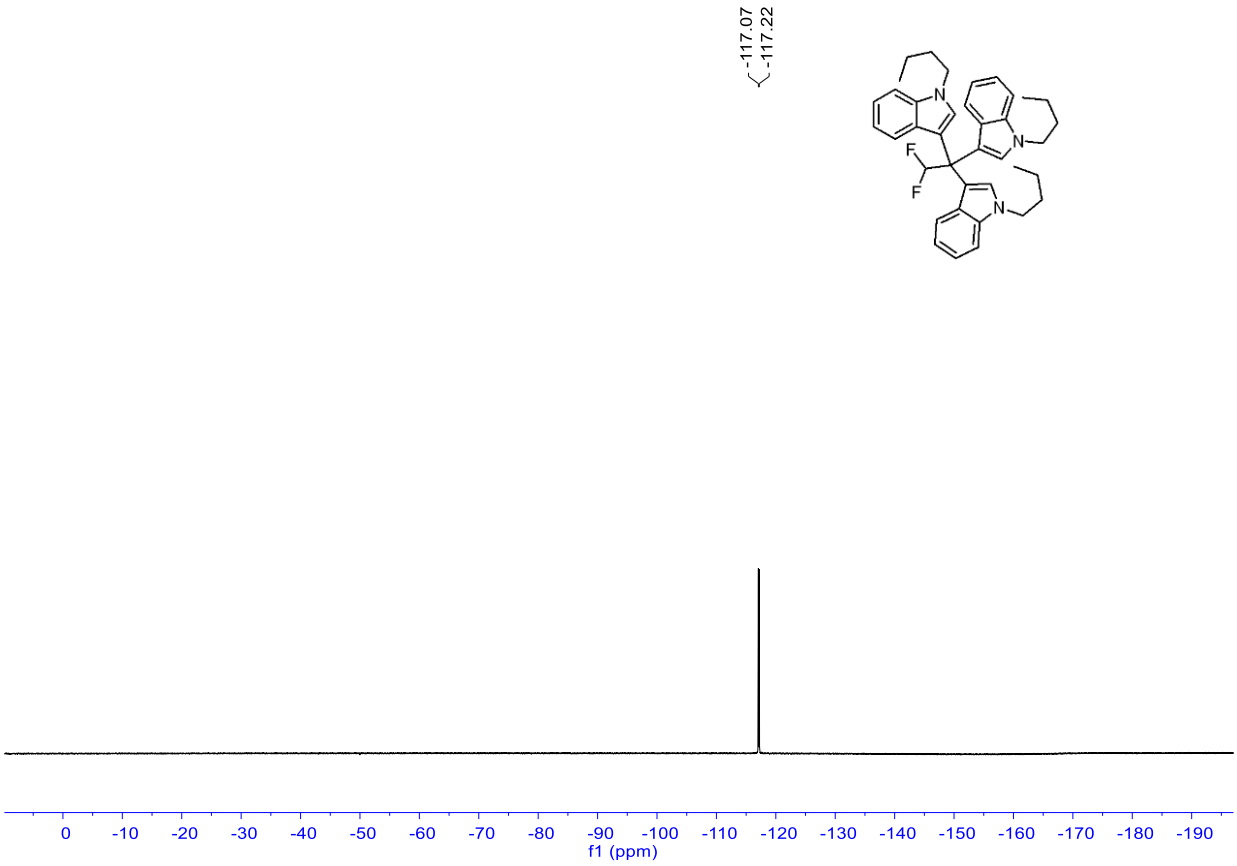
^{19}F NMR spectrum of **3c**



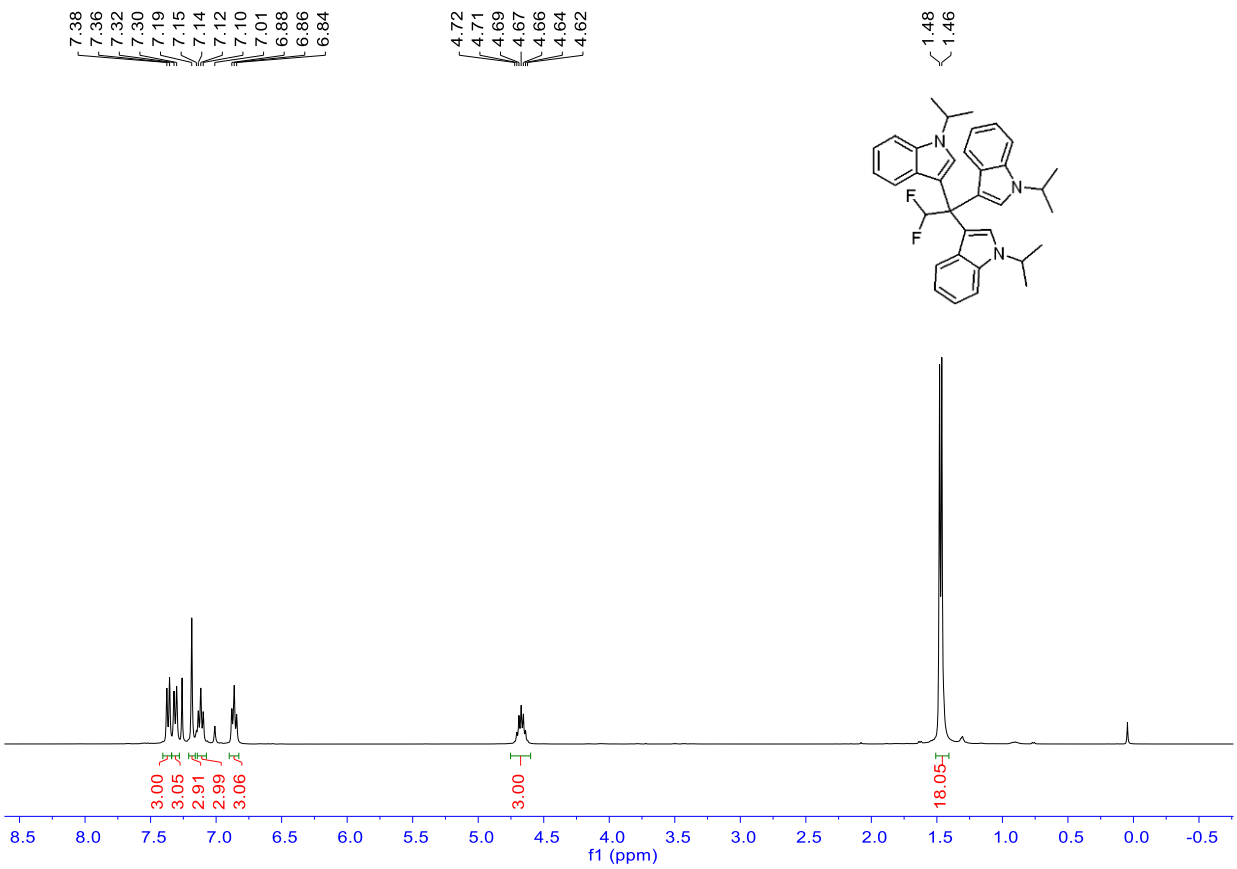
^{1}H NMR spectrum of **3d**



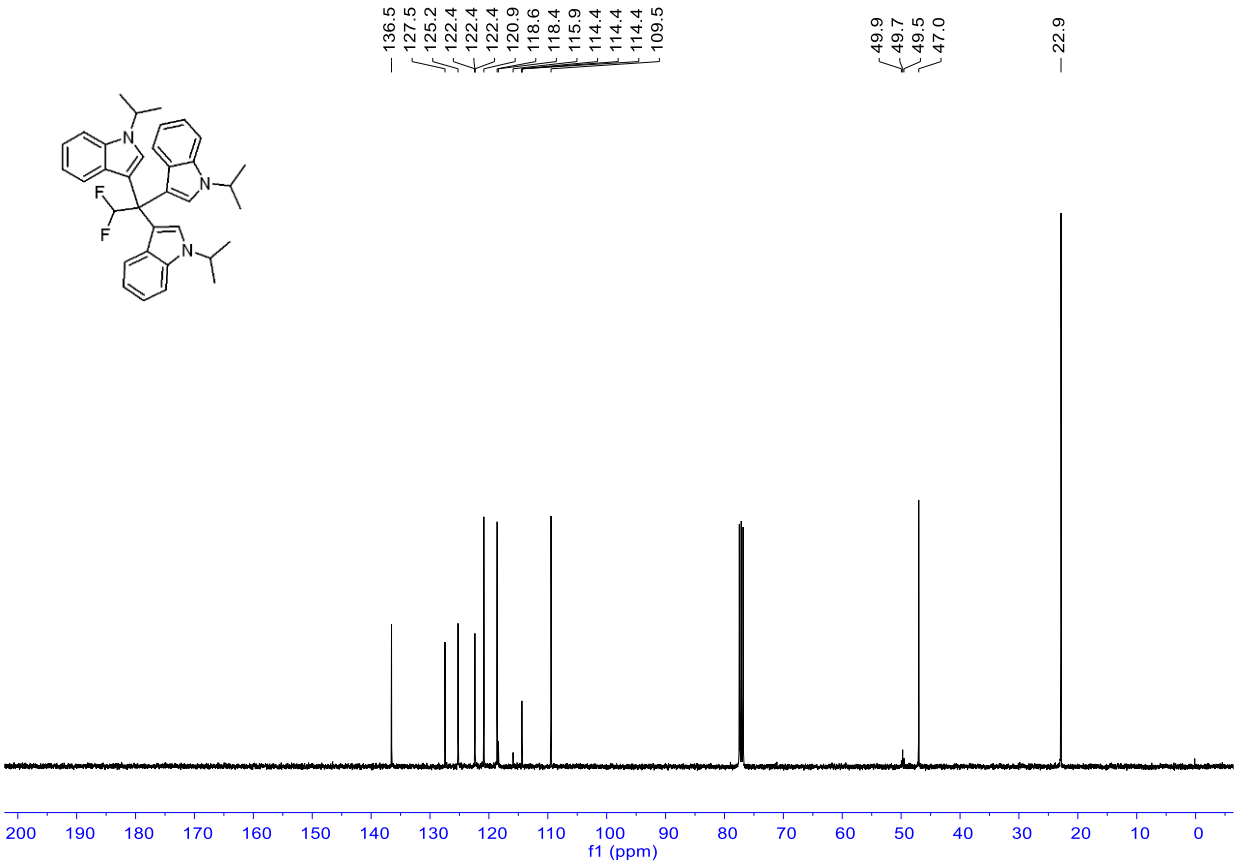
$^{13}C\{^{1}H\}$ NMR spectrum of **3d**



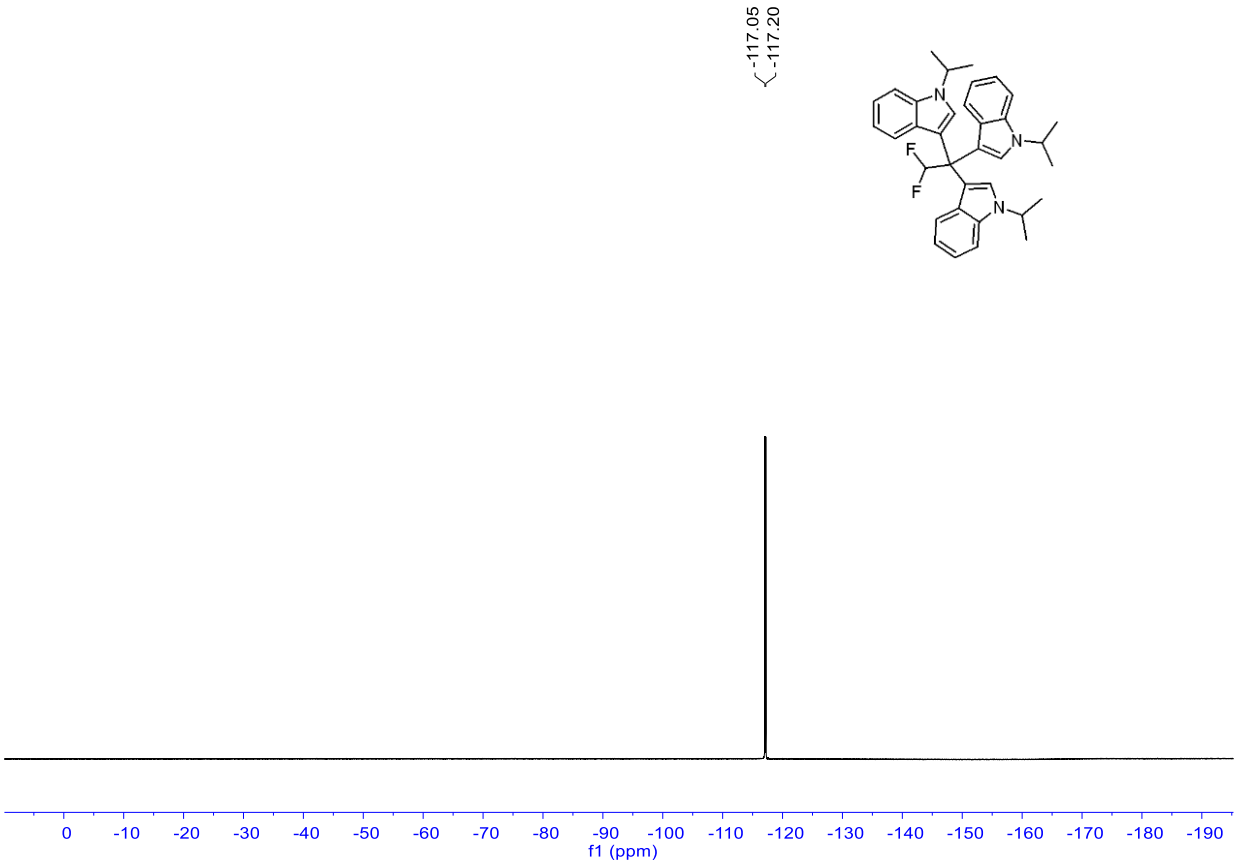
^{19}F NMR spectrum of **3d**



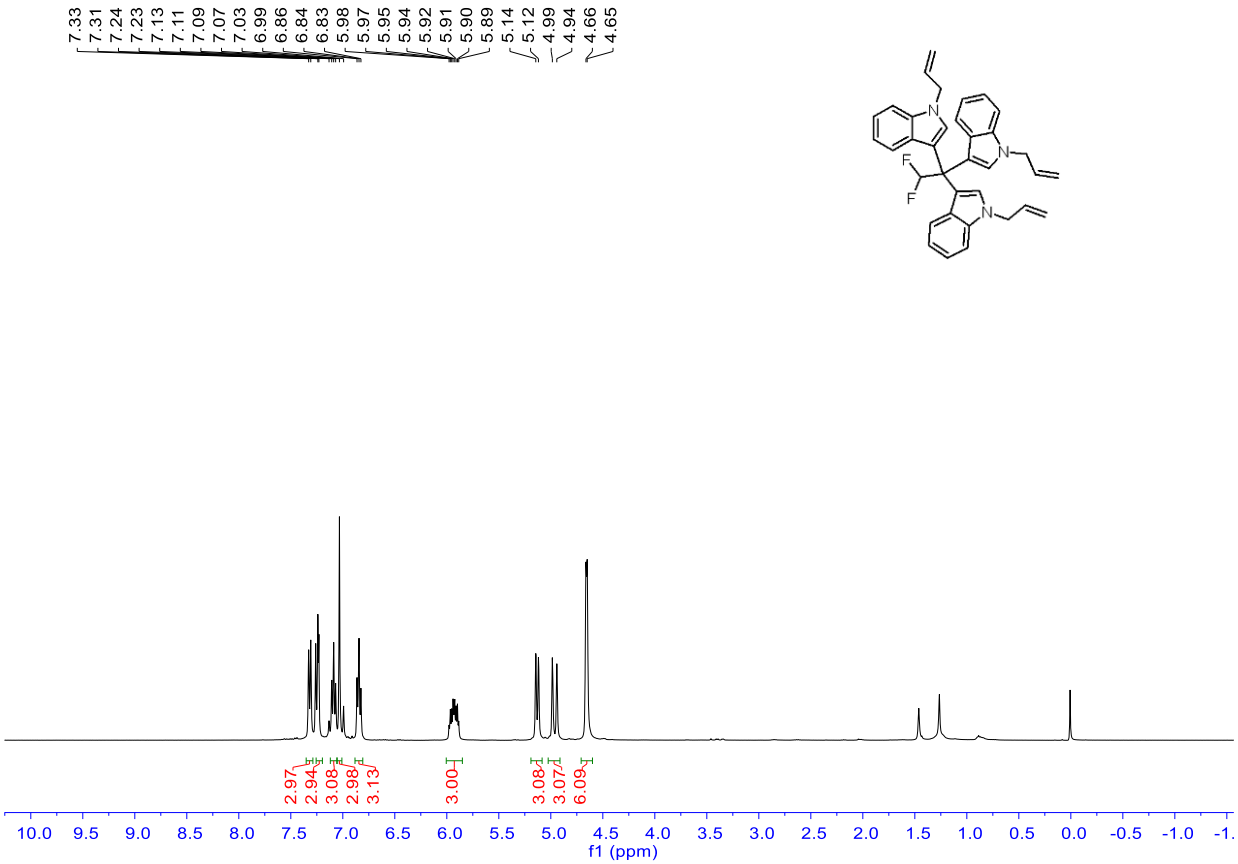
^{1}H NMR spectrum of **3e**



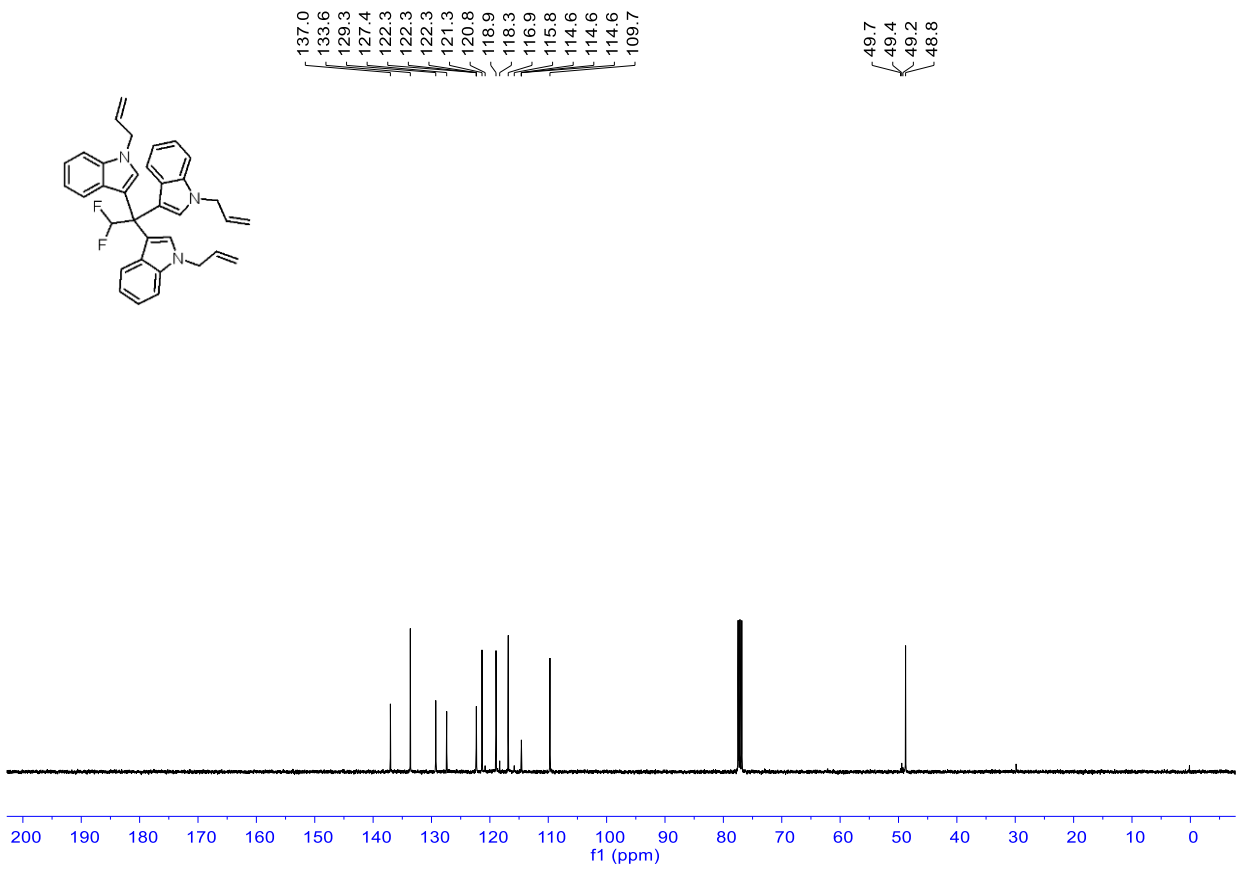
^{13}C{^{1}H} NMR spectrum of **3e**



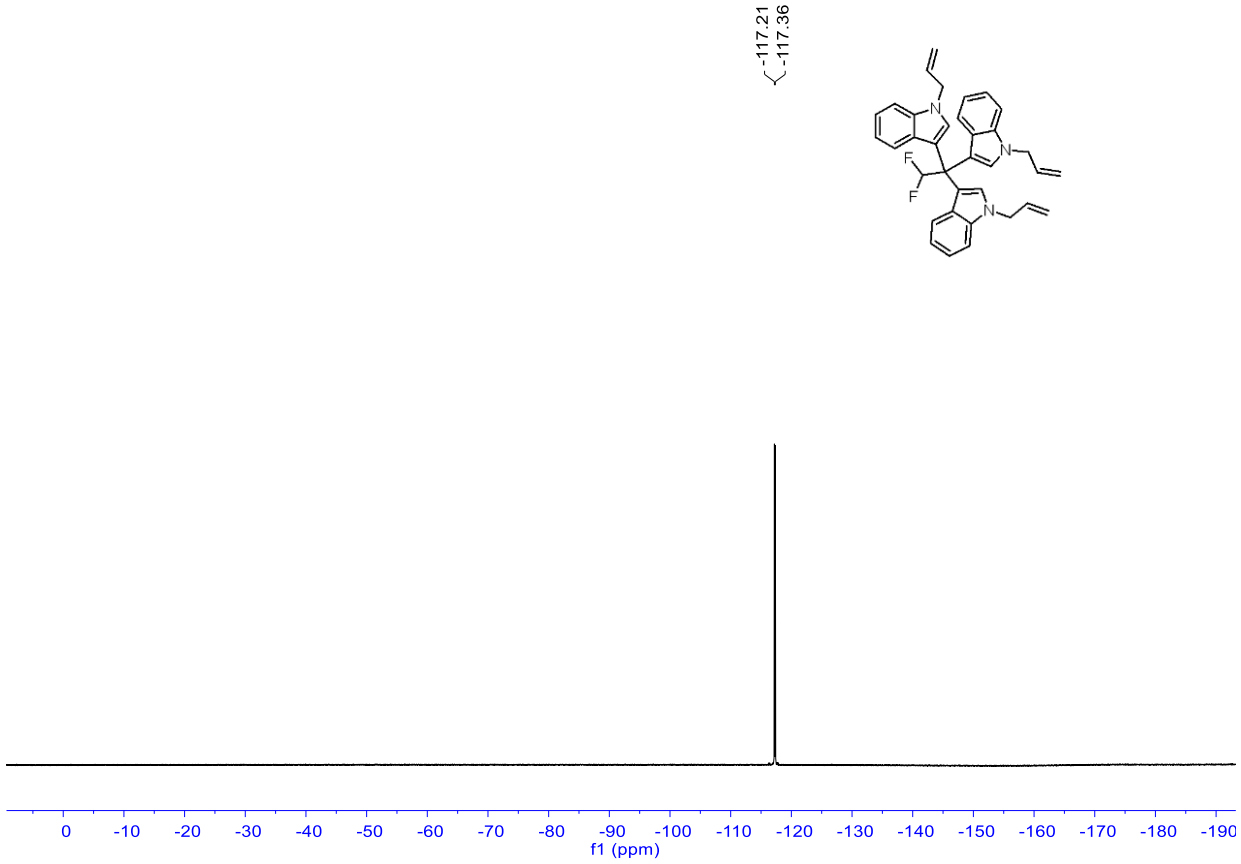
^{19}F NMR spectrum of **3e**



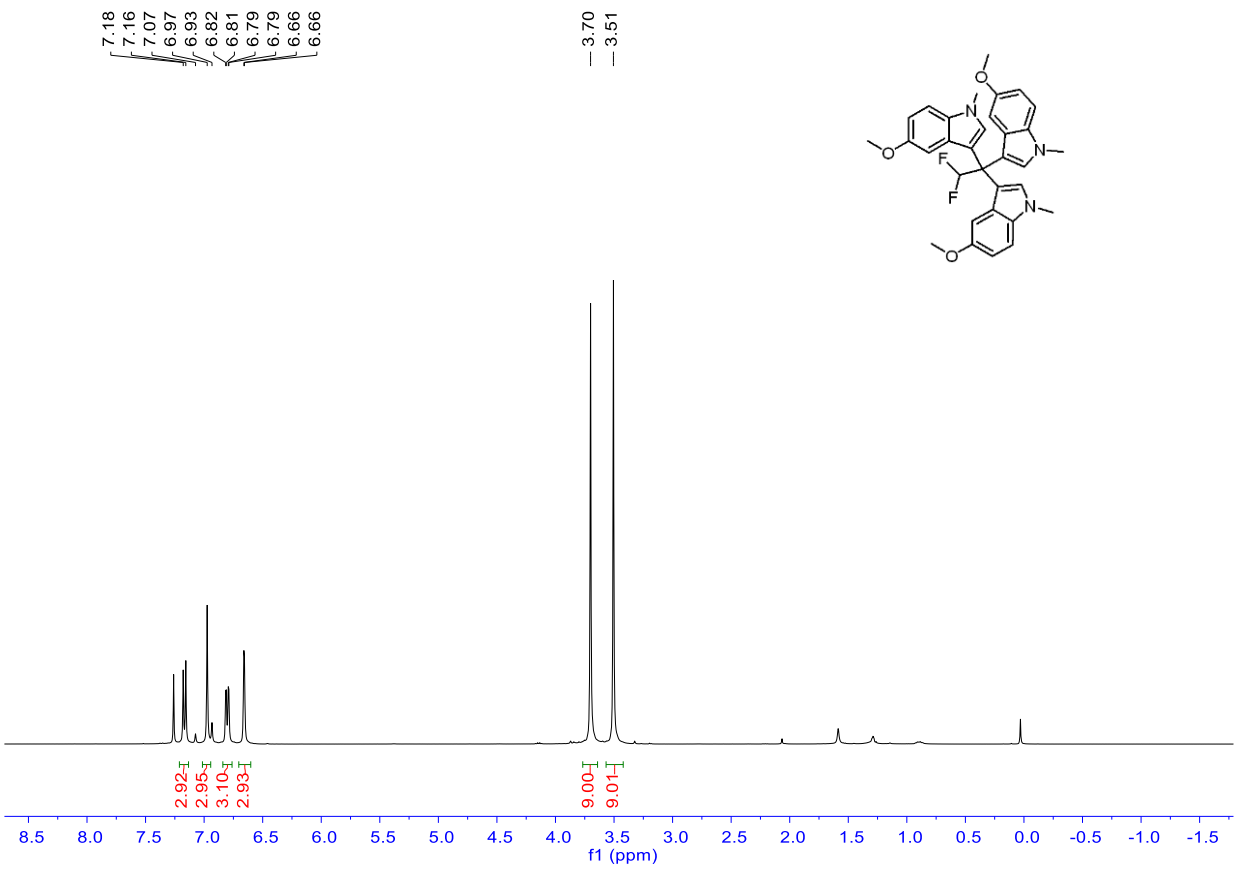
^{1}H NMR spectrum of **3f**



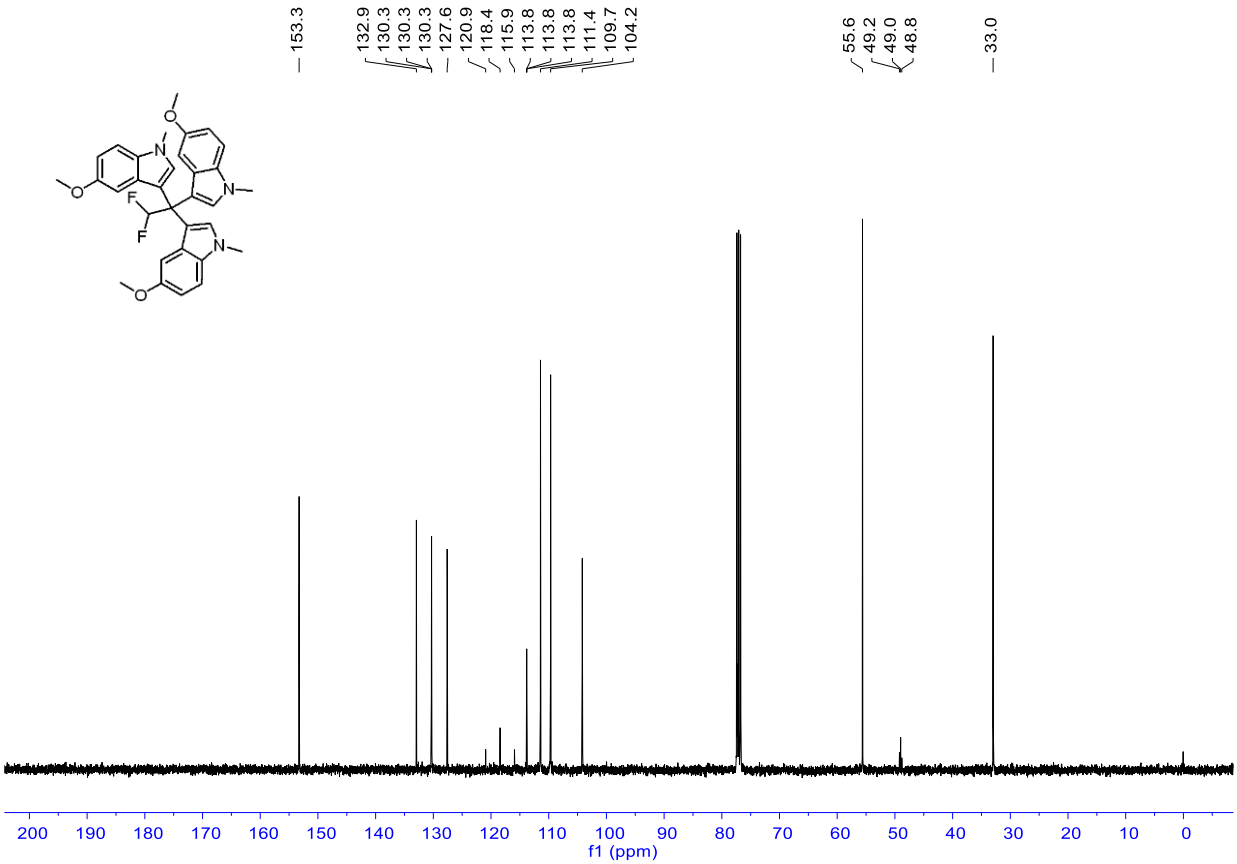
$^{13}C\{^{1}H\}$ NMR spectrum of **3f**



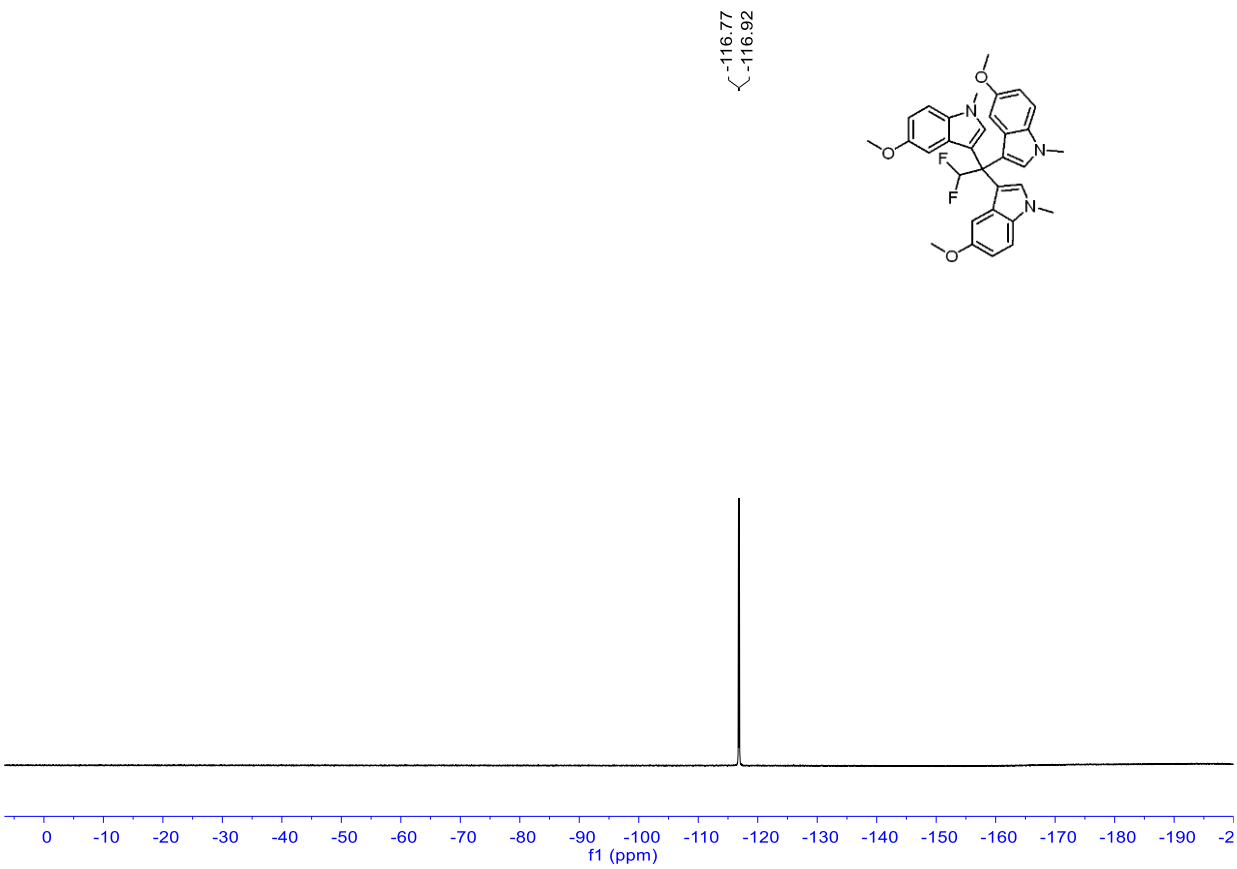
^{19}F NMR spectrum of **3f**



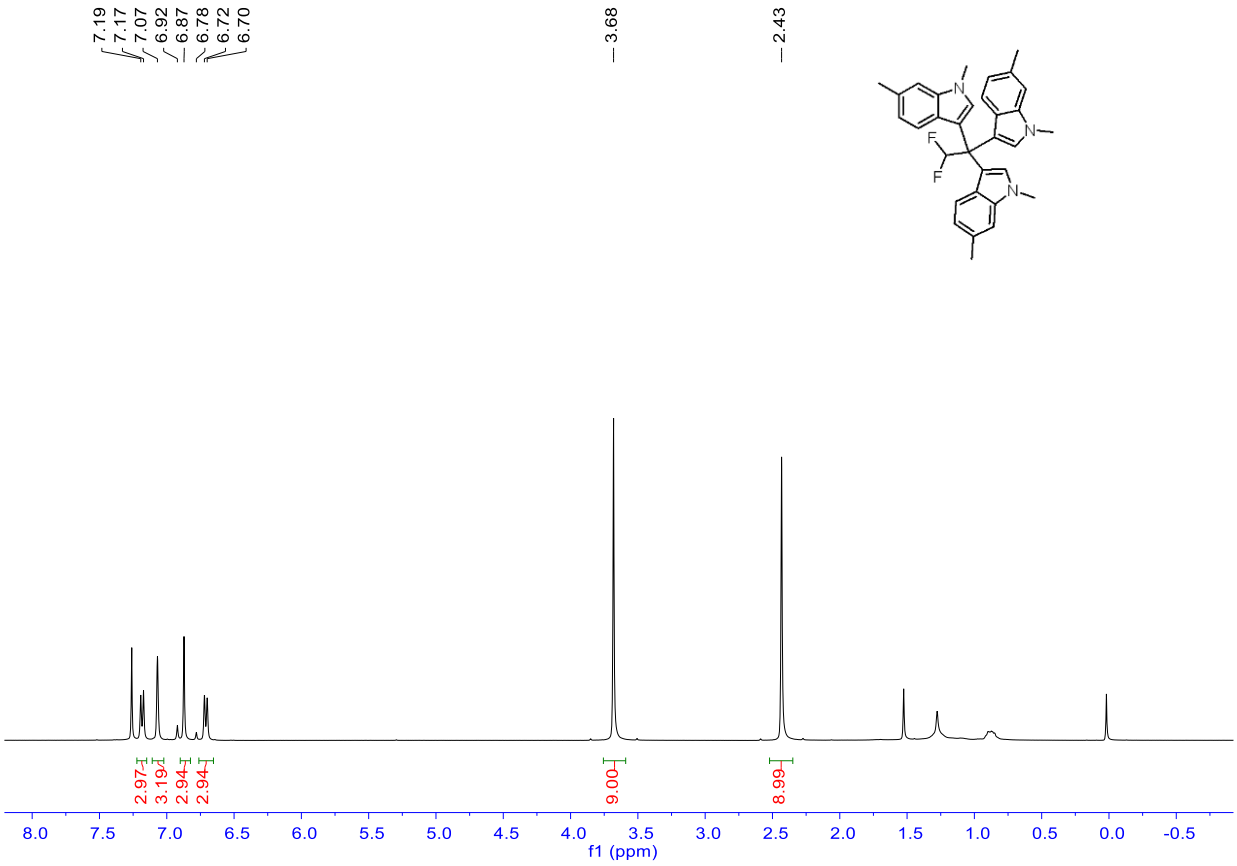
^{1}H NMR spectrum of **3g**



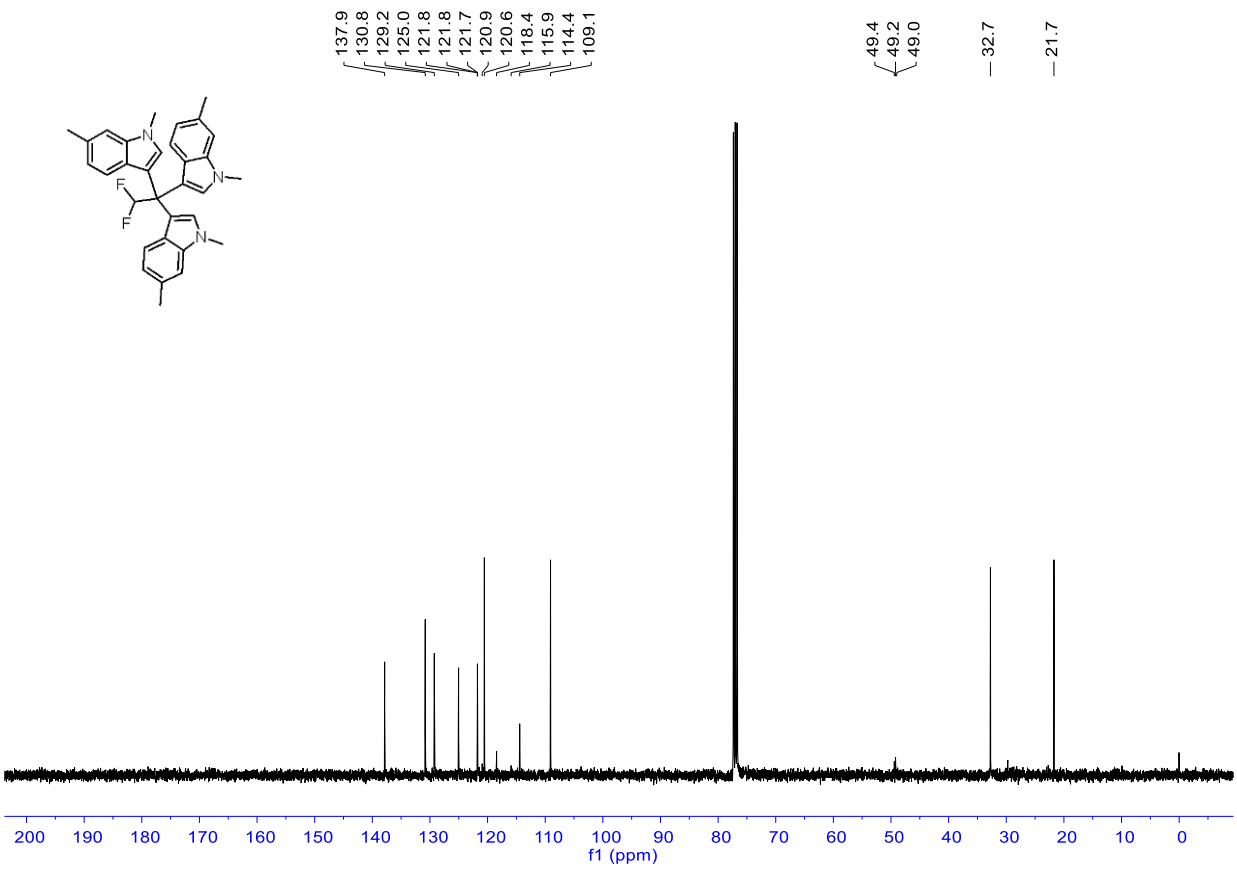
^{13}C{^{1}H} NMR spectrum of **3g**



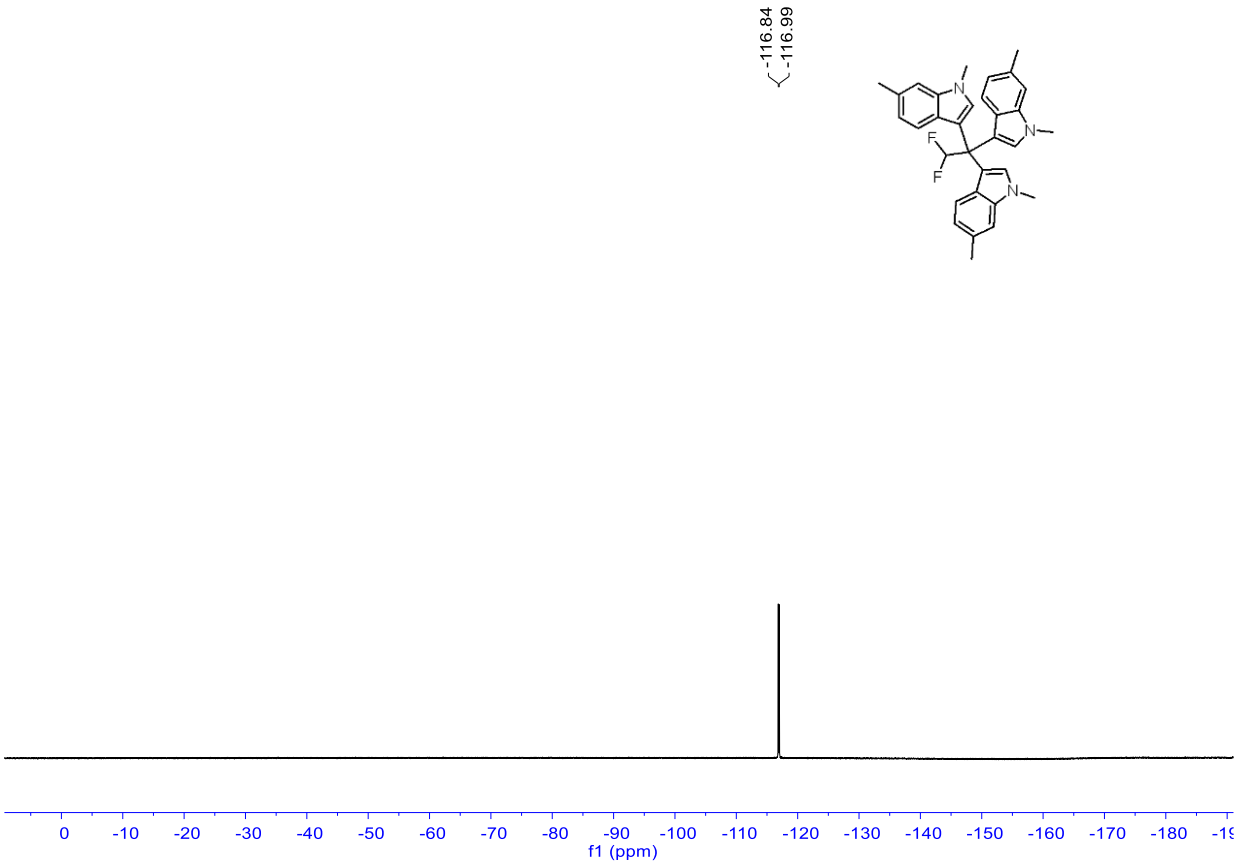
^{19}F NMR spectrum of **3g**



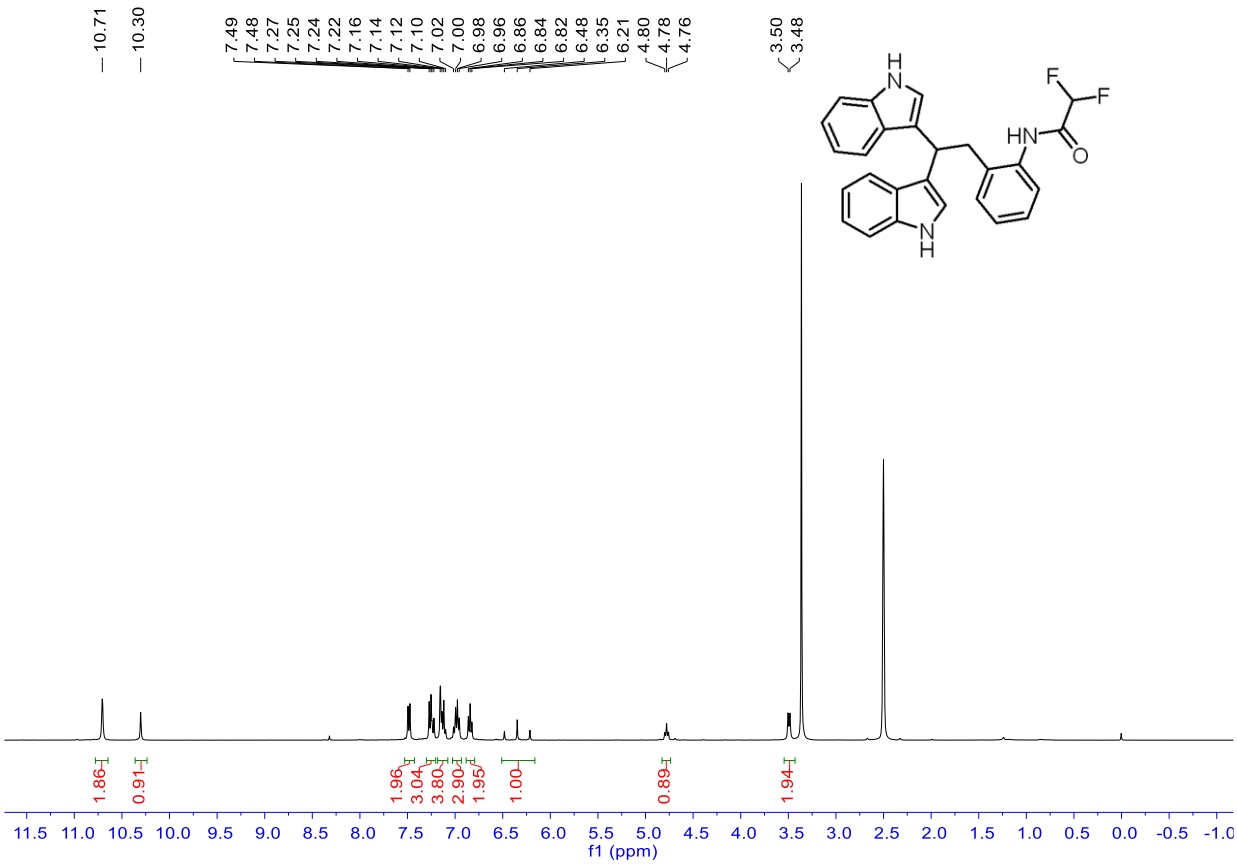
^{1}H NMR spectrum of **3h**



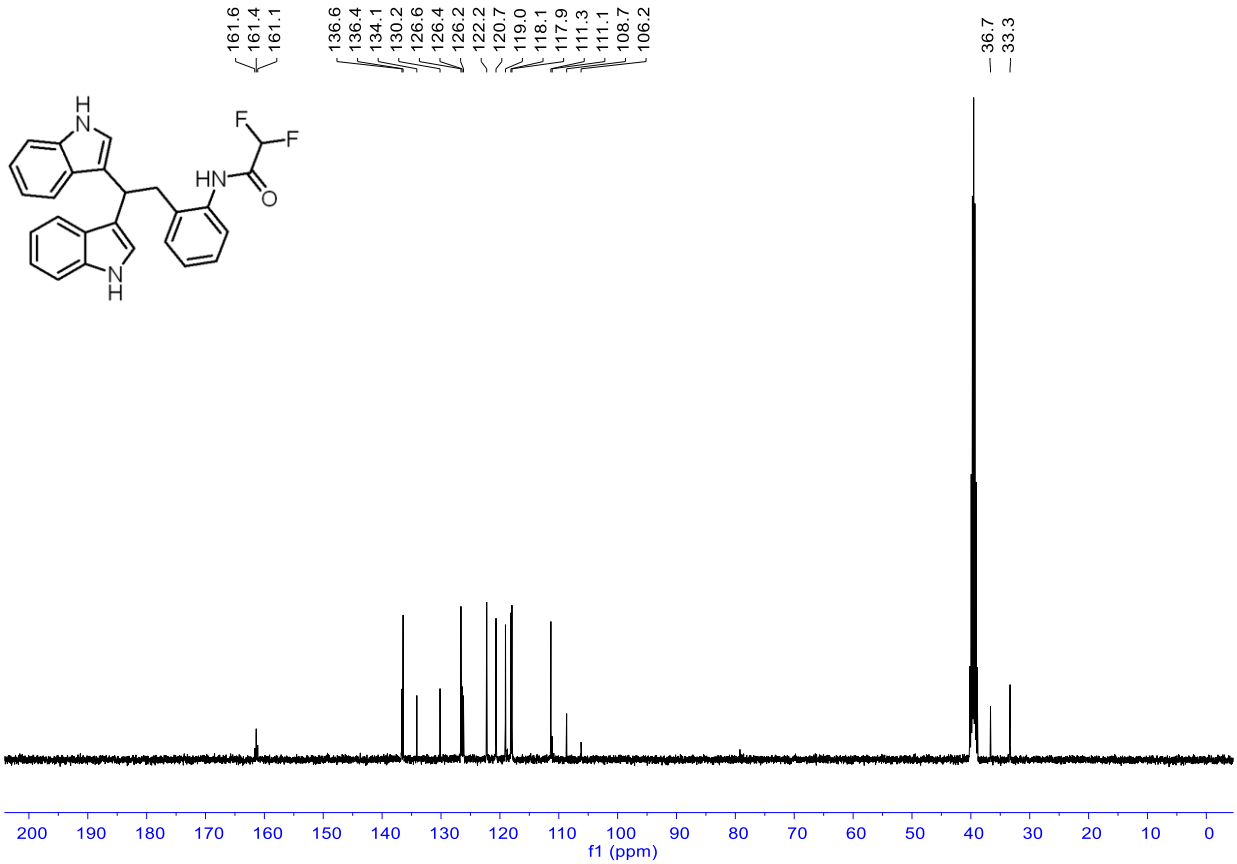
$^{13}C\{^{1}H\}$ NMR spectrum of **3h**



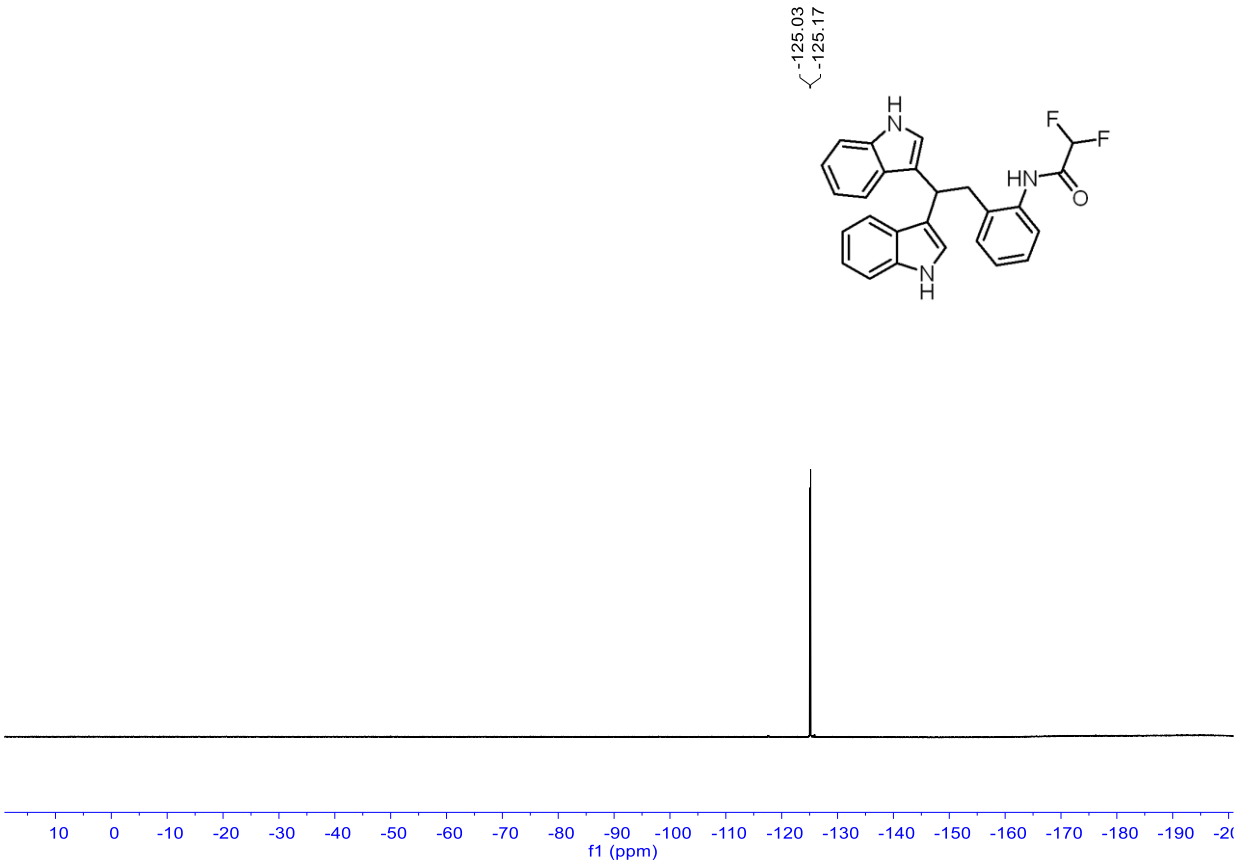
^{19}F NMR spectrum of **3h**



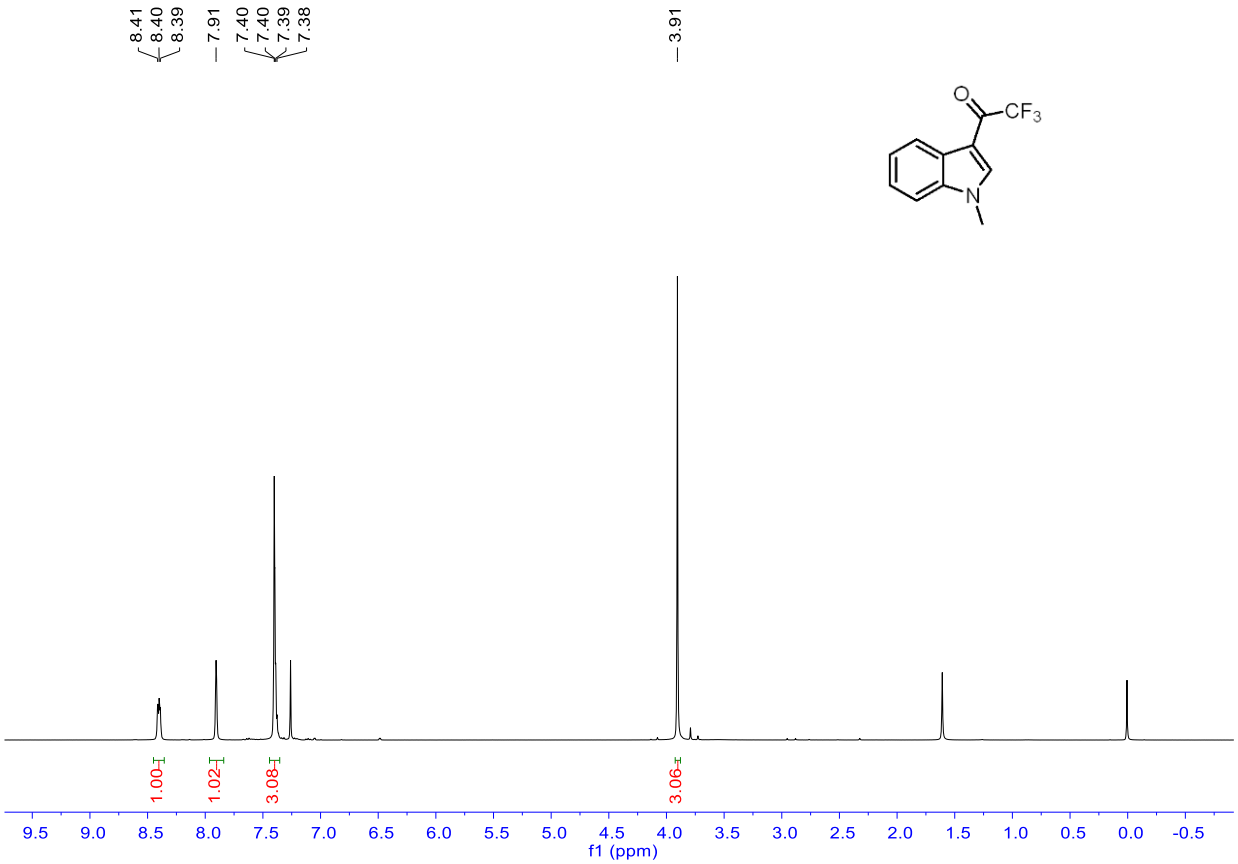
^{1}H NMR spectrum of **4**



^{13}C{^{1}H} NMR spectrum of **4**



^{19}F NMR spectrum of **4**



^{1}H NMR spectrum of **D**