Supplementary Information

Efficient Generation of Perfluoroalkyl Radicals from Sodium Perfluoroalkanesulfinates and a Hypervalent Iodine(III) Reagent: Mild, Metal-free Synthesis of Perfluoroalkylated Organic Molecules

Ryu Sakamoto, Hirotaka Kashiwagi, Selvakumar Sermadurai,
Shin A. Moteki, and Keiji Maruoka*

Laboratory of Synthetic Organic Chemistry and Special Laboratory of Organocatalytic Chemistry, Department of Chemistry, Graduate School of Science, Kyoto University, Sakyo, Kyoto 606-8502, Japan

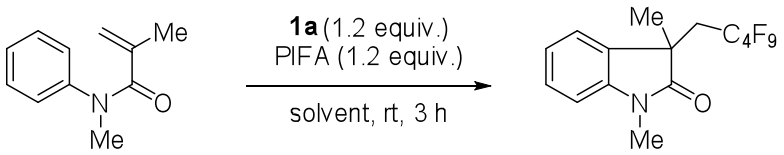
General Information

^{1}H NMR spectra were measured on JEOL JNM-ECA500 (500 MHz) spectrometer. Data were reported as follows: chemical shifts in ppm from tetramethylsilane as an internal standard in $CDCl_3$, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet-doublet, m = multiplet, br = broad), coupling constants (Hz), and assignment. ^{13}C NMR spectra were measured on JEOL JNM-ECA500 (125 MHz) spectrometer with complete proton decoupling. Chemical shifts were reported in ppm from the residual solvent as an internal standard. ^{19}F NMR spectra were measured on JEOL JNM-ECA500 (470 MHz) spectrometer. Infrared (IR) spectra were recorded on a Thermo Scientific Nicolet iS5 spectrometer. High-resolution mass spectra (HRMS) were performed on Brucker microTOF and Thermo Exactive plus. YMC syringe pump (model number: YSP-101) was used when slow addition of a solution was conducted. The products were purified by flash column chromatography (silica gel 60, Merck, 230-400 mesh) or preparative thin layer chromatography silica gel (PLC 60 F254. 0.5 mm). Hypervalent iodine(III) reagents were prepared according to the literature procedure.[1-2] Sodium sulfinates **1** were prepared according to the literature procedure.[3] *N*-Arylacrylamides **2**,[4] isocyanobiphenyls **4**,[5] 3,3-diarylacrylates **6a-e**,[6] were prepared according to the literature procedure. 4-Phenylcoumarin **6X** and 1-methyl-4-phenyl-2-quinolinone **6Y** were prepared according to the literature procedure.[7] Commercially available reagents were purchased from Wako, Aldrich, TCI and Alfa-aesar chemicals and used as received.

Optimization of Reaction Condition of Perfluoroalkylation/Cyclization of *N*-Methyl- *N*-acrylamide 2a with 1a.

The effect of solvents were summarized in Table S1. When the reaction of **2a** (1.0 equiv.) with **1a** (1.2 equiv.) in the presence of PIFA (1.2 equiv.) was carried out in acetonitrile, the desired product **3a** was obtained in 72% yield (entry 1). Other solvents, such as hexafluoroisopropanol, dichloromethane, DMF, DMSO or methanol were found to be less satisfactory than acetonitrile in term of chemical yield (entries 2-6).

Table S1. Perfluoroalkylation/cyclization of **2a** with **1a**[a]



2a **3a**

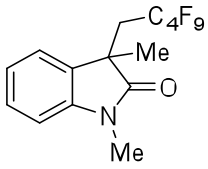
entry	solvent	Yield **3a** (%) [b]
1	CH_3CN	72
2	HFIP	8
3	CH_2Cl_2	49
4	DMF	56
5	DMSO	34
6	MeOH	30

The reactions of **2a** (1.0 equiv.) with **1a** (1.2 equiv.) were carried out in the presence of PIFA (1.2 equiv) in a solvent (0.1 M). [b] Yield was determined by ^{1}H NMR spectroscopy using 1,1,2,2-tetrachloroethane as an internal standard.

General Procedure for Perfluoroalkylation/Cyclization of *N*-Arylacrylamide 2 (Scheme 2)

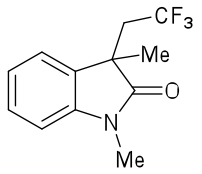
To a stirred solution of *N*-arylacrylamide **2** (0.1 mmol) and R_fSO_2Na **1** (0.12 mmol) in acetonitrile (1.5 mL) was added a solution of PIFA (51.6 mg, 0.12 mmol) in acetonitrile (0.5 mL) slowly over the course of 20 min with syringe pump at room temperature under argon atmosphere. The reaction mixture was then stirred for 3 h at the same temperature. The crude product was directly purified by flash column chromatography on silica gel to afford a corresponding product.

1,3-Dimethyl-3-(nonafluoropentyl)indolin-2-one (3a)



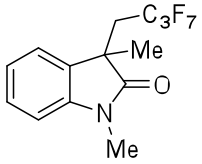
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34-7.26 (2H, m, Ar*H*), 7.10 (1H, t, *J* = 7.7 Hz, Ar*H*), 6.89 (1H, d, *J* = 7.7 Hz, Ar*H*), 3.25 (3H, s, NCH_3), 2.88 (1H, dd, *J* = 35.1 Hz, 15.3 Hz , C*H*HC_4F_9), 2.60 (1H, ddd, *J* = 31.2, 15.6, 7.9 Hz, CH*H*C_4F_9), 1.44 (3H, s, CCH_3). Other spectral data of **3a** were consistent with previously reported data.[8]

1,3-Dimethyl-3-(2,2,2-trifluoroethyl)indolin-2-one (3b)



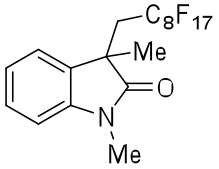
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 (1H, t, *J* = 7.8 Hz, Ar*H*), 7.27 (1H, d, *J* = 7.1 Hz, Ar*H*), 7.10 (1H, t, *J* = 7.5 Hz, Ar*H*), 6.90 (1H, d, *J* = 7.7 Hz, Ar*H*), 3.25 (3H, s, NCH_3), 2.83 (1H, dq, *J* = 15.3, 10.5 Hz, C*H*HCF_3), 2.66 (1H, dq, *J* = 15.5, 10.5 Hz, CH*H*CF_3), 1.41 (3H, s, CCH_3). Other spectral data of **3b** were consistent with previously reported data. [8]

3-(2,2,3,3,4,4,4-Heptafluorobutyl)-1,3-dimethylindolin-2-one (3c)



^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33-7.27 (2H, m, Ar*H*), 7.09 (1H, t, *J* = 7.5 Hz, Ar*H*), 6.89 (1H, d, *J* = 7.9 Hz, Ar*H*), 3.25 (3H, s, NCH_3), 2.87 (1H, dd, *J* = 35.0, 15.4 Hz , C*H*HC_3F_7), 2.59 (1H, ddd, *J* = 31.4, 15.8, 8.0 Hz, CH*H*C_3F_7), 1.44 (3H, s, CCH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 178.6, 142.8, 131.3, 128.5, 123.6, 122.6, 120.0-114.5 (m), 108.5, 44.2, 36.8 (t, $J_{C\text{-}F}$ = 20.3 Hz), 26.5, 25.8; ^{19}F NMR (470 MHz, $CDCl_3$) δ –80.1- –80.2 (3F, m), –109.1- –109.9 (1F, m), –115.0- –115.8 (1F, m), –127.1- –128.6 (2F, m); HRMS calculated for $C_{14}H_{12}ONF_7Na$: *m/z* 366.0699 ([M + Na]$^+$), found: *m/z* 366.0700 ([M + Na]$^+$); IR (neat) 1714, 1615, 1530, 1220, 1118 cm^{-1}.

3-(2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-Heptadecafluorononyl)-1,3-dimethylindolin-2-one



(3d); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35-7.25 (2H, m, Ar*H*), 7.10 (1H, t, *J* = 7.5 Hz, Ar*H*), 6.90 (1H, d, *J* = 7.7 Hz, Ar*H*), 3.26 (3H, s, NCH_3), 2.89 (1H, dd, *J* = 35.1, 15.3 Hz, C*H*HC_8F_{17}), 2.61 (1H, ddd, *J* = 31.1, 15.5, 8.0 Hz, CH*H*C_8F_{17}), 1.44 (3H, s, CCH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 178.6, 142.8, 131.3, 128.5, 123.6, 122.6, 120.0-110.0 (m), 108.5, 44.2, 37.0 (t, $J_{C\text{-}F}$ = 20.3 Hz), 26.5, 25.9; ^{19}F NMR (470 MHz, $CDCl_3$) δ –80.6- –80.7 (3F, m), –108.2- –109.0 (1F, m), –113.8- –114.6 (1F, m), –121.3- –126.2 (12F, m); HRMS calculated for $C_{19}H_{13}ONF_{17}$: *m/z* 594.0720 ([M + H]$^+$), found: *m/z* 594.0725 ([M + H]$^+$); IR (neat) 1715, 1616, 1474, 1351, 1237, 1200, 1145, 1133, 740 cm^{-1}.

3-(2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-Henicosafluoroundecyl)-1,3-dimethylindolin-2-one *(3e); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34-7.27 (2H, m, Ar*H*), 7.11-7.07 (1H, m, Ar*H*), 6.89 (1H, d, J = 7.7 Hz, Ar*H*), 3.25 (3H, s, NCH_3), 2.88 (1H, dd, J = 35.1, 15.3 Hz, C*H*H$C_{10}F_{21}$), 2.60 (1H, ddd, J = 31.5, 15.5, 8.0 Hz, CH*H*$C_{10}F_{21}$), 1.44 (3H, s, CCH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 178.6, 142.8, 131.3, 128.5, 123.6, 122.7, 120.0-110.0 (m), 108.5, 44.3, 37.1 (t, $J_{C\text{-}F}$ = 20.9 Hz), 26.5, 25.9; ^{19}F NMR (470 MHz, $CDCl_3$) δ –80.6- –80.8 (3F, m), –113.8- –114.1 (1F, m), –114.4- –114.6 (1F, m), –121.3- –122.9 (10F, m), –122.5- –122.8 (2F, m), –123.4- –123.7 (2F, m), –126.0- –126.2 (2F, m); HRMS calculated for $C_{21}H_{12}ONF_{21}Na$: *m/z* 716.0476 ([M + Na]$^+$), found: *m/z* 716.0475 ([M + Na]$^+$); IR (neat) 1715, 1615, 1495, 1473, 1375, 1350, 1148, cm^{-1}.

*The reaction was conducted in AcOEt as a solvent instead of MeCN.

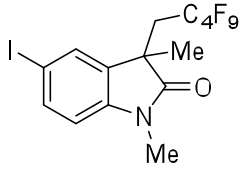
5-Methoxy-1,3-dimethyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)indolin-2-one (3f)

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.90 (1H, d, J = 2.3 Hz, Ar*H*), 6.84 (1H, dd, J = 8.5, 2.6 Hz, Ar*H*), 6.79 (1H, d, J = 8.5 Hz, Ar*H*), 3.81 (3H, s, OCH_3), 3.22 (3H, s, NCH_3), 2.87 (1H, dd, J = 35.3, 15.2 Hz, C*H*HC_4F_9), 2.58 (1H, ddd, J = 31.5, 15.5, 8.0 Hz, CH*H*C_4F_9), 1.43 (3H, s, CCH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 178.2, 156.1, 136.4, 132.7, 120.0-108.0 (m), 112.6, 111.4, 108.8, 55.9, 44.6, 36.9 (t, $J_{C\text{-}F}$ = 20.3 Hz), 26.6, 25.9; ^{19}F NMR (470 MHz, $CDCl_3$) δ –80.9- –81.0 (3F, m), –108.3- –109.1 (1F, m), –114.1- –114.9 (1F, m), –124.4- –124.5 (2F, m), –125.0- –126.5 (2F, m); HRMS calculated for $C_{16}H_{14}O_2NF_9Na$: *m/z* 446.0773 ([M + Na]$^+$), found: *m/z* 446.0785 ([M + Na]$^+$) ; IR (neat) 1709, 1501, 1287, 1219, 1130, 1037 cm^{-1}.

1,3-Dimethyl-5-nitro-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)indolin-2-one (3g)

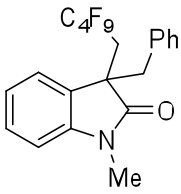
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.32 (1H, dd, J = 8.8, 2.3 Hz, Ar*H*), 8.19 (1H, m, Ar*H*), 6.99 (1H, d, J = 8.8 Hz, Ar*H*), 3.33 (3H, s, NCH_3), 2.98 (1H, dd, J = 35.1, 15.3 Hz, C*H*HC_4F_9), 2.69 (1H, ddd, J = 30.8, 15.0, 8.0 Hz, CH*H*C_4F_9), 1.50 (3H, s, CCH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 178.6, 148.4, 143.6, 132.0, 125.9, 119.6, 119.8-115.0 (m), 108.2, 44.1, 37.1 (t, $J_{C\text{-}F}$ = 20.3 Hz), 27.0, 25.8; ^{19}F NMR (470 MHz, $CDCl_3$) δ –80.9- –81.0 (3F, m), –107.7- –108.6 (1F, m), –113.9- –114.7 (1F, m), –124.3- –124.4 (2F, m), –125.0- –126.5 (2F, m); HRMS calculated for $C_{15}H_{11}O_3N_2F_9Na$: *m/z* 461.0518 ([M + Na]$^+$), found: *m/z* 461.0520 ([M + Na]$^+$) ; IR (neat) 1731, 1616, 1523, 1337, 1221, 1132 cm^{-1}.

5-Iodo-1,3-dimethyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)indolin-2-one (3h)



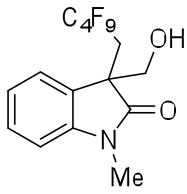
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66-7.62 (1H, m, Ar*H*), 7.56 (1H, brs, Ar*H*), 6.68 (1H, d, J = 8.2 Hz, Ar*H*), 3.22 (3H, s, NCH_3), 2.88 (1H, dd, J = 35.1, 15.3 Hz, C*H*HC$_4$F$_9$), 2.56 (1H, ddd, J = 31.3, 15.5, 8.0 Hz, CH*H*C$_4$F$_9$), 1.43 (3H, s, CCH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 177.8, 142.6, 137.4, 133.7, 132.4, 120.0-115.0 (m), 110.6, 85.0, 44.2, 37.0 (t, $J_{C\text{-}F}$ = 20.3 Hz), 26.5, 25.9; ^{19}F NMR (470 MHz, $CDCl_3$) δ –80.9- –81.0 (3F, m), –108.0- –108.9 (1F, m), –114.2- –115.0 (1F, m), –124.3- –124.5 (2F, m), –125.0- –126.5 (2F, m); HRMS calculated for $C_{15}H_{11}ONF_9INa$: *m/z* 541.9634 ([M + Na]$^+$), found: *m/z* 541.9646 ([M + Na]$^+$) ; IR (neat) 1717, 1220, 1131 cm^{-1}.

3-Benzyl-1-methyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)indolin-2-one (3i)

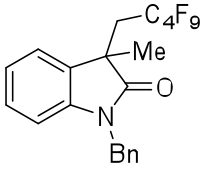


^{1}H NMR (500 MHz, $CDCl_3$) δ 7.22 (2H, t, J = 7.9 Hz, Ar*H*), 7.11-7.02 (4H, m, Ar*H*), 6.75 (2H, d, J = 7.1 Hz, Ar*H*), 6.59 (1H, d, J = 7.9 Hz, Ar*H*), 3.09 (1H, d, J = 12.8 Hz, C*H*HPh), 3.06 (1H, m, C*H*HC$_4$F$_9$), 3.03 (1H, d, J = 12.8 Hz, CH*H*Ph), 2.94 (3H, s, NCH_3), 2.73 (1H, ddd, J = 30.6, 15.5, 8.5 Hz, C*H*HC$_4$F$_9$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 177.1, 143.5, 133.8, 130.0, 128.6, 128.3, 127.6, 127.0, 124.6, 122.1, 120.0-108.5 (m), 108.1, 49.8, 45.4, 35.9 (t, $J_{C\text{-}F}$ = 19.7 Hz), 26.0; ^{19}F NMR (470 MHz, $CDCl_3$) δ –80.9- –81.0 (3F, m), –107.1- –108.0 (1F, m), –113.2- –114.1 (1F, m), –124.3- –124.5 (2F, m), –124.9- –126.6 (2F, m); HRMS calculated for $C_{21}H_{16}ONF_9Na$: *m/z* 492.0980 ([M + Na]$^+$), found: *m/z* 492.0989 ([M + Na]$^+$); IR (neat) 1713, 1614, 1221, 1133, 752 cm^{-1}.

3-(Hydroxymethyl)-1-methyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)indolin-2-one (3j); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39-7.35 (1H, m, Ar*H*), 7.30 (1H, d, J = 7.4 Hz, Ar*H*), 7.14-7.10 (1H, m, Ar*H*), 6.93 (1H, d, J = 7.7 Hz, Ar*H*), 3.75 (1H, d, J = 11.3 Hz, C*H*HOH), 3.67 (1H, d, J = 11.1 Hz, CH*H*OH), 3.81 (3H, s, OCH_3), 3.26 (3H, s, NCH_3), 3.14 (1H, dd, J = 35.0, 16.0 Hz, C*H*HC$_4$F$_9$), 2.78 (1H, ddd, J = 31.3, 15.8, 7.5 Hz, CH*H*C$_4$F$_9$), 2.37 (1H, br, O*H*); ^{13}C NMR (125 MHz, $CDCl_3$) δ 177.2, 143.6, 129.2, 127.3, 124.1, 122.9, 120.5-109.5 (m), 108.8, 67.9, 49.5, 32.9 (t, $J_{C\text{-}F}$ = 20.3 Hz), 26.5; ^{19}F NMR (470 MHz, $CDCl_3$) δ –80.9- –81.0 (3F, m), –107.7- –108.6 (1F, m), –113.3- –114.1 (1F, m), –124.4- –124.5 (2F, m), –125.0- –126.5 (2F, m); HRMS calculated for $C_{15}H_{12}O_2NF_9Na$: *m/z* 432.0617 ([M + Na]$^+$), found: *m/z* 432.0614 ([M + Na]$^+$) ; IR (neat) 3300 (br), 1698, 1615, 1219, 1132 cm^{-1}.



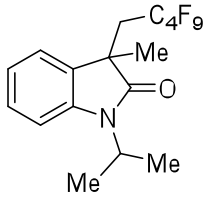
1-Benzyl-3-methyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)indolin-2-one (3k)



^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34-7.24 (6H, m, Ar*H*), 7.19-7.16 (1H, m, Ar*H*), 7.05 (1H, t, J = 7.5 Hz, Ar*H*), 6.76 (1H, d, J = 7.9 Hz, Ar*H*), 4.97 (1H, d, J = 15.6 Hz, NCH_2Ph), 4.92 (1H, d, J = 15.6 Hz,

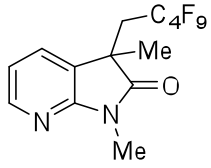
NCH_2Ph), 2.96 (1H, dd, J = 35.1, 15.3 Hz, CHHC$_4$F$_9$), 2.65 (1H, ddd, J = 31.5, 15.5, 8.0 Hz, CHHC$_4$F$_9$), 1.49 (3H, s, CCH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 178.6, 141.9, 135.7, 131.3, 128.8, 128.4, 127,6, 127.3, 123.5, 122.6, 120.0-115.0 (m), 109.6, 44.2, 44.0 (t, J = 6.6 Hz), 36.8 (t, $J_{C\text{-}F}$ = 20.3 Hz) 26.5; ^{19}F NMR (470 MHz, $CDCl_3$) δ –80.9- –81.0 (3F, m), –108.3- –109.1 (1F, m), –113.3- –114.1 (1F, m), –124.3- –124.6 (2F, m), –125.0- –126.5 (2F, m); HRMS calculated for $C_{21}H_{16}ONF_9Na$: *m/z* 492.0980 ([M + Na]$^+$), found: *m/z* 492.0991 ([M + Na]$^+$); IR (neat) 1715, 1614, 1489, 1353, 1220, 1132, 754 cm^{-1}.

1-Isopropyl-3-methyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)indolin-2-one (3l)



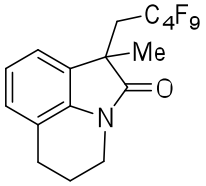
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30-7.26 (2H, m, ArH), 7.08-7.04 (2H, m, ArH), 4.64 (1H, m, J = 7.0 Hz, NCH(CH$_3$)$_2$), 2.89 (1H, dd, J = 35.0, 15.2 Hz, CHHC$_4$F$_9$), 2.56 (1H, ddd, J = 31.4, 15.8, 8.5 Hz, CHHC$_4$F$_9$), 1.48 (6H, t, J = 6.7 Hz, NCH (CH_3)$_2$), 1.41 (3H, s, CCH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 178.2, 141.6, 131.8, 128.2, 123.8, 122.0, 120.0-107.5 (m), 110.2, 44.0, 37.1 (t, $J_{C\text{-}F}$ = 20.3 Hz), 26.2, 19.2, 19.0; ^{19}F NMR (470 MHz, $CDCl_3$) δ –80.9- –81.1 (3F, m), –108.3- –109.2 (1F, m), –114.1- –114.9 (1F, m), –124.4- –124.6 (2F, m), –125.0- –126.6 (2F, m); HRMS calculated for $C_{17}H_{16}ONF_9Na$: *m/z* 444.0980 ([M + Na]$^+$), found: *m/z* 444.0987 ([M + Na]$^+$) ; IR (neat) 1709, 1354, 1216, 1129, 733 cm^{-1}.

1,3-Dimethyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-1,3-dihydro-2H-pyrrolo[2,3-*b*]pyridin-2-one (3m);



^{1}H NMR (500 MHz, $CDCl_3$) δ 8.24 (1H, dd, J = 5.4, 1.4 Hz, ArH), 7.53 (1H, d, J = 7.4 Hz, ArH), 7.00 (1H, dd, J = 7.2, 5.2 Hz, ArH), 3.34 (3H, s, NCH_3), 2.88 (1H, dd, J = 35.3, 15.4 Hz, CHHC$_4$F$_9$), 2.62 (1H, ddd, J = 31.6, 16.0, 8.0 Hz, CHHC$_4$F$_9$), 1.47 (3H, s, CCH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 178.2, 156.3, 147.6, 131.3, 125.7, 118.3, 120.0-108.0 (m), 44.0, 36.6 (t, $J_{C\text{-}F}$ = 20.9 Hz), 25.7, 25.1; ^{19}F NMR (470 MHz, $CDCl_3$) δ –80.9- –81.1 (3F, m), –108.0- –108.8 (1F, m), –113.7- –114.5 (1F, m), –124.4- –124.5 (2F, m), –125.0- –126.5 (2F, m); HRMS calculated for $C_{14}H_{11}ON_2F_9Na$: *m/z* 417.0620 ([M + Na]$^+$), found: *m/z* 417.0627 ([M + Na]$^+$); IR (neat) 1724, 1597, 1471, 1220, 1134 cm^{-1}.

1-Methyl-1-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-5,6-dihydro-4H-pyrrolo[3,2,1-*ij*]-quinolin-2(1H)-one (3n);



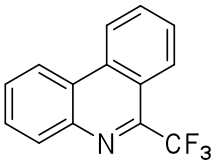
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.12 (1H, d, J = 7.4 Hz, ArH), 7.06 (1H, d, J = 7.7 Hz, ArH), 6.98 (1H, t, J = 7.7 Hz, ArH), 3.74 (2H, t, J = 5.8 Hz, NCH_2), 2.90-2.75 (3H, m, CHHC$_4$F$_9$, ArCH_2), 2.60 (1H, ddd, J = 31.8, 15.8, 8.0 Hz, CHHC$_4$F$_9$), 2.02 (2H, m, CH$_2$CH_2CH$_2$), 1.45 (3H, s, CCH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 177.5, 138.6, 130.0, 127.3, 122.1, 121.5, 120.6, 120.0-108.0 (m), 45.6, 39.1, 36.8 (t, $J_{C\text{-}F}$ = 20.3 Hz), 25.5, 24.7, 21.2; ^{19}F NMR (470 MHz, $CDCl_3$) δ –80.9- –81.0 (3F, m), –108.4- –109.2 (1F, m), –114.1- –114.9 (1F, m), –124.4- –124.5 (2F, m), –125.0- –126.5 (2F, m); HRMS calculated for $C_{17}H_{14}ONF_9Na$: *m/z* 442.0824

([M + Na]$^+$), found: *m/z* 442.0809 ([M + Na]$^+$); IR (neat) 1715, 1483, 1355, 1221, 1133 cm^{-1}.

General Procedure for Perfluoroalkylation of 2-Isocyanobiphenyl 4 (Scheme 3)

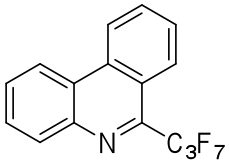
To a stirred solution of 2-isocyanobiphenyl **4** (0.1 mmol), R_fSO_2Na **1** (0.2 mmol), AcONa (0.1 mmol, 8.2 mg) in ethyl acetate (1.5 mL) was added a solution of PIFA (51.6 mg, 0.12 mmol) in ethyl acetate (0.5 mL) slowly over the course of 50 minutes with syringe pump at room temperature under argon atmosphere. The reaction mixture was then stirred for 40 minutes at the same temperature. After the reaction completed, the reaction was quenched with saturated $NaHCO_3$ aq. and extracted with ethyl acetate. The combined organic layer was dried over Na_2SO_4 and concentrated. The residue was purified by flash column chromatography on silica gel to provide the product.

6-(Trifluoromethyl)phenanthridine (5a)



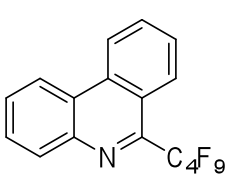
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.74 (1H, d, J = 8.5 Hz, Ar*H*), 8.66-8.62 (1H, m, Ar*H*), 8.42-8.38 (1H, m, Ar*H*), 8.32-8.29 (1H, m, Ar*H*), 7.97-7.93 (1H, m, Ar*H*), 7.85-7.77 (3H, m, Ar*H*). Other spectral data of this compound were consistent with previously reported data.[9]

6-(Heptafluoropropyl)phenanthridine (5b)



^{1}H NMR (500 MHz, $CDCl_3$) δ 8.71 (1H, d, J = 8.3 Hz, Ar*H*), 8.62-8.59 (1H, m, Ar*H*), 8.46 (1H, d, J = 8.5 Hz, Ar*H*), 8.29-8.26 (1H, m, Ar*H*), 7.91 (1H, t, J = 7.7 Hz, Ar*H*), 7.82-7.73 (3H, m, Ar*H*); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.5 (t, $J_{C\text{-}F}$ = 24.4 Hz), 141.8, 134.0, 131.3, 131.2, 129.4, 129.3, 128.0, 126.3-126.1 (m), 124.8, 123.0, 122.6, 122.0, 120-106 (m); ^{19}F NMR (470 MHz, $CDCl_3$) δ –78.9 (3F, t, J = 9.6 Hz), –105.6- –105.7 (2F, m), –123.5- –123.6 (2F, m); HRMS calculated for $C_{16}H_8NF_7Na$: *m/z* 370.0437 ([M + Na]$^+$), found: *m/z* 370.0436 ([M + Na]$^+$); IR (neat) 1219, 1192, 1162, 1086, 997, 887, 759, 745, 723 cm^{-1}.

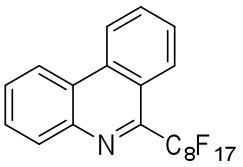
6-(Nonafluorobutyl)phenanthridine (5c)



^{1}H NMR (500 MHz, $CDCl_3$) δ 8.74 (1H, d, J = 8.3 Hz, Ar*H*), 8.65-8.61 (1H, m, Ar*H*), 8.47 (1H, d, J = 8.5 Hz, Ar*H*), 8.30-8.26 (1H, m, Ar*H*), 7.95-7.91 (1H, m, Ar*H*), 7.84-7.75 (3H, m, Ar*H*); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.7 (t, $J_{C\text{-}F}$ = 25.0 Hz), 141.8, 134.0, 131.3, 131.2, 129.4, 129.3, 128.0, 126.3-126.1 (m), 124.8, 123.0, 122.6, 122.0, 120-105 (m); ^{19}F NMR (470 MHz, $CDCl_3$) δ –80.8- –80.9 (3F, m), –104.7- –

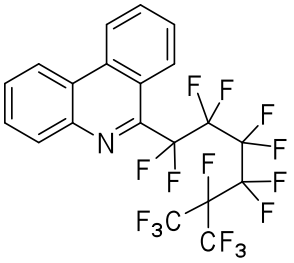
104.9 (2F, m), –119.6- –119.7 (2F, m), –123.5- –123.6 (2F, m); HRMS calculated for $C_{17}H_9NF_9$: *m/z* 398.0586 ($[M + H]^+$), found: *m/z* 398.0593 ($[M + H]^+$); IR (neat) 1349, 1229, 1206, 1133, 864, 761, 726 cm^{-1}.

6-(Perfluorooctyl)phenanthridine (5d)



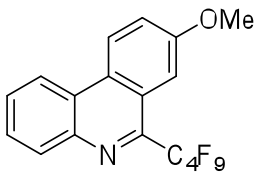
^1H NMR (500 MHz, $CDCl_3$) δ 8.74 (1H, d, J = 8.5 Hz, Ar*H*), 8.64-8.62 (1H, m, Ar*H*), 8.47 (1H, d, J = 8.2 Hz, Ar*H*), 8.30-8.27 (1H, m, Ar*H*), 7.92 (1H, t, J = 7.8 Hz, Ar*H*), 7.84-7.74 (3H, m, Ar*H*); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.7 (t, $J_{C\text{-}F}$ = 24.4 Hz), 141.8, 134.1, 131.3, 131.2, 129.4, 129.3, 128.0, 126.3-126.1 (m), 124.9, 123.1, 122.7, 122.0, 120-105 (m); ^{19}F NMR (470 MHz, $CDCl_3$) δ –80.6- –80.7 (3F, m), –104.7- –104.9 (2F, m), –118.8- –119.0 (2F, m), –119.5- –119.7 (2F, m), –121.4- –121.7 (4F, m), –122.5- –122.7 (2F, m), –125.9- –126.0 (2F, m); HRMS calculated for $C_{21}H_9NF_{17}$: *m/z* 598.0458 ($[M + H]^+$), found: *m/z* 598.0461 ($[M + H]^+$); IR (neat) 1240, 1205, 1149, 761, 725 cm^{-1}.

6-(1,1,2,2,3,3,4,4,5,6,6,6-Dodecafluoro-5-(trifluoromethyl)hexyl)phenanthridine



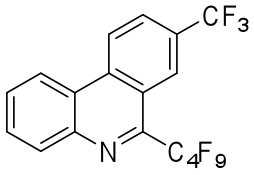
(5e); ^1H NMR (500 MHz, $CDCl_3$) δ 8.72 (1H, d, J = 8.2 Hz, Ar*H*), 8.63-8.60 (1H, m, Ar*H*), 8.46 (1H, d, J = 8.5 Hz, Ar*H*), 8.28-8.26 (1H, m, Ar*H*), 7.91 (1H, t, J = 7.7 Hz, Ar*H*), 7.82-7.74 (3H, m, Ar*H*); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.8 (t, $J_{C\text{-}F}$ = 24.4 Hz), 141.8, 134.0, 131.23, 131.18, 129.4, 129.3, 128.0, 126.3-126.1 (m), 124.8, 123.1, 122.6, 122.0, 120-105 (m); ^{19}F NMR (470 MHz, $CDCl_3$) δ –71.6- –71.8 (6F, m), –104.6- –104.8 (2F, m), –114.6- –114.9 (2F, m), –118.3- –118.7 (4F, m), –185.6- –185.7 (1F, m); HRMS calculated for $C_{20}H_8NF_{15}Na$: *m/z* 570.0309 ($[M + Na]^+$), found: *m/z* 570.0316 ($[M + Na]^+$); IR (neat) 1251, 1198, 1153, 984 cm^{-1}.

8-Methoxy-6-(nonafluorobutyl)phenanthridine (5f)



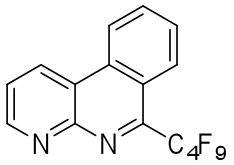
^1H NMR (500 MHz, $CDCl_3$) δ 8.59 (1H, d, J = 9.1 Hz, Ar*H*), 8.51-8.48 (1H, m, Ar*H*), 8.24-8.21 (1H, m, Ar*H*), 7.78-7.70 (3H, m, Ar*H*), 7.52 (1H, dd, J = 9.1, 2.6 Hz, Ar*H*), 3.98 (3H, s, O*CH*$_3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.9, 145.7 (t, $J_{C\text{-}F}$ = 25.0 Hz), 141.0, 134.0, 131.1, 129.5, 128.5, 128.3, 125.0, 124.3, 124.2, 122.3, 121.5, 119-108 (m), 106.0-105.8 (m), 55.5; ^{19}F NMR (470 MHz, $CDCl_3$) δ –80.9 (3F, t, J = 10.5 Hz), –105.4 (2F, t, J = 12.3 Hz), –119.5- –119.6 (2F, m), –123.4- –123.5 (2F, m); HRMS calculated for $C_{18}H_{10}ONF_9Na$: *m/z* 450.0511 ($[M + Na]^+$), found: *m/z* 450.0517 ($[M + Na]^+$); IR (neat) 1622, 1466, 1222, 1104, 829, 744 cm^{-1}.

6-(Nonafluorobutyl)-8-(trifluoromethyl)phenanthridine (5g)



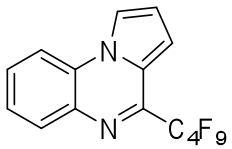
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.83 (1H, d, J = 8.8 Hz, Ar*H*), 8.73 (1H, s, Ar*H*), 8.64-8.61 (1H, m, Ar*H*), 8.32-8.29 (1H, m, Ar*H*), 8.12-8.09 (1H, m, Ar*H*), 7.91-7.84 (2H, m, Ar*H*); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.6 (t, $J_{C\text{-}F}$ = 25.0 Hz), 142.4, 136.1, 131.5, 130.6, 130.1, 130.0 (q, $J_{C\text{-}F}$ = 33.0 Hz), 127.1 (q, $J_{C\text{-}F}$ = 3.2 Hz), 123.9, 123.9, 123.8-123.6 (m), 123.7 (q, $J_{C\text{-}F}$ = 272.6 Hz), 122.4, 122.2, 119-108 (m); ^{19}F NMR (470 MHz, $CDCl_3$) δ –62.6, (3F, s), –80.9 (3F, t, J = 10.2 Hz), –104.5 (2F, t, J = 12.5 Hz), –119.7- –119.8 (2F, m), –123.5- –123.6 (2F, m); HRMS calculated for $C_{18}H_8NF_{12}$: *m/z* 466.0460 ([M + H]$^+$), found: *m/z* 466.0461 ([M + H]$^+$); IR (neat) 1320, 1235, 1133, 1087, 735 cm^{-1}.

6-(Nonafluorobutyl)benzo[*c*][1,8]naphthyridine (5h)



^{1}H NMR (500 MHz, $CDCl_3$) δ 9.18 (1H, dd, J= 4.4, 1.8 Hz, Ar*H*), 8.98 (1H, dd, J= 8.5, 1.7 Hz, Ar*H*), 8.71 (1H, d, J = 8.5 Hz, Ar*H*), 8.54 (1H, d, J = 8.2 Hz, Ar*H*), 8.01-7.97 (1H, m, Ar*H*), 7.86-7.82 (1H, m, Ar*H*), 7.74 (1H, dd, J= 8.2, 4.3 Hz, Ar*H*); ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.6, 151.1, 150.3 (t, $J_{C\text{-}F}$ = 24.4 Hz), 134.5, 131.9, 131.5, 128.9, 126.8-126.5 (m), 124.3, 123.2, 122.7, 120.1, 119-108 (m); ^{19}F NMR (470 MHz, $CDCl_3$) δ –80.7- –80.8 (3F, m), –105.2- –105.3 (2F, m), –119.8- –119.9 (2F, m), –124.4- –124.6 (2F, m); HRMS calculated for $C_{16}H_7N_2F_9Na$: *m/z* 421.0358 ([M + Na]$^+$), found: *m/z* 421.0368 ([M + Na]$^+$); IR (neat) 1567, 1348, 1213, 1133 cm^{-1}.

4-(Nonafluorobutyl)pyrrolo[1,2-*a*]quinoxaline (5i)



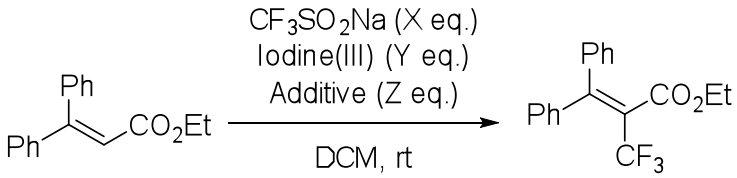
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10-8.04 (2H, m, Ar*H*), 7.90 (1H, dd, J= 8.2, 1.1 Hz, Ar*H*), 7.66-7.61 (1H, m, Ar*H*), 7.53-7.49 (1H, m, Ar*H*), 7.16-7.13 (1H, m, Ar*H*), 6.98 (1H, dd, J= 4.1, 2.7 Hz, Ar*H*); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.7 (t, $J_{C\text{-}F}$ = 25.6 Hz), 134.2, 131.3, 130.1, 127.7, 125.8, 122.8, 122-110 (m), 115.4, 115.0, 113.8, 108.8 (t, $J_{C\text{-}F}$ = 4.8 Hz); ^{19}F NMR (470 MHz, $CDCl_3$) δ –80.7- –80.8 (3F, m), –113.2- –113.3 (2F, m), –121.7- –121.9 (2F, m), –125.2- –125.4 (2F, m); HRMS calculated for $C_{15}H_8N_2F_9$: *m/z* 387.0538 ([M + H]$^+$), found: *m/z* 387.0538 ([M + H]$^+$); IR (neat) 1481, 1376, 1220, 1135, 756 cm^{-1}.

Optimization of Direct Perfluoroalkylation of sp2–Hybridized C–H Bond

The effect of hypervalent iodine reagent and oxidants were summarized in Table S2. When the reaction of ethyl 3,3-diphenylacrylate **6a** with sodium trifluoromethansulinate **1b** was conducted in the presence of PIFA, the desired product **7a** was obtained in 17% yield (entry 1). Use of F_5-PIFA improved the yield of **7a** (entry 2). Although addition of

ammonium hexanitratocerate (CAN) as an oxidant slightly decreased yield, use of 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) gave **7a** in 76% yield. After the survey of equivalent of F_5-PIFA and DDQ, the combination of 2.0 equivalent F_5-PIFA and 0.6 equivalent of DDQ gave the best result in terms of yield (entries 3-6).

Table S2



6a **7a**

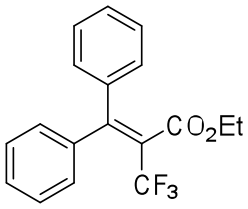
Entry	X eq.	Iodine(III) (Y eq.)	Additive (Z eq.)	Yield (%)[b]
1	1.5	PIFA (1.5)	-	17
2	1.5	F_5-PIFA (1.5)		43
3	1.5	F_5-PIFA (1.5)	CAN (1.0)	36
4[c]	1.5	F_5-PIFA (1.5)	DDQ (1.0)	33
5	1.5	F_5-PIFA (1.5)	DDQ (1.0)	76
6	1.5	F_5-PIFA (1.5)	DDQ (0.6)	71
7	2.0	F_5-PIFA (2.0)	DDQ (0.6)	80

The reactions of **6a** (1.0 equiv.) with CF_3SO_2Na (X equiv.) were carried out in the presence of iodine(III) reagent (Y equiv) and additive (Z equiv.) in a dichloromethane (0.1 M). [b] Yield was determined by ^{1}H NMR spectroscopy using 1,1,2,2-tetrachloroethane as an internal standard. [c] The reaction was carried out at 60 °C.

Typical Procedure for Direct Perfluoroalkylation of sp2–Hybridized C–H Bond (Scheme 4, 7a-h).

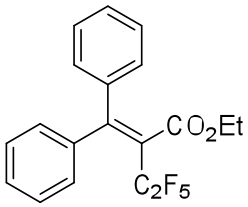
Ethyl 3,3-diarylacrylate **6a** (0.2 mmol), R_fSO_2Na **1** (0.4 mmol), DDQ (27.2 mg, 0.12 mmol) and F_5-PIFA (208 mg, 0.4 mmol) were added subsequently in a test tube under argon atmosphere. Then DCM (1 mL) was added and the reaction mixture was stirred at room temperature for 8~15 hours. Upon completion of the reaction, the resulting mixture was directly purified by flash column chromatography on silica gel to afford the corresponding product.

Ethyl 3,3-Diphenyl-2-(trifluoromethyl)acrylate (7a)



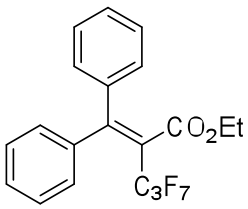
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36-7.22 (10H, m, Ar*H*), 4.03 (2H, q, J = 7.1 Hz, OCH_2CH_3), 0.97 (3H, t, J = 7.1 Hz, OCH_2CH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.2, 154.3 (q, $J_{C\text{-}F}$ = 3.6 Hz), 139.7, 138.0, 129.0, 128.7, 128.3, 128.1, 128.1, 121.7 (q, $J_{C\text{-}F}$ = 275.0 Hz), 61.8, 13.5; ^{19}F NMR (470 MHz, $CDCl_3$) δ –55.4 (3F, s); HRMS calculated for $C_{18}H_{15}O_2F_3Na$: *m/z* 343.0916 ([M + Na]$^+$), found: *m/z* 343.0928 ([M + Na]$^+$); IR (neat) 1730, 1327, 1244, 1148, 1126, 1045 cm^{-1}.

Ethyl 3,3-Diphenyl-2-(pentafluoroethyl)acrylate (7b)



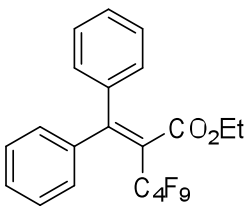
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34-7.18 (10H, m, Ar*H*), 3.96 (2H, q, J = 7.2 Hz, OCH_2CH_3), 0.90 (3H, t, J = 7.1 Hz, OCH_2CH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.4 (t, $J_{C\text{-}F}$ = 4.2 Hz), 156.8 (t, $J_{C\text{-}F}$ = 4.2 Hz), 140.8, 138.1, 129.1, 128.4, 128.3, 128.1, 128.1, 128.0, 127.8, 123-109 (m), 61.8, 13.4; ^{19}F NMR (470 MHz, $CDCl_3$) δ –82.5 (3F, t, J = 2.9 Hz), –105.0- –105.1 (2F, m); HRMS calculated for $C_{19}H_{15}O_2F_5Na$: *m/z* 393.0884 ([M + Na]$^+$), found: *m/z* 343.0874 ([M + Na]$^+$); IR (neat) 1732, 1303, 1202, 1127, 1072, 1018 cm^{-1}.

Ethyl 3,3-Diphenyl-2-(heptafluoropropyl)acrylate (7c)



^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34-7.18 (10H, m, Ar*H*), 3.95 (2H, q, J = 7.1 Hz, OCH_2CH_3), 0.90 (3H, t, J = 7.1 Hz, OCH_2CH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.4 (t, $J_{C\text{-}F}$ = 4.2 Hz), 157.2 (t, $J_{C\text{-}F}$ = 4.8 Hz), 140.9, 138.1, 129.1, 128.4, 128.4, 128.1, 128.0, 127.7, 125-106 (m), 61.8, 13.4; ^{19}F NMR (470 MHz, $CDCl_3$) δ –80.3 (3F, t, J = 10.2 Hz), –101.7- –101.9 (2F, m), –123.4- –123.5 (2F, m); HRMS calculated for $C_{20}H_{15}O_2F_7Na$: *m/z* 443.0852 ([M + Na]$^+$), found: *m/z* 443.0836 ([M + Na]$^+$); IR (neat) 1732, 1344, 1226, 1187, 1113, 1054 cm^{-1}.

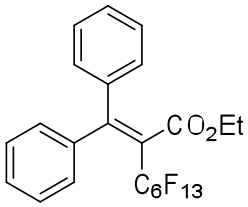
Ethyl 2-(Diphenylmethylene)-3,3,4,4,5,5,6,6,6-nonafluorohexanoate (7d)



^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33-7.28 (6H, m, Ar*H*), 7.23-7.19 (4H, m, Ar*H*), 3.95 (2H, q, J = 7.2 Hz, OCH_2CH_3), 0.89 (3H, t, J = 7.2 Hz, OCH_2CH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.4 (t, $J_{C\text{-}F}$ = 3.6 Hz), 157.2 (q, $J_{C\text{-}F}$ = 4.2 Hz), 140.9, 138.1, 129.0, 128.4, 128.4, 128.0, 128.0, 127.7, 125-110 (m), 61.8, 13.4; ^{19}F NMR (470 MHz, $CDCl_3$) δ –80.8- –80.9 (3F, m), –101.4 (2F, t, J =14.0 Hz), –119.7- –119.9 (2F, m), –125.9- –126.0 (2F, m); HRMS calculated for $C_{21}H_{15}O_2F_9Na$: *m/z*

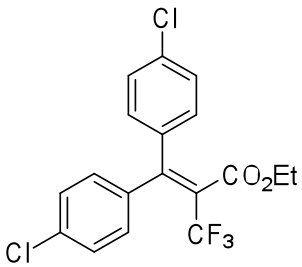
493.0821 ([M + Na]$^+$), found: *m/z* 493.0827 ([M + Na]$^+$); IR (neat) 1733, 1234, 1135 cm^{-1}.

Ethyl 3,3-Diphenyl-2-(tridecafluorohexyl)acrylate (7e)



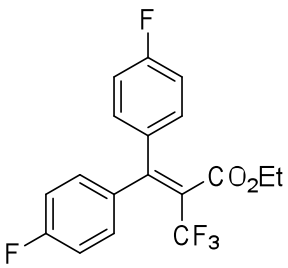
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34-7.19 (10H, m, Ar*H*), 3.95 (2H, q, J = 7.1 Hz, OCH_2CH$_3$), 0.89 (3H, t, J = 7.1 Hz, OCH$_2$CH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.4 (t, $J_{C\text{-}F}$ = 4.2 Hz), 157.2 (t, $J_{C\text{-}F}$ = 4.8 Hz), 140.9, 138.2, 129.1, 128.4, 128.4, 128.0, 128.0, 127.7, 124-108 (m), 61.8, 13.3; ^{19}F NMR (470 MHz, $CDCl_3$) δ –80.6- –80.8 (3F, m), –101.2- –101.3 (2F, m), –118.8- –119.0 (2F, m), –121.7- –121.9 (2F, m), –122.5- –122.7 (2F, m), –125.9- –126.1 (2F, m); HRMS calculated for $C_{23}H_{15}O_2F_{13}Na$: *m/z* 593.0757 ([M + Na]$^+$), found: *m/z* 593.0762 ([M + Na]$^+$); IR (neat) 1733, 1234, 1196, 1144, 1075, 1038 cm^{-1}.

Ethyl 3,3-Bis(4-chlorophenyl)-2-(trifluoromethyl)acrylate (7f)



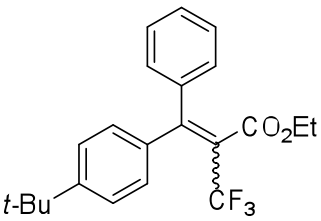
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36-7.28 (4H, m, Ar*H*), 7.19-7.15 (4H, m, Ar*H*), 4.08 (2H, q, J = 7.1 Hz, OCH_2CH$_3$), 1.05 (3H, t, J = 7.1 Hz, OCH$_2$CH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.8 (t, $J_{C\text{-}F}$ = 3.0 Hz), 151.7 (q, $J_{C\text{-}F}$ = 3.6 Hz), 137.6, 136.0, 135.6, 135.3, 129.7, 129.7, 129.7, 128.7, 128.6, 121.4 (q, $J_{C\text{-}F}$ = 275.4 Hz), 62.2, 13.6; ^{19}F NMR (470 MHz, $CDCl_3$) δ –55.4 (3F, s); HRMS calculated for $C_{18}H_{13}O_2Cl_2F_3Na$: *m/z* 411.0137 ([M + Na]$^+$), found: *m/z* 411.0142 ([M + Na]$^+$); IR (neat) 1729, 1490, 1324, 1246, 1130, 1090, 1043, 826 cm^{-1}.

Ethyl 3,3-Bis(4-fluorophenyl)-2-(trifluoromethyl)acrylate (7g)



^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24-7.20 (4H, m, Ar*H*), 7.08-6.98 (4H, m, Ar*H*), 4.07 (2H, q, J = 7.1 Hz, OCH_2CH$_3$), 1.04 (3H, t, J = 7.1 Hz, OCH$_2$CH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.2, 164.0 (d, $J_{C\text{-}F}$ = 11.9 Hz), 162.1 (d, $J_{C\text{-}F}$ = 17.9 Hz), 152.1 (q, $J_{C\text{-}F}$ = 3.6 Hz), 135.5 (d, $J_{C\text{-}F}$ = 3.6 Hz), 133.8 (d, $J_{C\text{-}F}$ = 3.6 Hz), 130.5, 130.4, 130.3, 124.3 (q, $J_{C\text{-}F}$ = 31.8 Hz), 121.5 (q, $J_{C\text{-}F}$ = 275.4 Hz), 115.6, 115.5, 115.4, 115.3, 62.1, 13.6; ^{19}F NMR (470 MHz, $CDCl_3$) δ –55.4 (3F, s), –111.0- –111.2 (1F, m), –111.7- –111.8 (1F, m); HRMS calculated for $C_{18}H_{13}O_2F_5Na$: *m/z* 379.0728 ([M + Na]$^+$), found: *m/z* 379.0733 ([M + Na]$^+$); IR (neat) 1730, 1603, 1507, 1328, 1233, 1149, 1044, 838 cm^{-1}.

Ethyl 3-(4-(*tert*-Butyl)phenyl)-3-phenyl-2-(trifluoromethyl)acrylate (7h)



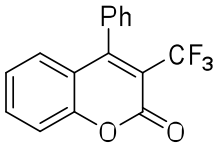
^{1}H NMR (500 MHz, $CDCl_3$) (data given for E and Z mixture) δ 7.37-7.13 (9H, m, Ar*H*, E,Z-mixture), 4.03, 4.01 (2H, q, J = 7.1 Hz, OCH_2CH$_3$), 1.30, 1.28 (9H, s, C(CH_3)$_3$),

0.95, 0.91 (3H, t, J = 7.1 Hz, OCH_2CH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.5-164.4 (m), 164.4-164.3 (m), 154.7 (q, $J_{C\text{-}F}$ = 3.6 Hz), 154.4 (q, $J_{C\text{-}F}$ = 3.6 Hz), 152.4, 151.8, 140.1, 138.2, 136.8, 135.0, 128.9, 128.6, 128.2, 128.2, 128.2, 128.0, 127.9, 125.2, 125.0, 121.7 (q, $J_{C\text{-}F}$ = 275.4 Hz), 121.7 (q, $J_{C\text{-}F}$ = 275.4 Hz), 61.7, 61.7, 34.7, 31.2, 31.2, 13.5, 13.4; ^{19}F NMR (470 MHz, $CDCl_3$) δ –55.29, –55.30 (3F, s); HRMS calculated for $C_{22}H_{23}O_2F_3Na$: *m/z* 399.1542 ($[M + Na]^+$), found: *m/z* 399.1538 ($[M + Na]^+$); IR (neat) 2965, 1730, 1367, 1329, 1243, 1151, 1129, 1045, 831, 699 cm^{-1}.

Typical Procedure for Direct Perfluoroalkylation of Heterocycles (Scheme 4, 7i-p).

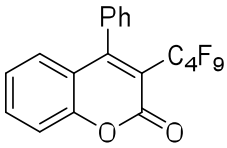
4-Phenylcoumarin (44.4 mg, 0.2 mmol), DDQ (27.2 mg, 0.12 mmol), R_fSO_2Na (0.4 mmol) and F_5-PIFA (208 mg, 0.4 mmol) were added subsequently in a test tube under argon atmosphere. Then 2,6-lutidine (23.0 μL , 0.2 mmol) and DCM (1 mL) was added and the reaction mixture was stirred at room temperature overnight. Upon completion of the reaction, the resulting mixture was directly purified by flash column chromatography on silica gel to afford the corresponding product.

4-Phenyl-3-(trifluoromethyl)-2*H*-chromen-2-one (7i)



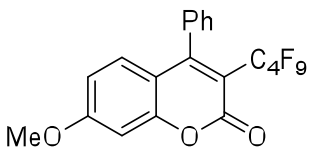
^1H NMR (500 MHz, $CDCl_3$) δ 7.65-7.60 (1H, m, Ar*H*), 7.55-7.51 (3H, m, Ar*H*), 7.42-7.39 (1H, m, Ar*H*), 7.27-7.24 (2H, m, Ar*H*), 7.22-7.18 (1H, m, Ar*H*), 7.03-7.00 (1H, m, Ar*H*).
Other spectral data of this compound were consistent with previous reported data. [10]

3-(Nonafluorobutyl)-4-phenyl-2*H*-chromen-2-one (7j)



^1H NMR (500 MHz, $CDCl_3$) δ 7.64-7.60 (1H, m, Ar*H*), 7.53-7.47 (3H, m, Ar*H*), 7.40 (1H, d, J = 8.2 Hz, Ar*H*), 7.24-7.20 (2H, m, Ar*H*), 7.19-7.14 (1H, m, Ar*H*), 6.85 (1H, q, J = 8.2 Hz, Ar*H*); ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.0 (m), 156.1, 153.5, 134.3, 133.0, 129.4, 128.9, 128.0, 127.3, 124.7, 120.2, 119-108 (m), 116.7; ^{19}F NMR (470 MHz, $CDCl_3$) δ –80.7- –80.8 (3F, m), –102.3 (2F, t, J =14.7 Hz), –118.8- –119.0 (2F, m), –126.0- –126.1 (2F, m); HRMS calculated for $C_{19}H_9O_2F_9Na$: *m/z* 463.0351 ($[M + Na]^+$), found: *m/z* 463.0343 ($[M + Na]^+$); IR (neat) 1742, 1605, 1560, 1354, 1230, 1200, 1134, 756 cm^{-1}.

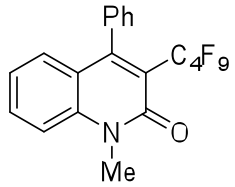
7-Methoxy-3-(perfluorobutyl)-4-phenyl-2*H*-chromen-2-one (7k)



^1H NMR (500 MHz, $CDCl_3$) δ 7.49-7.46 (3H, m, Ar*H*), 7.21-7.18 (2H, m, Ar*H*), 6.86-6.84 (1H, m, Ar*H*), 6.73-6.70 (2H, m, Ar*H*), 3.89 (3H, s, OCH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.8, 159.9 (q, $J_{C\text{-}F}$ = 2.4 Hz), 156.6 (q, $J_{C\text{-}F}$ = 2.4 Hz), 155.7,

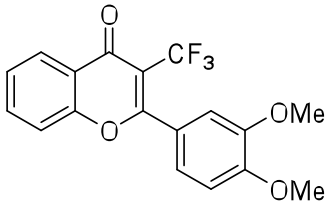
133.4, 130.6, 128.8, 127.9, 127.3, 120-105 (m), 113.8, 113.3, 100.1, 56.1; ^{19}F NMR (470 MHz, $CDCl_3$) δ –80.7- –80.8 (3F, m), –102.1 (2F, t, J =14.7 Hz), –119.0- –119.2 (2F, m), –126.0- –126.1 (2F, m); HRMS calculated for $C_{20}H_{11}O_3F_9Na$: *m/z* 493.0457 ([M + Na]$^+$), found: *m/z* 493.0461 ([M + Na]$^+$); IR (neat) 1738, 1616, 1591, 1546, 1372, 1205, 1133 cm^{-1}.

1-Methyl-3-(perfluorobutyl)-4-phenylquinolin-2(1*H*)-one (7l)



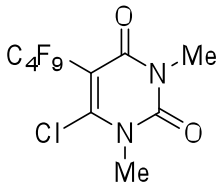
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66-7.62 (1H, m, Ar*H*), 7.48-7.45 (3H, m, Ar*H*), 7.42 (1H, d, J = 8.2 Hz, Ar*H*), 7.22-7.19 (2H, m, Ar*H*), 7.12-7.08 (1H, m, Ar*H*), 6.96 (1H, dd, J= 8.2, 1.4 Hz, Ar*H*), 3.81 (3H, s, NCH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.5 (t, $J_{C\text{-}F}$ = 2.4 Hz), 154.8-154.7 (m), 140.4, 135.0, 133.0, 130.2, 128.2, 128.0, 127.8, 122.4, 121.1, 119-108 (m), 114.0, 29.9; ^{19}F NMR (470 MHz, $CDCl_3$) δ –80.6- –80.7 (3F, m), –101.0- –101.2 (2F, m), –117.8- –118.0 (2F, m), –126.0- –126.2 (2F, m); HRMS calculated for $C_{20}H_{12}ONF_9Na$: *m/z* 476.0667 ([M + Na]$^+$), found: *m/z* 476.0675 ([M + Na]$^+$); IR (neat) 1655, 1603, 1367, 1231, 1199, 1132 cm^{-1}.

2-(3,4-Dimethoxyphenyl)-3-(trifluoromethyl)-4*H*-chromen-4-one (7m)



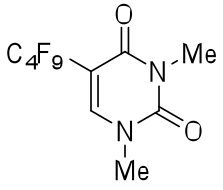
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.27 (1H, dd, J = 7.9, 1.7 Hz, Ar*H*), 7.76-7.71 (1H, m, Ar*H*), 7.50-7.46 (2H, m, Ar*H*), 7.24 (1H, dd, J = 8.4 Hz, 1.8 Hz, Ar*H*), 7.12 (1H, d, J = 2.0 Hz, Ar*H*), 6.99 (1H, d, J = 8.0 Hz, Ar*H*), 3.98 (3H, s, OCH_3) 3.95 (3H, s, OCH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.6, 166.8-166.9 (m), 155.4, 151.8, 148.7, 134.6, 126.2, 126.1, 124.6, 123.4, 122.9 (q, $J_{C\text{-}F}$ = 275.3 Hz), 122.5, 121.8, 117.9, 111.7, 110.6, 56.13, 56.08; ^{19}F NMR (470 MHz, $CDCl_3$) δ –56.0 (3F, s); HRMS calculated for $C_{18}H_{13}O_4F_3Na$: *m/z* 373.0658 ([M + Na]$^+$), found: *m/z* 373.0664 ([M + Na]$^+$); IR (neat) 1654, 1516, 1467, 1385, 1267, 1125, 1069, 1022, 762 cm^{-1}.

6-Chloro-1,3-dimethyl-5-(perfluorobutyl)pyrimidine-2,4(1*H*,3*H*)-dione (7n)



^{1}H NMR (500 MHz, $CDCl_3$) δ 3.71 (3H, s, NCH_3), 3.37 (3H, s, NCH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.1, 150.8, 149.7, 119-106 (m), 101.6 (t, $J_{C\text{-}F}$ = 23.2 Hz), 34.8, 29.0; ^{19}F NMR (470 MHz, $CDCl_3$) δ –80.7- –80.8 (3F, m), –104.7- –104.9 (2F, m), –121.2- –121.4 (2F, m), –126.0- –126.2 (2F, m); HRMS calculated for $C_{10}H_6O_2N_2ClF_9Na$: *m/z* 414.9866 ([M + Na]$^+$), found: *m/z* 414.9878 ([M + Na]$^+$); IR (neat) 1720, 1662, 1582, 1429, 1350, 1231, 1198, 1128 cm^{-1}.

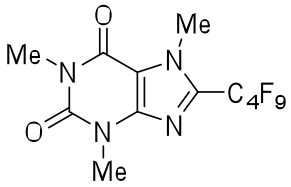
1,3-Dimethyl-5-(perfluorobutyl)pyrimidine-2,4(1*H*,3*H*)-dione (7o)



^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 (1H, s, NC*H*=C), 3.52 (3H, s, NCH_3), 3.37 (3H, s, NCH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.5 (t, $J_{C\text{-}F}$ = 2.4 Hz), 150.9, 145.7 (t, $J_{C\text{-}F}$ = 10.1 Hz), 120-106 (m), 102.3 (t,

$J_{C\text{-}F}$ = 24.4 Hz), 37.9, 28.2; ^{19}F NMR (470 MHz, $CDCl_3$) δ –80.8- –80.9 (3F, m), –109.8- –109.9 (2F, m), –121.7- –121.9 (2F, m), –125.8- –126.0 (2F, m); HRMS calculated for $C_{10}H_7O_2N_2F_9Na$: *m/z* 381.0256 ([M + Na]$^+$), found: *m/z* 381.0267 ([M + Na]$^+$); IR (neat) 1721, 1668, 1454, 1372, 1350, 1231, 1204, 1131 cm^{-1}.

1,3,7-Trimethyl-8-(perfluorobutyl)-3,7-dihydro-1*H*-purine-2,6-dione (7p)



^{1}H NMR (500 MHz, $CDCl_3$) δ 4.20-4.19 (3H, m, NCH_3), 3.60 (3H, s, NCH_3), 3.43 (3H, s, NCH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.5, 151.3, 147.1, 137.8 (t, $J_{C\text{-}F}$ = 29.2 Hz), 119-108 (m), 110.2, 33.8, 29.9, 28.2; ^{19}F NMR (470 MHz, $CDCl_3$) δ –80.7- –80.8 (3F, m), –108.9- –109.1 (2F, m), –121.7- –121.9 (2F, m), –125.3- –125.5 (2F, m); HRMS calculated for $C_{12}H_9O_2N_4F_9Na$: *m/z* 435.0474 ([M + Na]$^+$), found: *m/z* 435.0474 ([M + Na]$^+$); IR (neat) 1706, 1671, 1231, 1199, 1136 cm^{-1}.

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(b) Z. He, M. Bae, J. Wu ,and T. F. Jamison *Angew. Chem. Int. Ed.* **2014**, *53*, 14451.

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(a) R. Wu, M. G. Beauchamps, J. M. Laquidara, and J. R. Sowa Jr. *Angew. Chem. Int. Ed.* **2012**, *51*, 2106.

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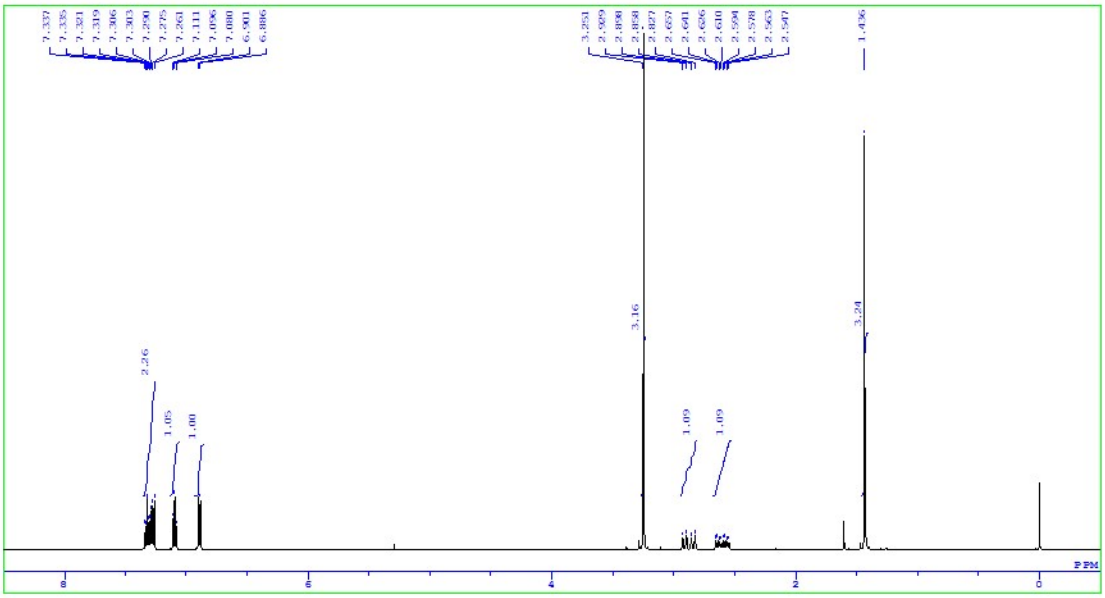
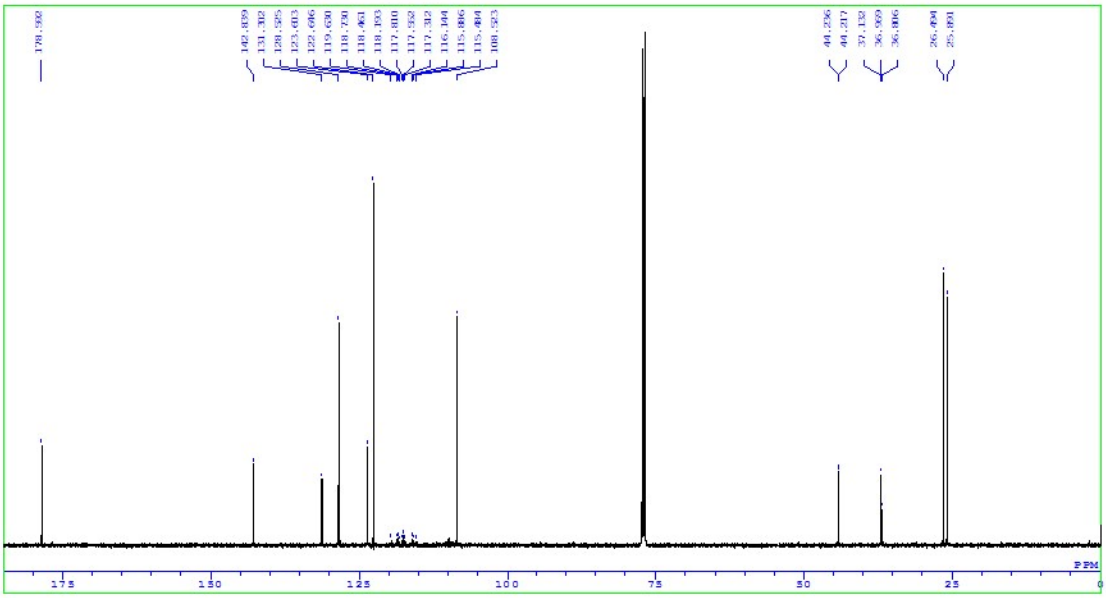
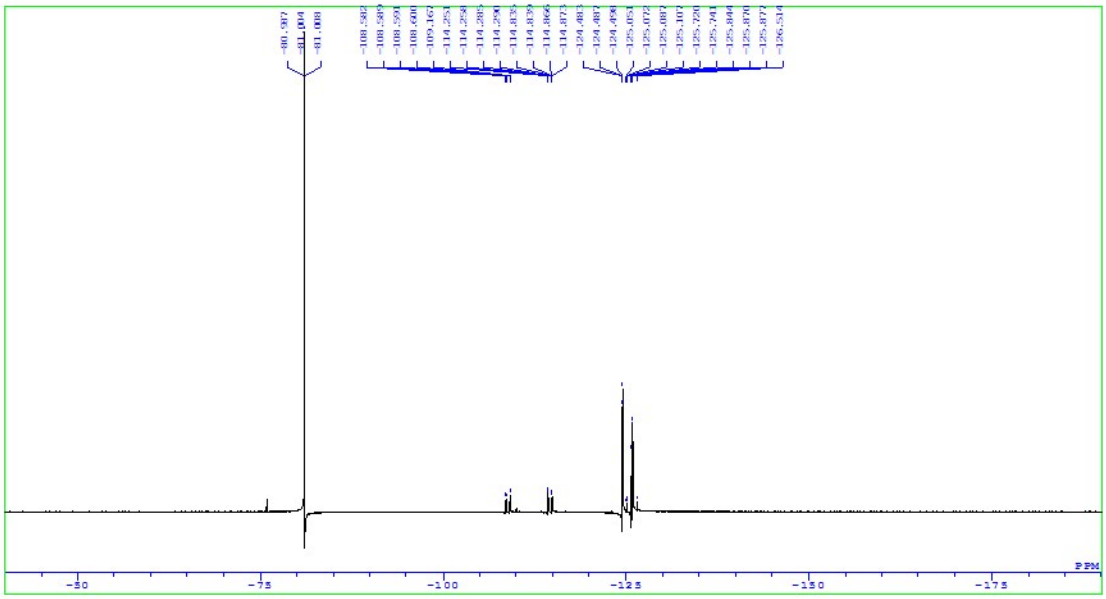
^{1}H NMR spectrum of **3a**



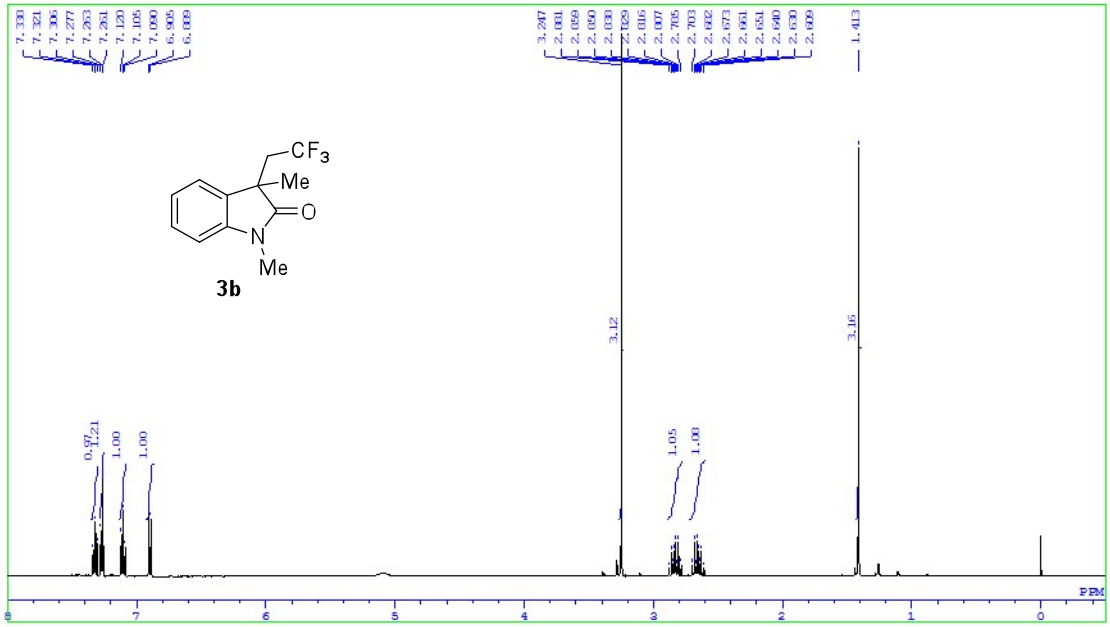
^{13}C NMR spectrum of **3a**



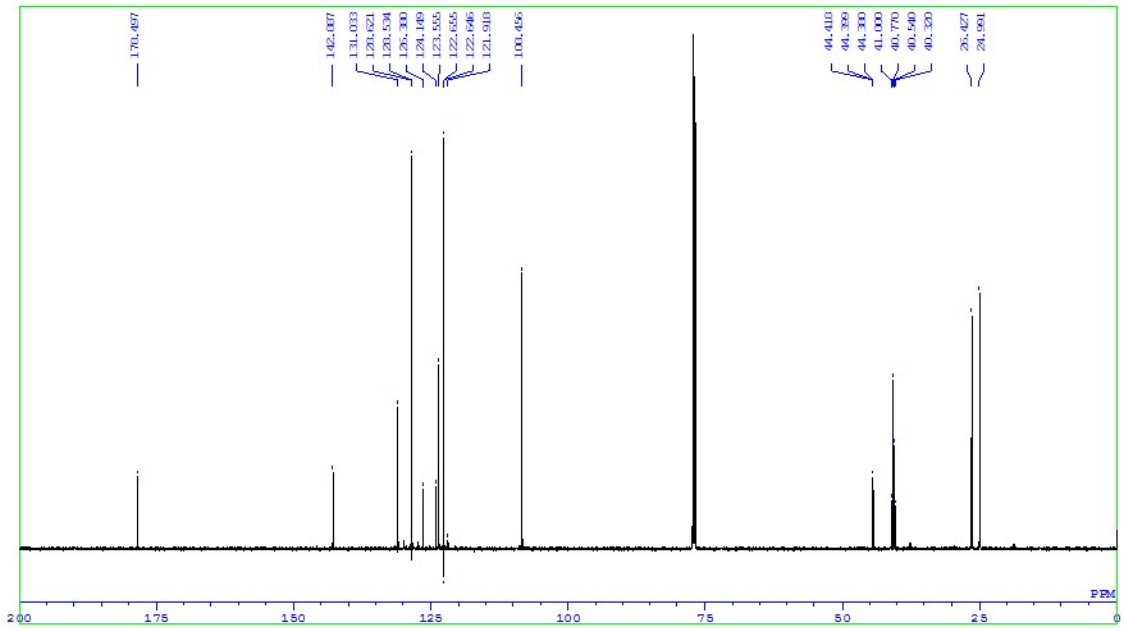
^{19}F NMR of spectrum of **3a**



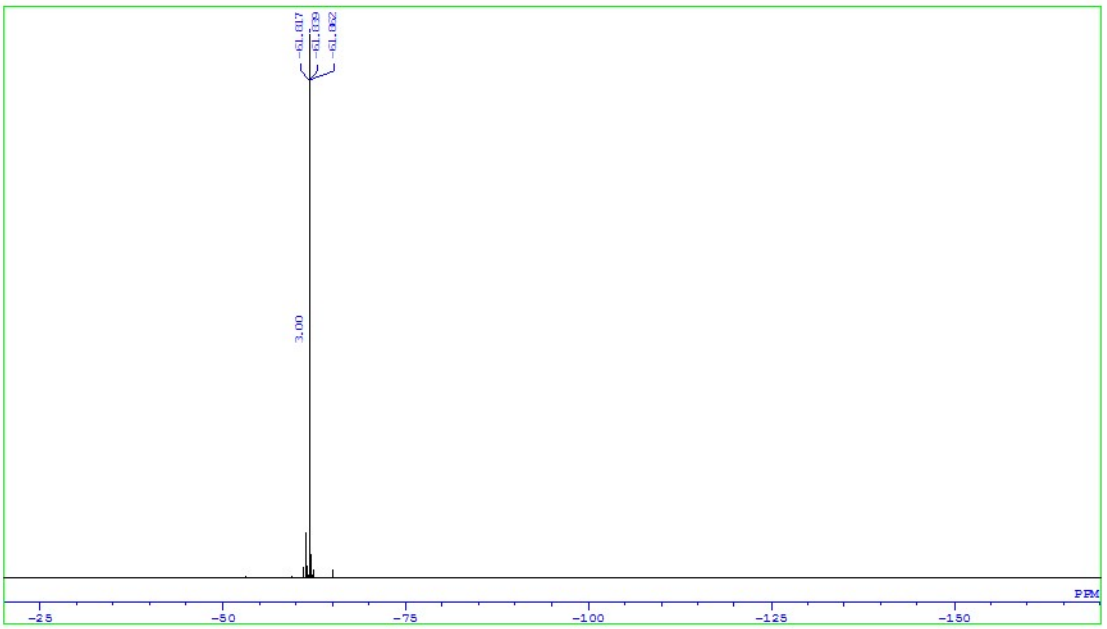
^{1}H NMR spectrum of **3b**



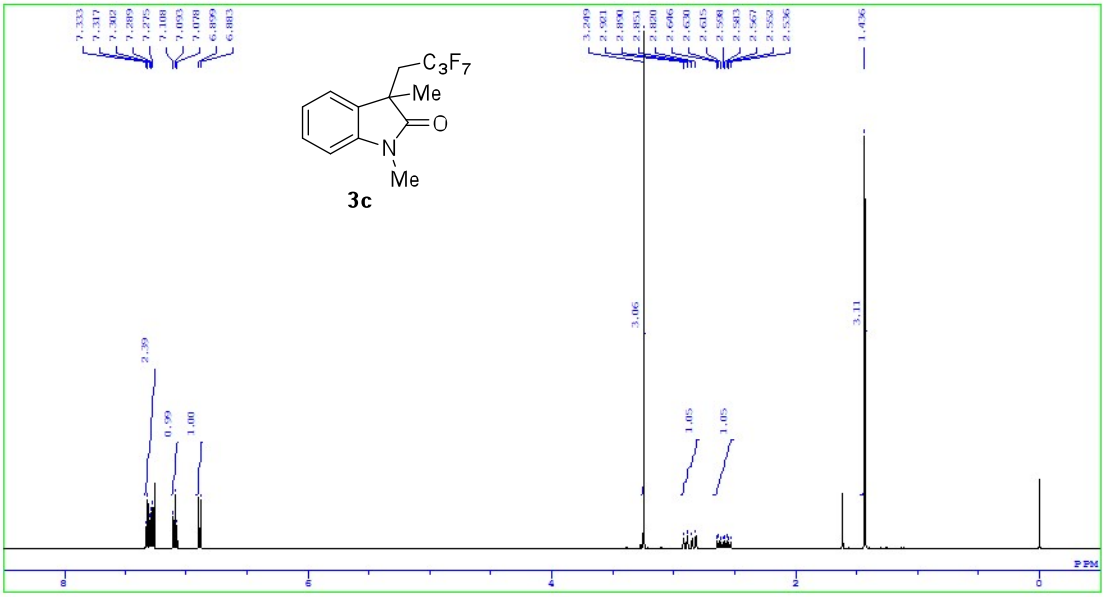
^{13}C NMR of spectrum of **3b**



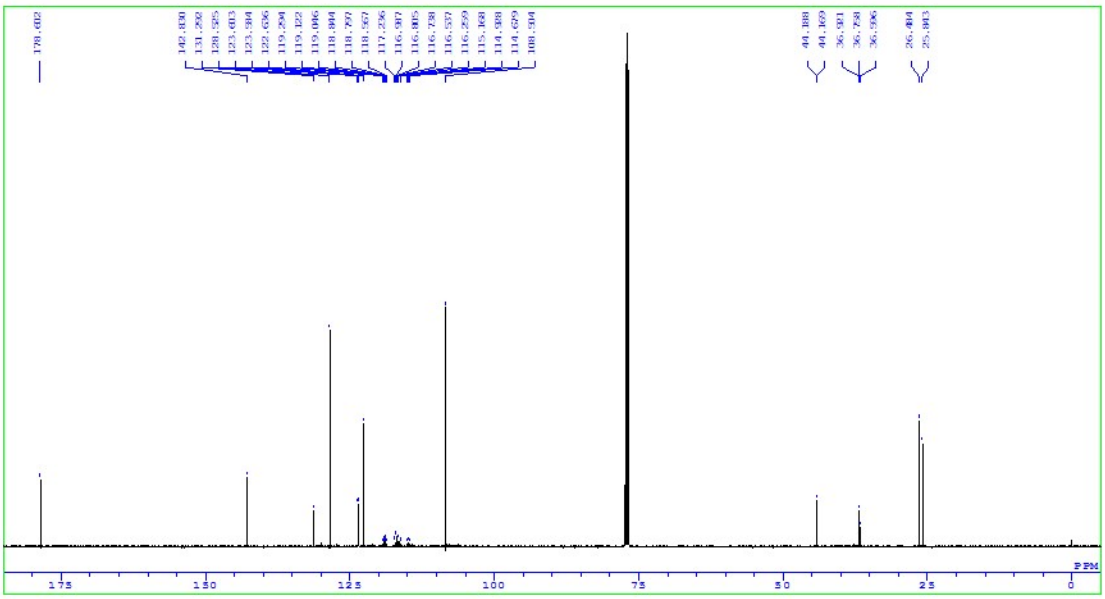
^{19}F NMR of spectrum of **3b**



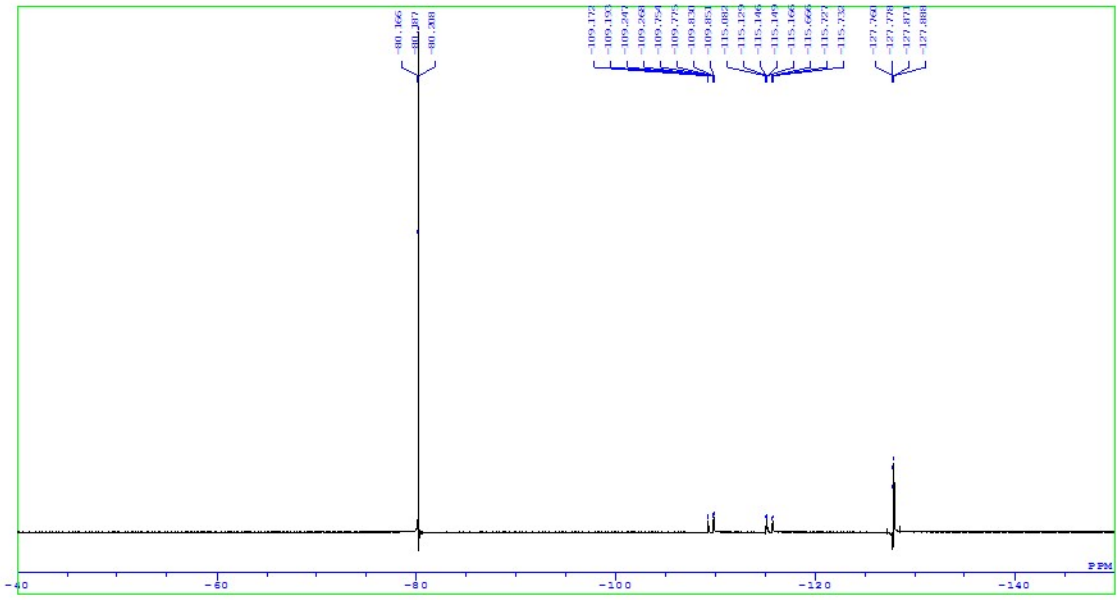
^{1}H NMR spectrum of **3c**



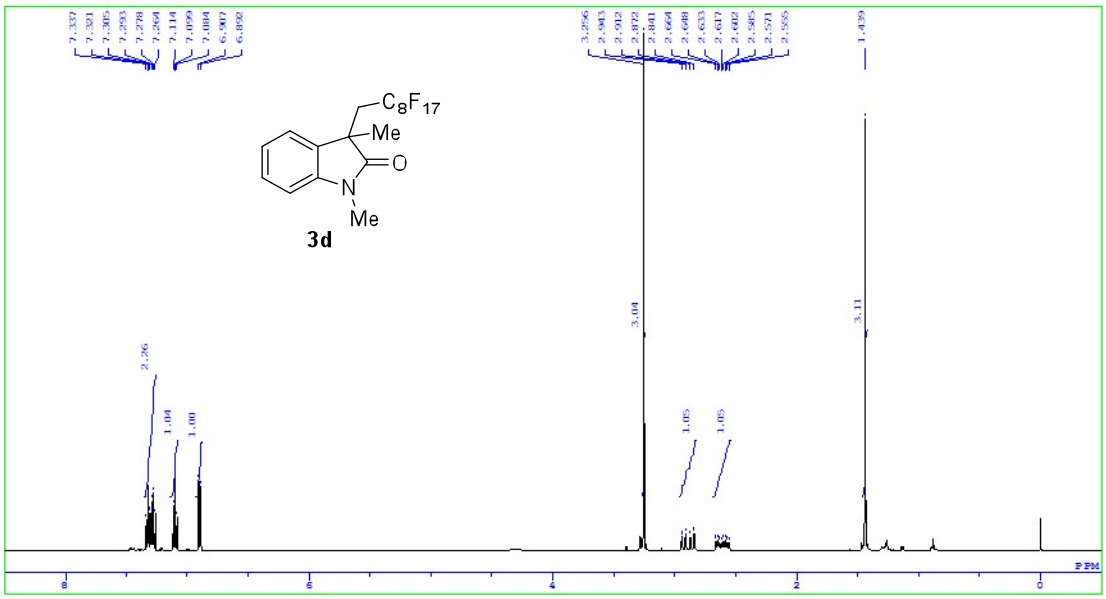
^{13}C NMR spectrum of **3c**



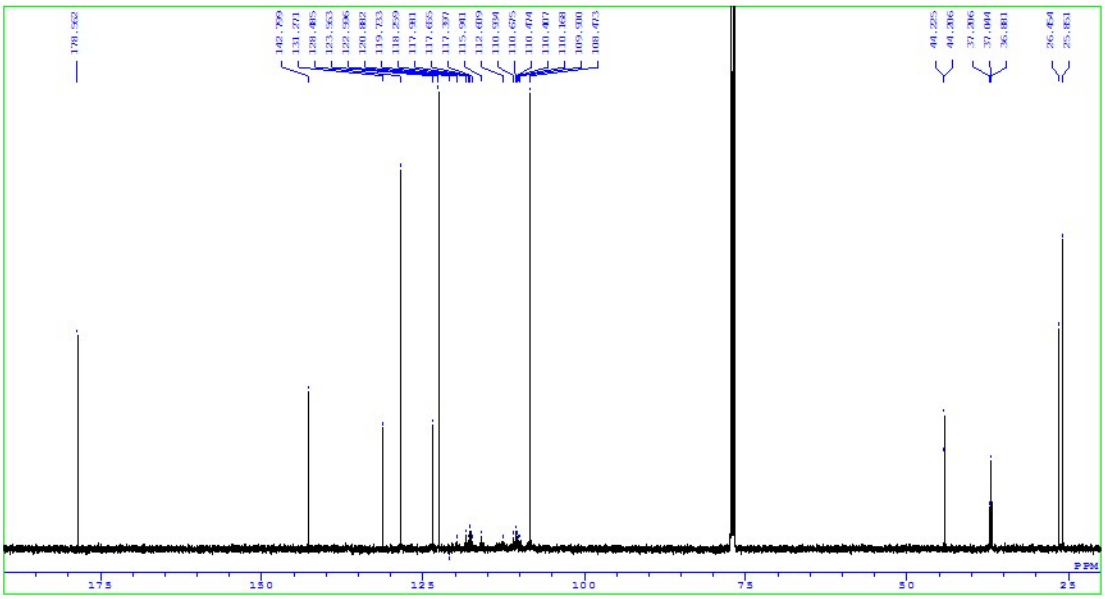
^{19}F NMR of spectrum of **3c**



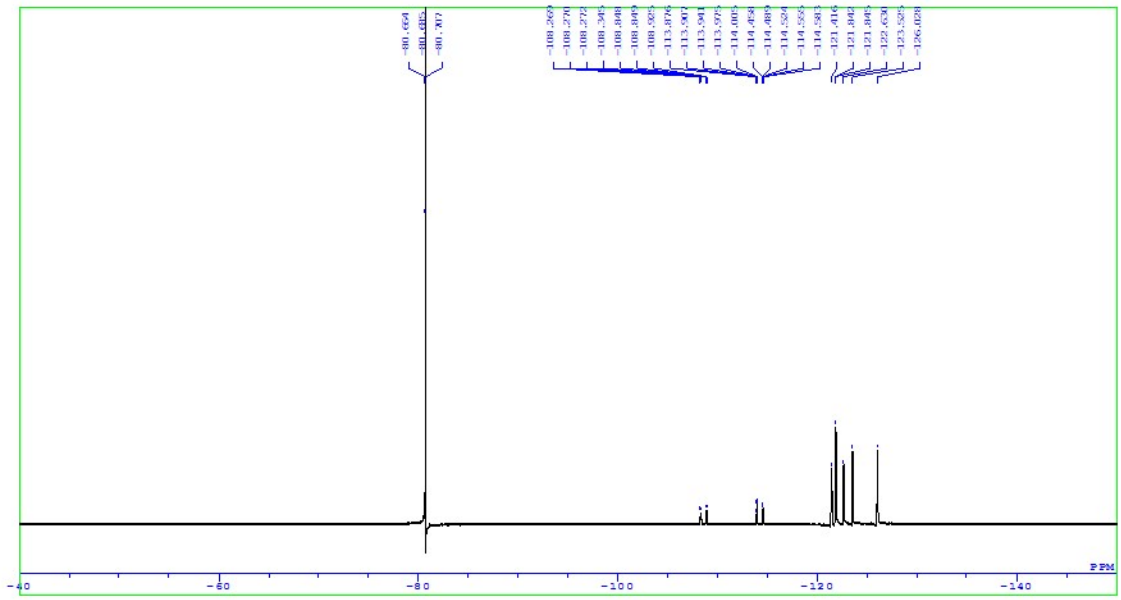
^{1}H NMR of spectrum of **3d**



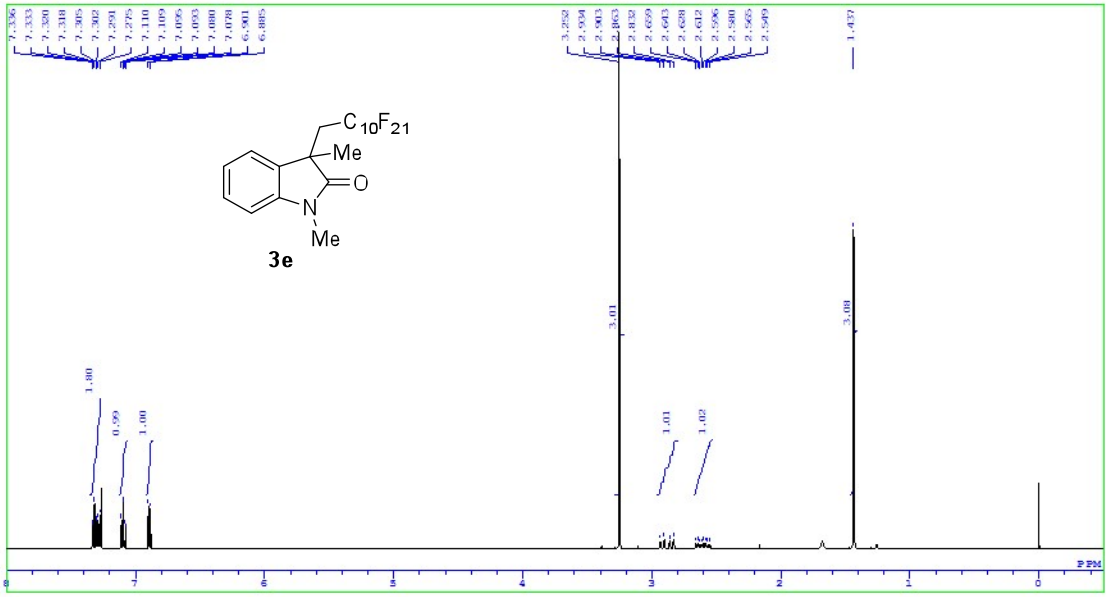
^{13}C NMR of spectrum of **3d**



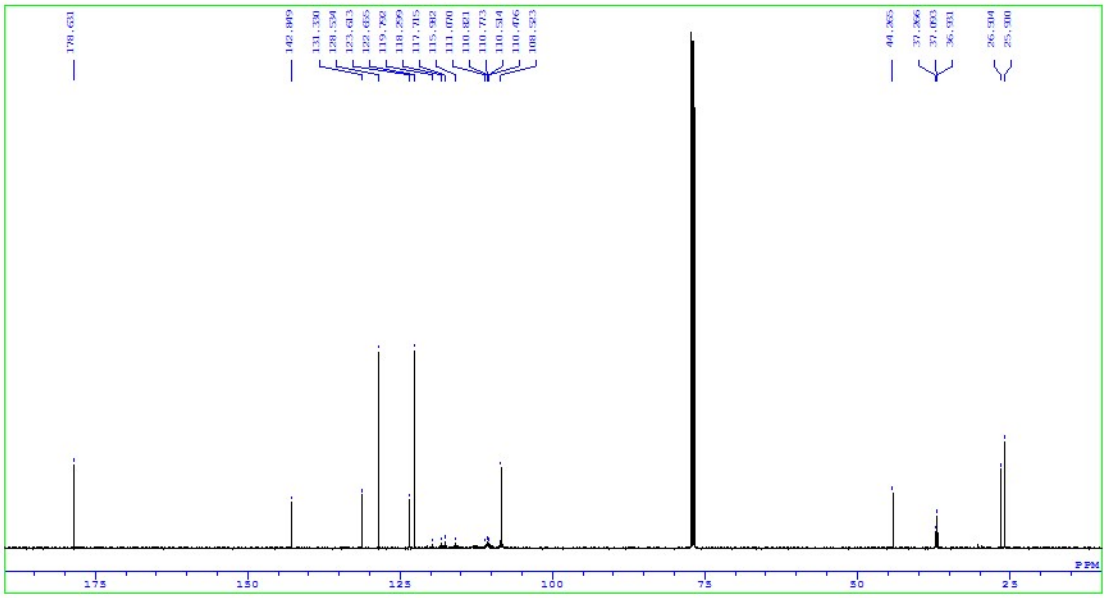
^{19}F NMR of spectrum of **3d**



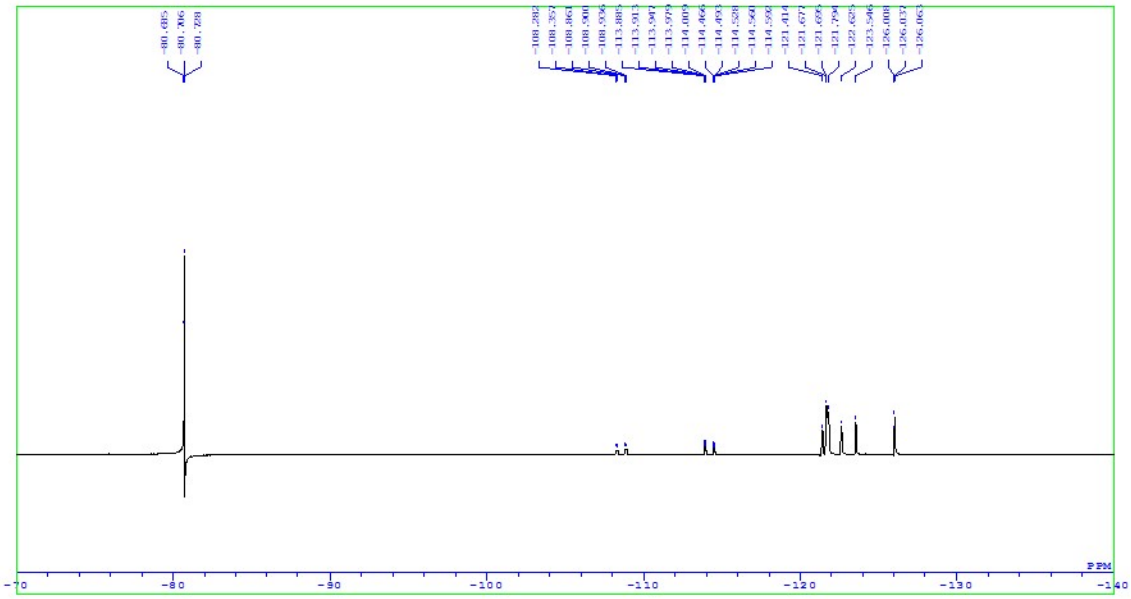
^{1}H NMR of spectrum of **3e**



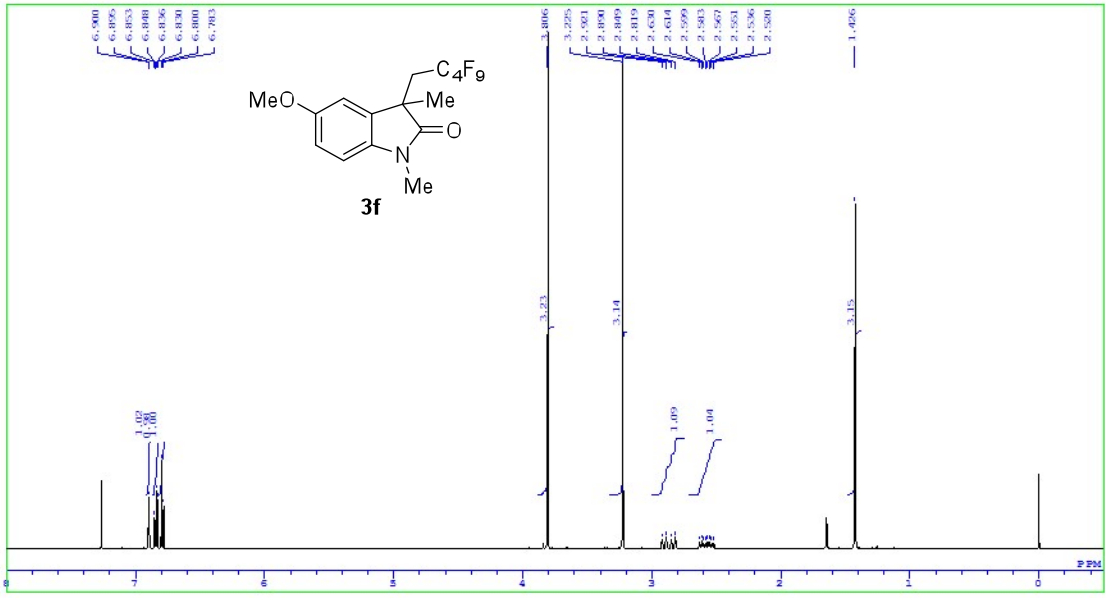
^{13}C NMR of spectrum of **3e**



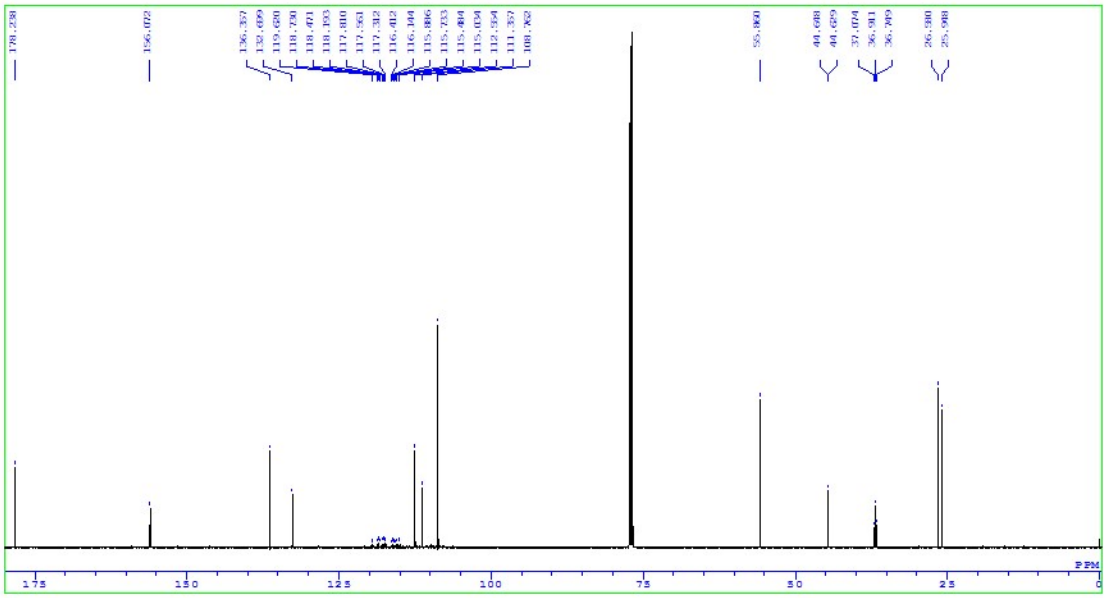
^{19}F NMR of spectrum of **3e**



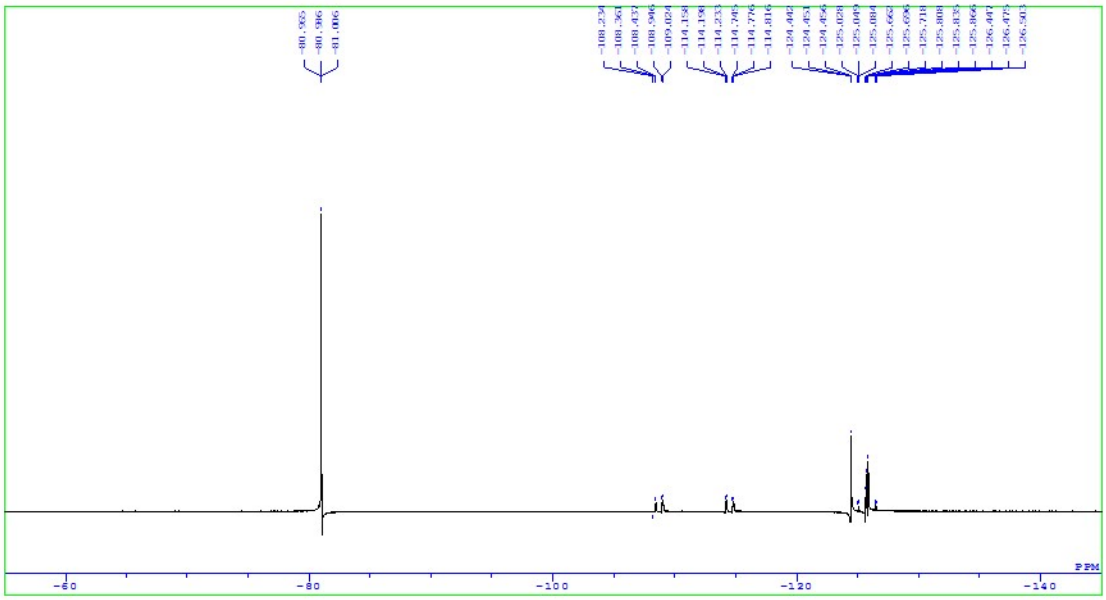
^{1}H NMR of spectrum of **3f**



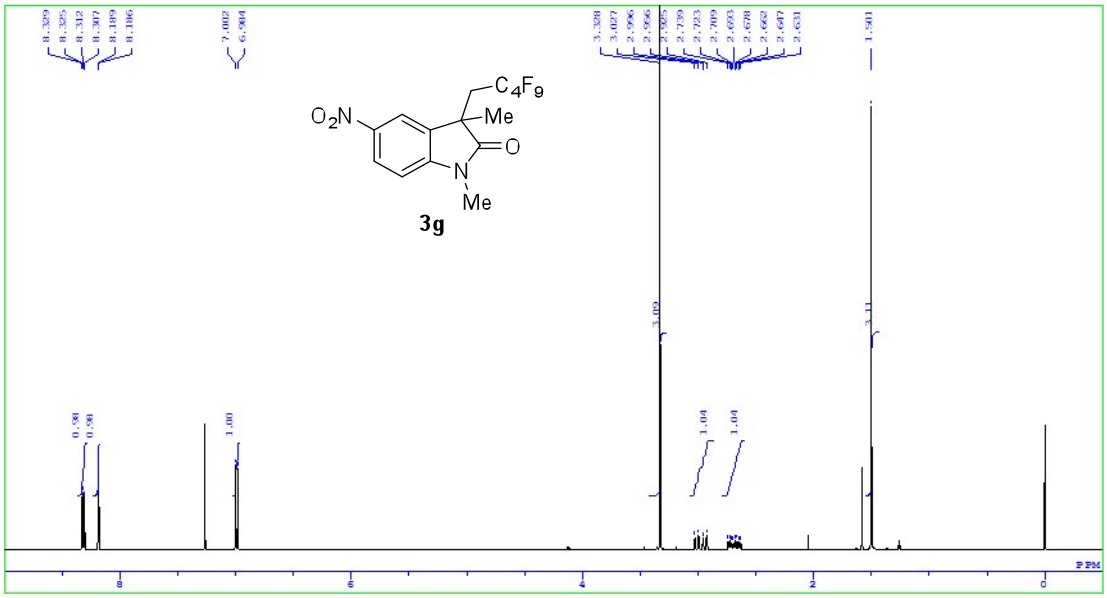
^{13}C NMR of spectrum of **3f**



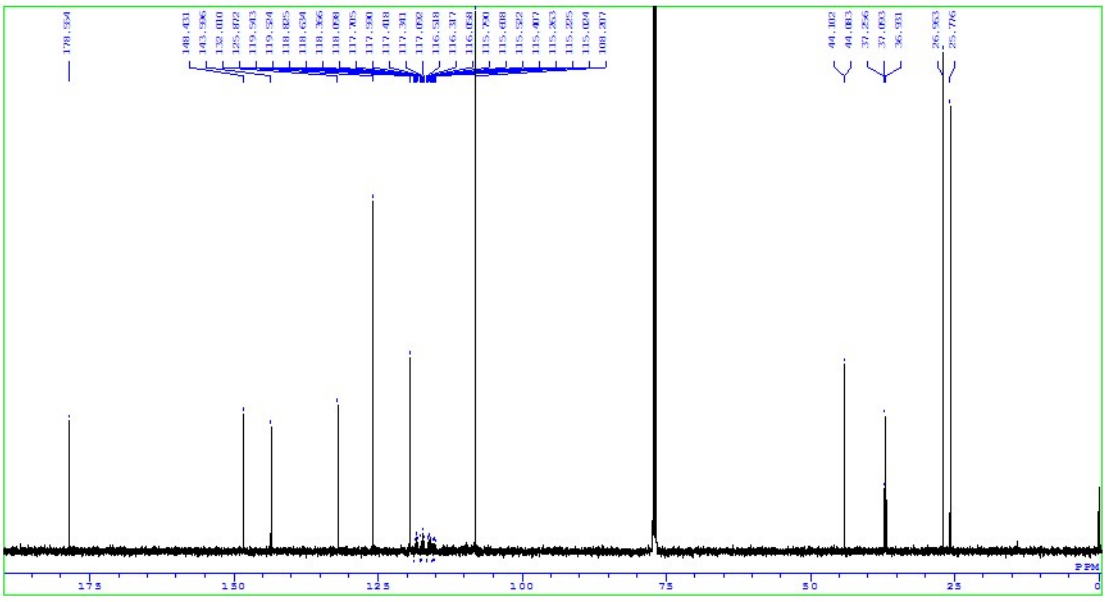
^{19}F NMR of spectrum of **3f**



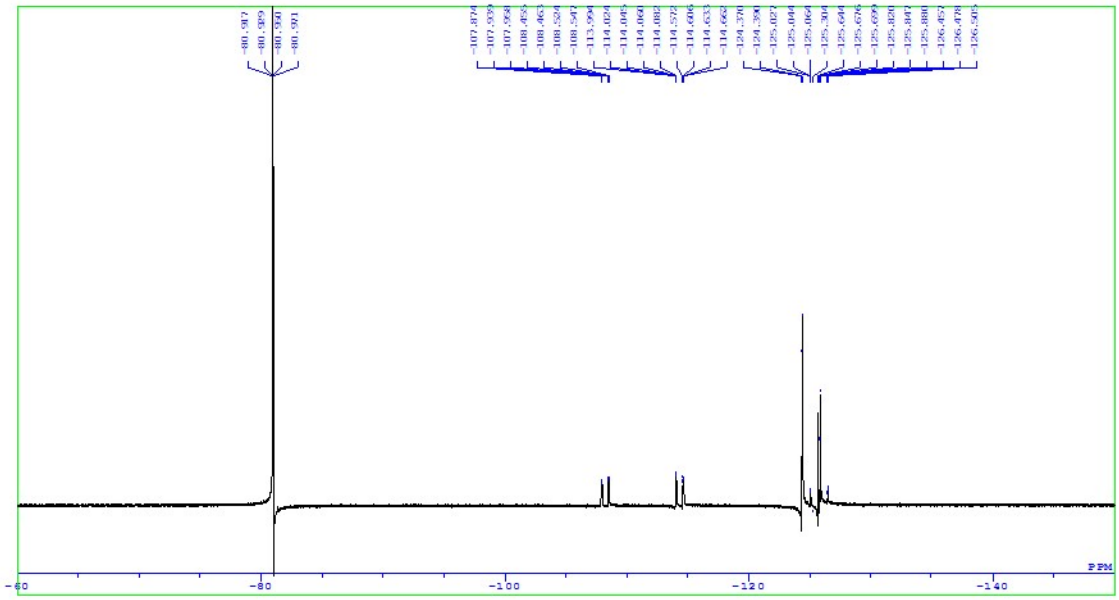
^{1}H NMR of spectrum of **3g**



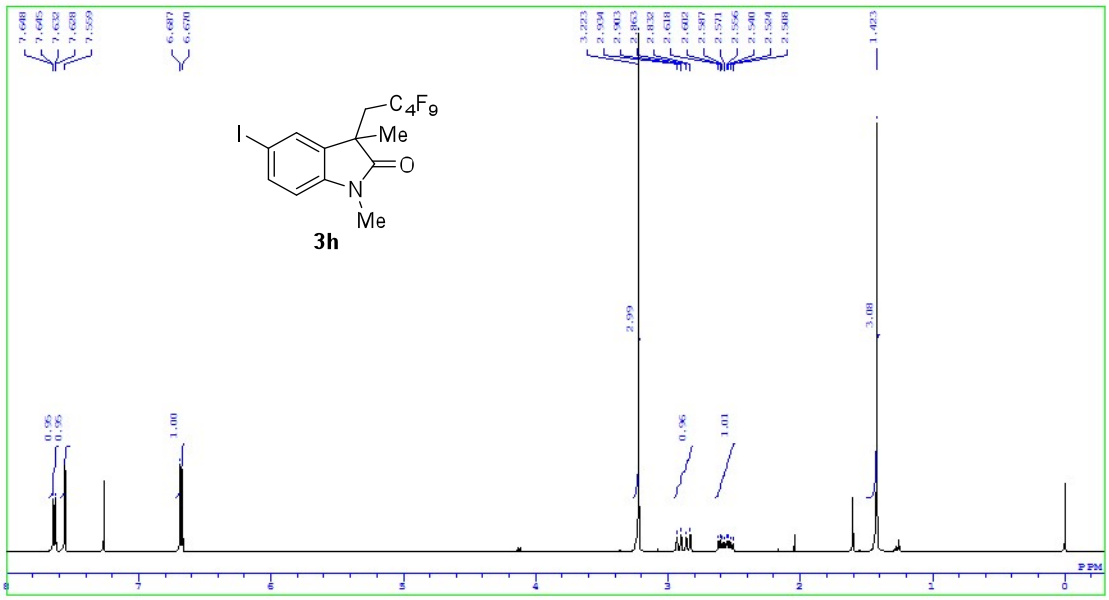
^{13}C NMR of spectrum of **3g**



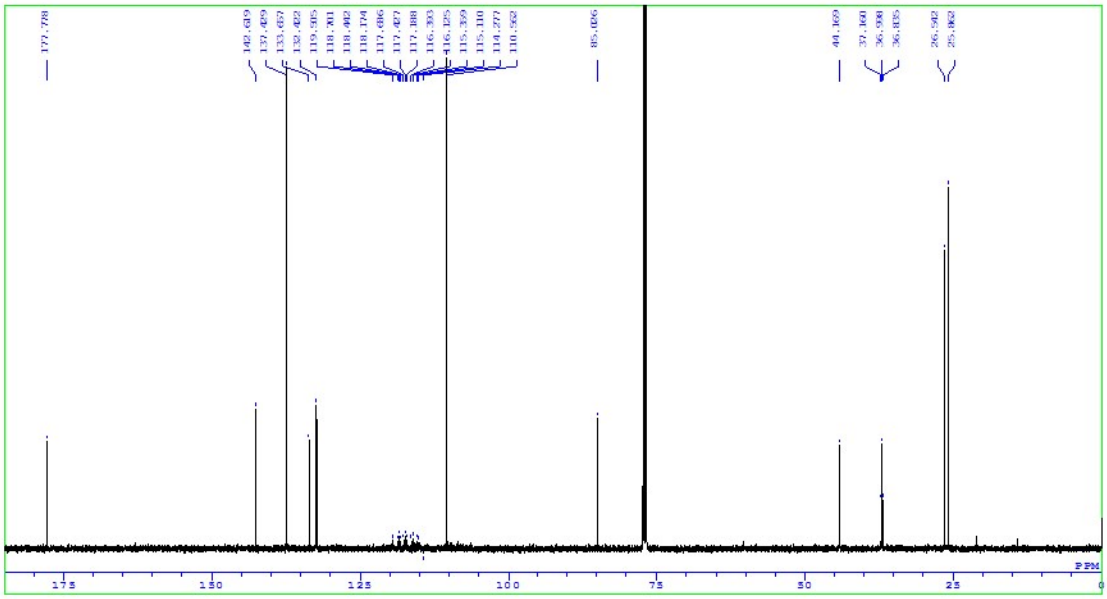
^{19}F NMR of spectrum of **3g**



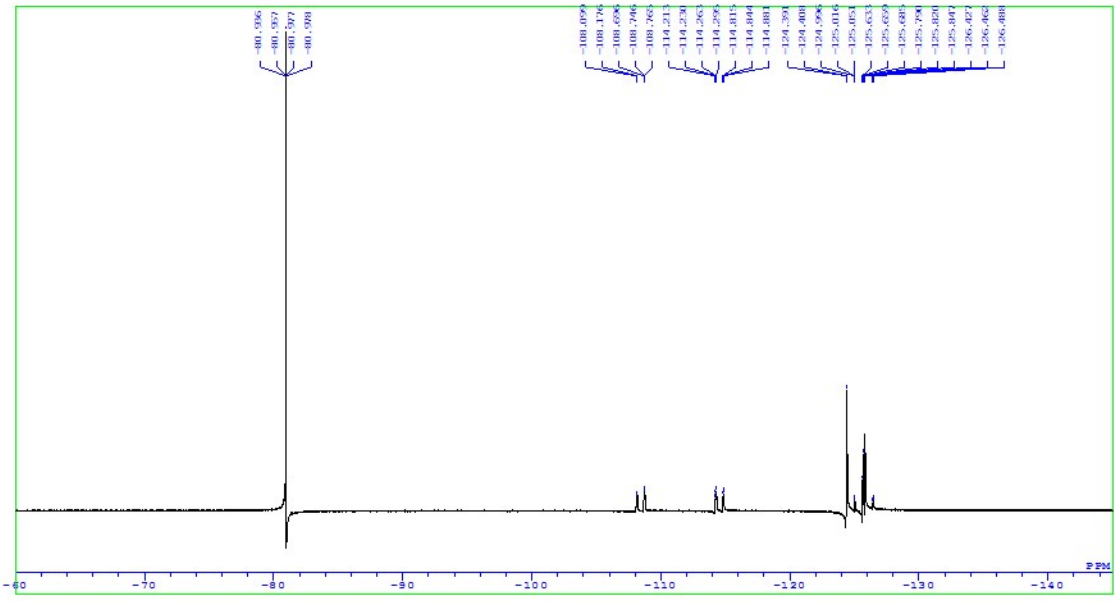
^{1}H NMR of spectrum of **3h**



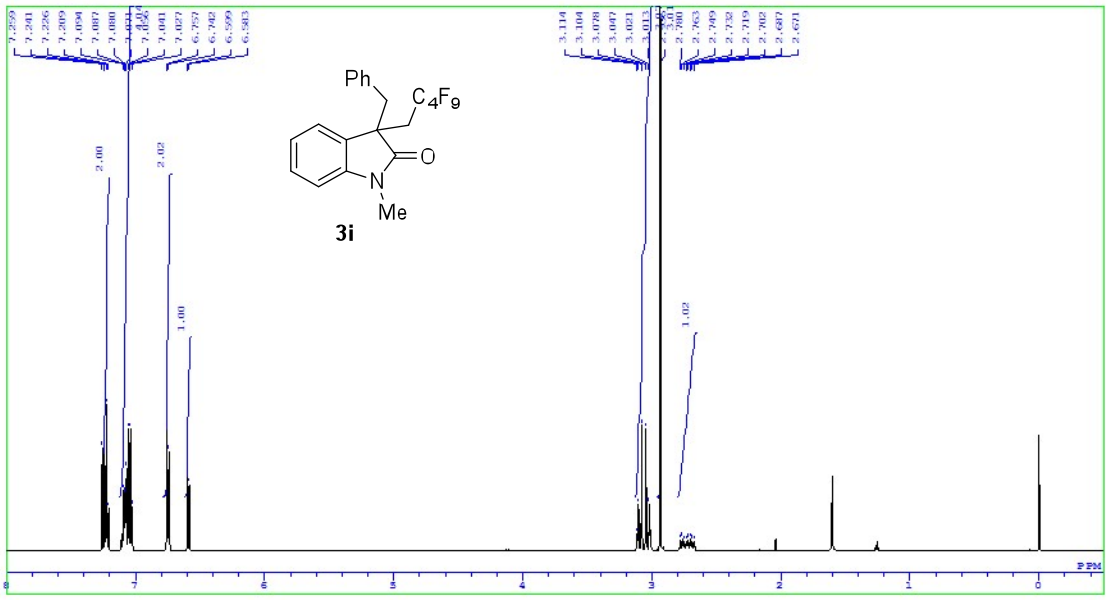
^{13}C NMR of spectrum of **3h**



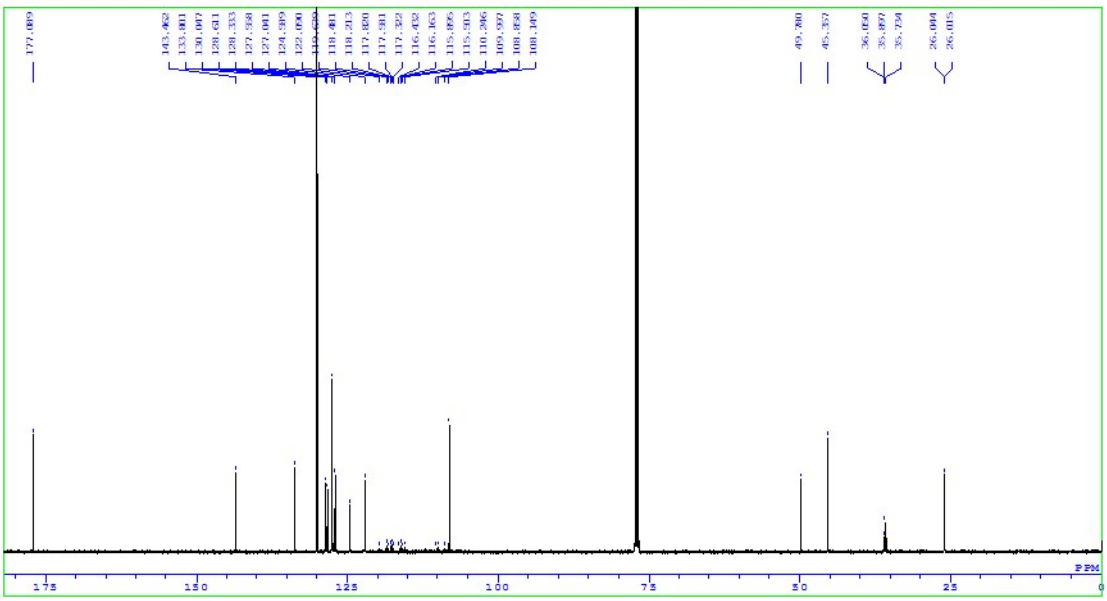
^{19}F NMR of spectrum of **3h**



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



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



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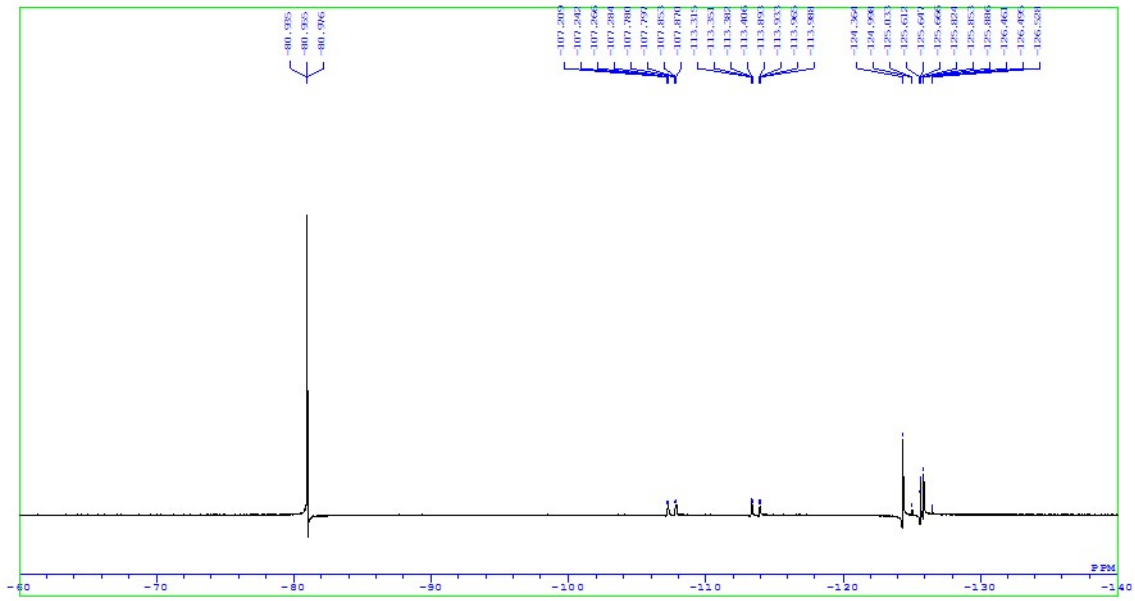

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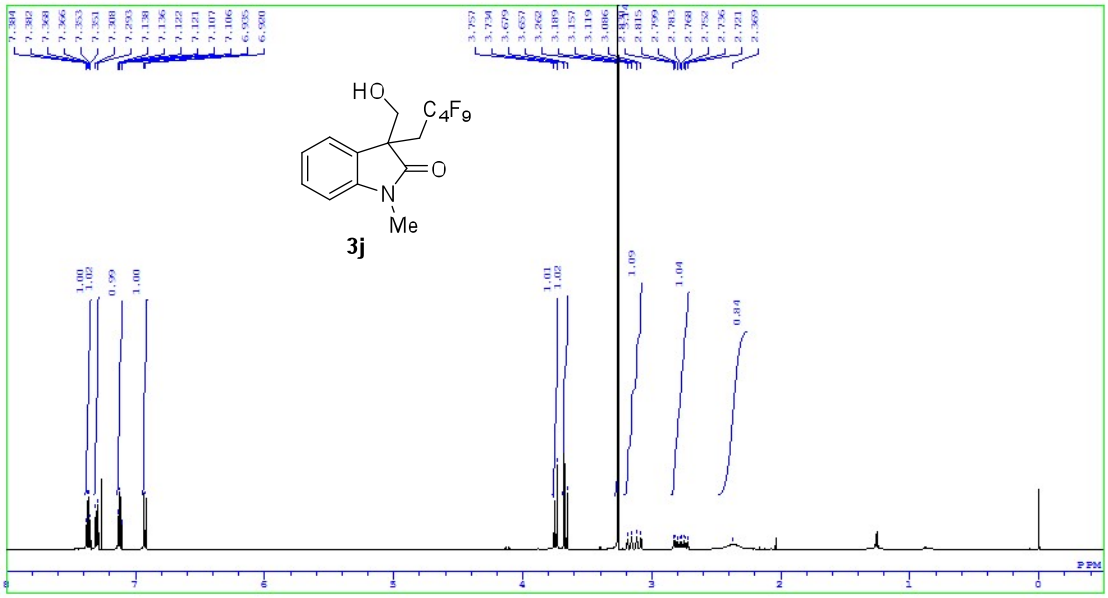
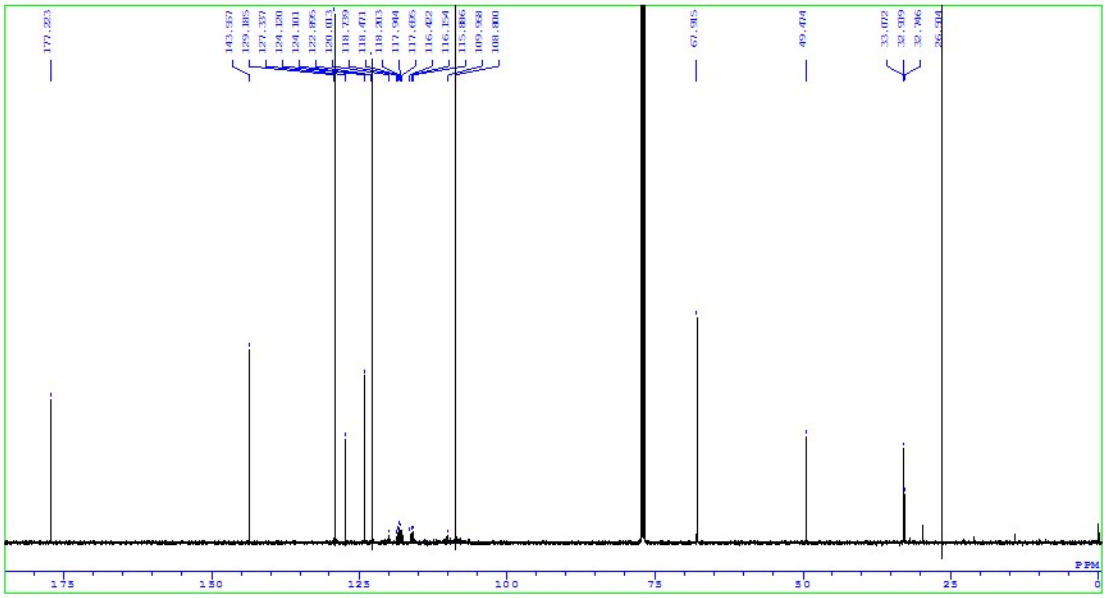


^{13}C NMR of spectrum of **3j**



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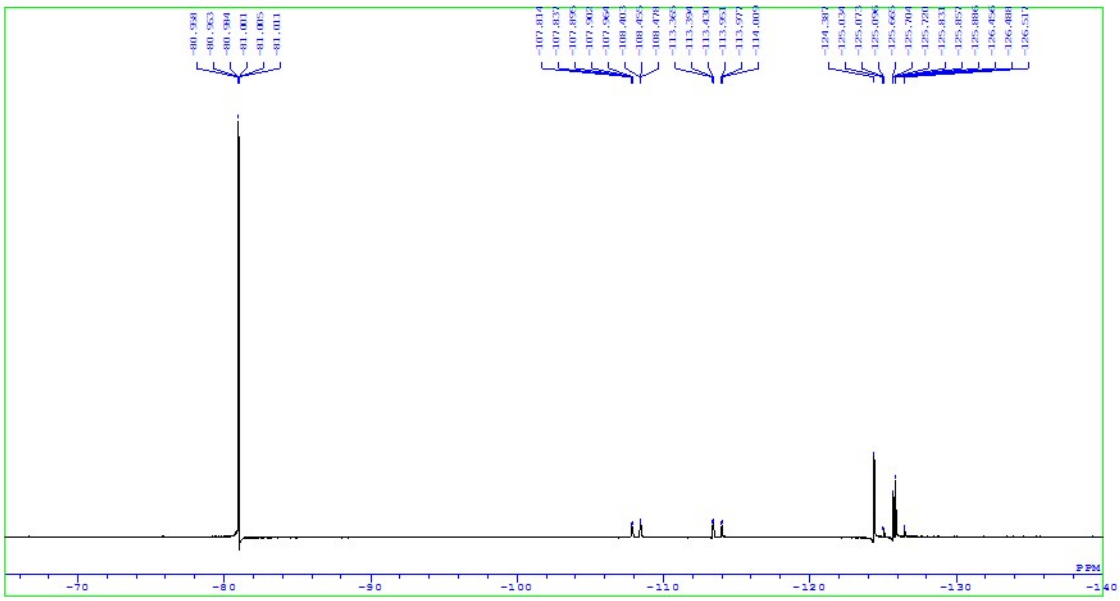
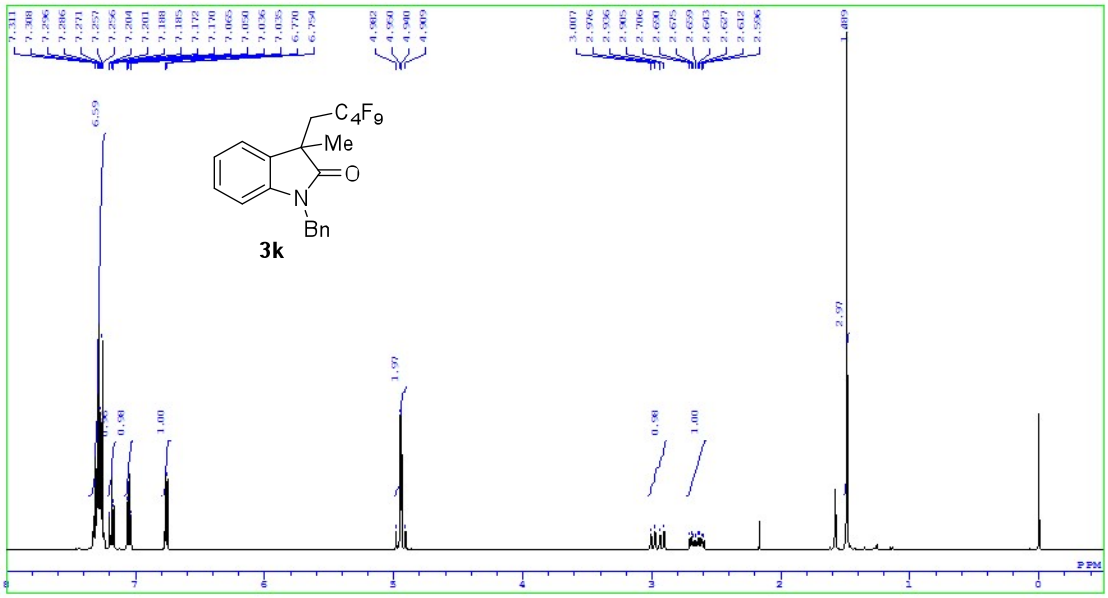
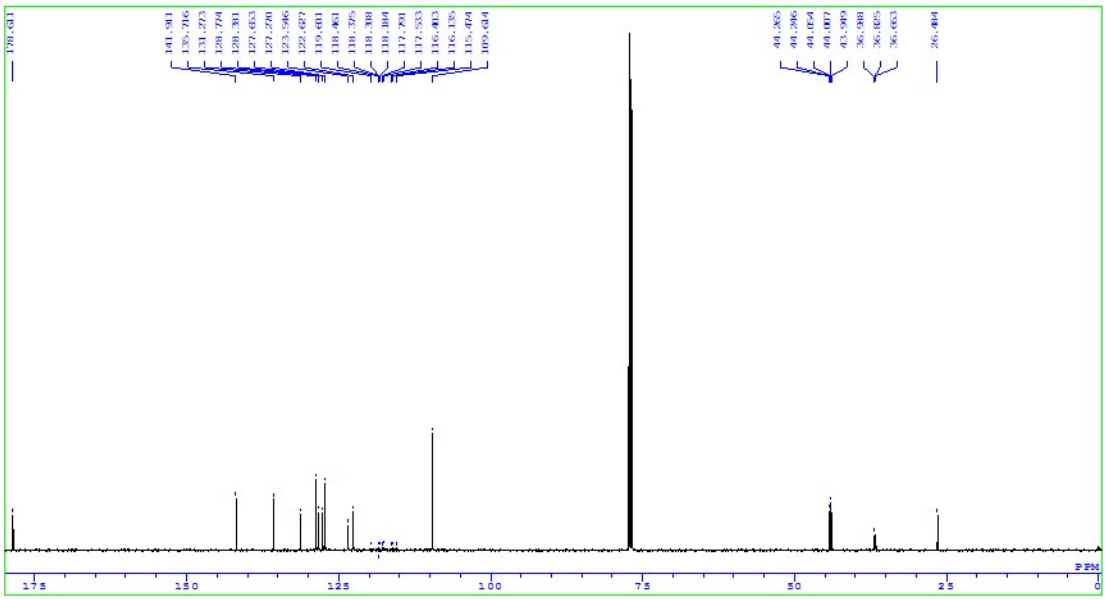


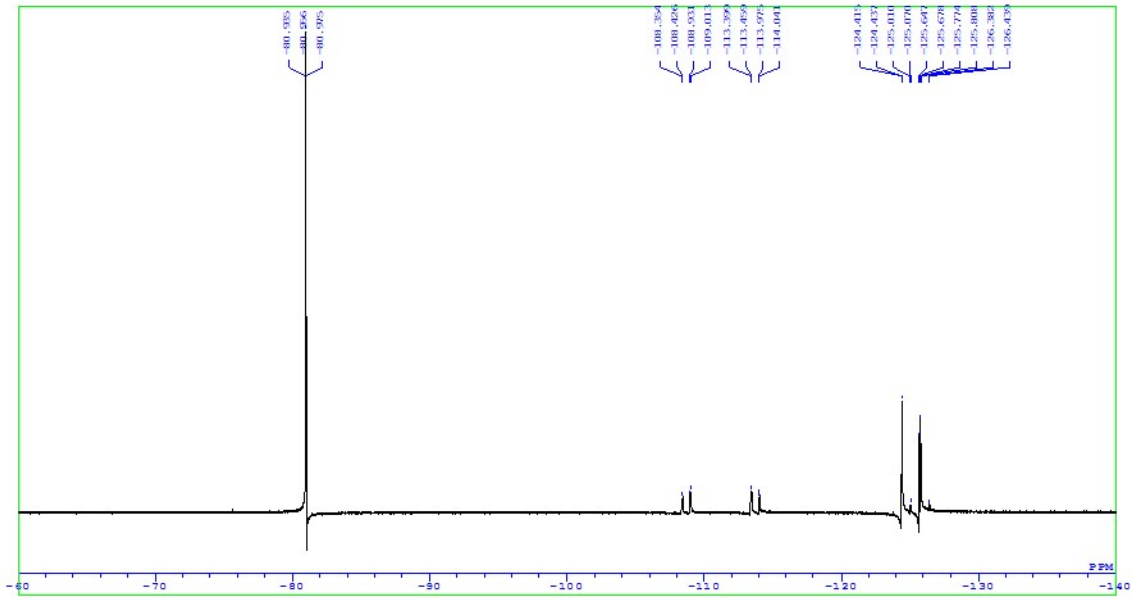
^{1}H NMR of spectrum of **3k**



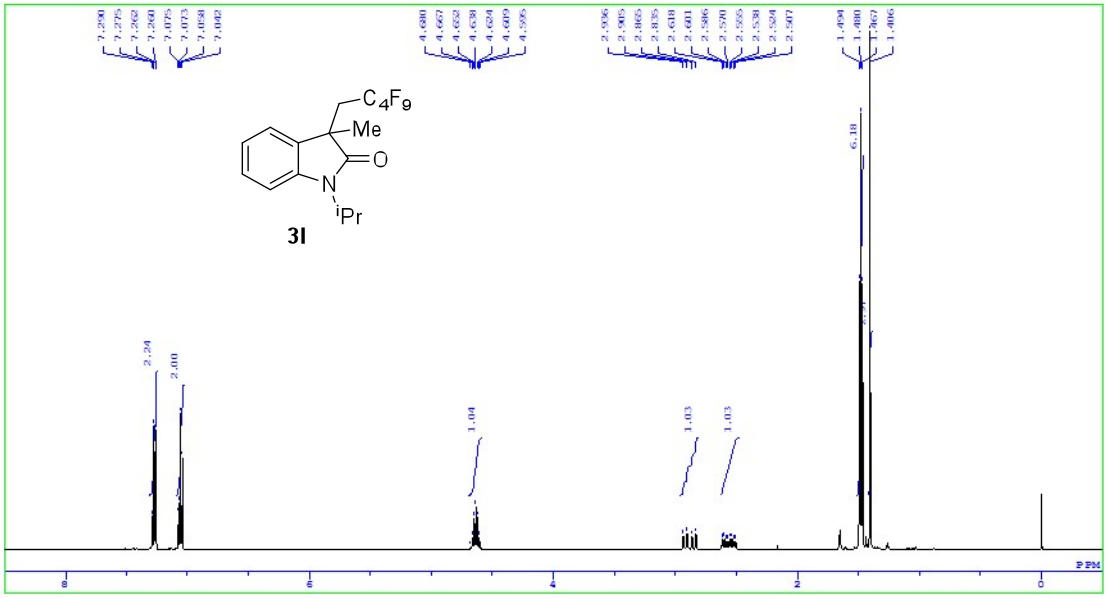
^{13}C NMR of spectrum of **3k**



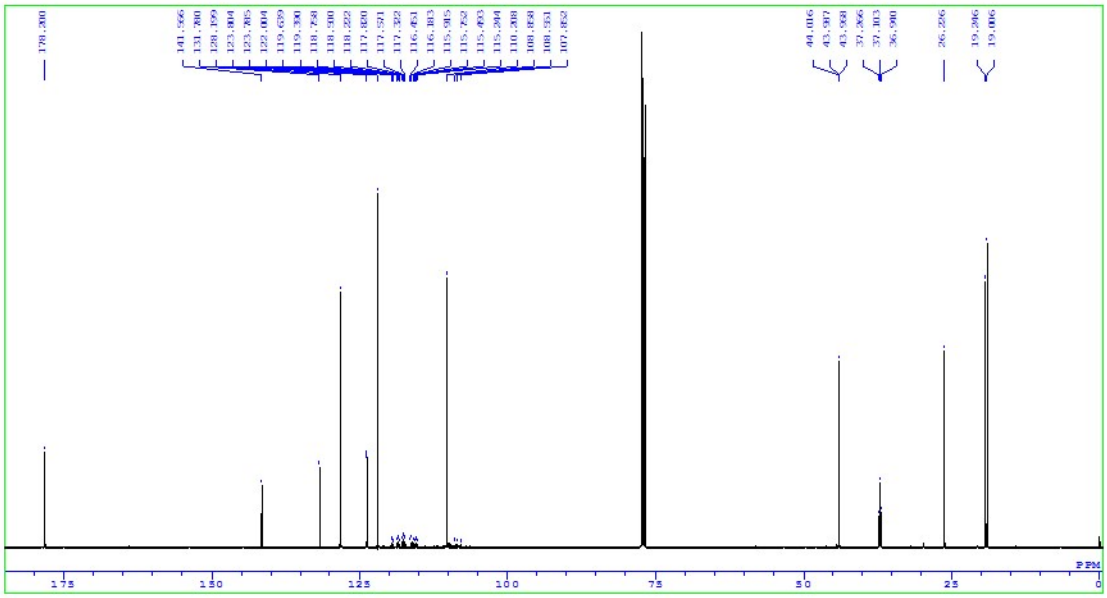
^{19}F NMR of spectrum of **3k**



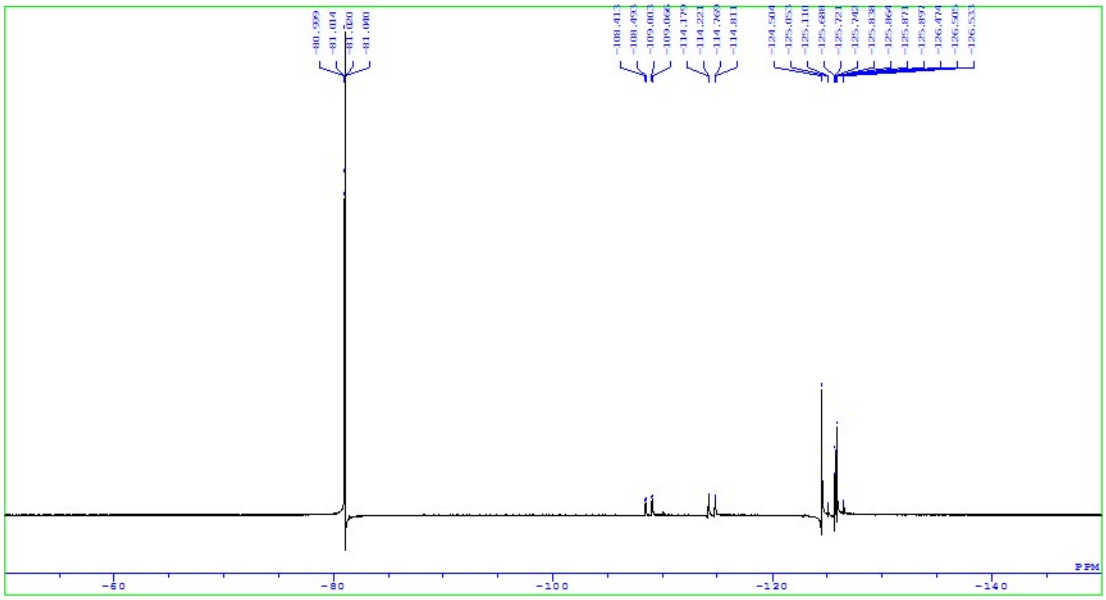
^{1}H NMR of spectrum of **3l**



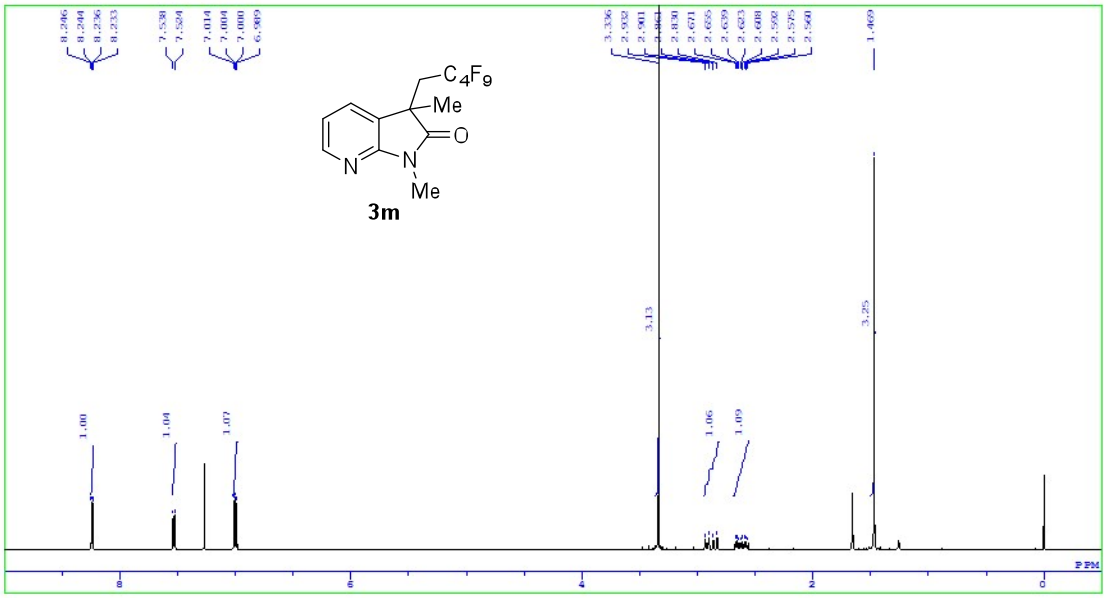
^{13}C NMR of spectrum of **3l**



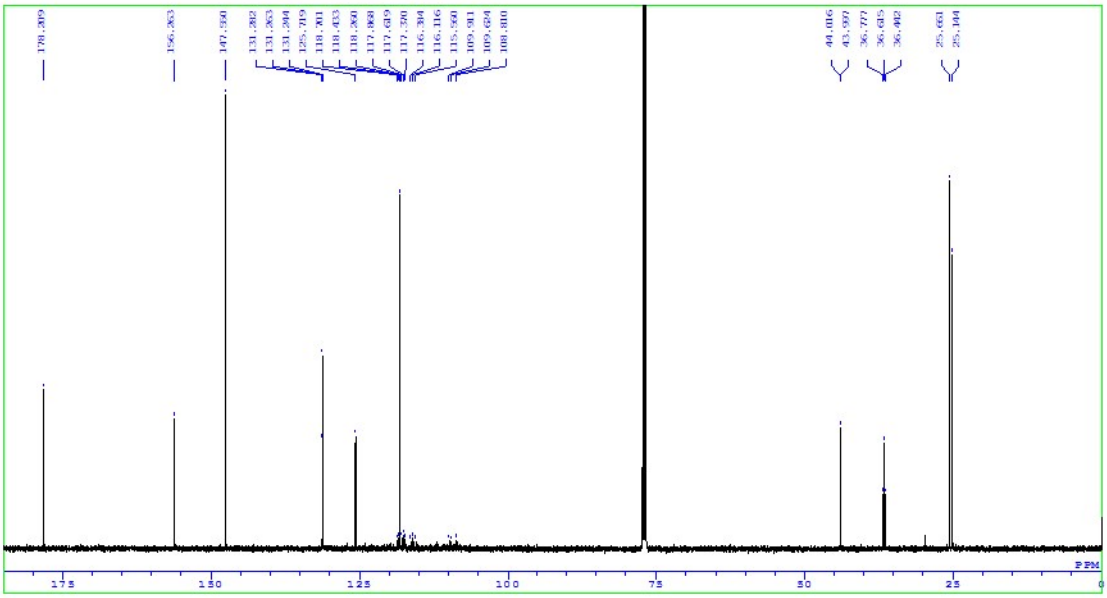
^{19}F NMR of spectrum of **3l**



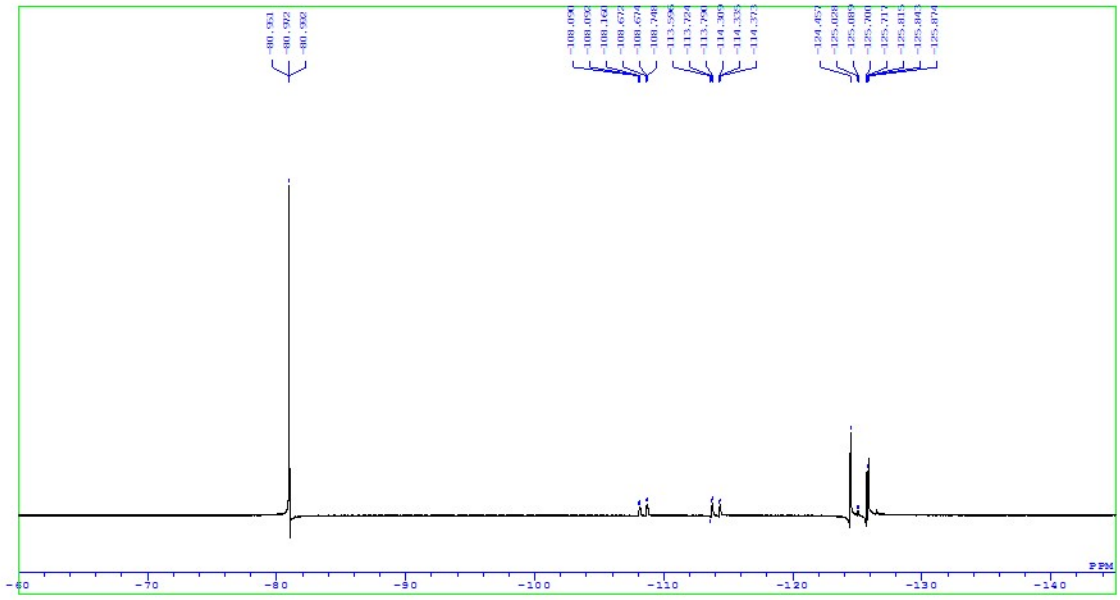
^{1}H NMR of spectrum of **3m**



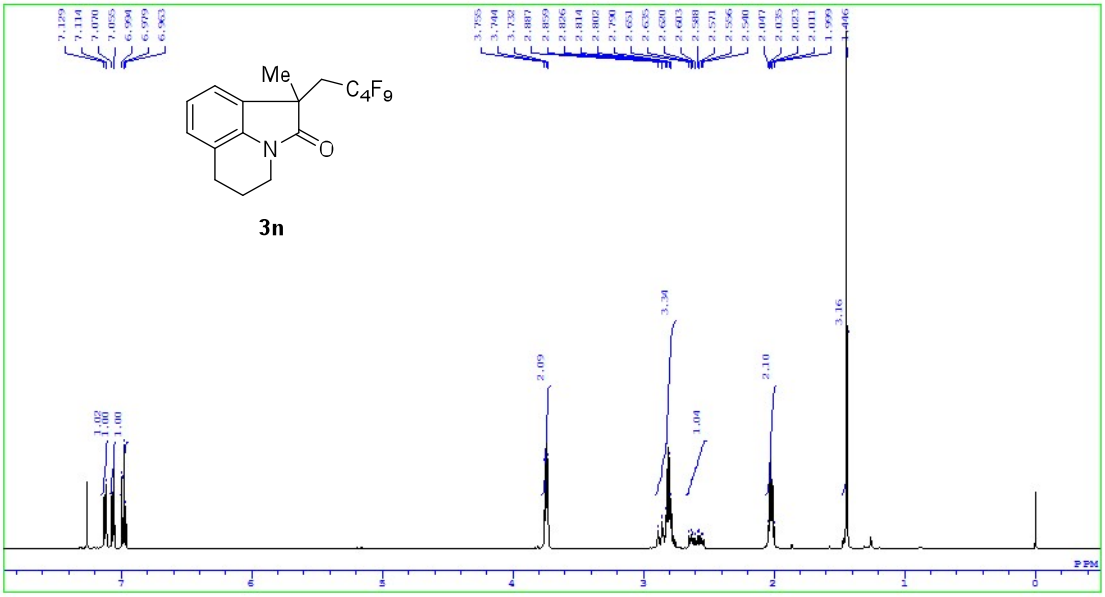
^{13}C NMR of spectrum of **3m**



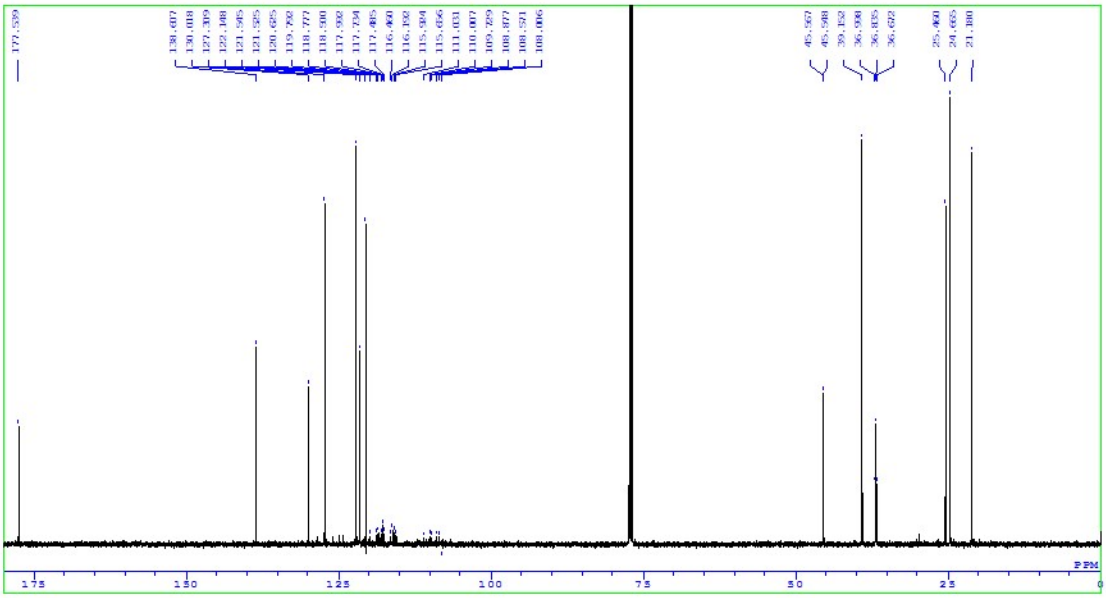
^{19}F NMR of spectrum of **3m**



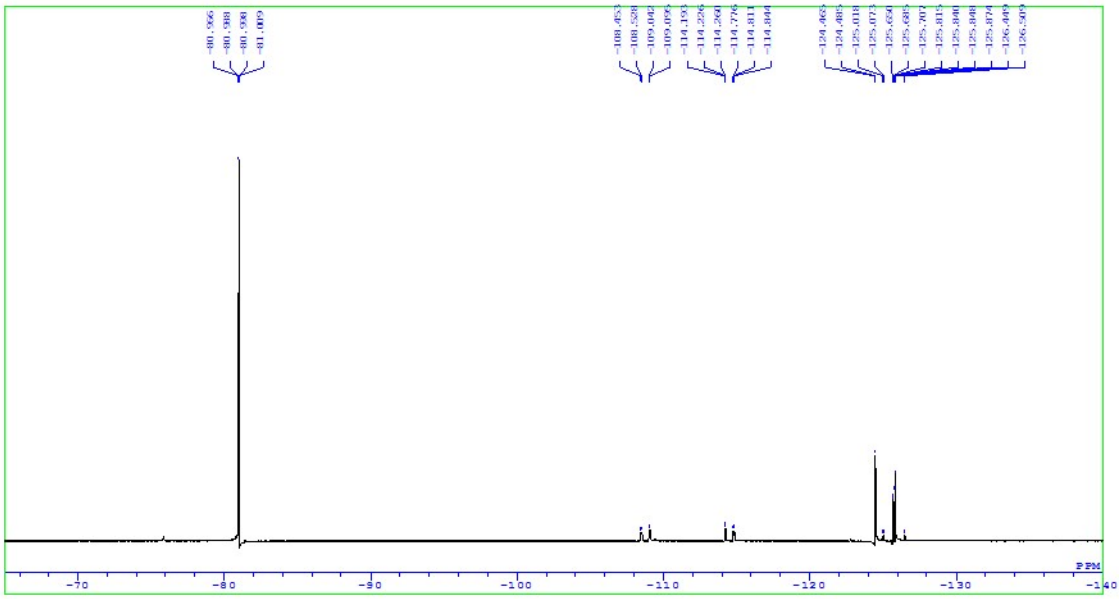
^{1}H NMR of spectrum of **3n**



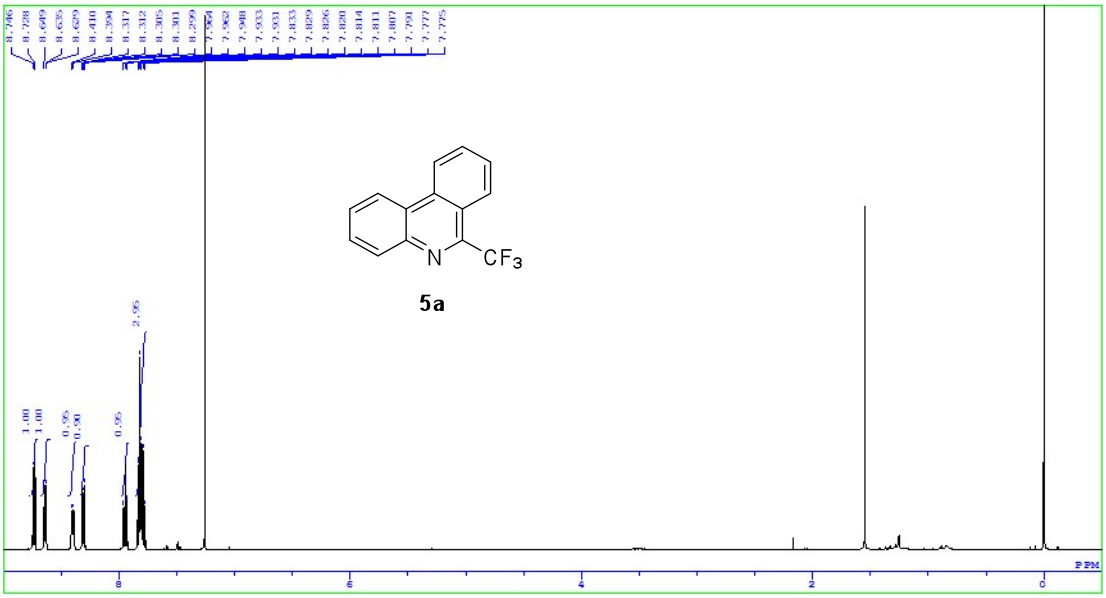
^{13}C NMR of spectrum of **3n**



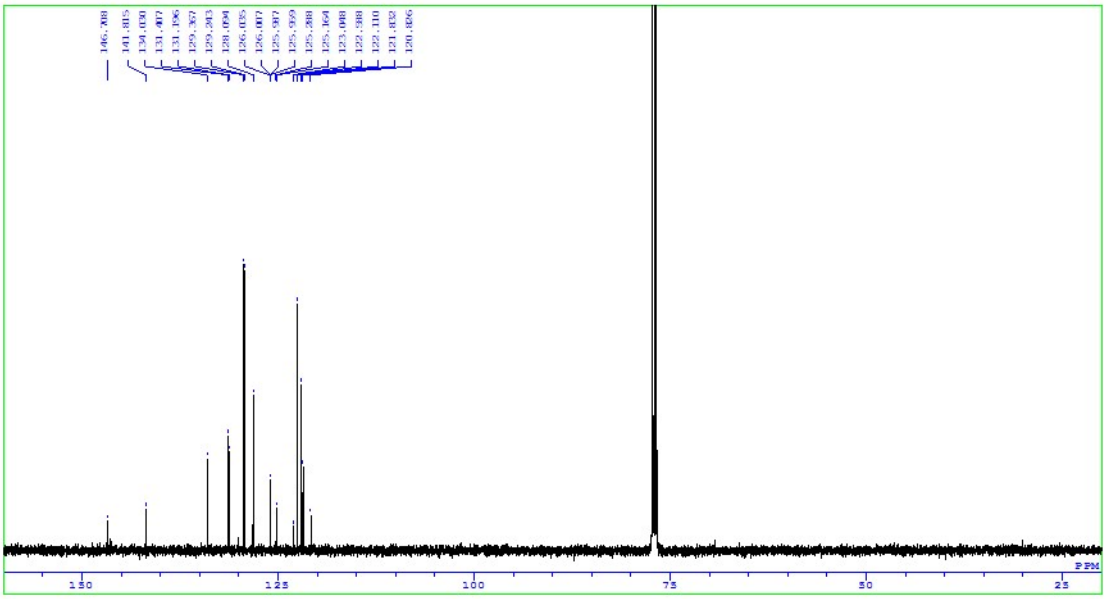
^{19}F NMR of spectrum of **3n**



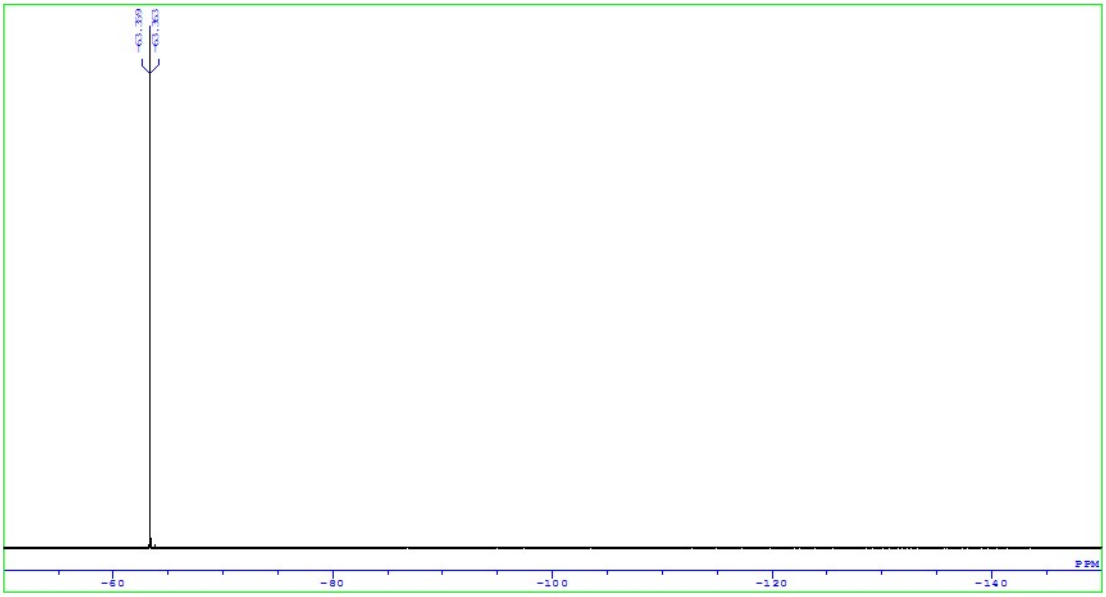
^{1}H NMR of spectrum of **5a**



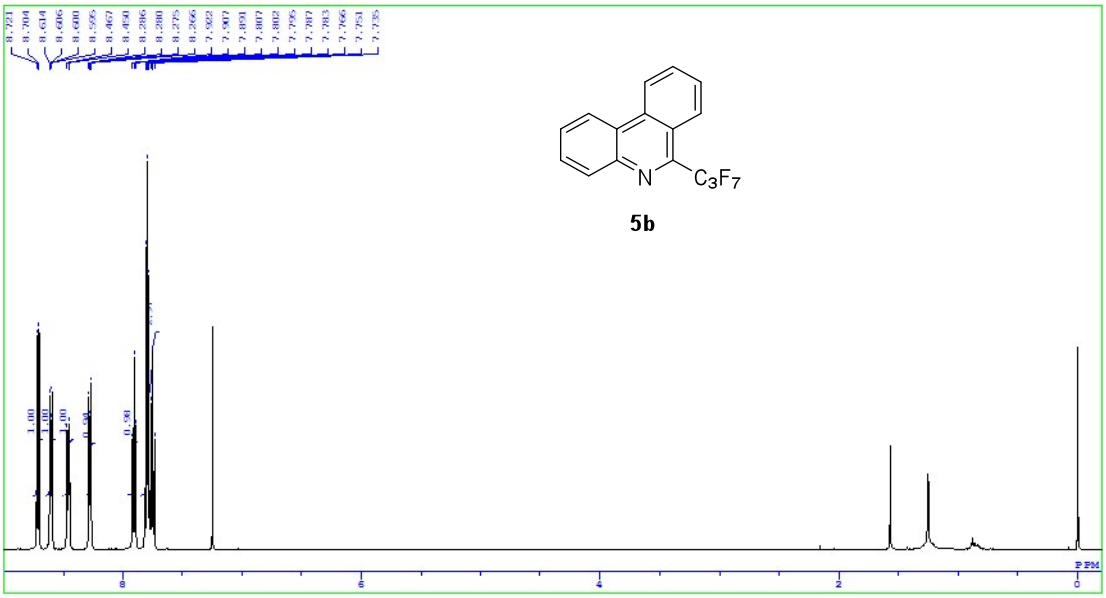
^{13}C NMR of spectrum of **5a**



^{19}F NMR of spectrum of **5a**



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



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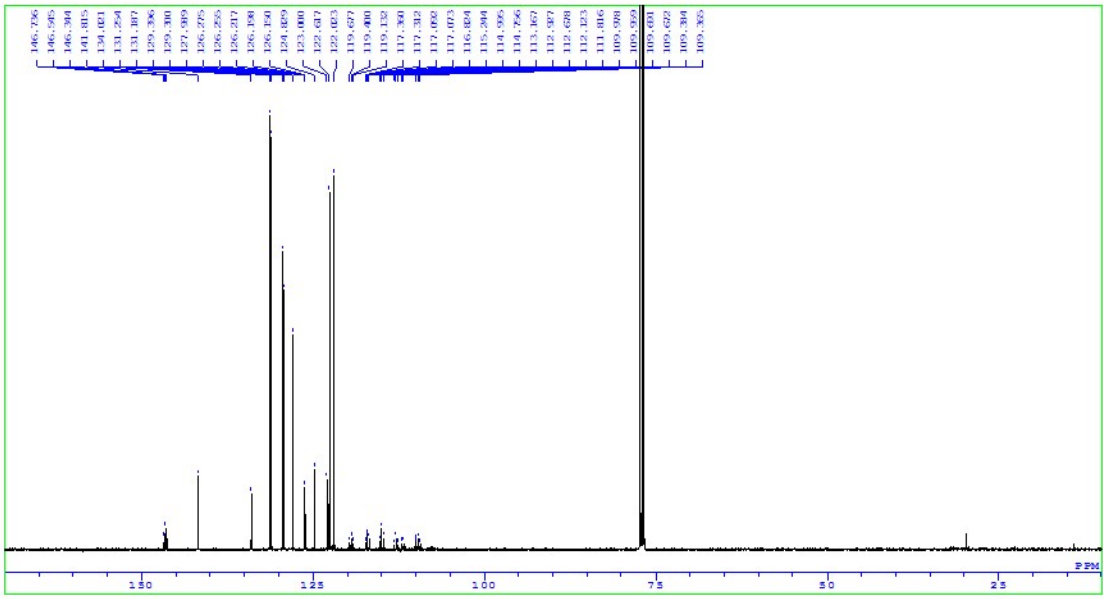
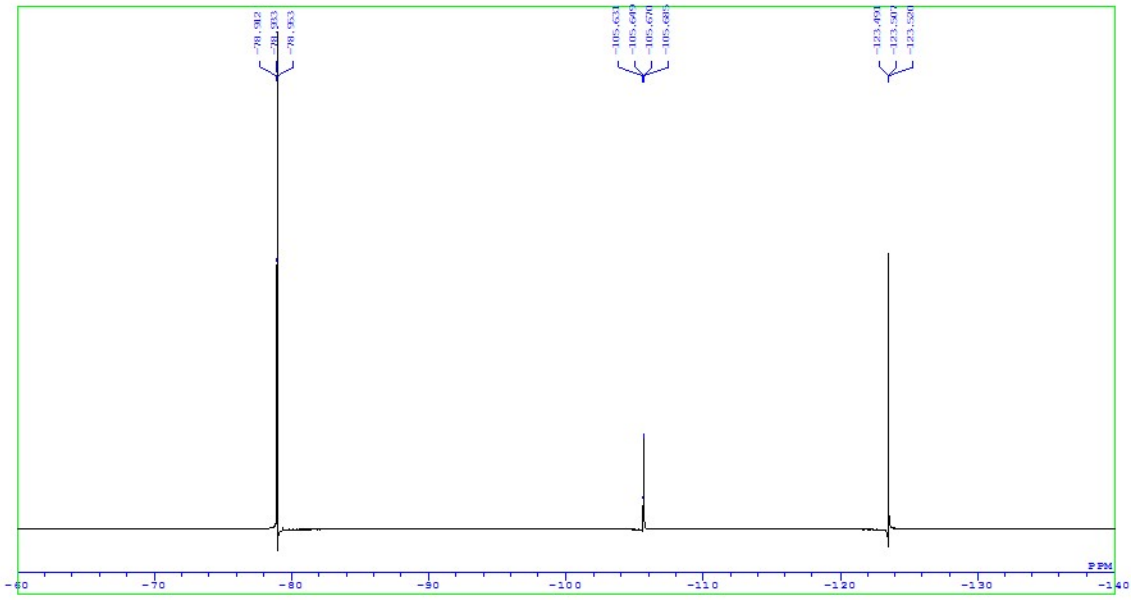
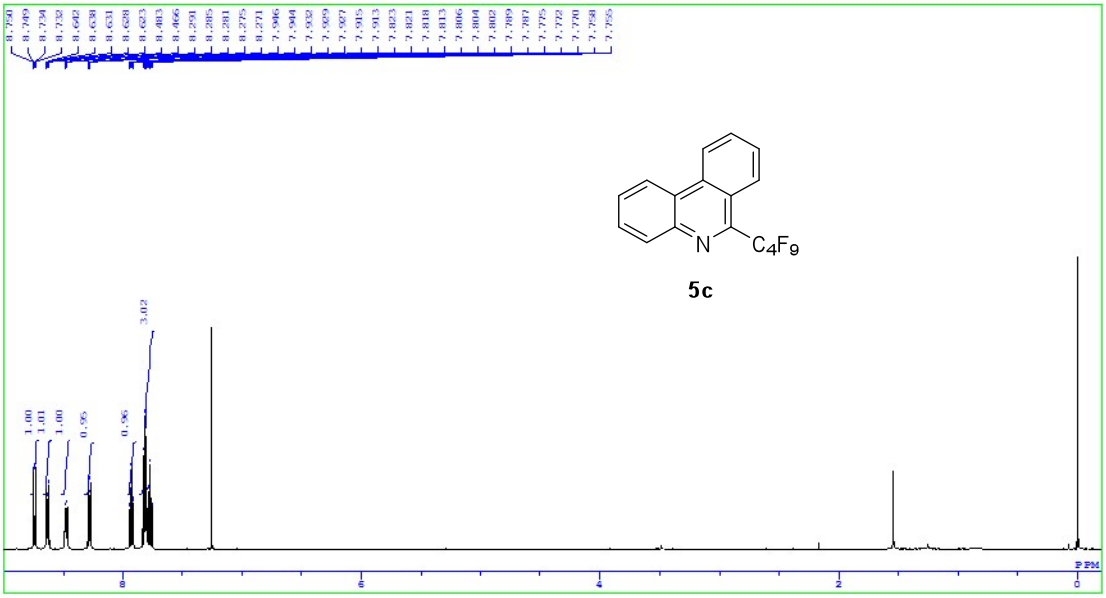


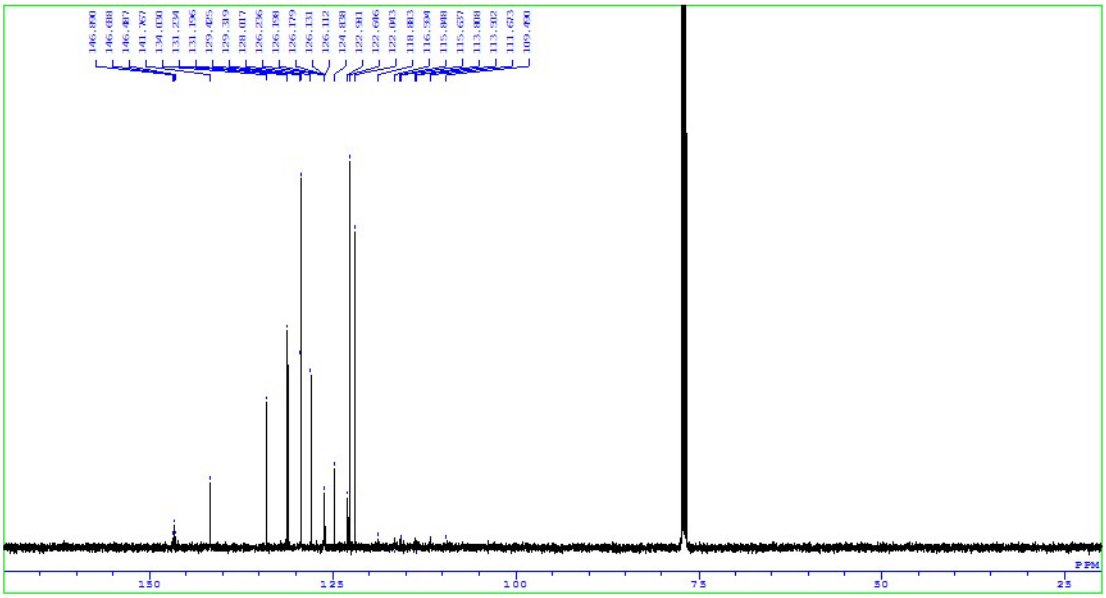
^{19}F NMR of spectrum of **5b**



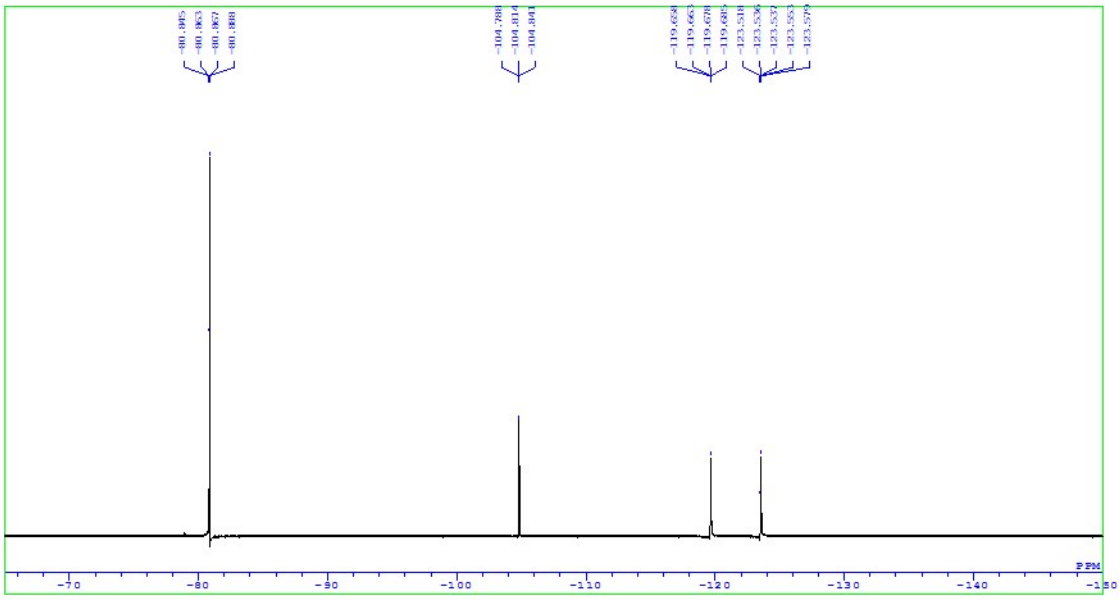
^{1}H NMR of spectrum of **5c**



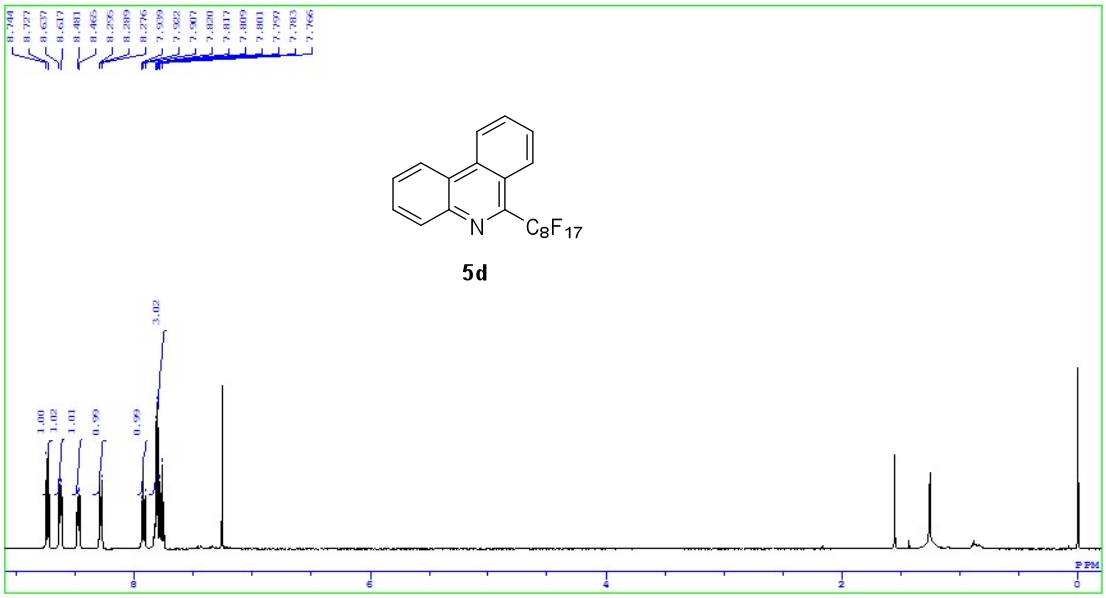
^{13}C NMR of spectrum of **5c**



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

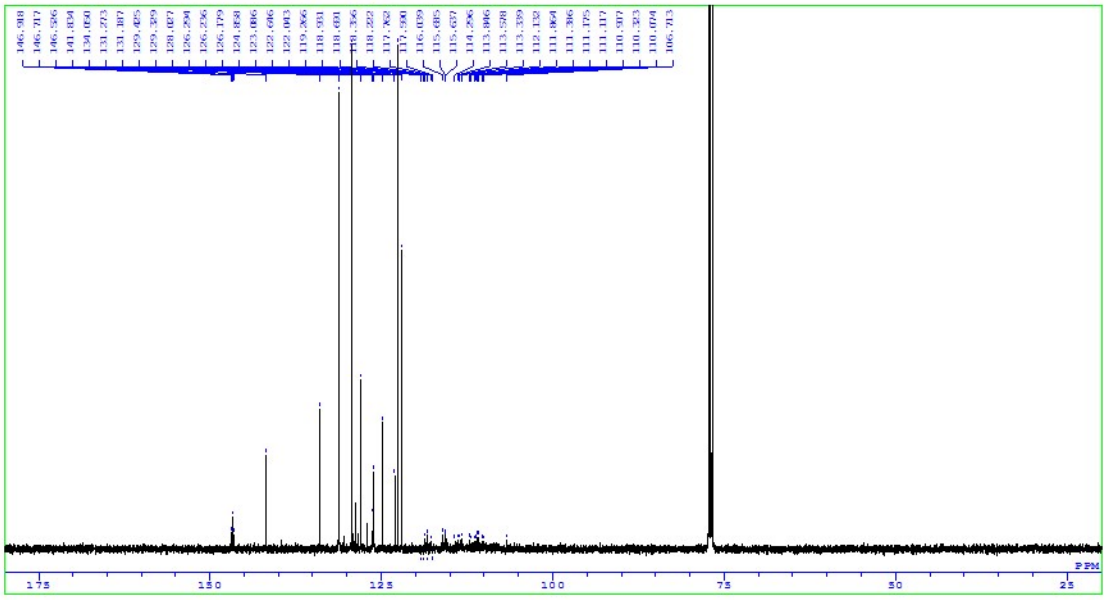


^{1}H NMR of spectrum of **5d**

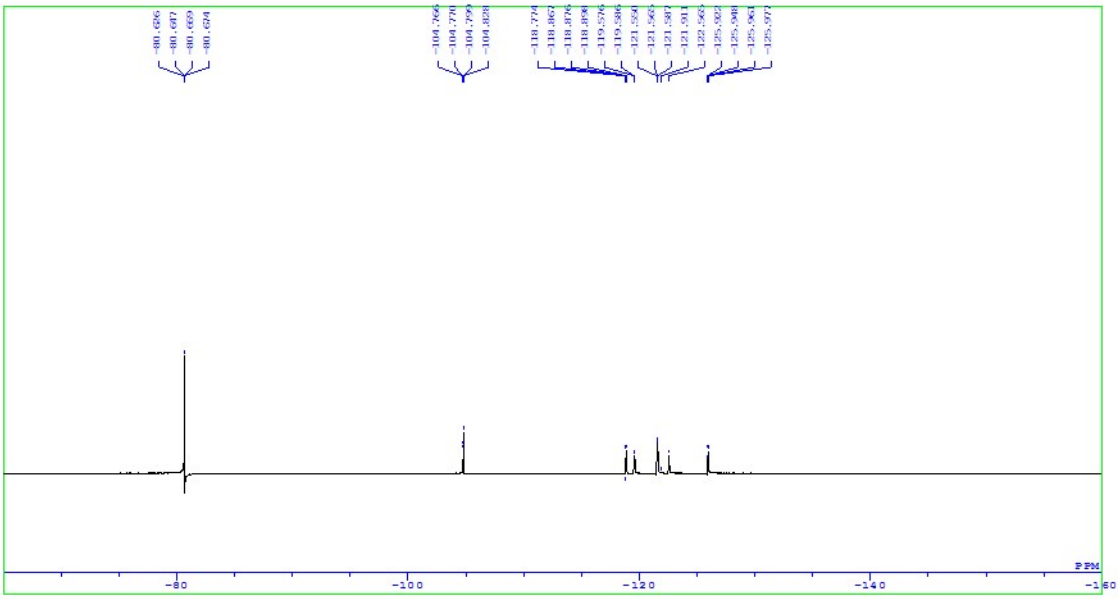


5d

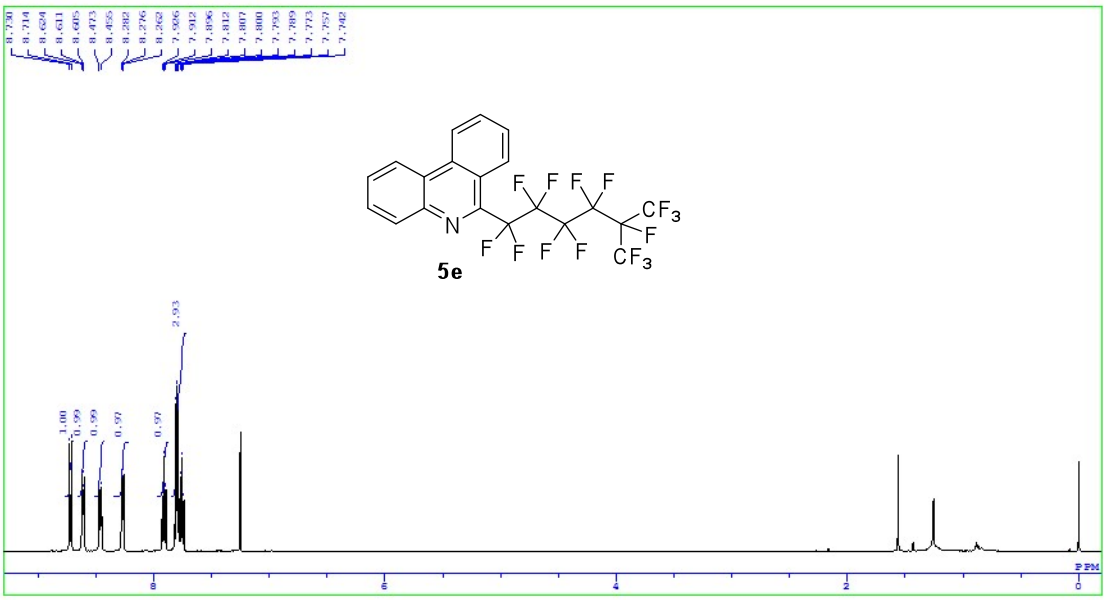
^{13}C NMR of spectrum of **5d**



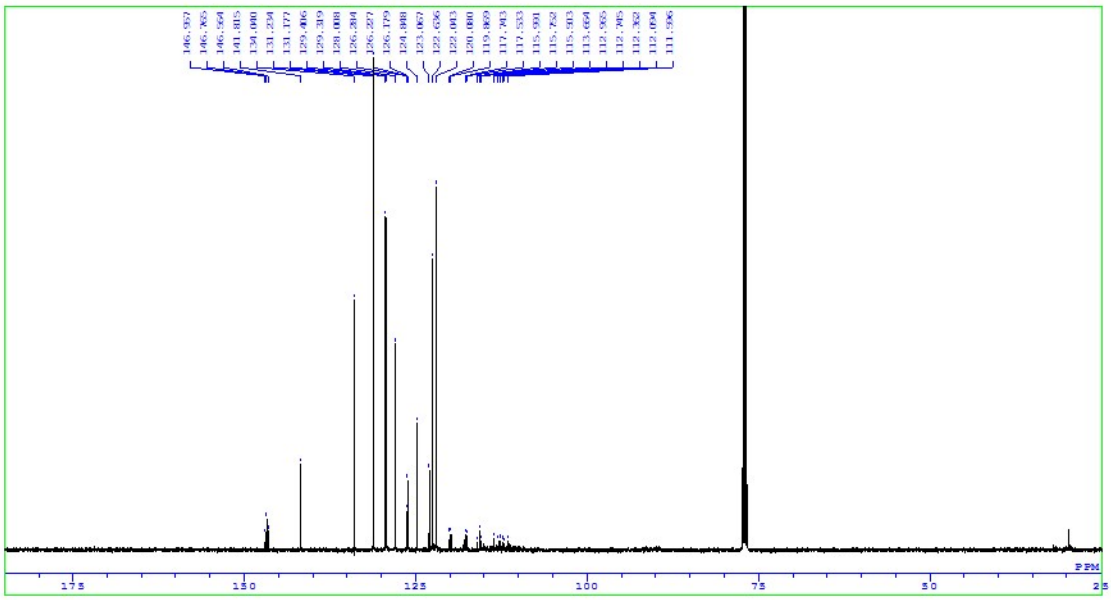
^{19}F NMR of spectrum of **5d**



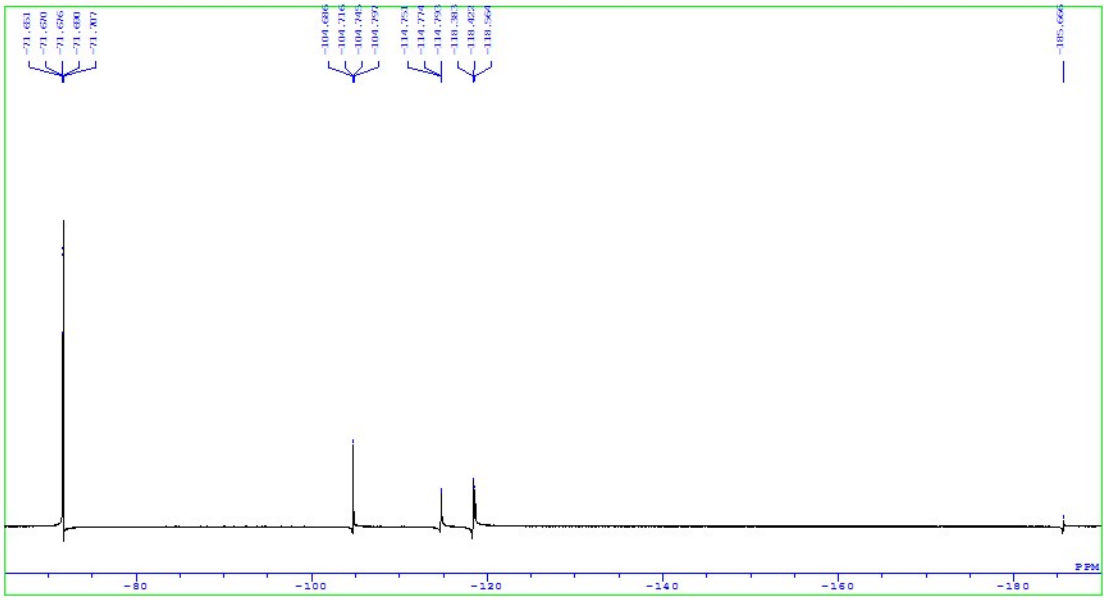
^{1}H NMR of spectrum of **5e**



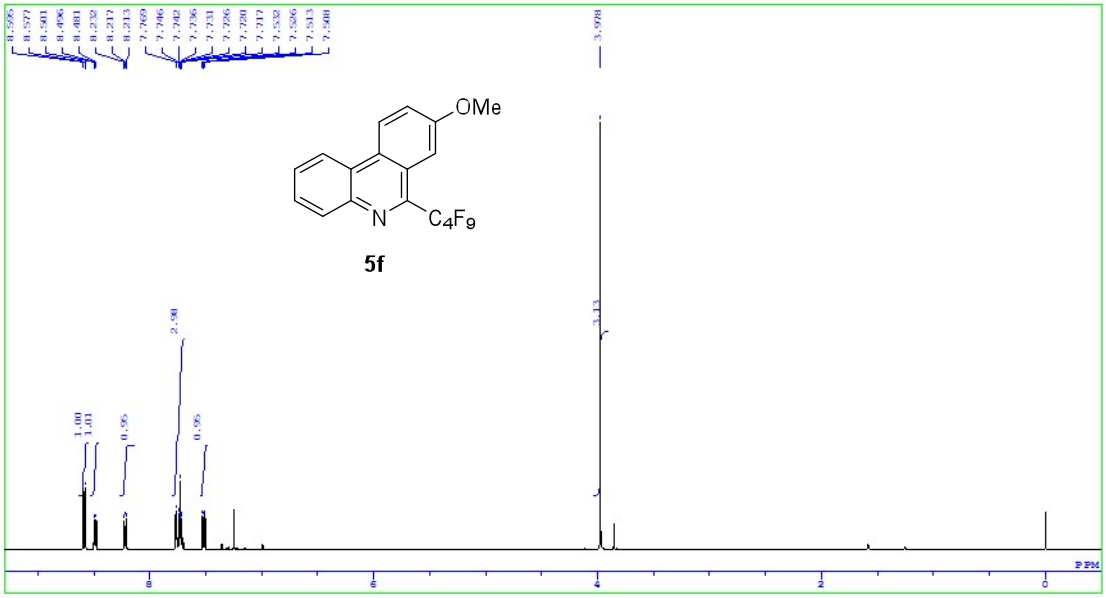
^{13}C NMR of spectrum of **5e**



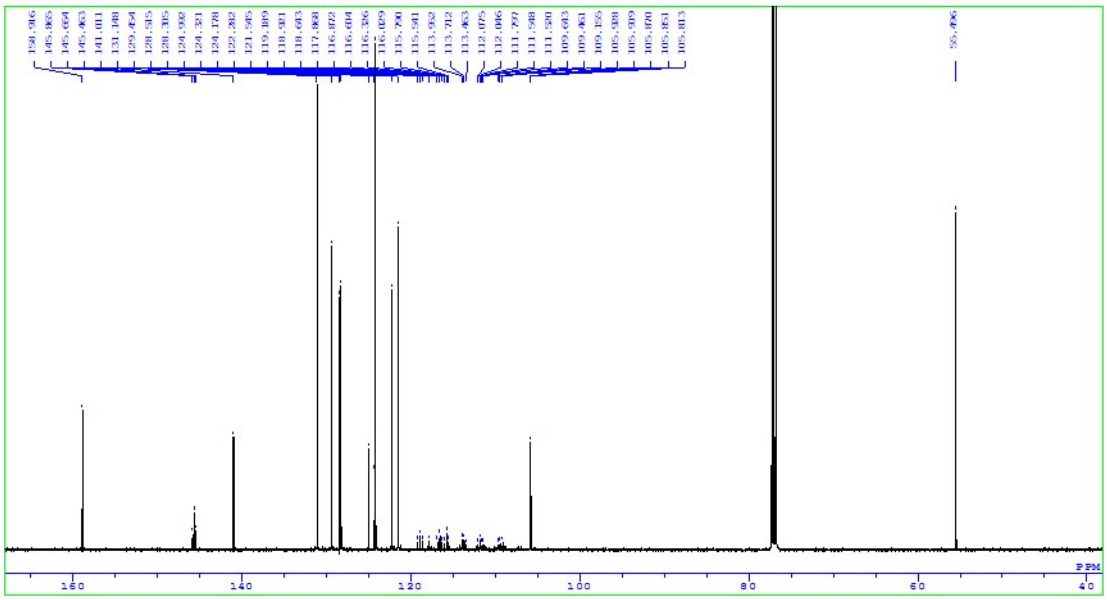
^{19}F NMR of spectrum of **5e**



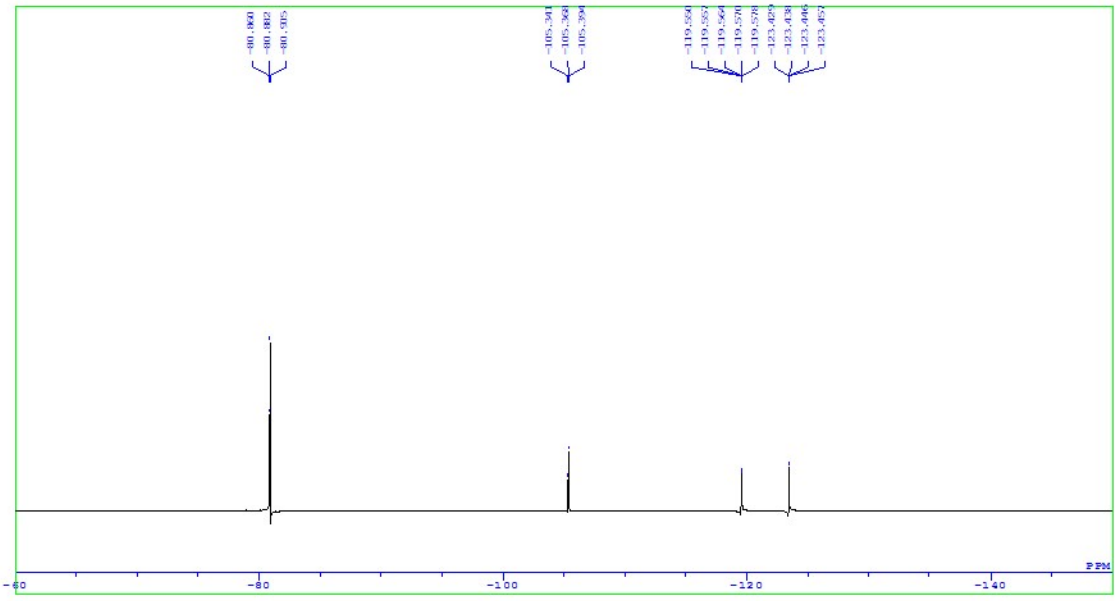
^{1}H NMR of spectrum of **5f**



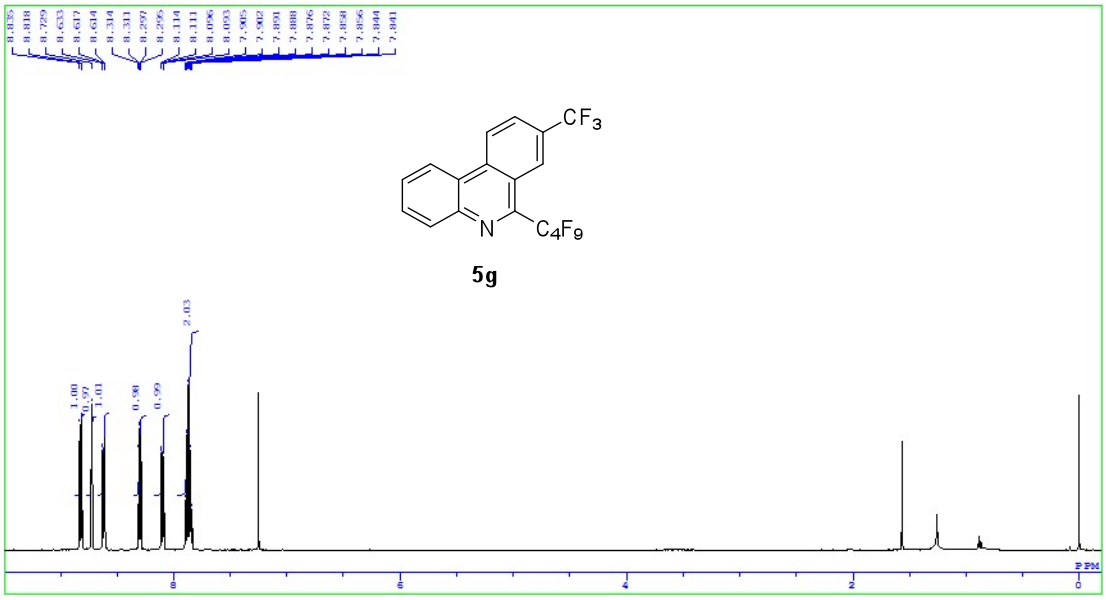
^{13}C NMR of spectrum of **5f**



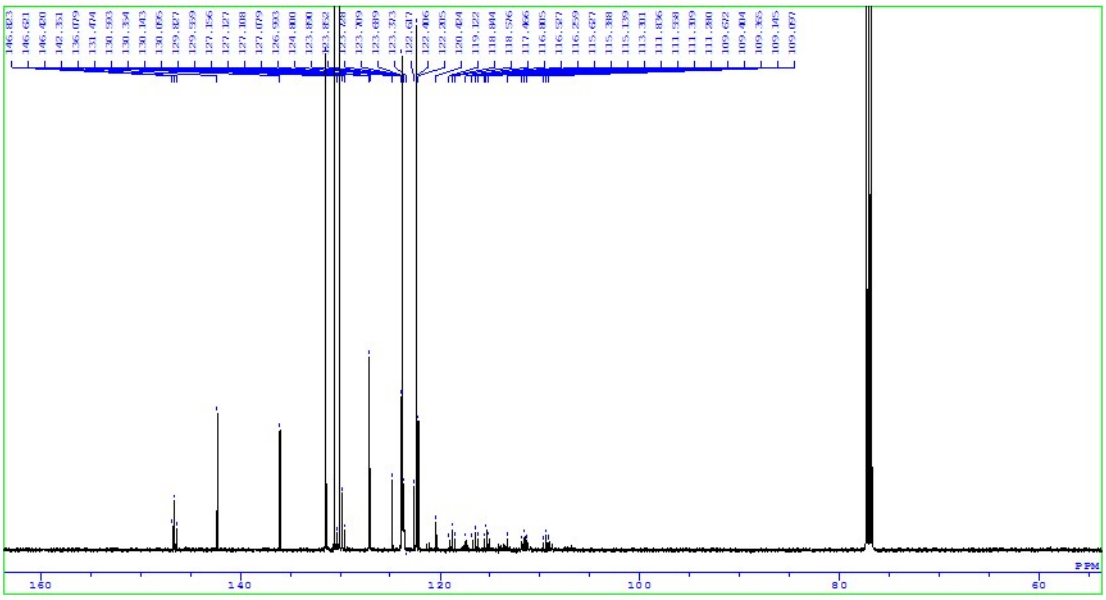
^{19}F NMR of spectrum of **5f**



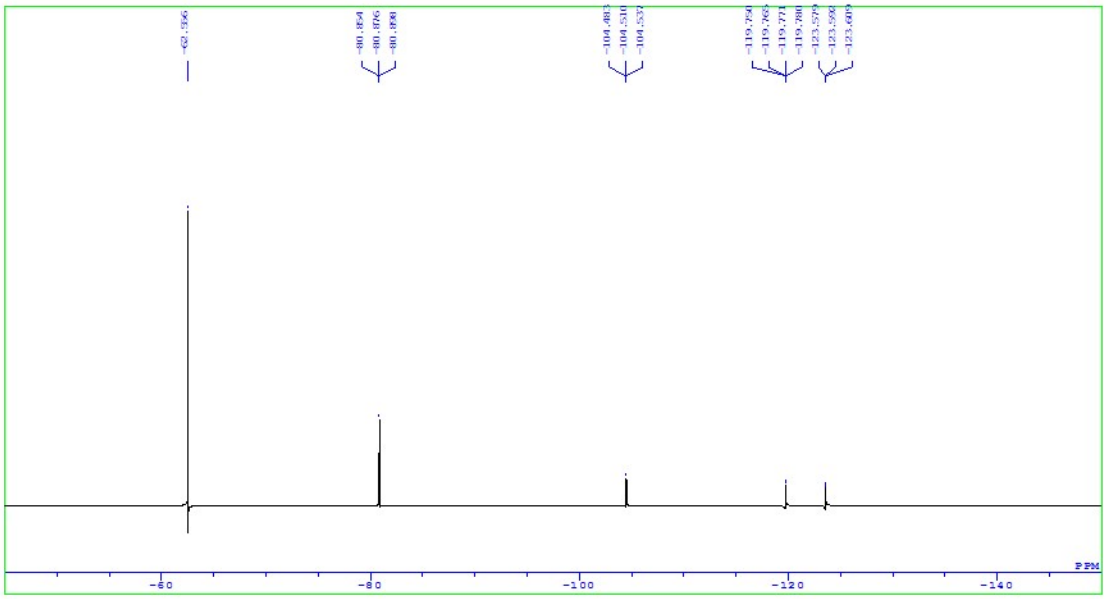
^{1}H NMR of spectrum of **5g**



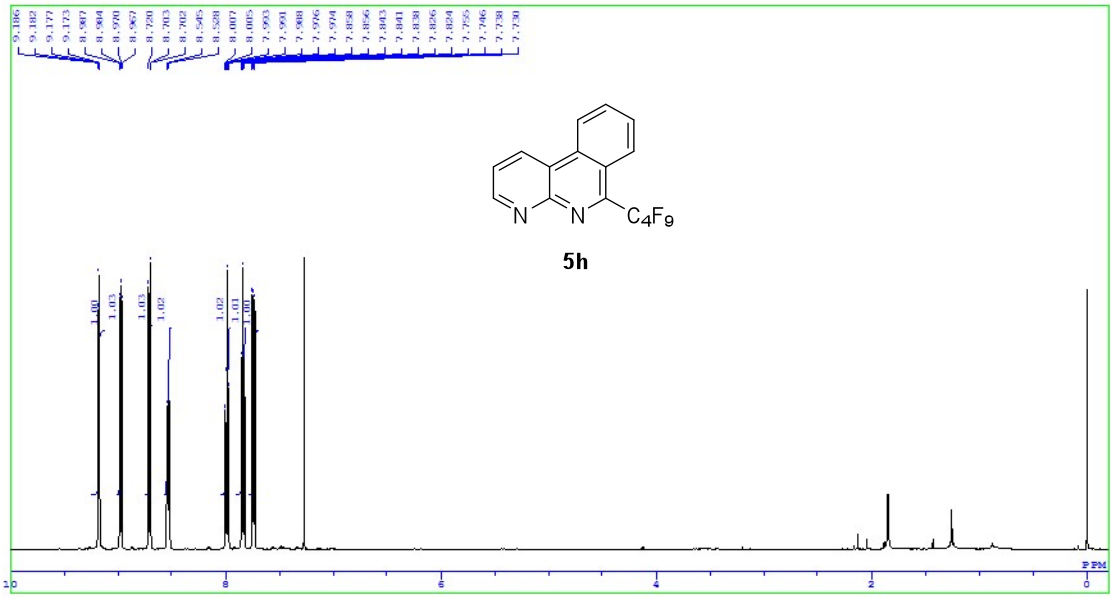
^{13}C NMR of spectrum of **5g**



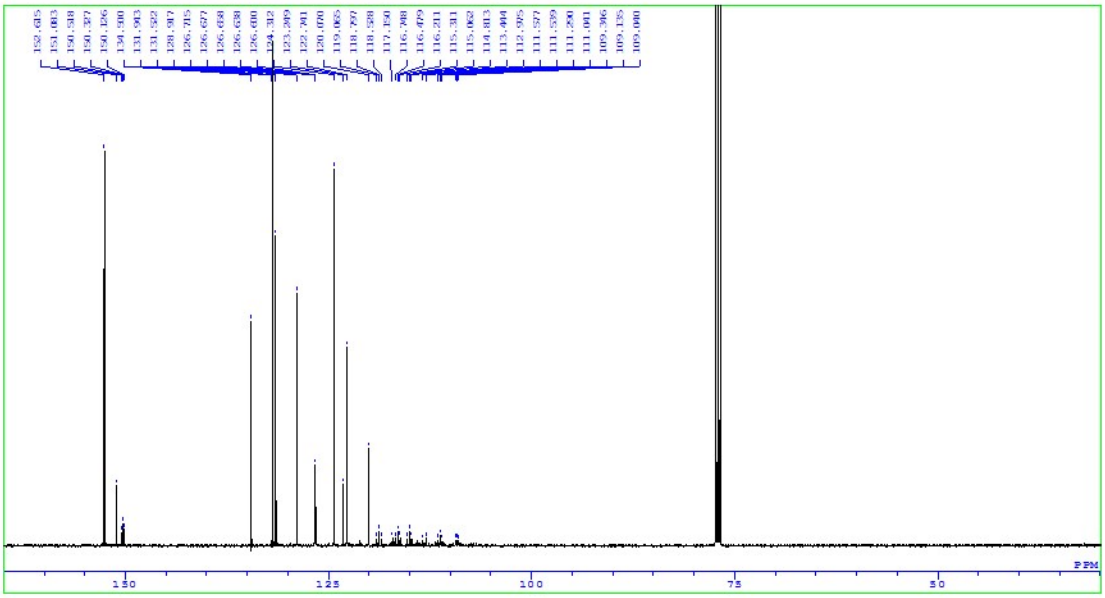
^{19}F NMR of spectrum of **5g**



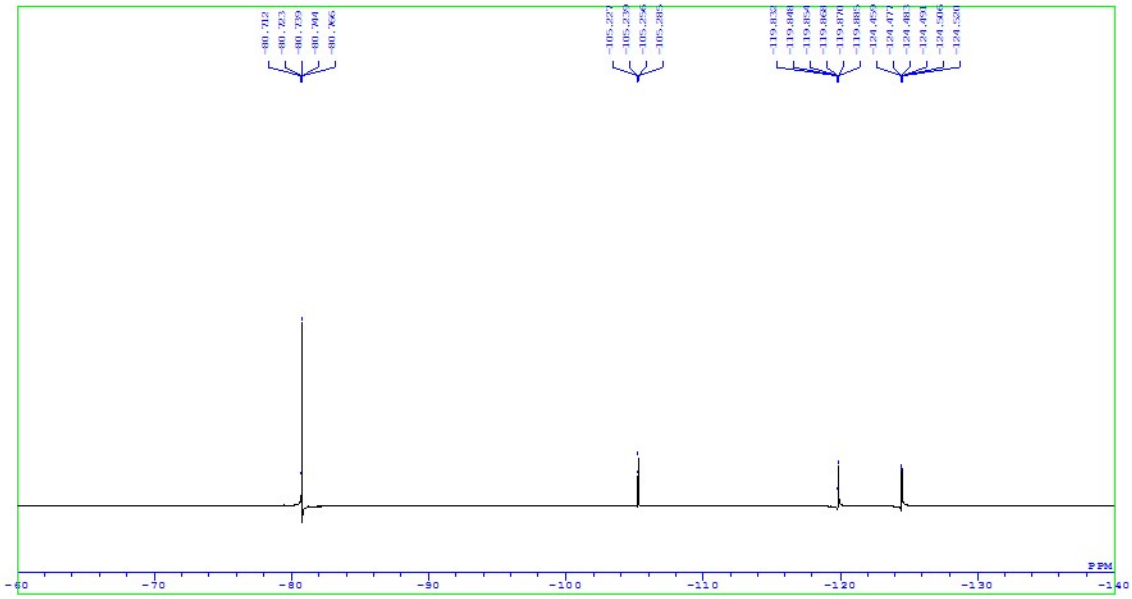
^{1}H NMR of spectrum of **5h**



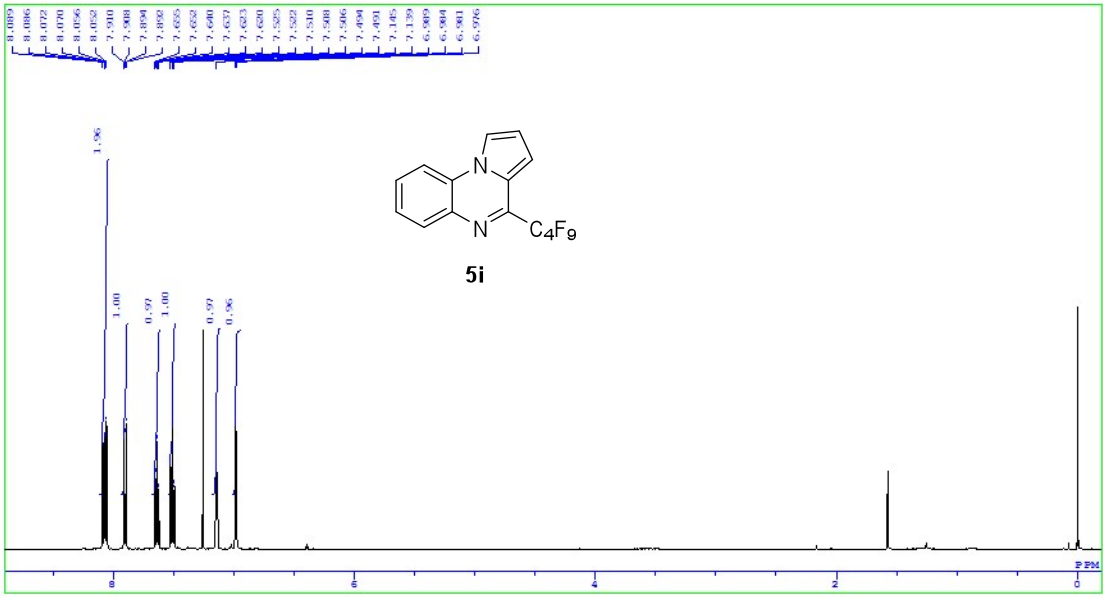
^{13}C NMR of spectrum of **5h**



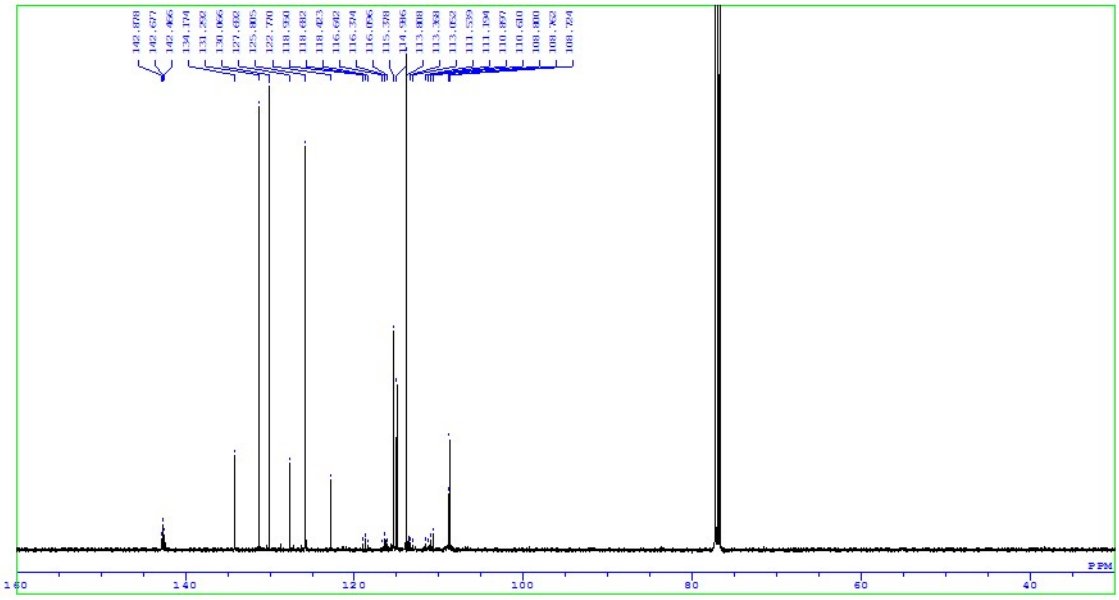
^{19}F NMR of spectrum of **5h**



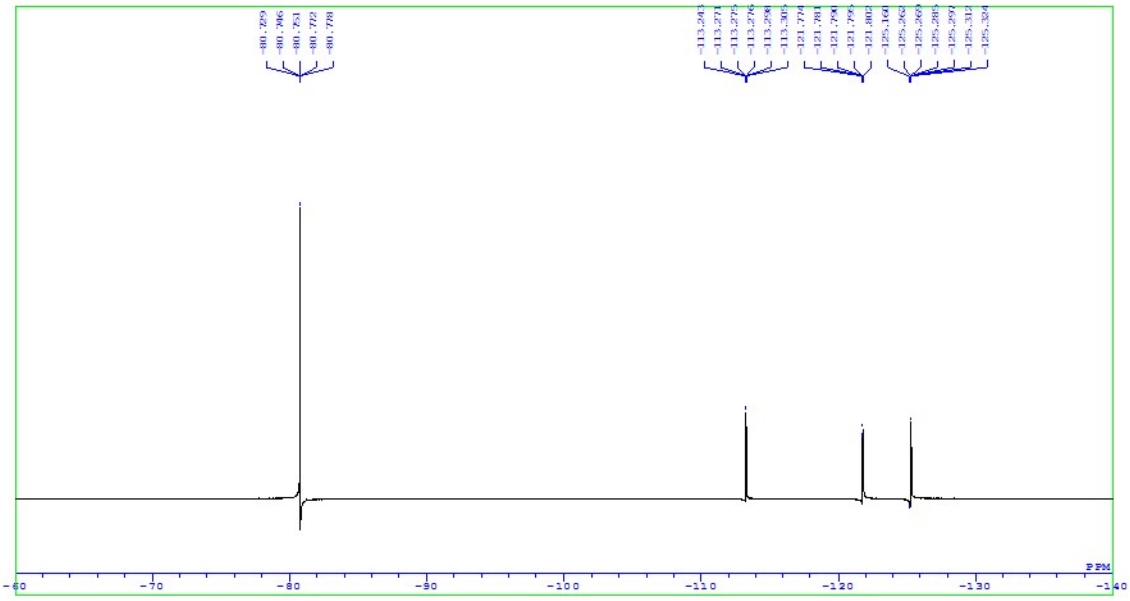
^{1}H NMR of spectrum of **5i**



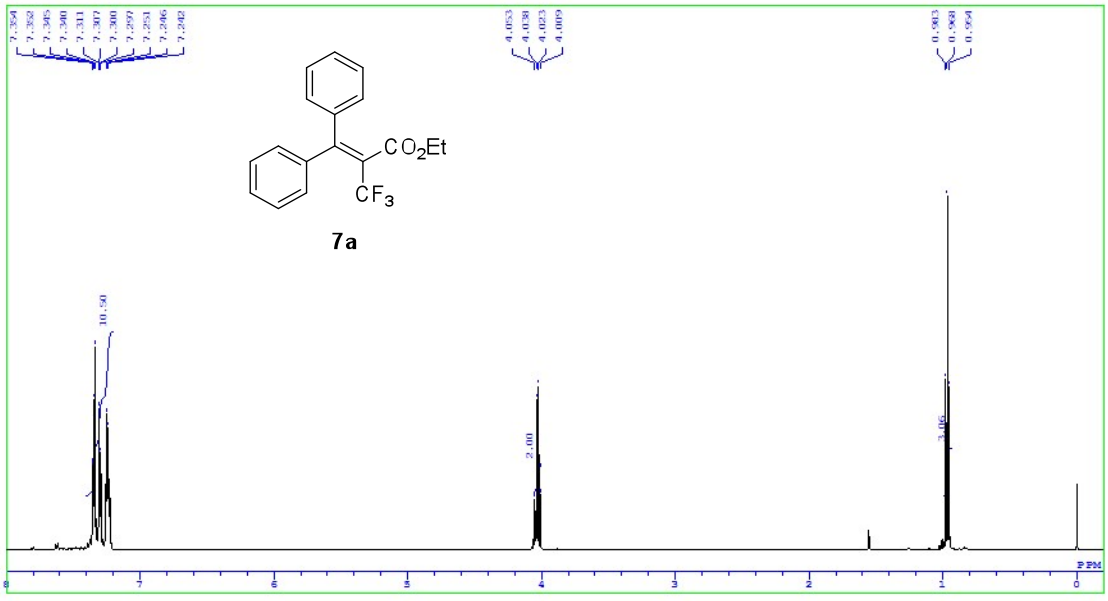
^{13}C NMR of spectrum of **5i**



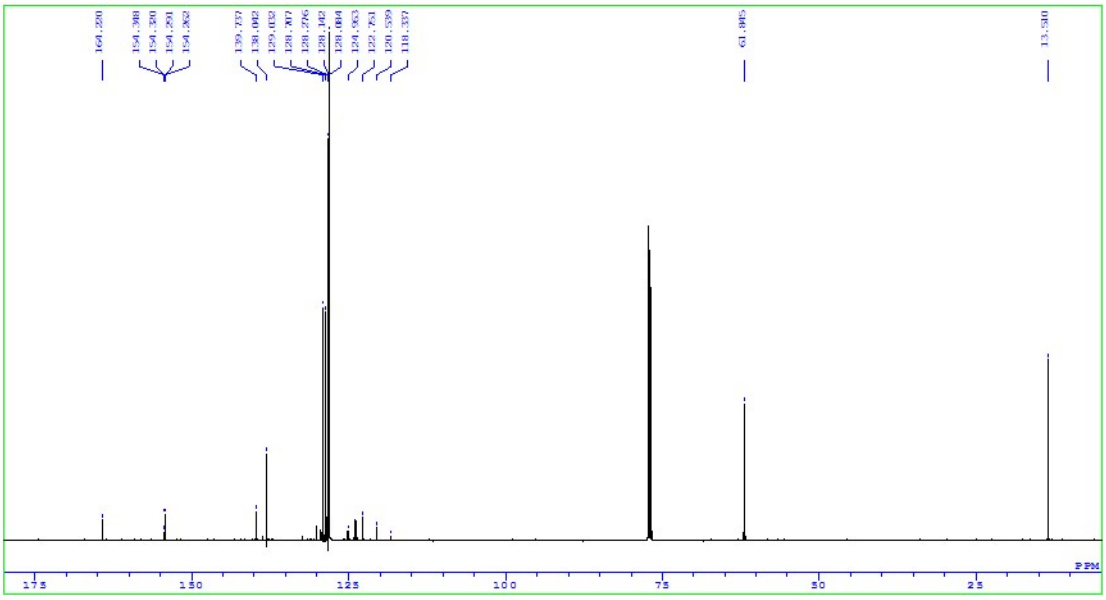
^{19}F NMR of spectrum of **5i**



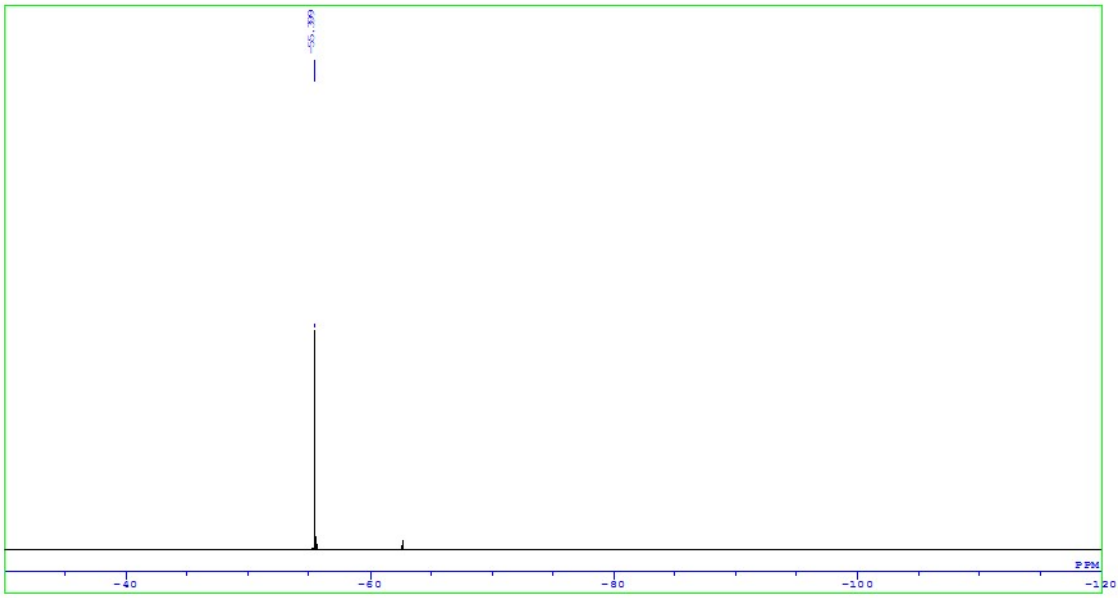
^{1}H NMR of spectrum of **7a**



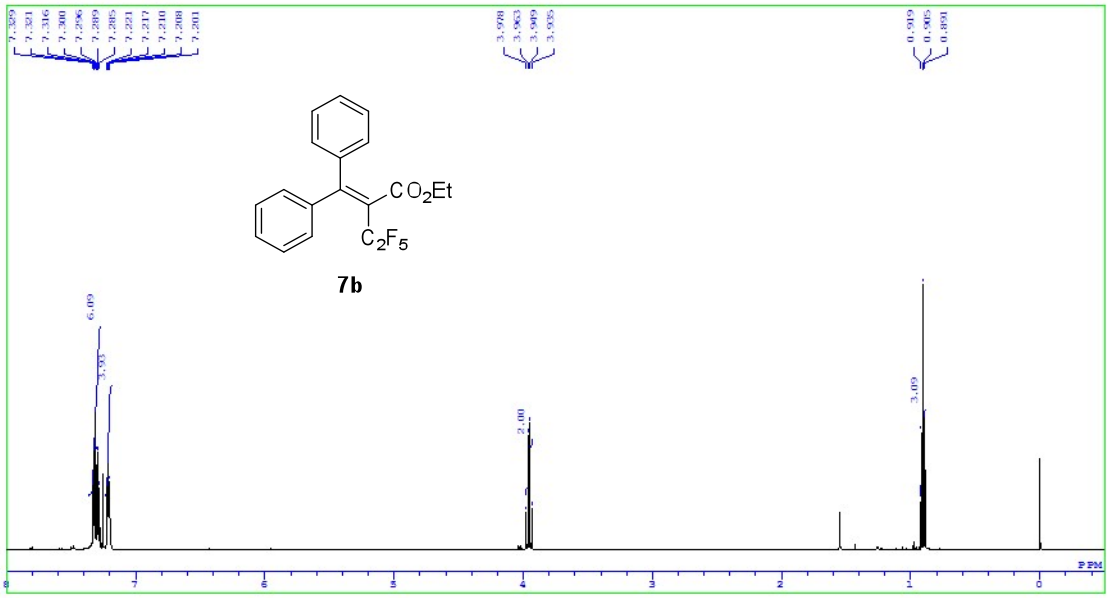
^{13}C NMR of spectrum of **7a**



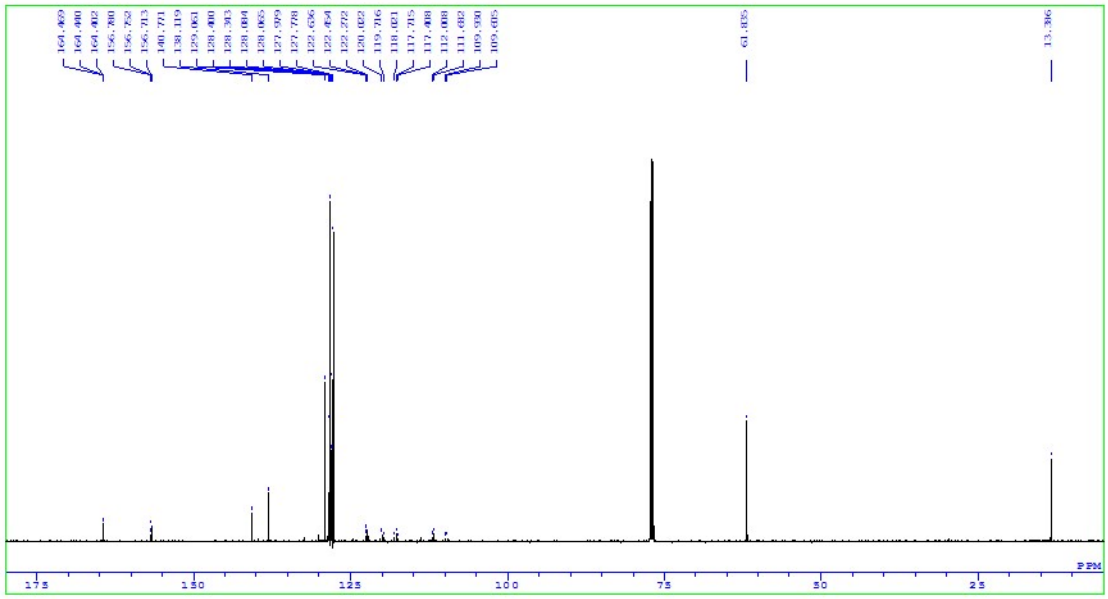
^{19}F NMR of spectrum of **7a**



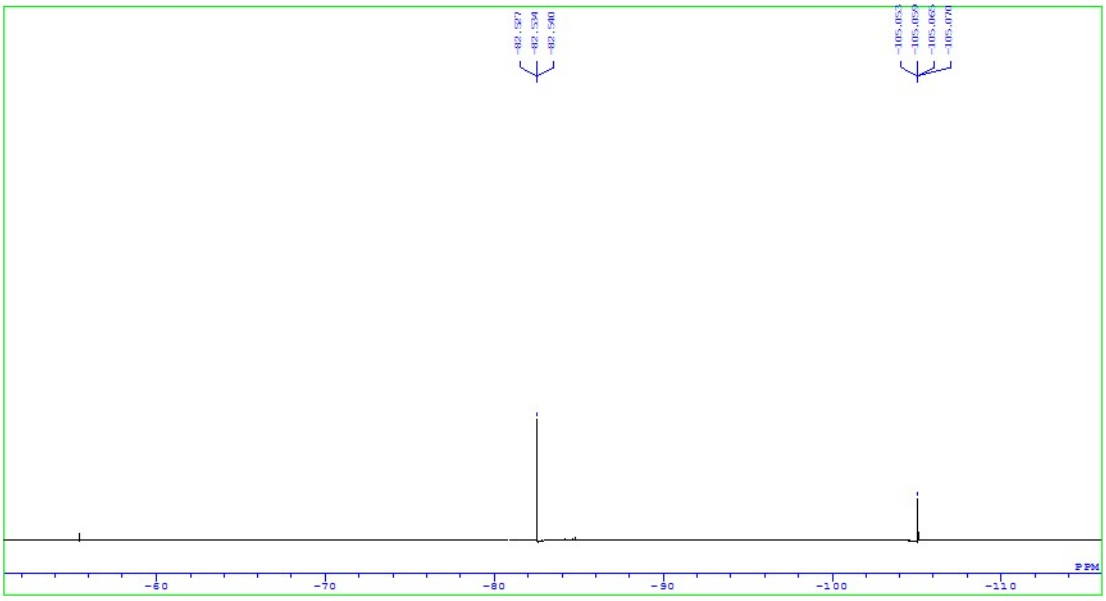
^{1}H NMR of spectrum of **7b**



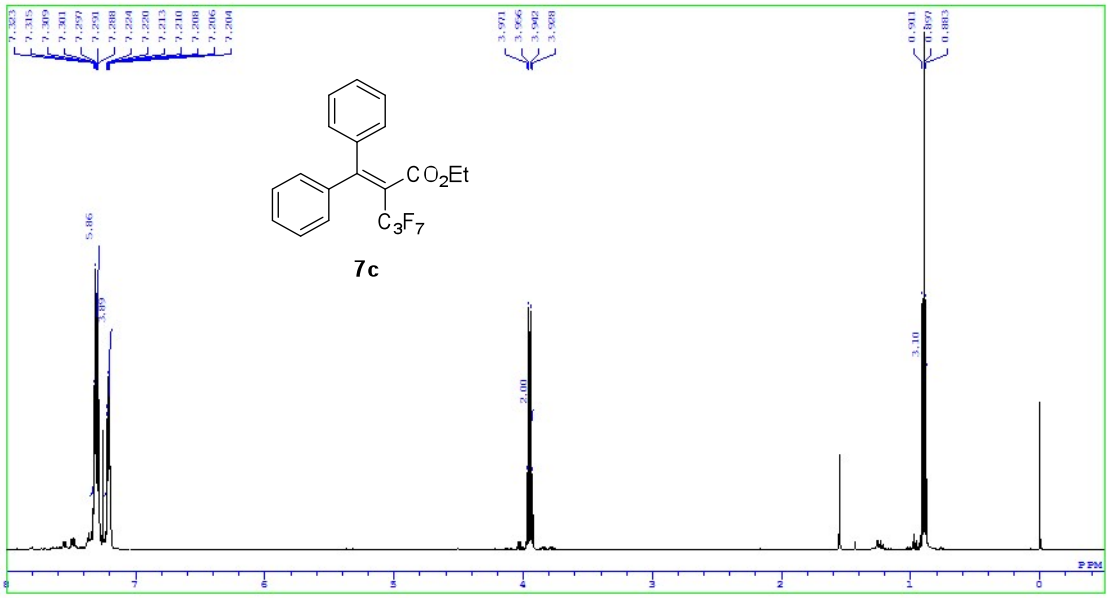
^{13}C NMR of spectrum of **7b**



^{19}F NMR of spectrum of **7b**

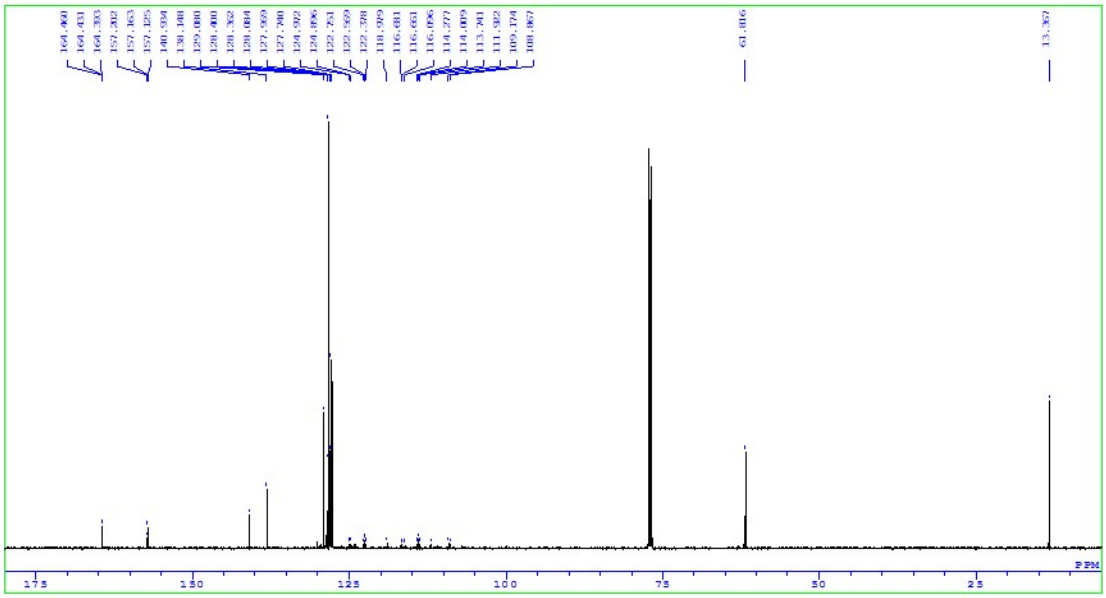


^{1}H NMR of spectrum of **7c**

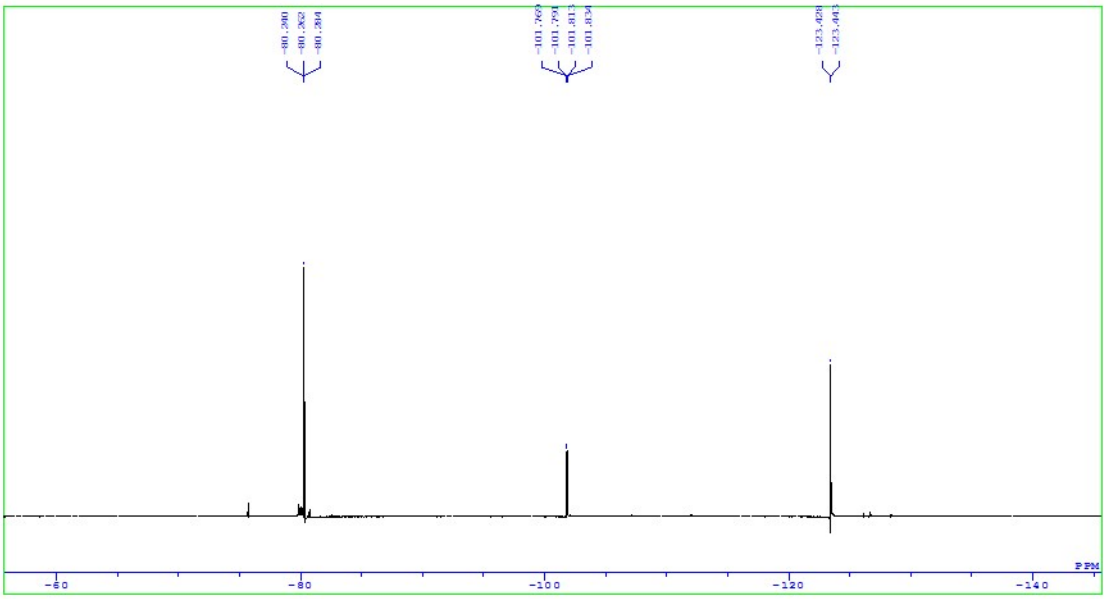


7c

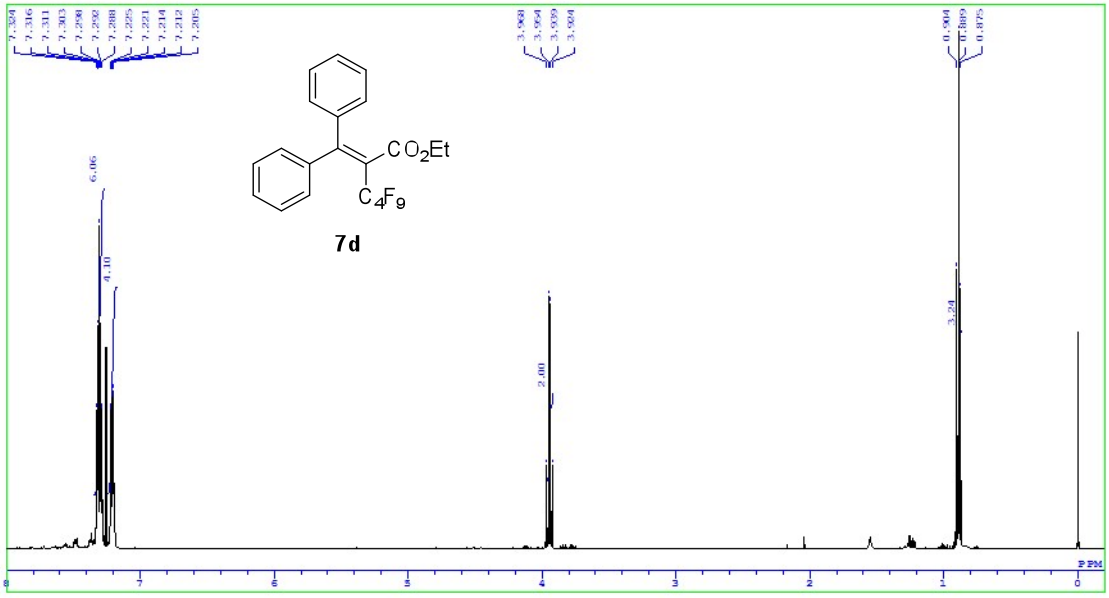
^{13}C NMR of spectrum of **7c**



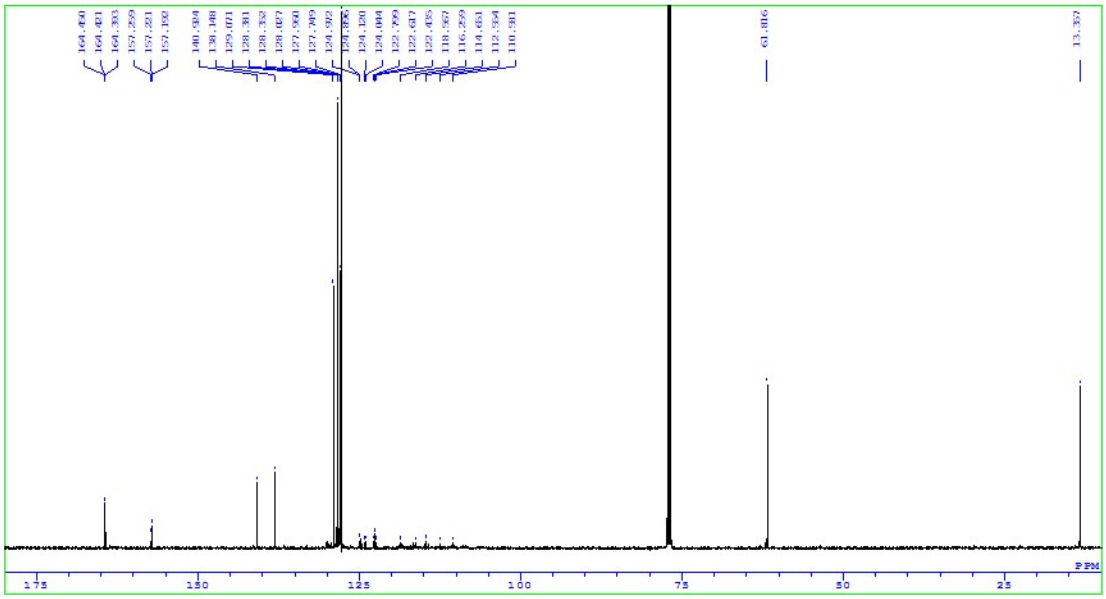
^{19}F NMR of spectrum of **7c**



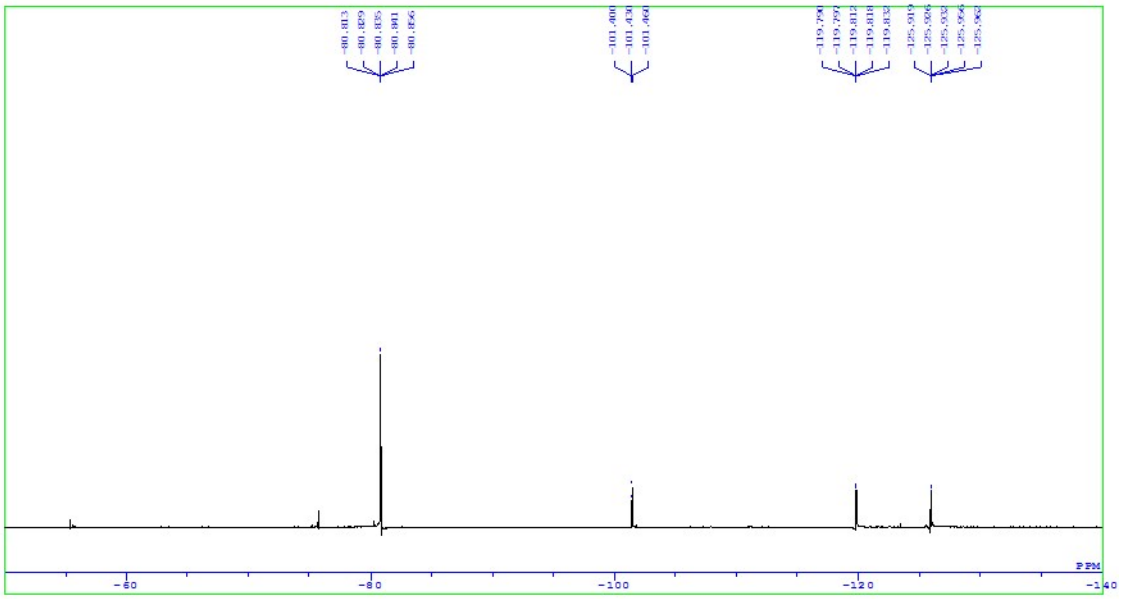
^{1}H NMR of spectrum of **7d**



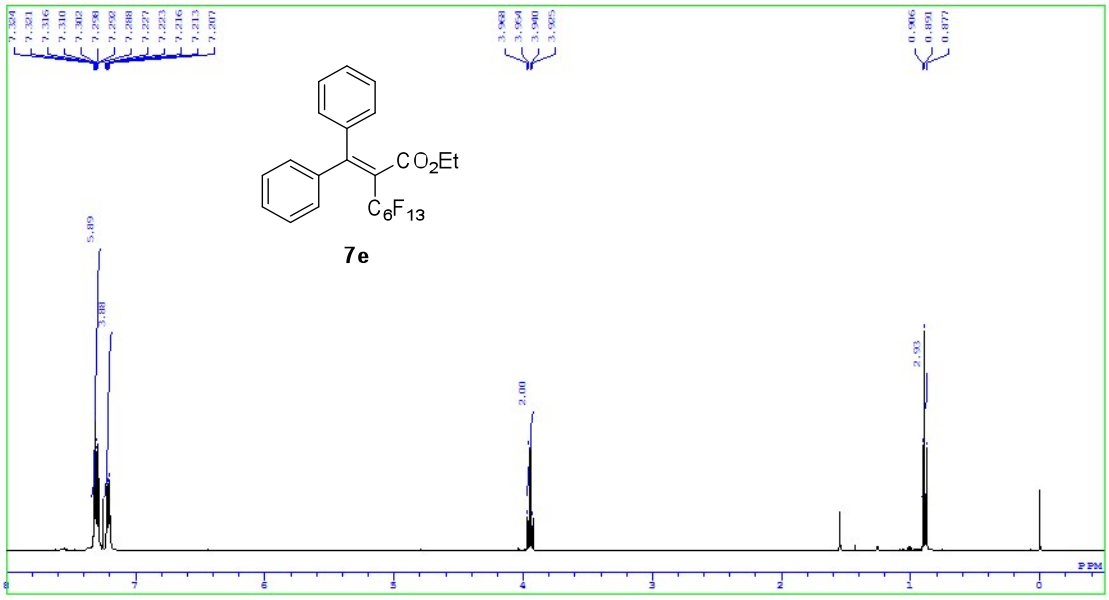
^{13}C NMR of spectrum of **7d**



^{19}F NMR of spectrum of **7d**

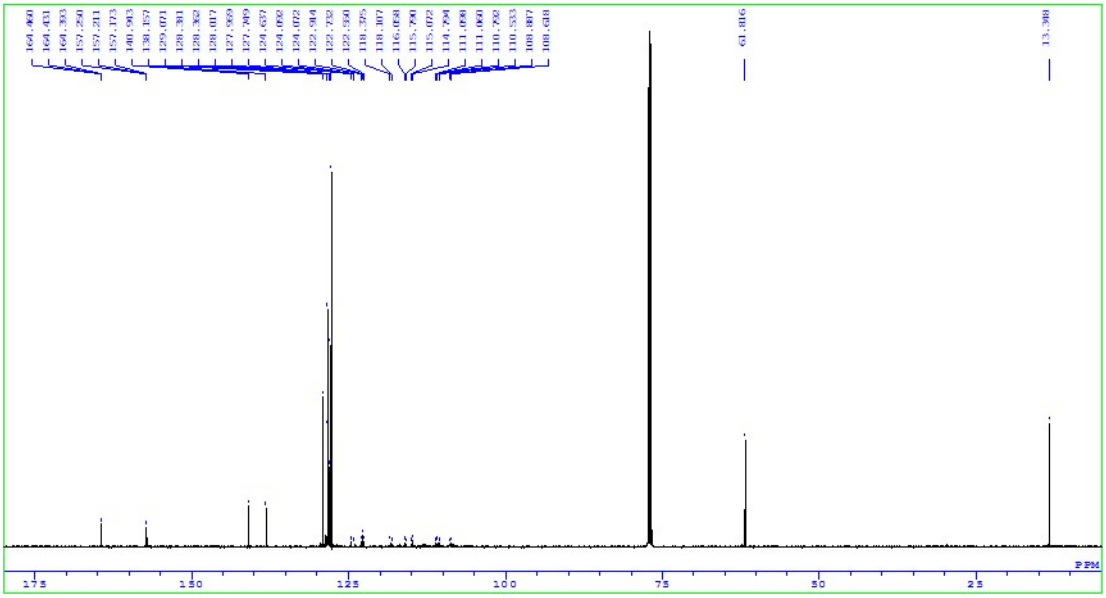


^{1}H NMR of spectrum of **7e**

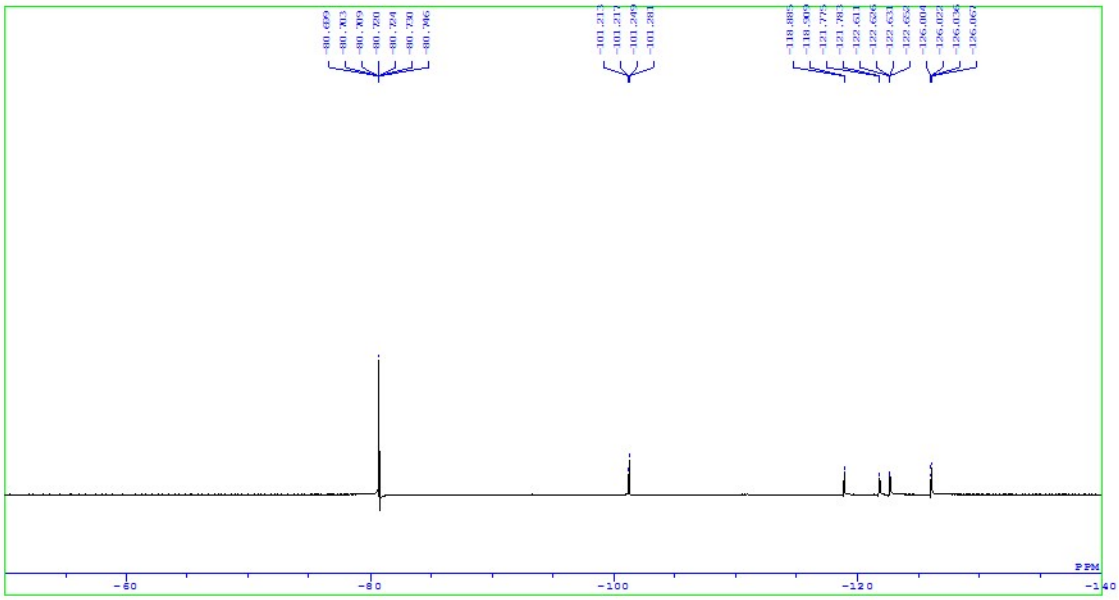


7e

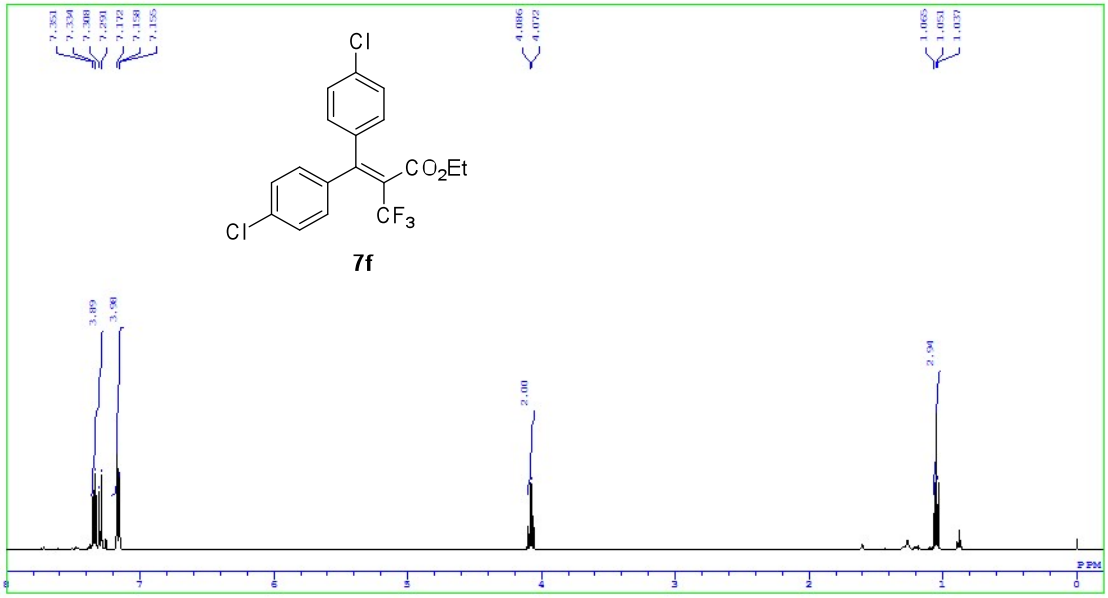
^{13}C NMR of spectrum of **7e**



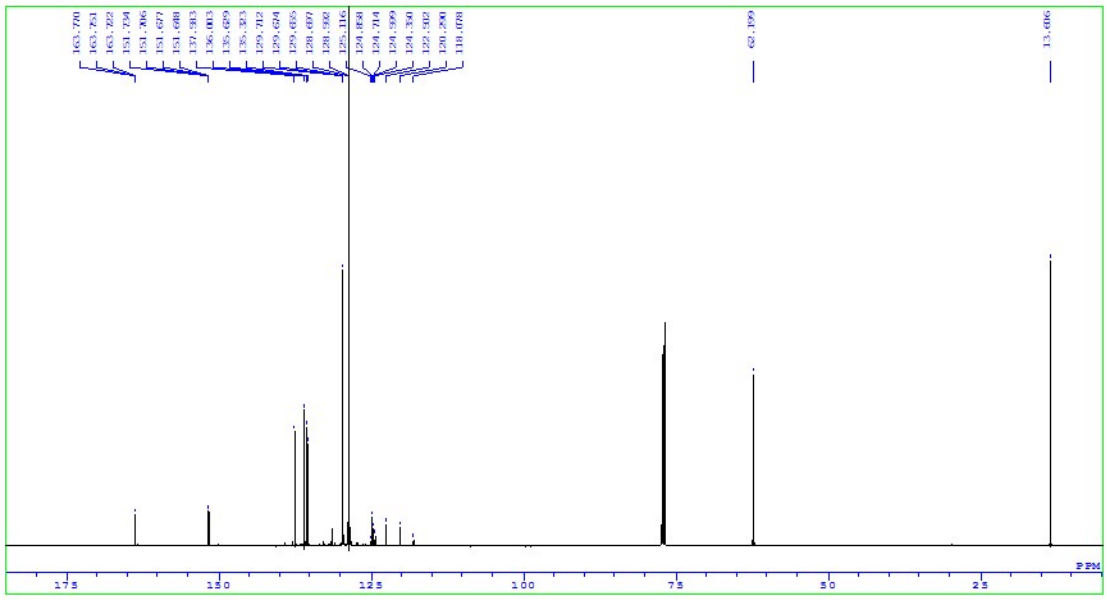
^{19}F NMR of spectrum of **7e**



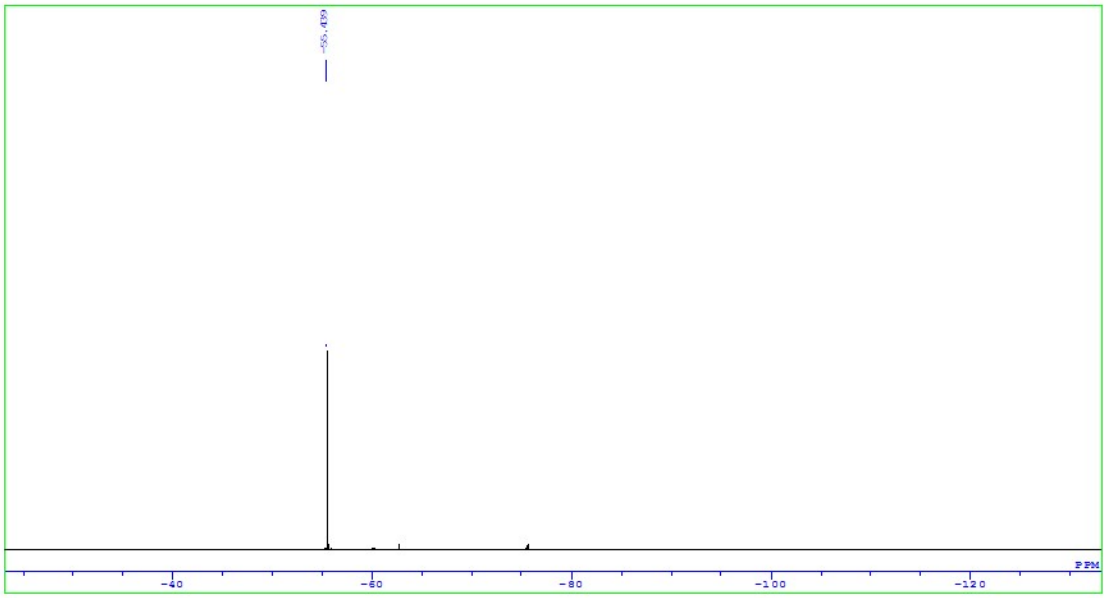
^{1}H NMR of spectrum of **7f**



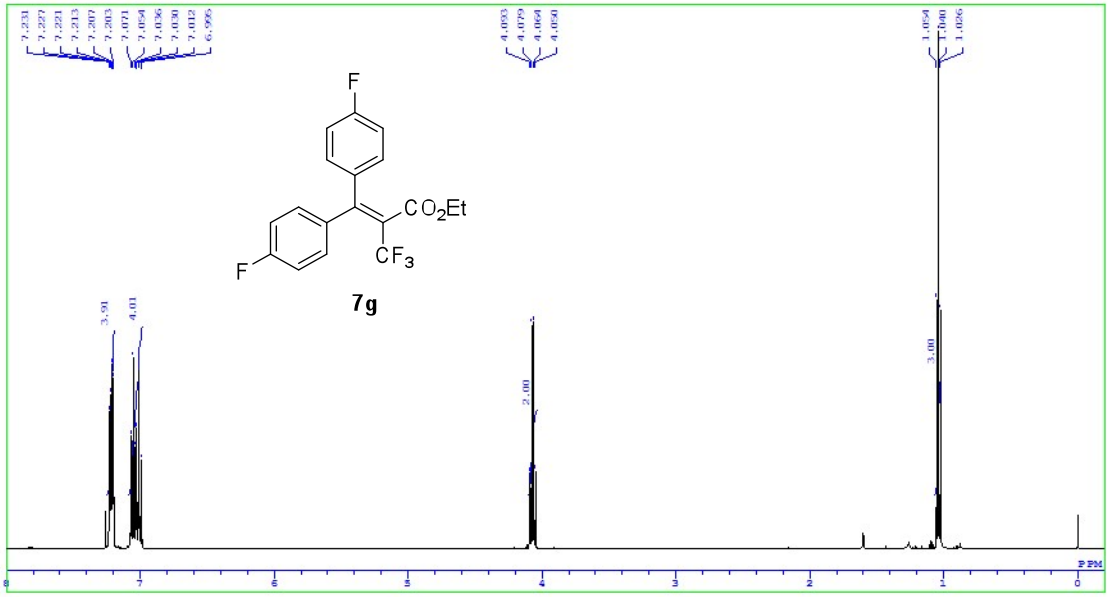
^{13}C NMR of spectrum of **7f**



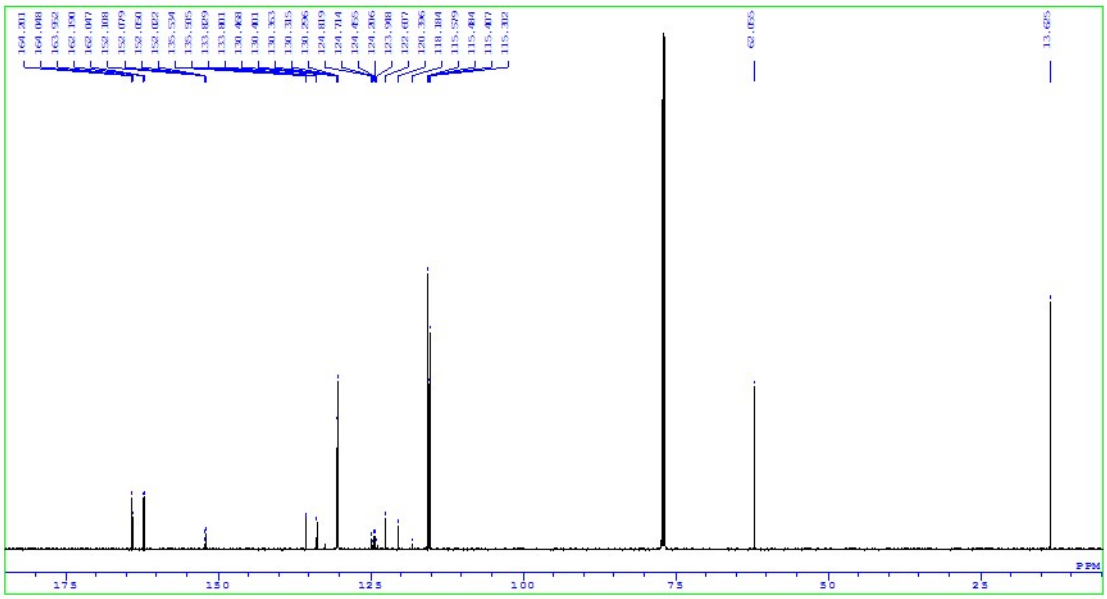
^{19}F NMR of spectrum of **7f**



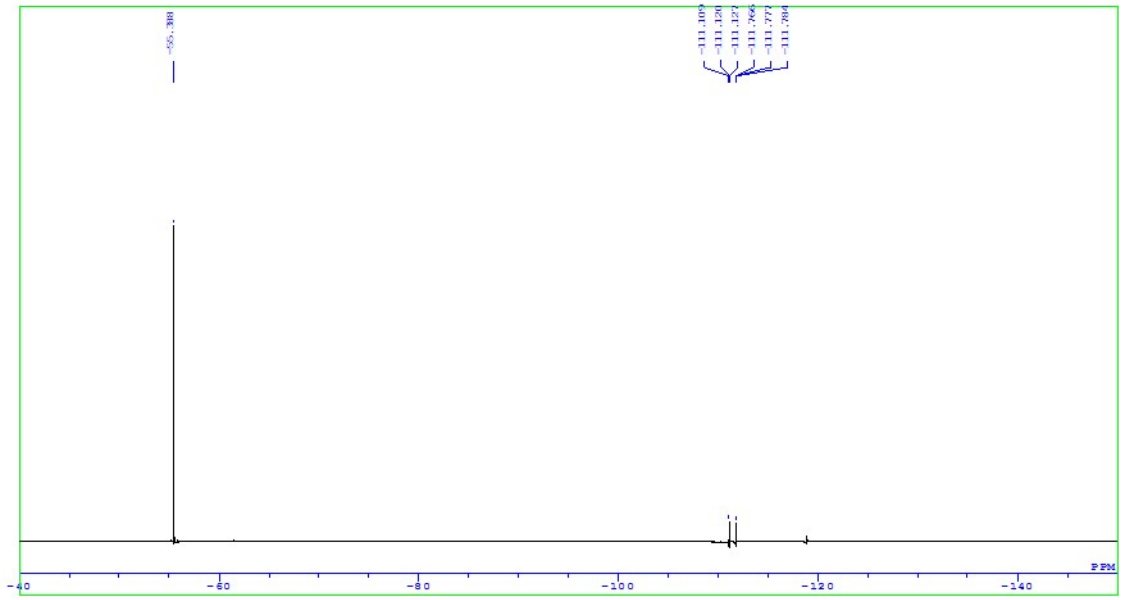
^{1}H NMR of spectrum of **7g**



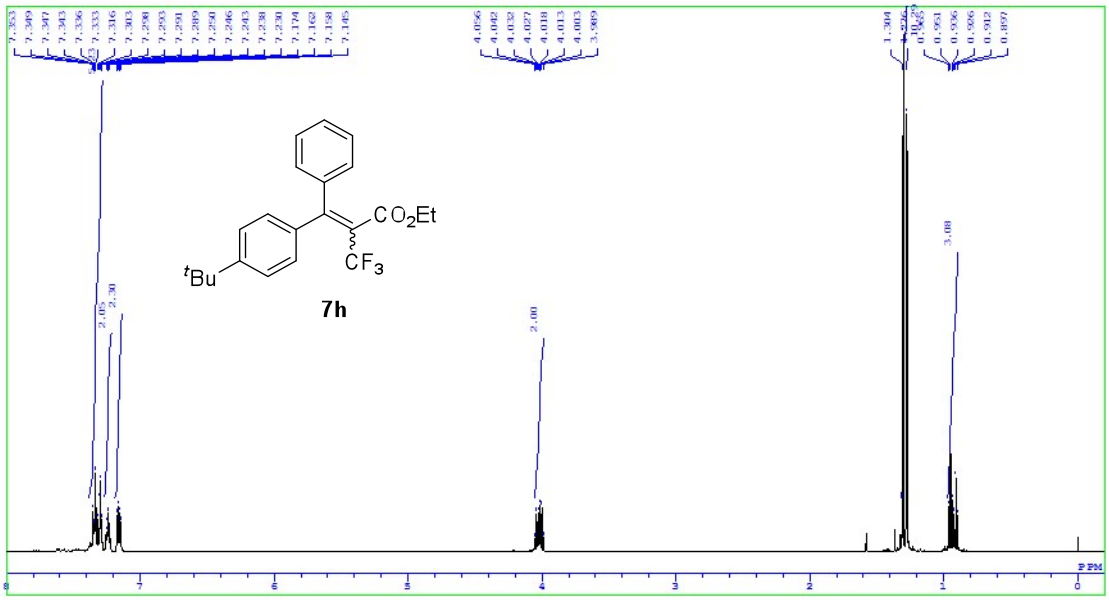
^{13}C NMR of spectrum of **7g**



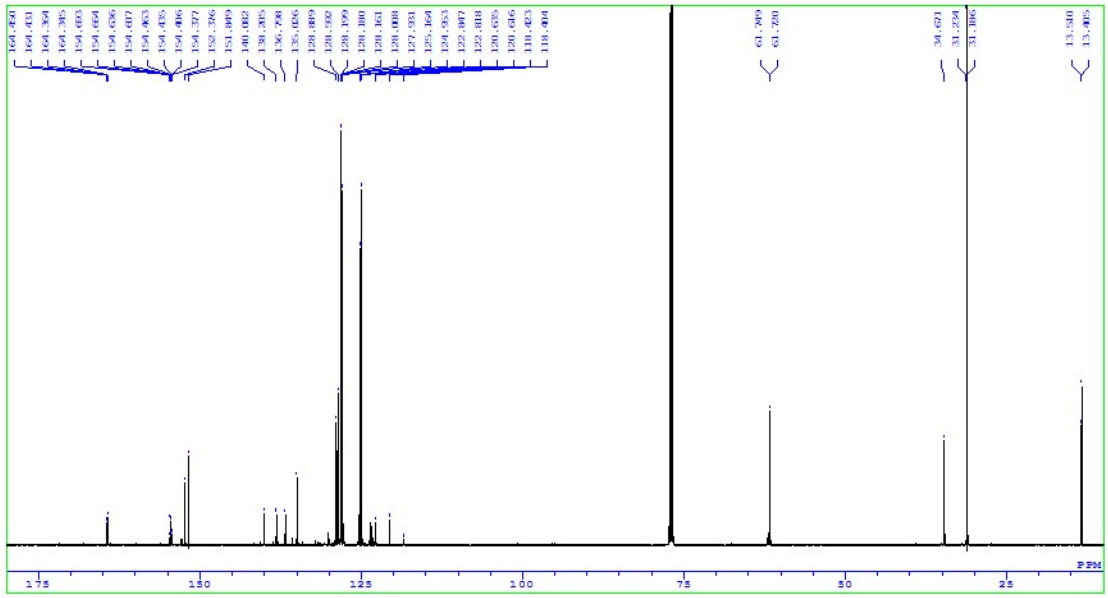
^{19}F NMR of spectrum of **7g**



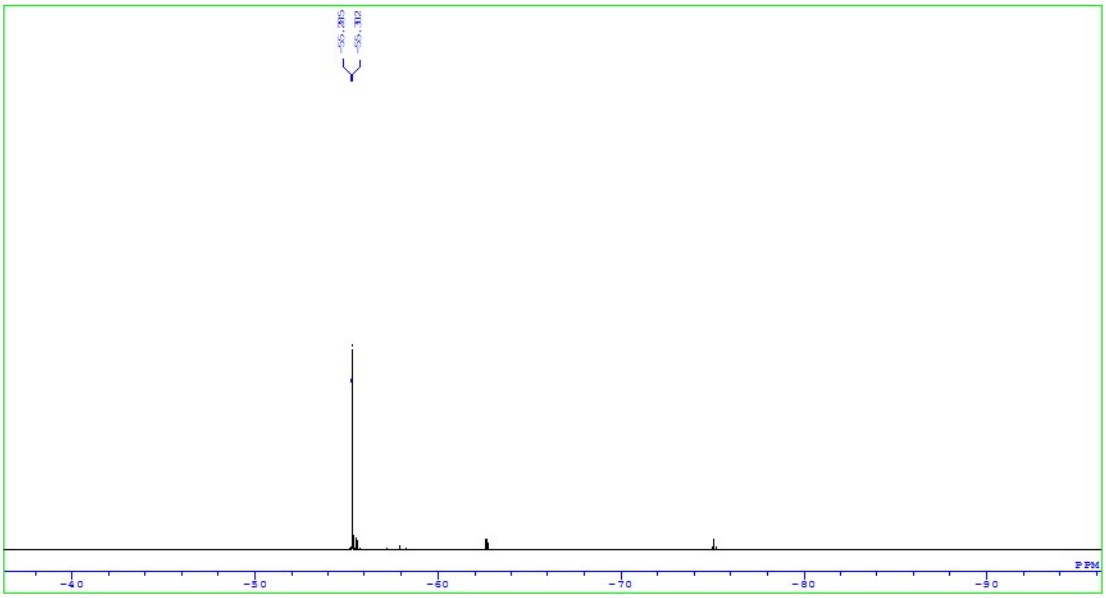
^{1}H NMR of spectrum of **7h**



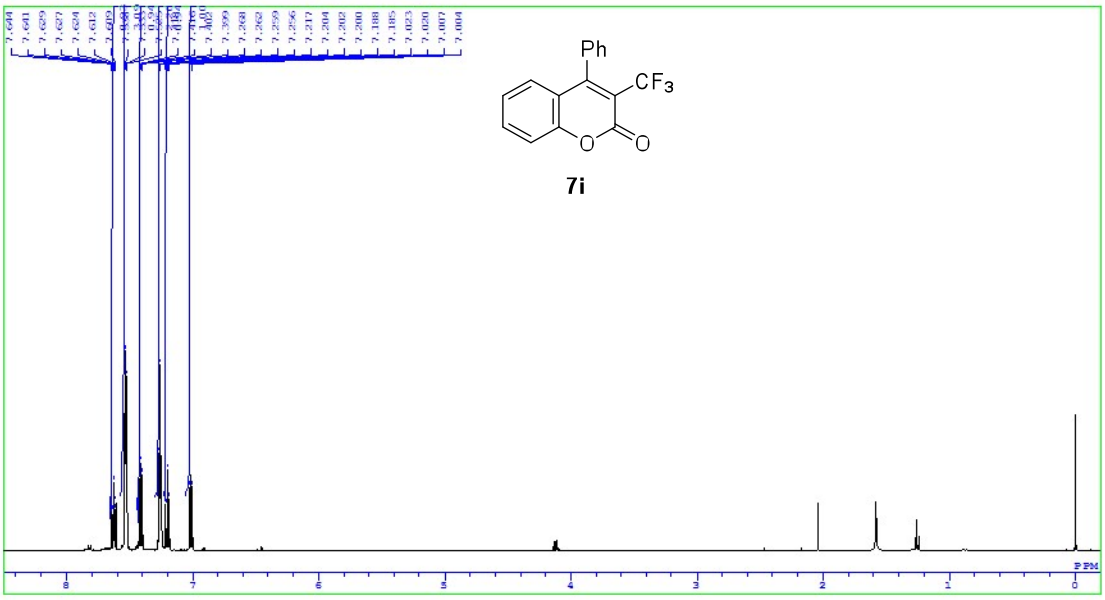
^{13}C NMR of spectrum of **7h**



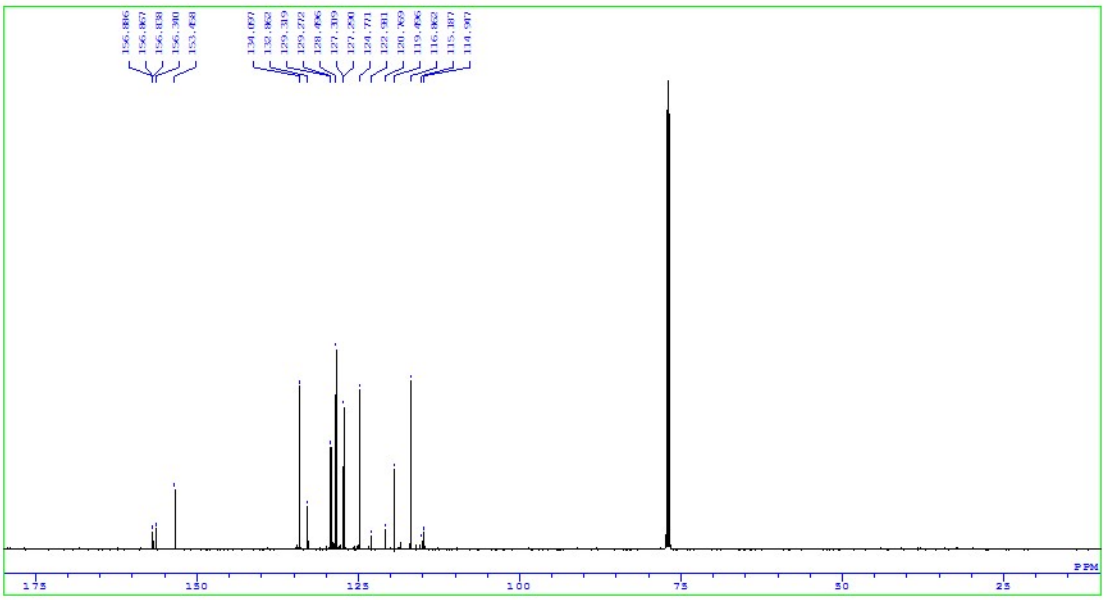
^{19}F NMR of spectrum of **7h**



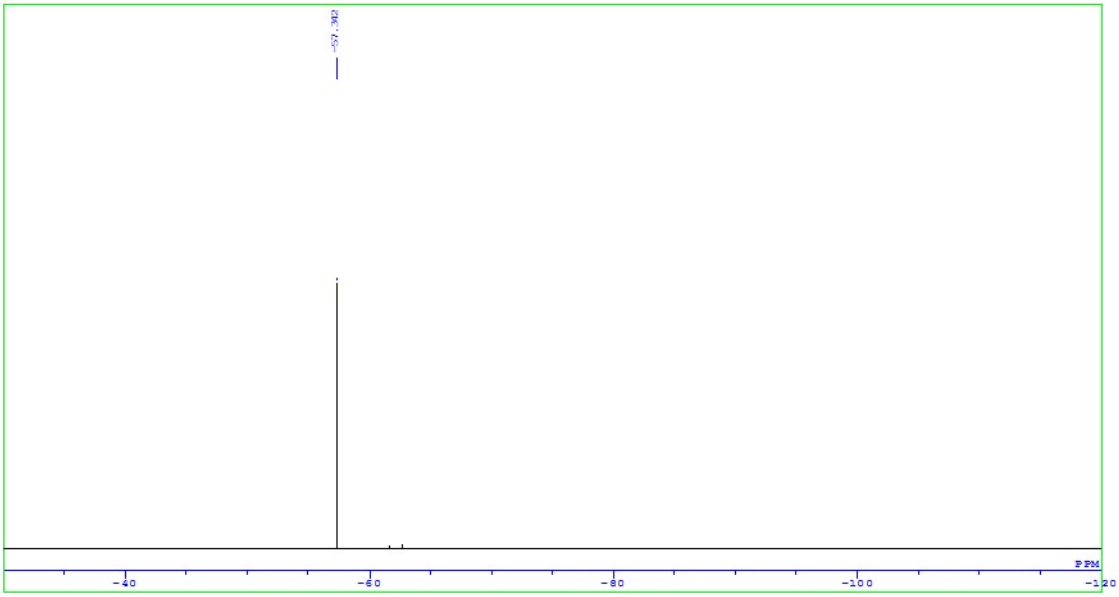
^{1}H NMR of spectrum of **7i**



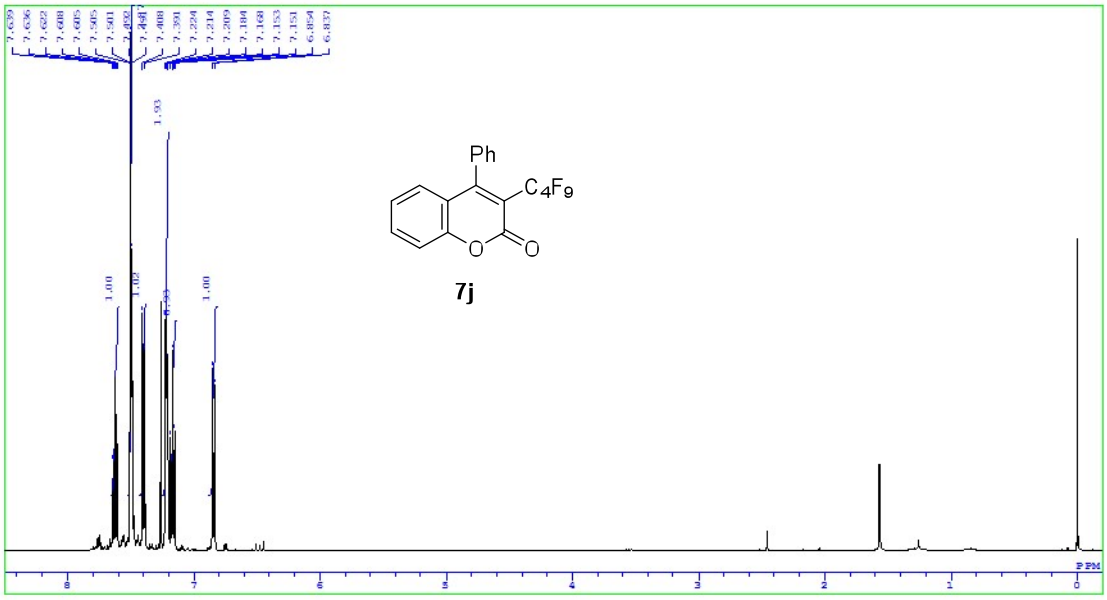
^{13}C NMR of spectrum of **7i**



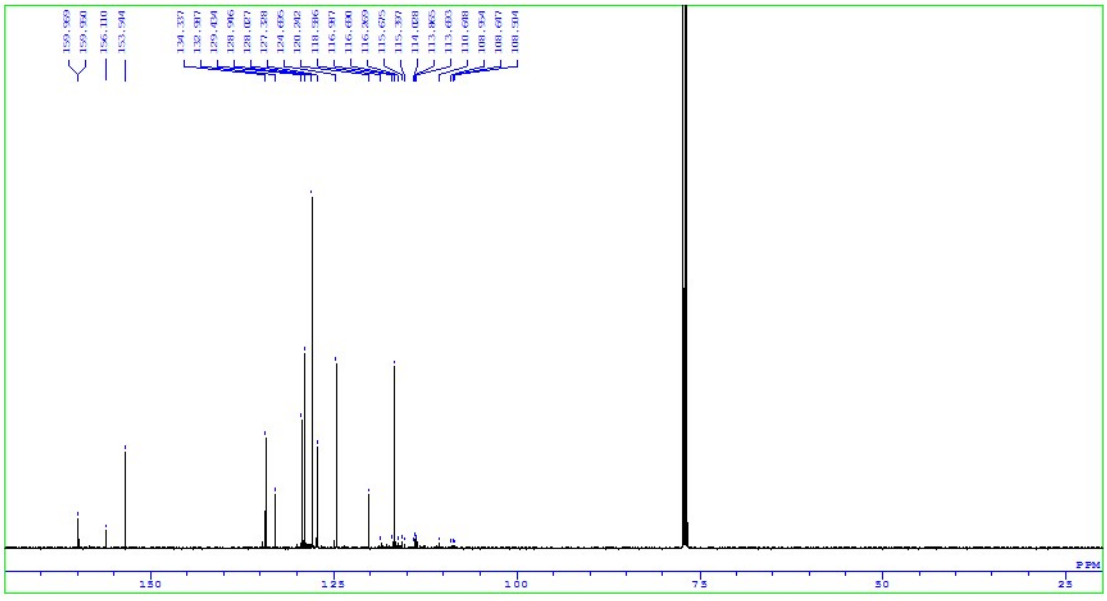
^{19}F NMR of spectrum of **7i**



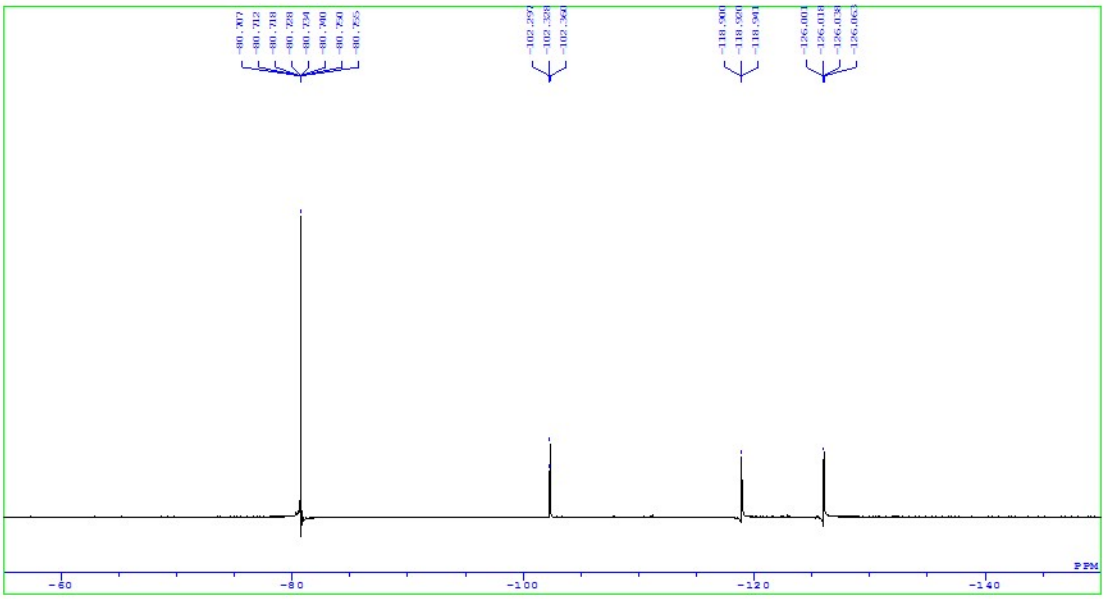
^{1}H NMR of spectrum of **7j**



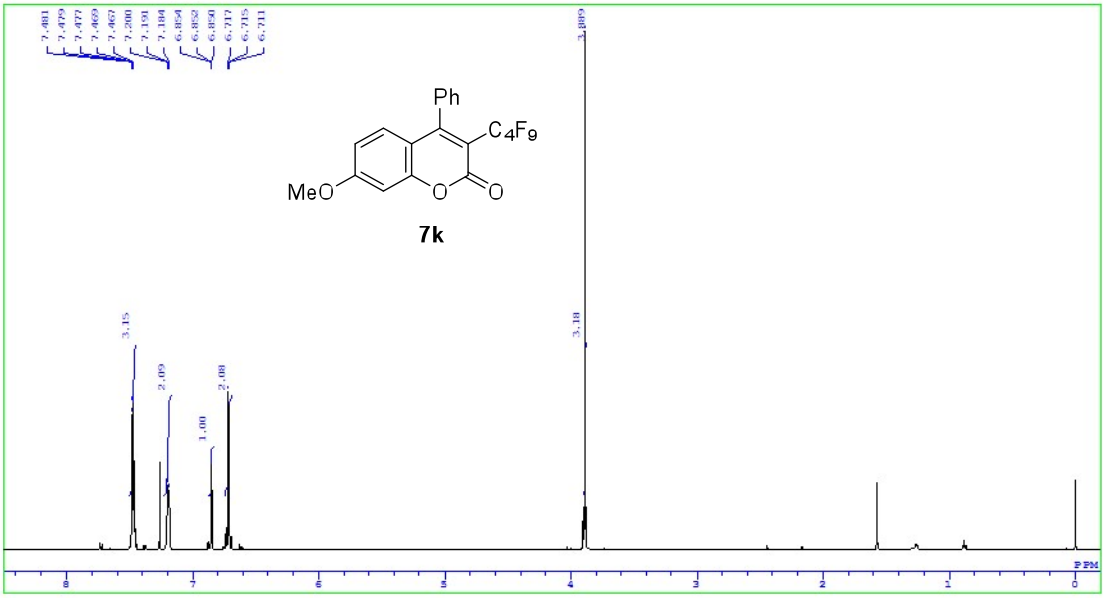
^{13}C NMR of spectrum of **7j**



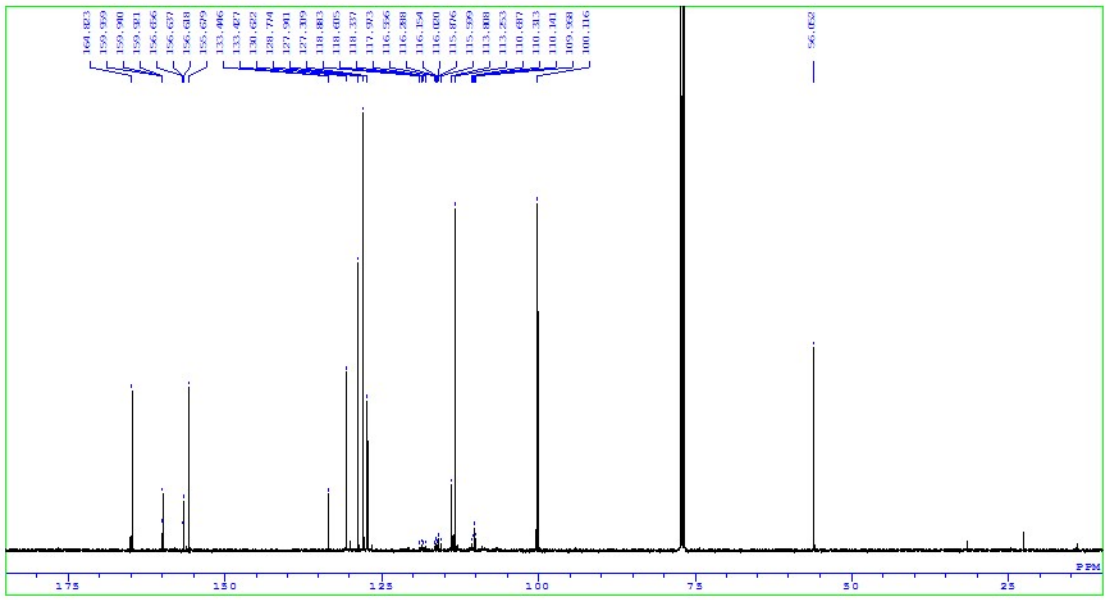
^{19}F NMR of spectrum of **7j**



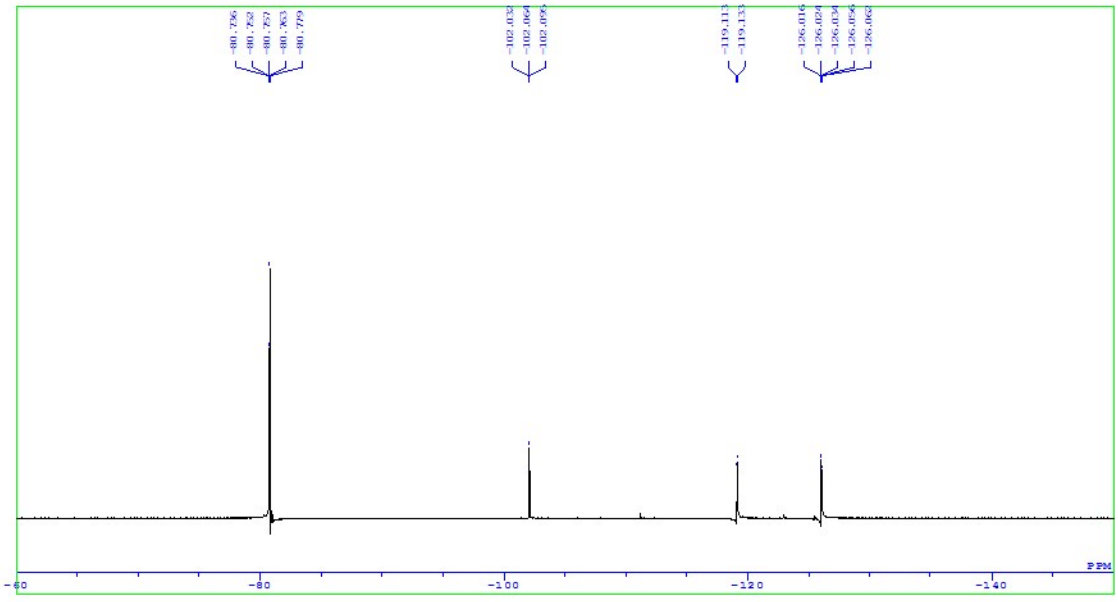
^{1}H NMR of spectrum of **7k**



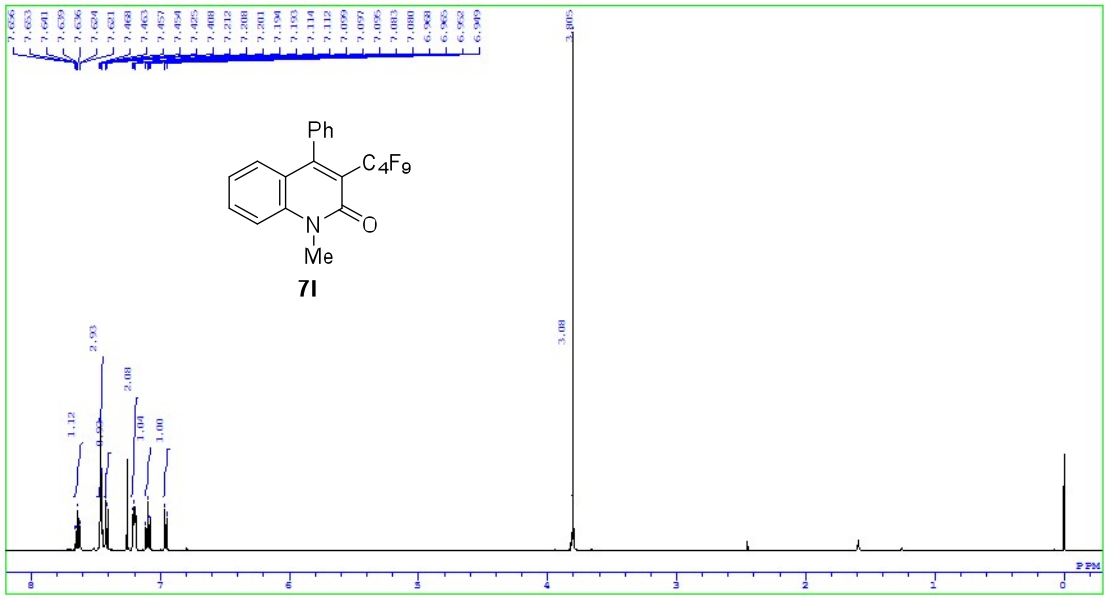
^{13}C NMR of spectrum of **7k**



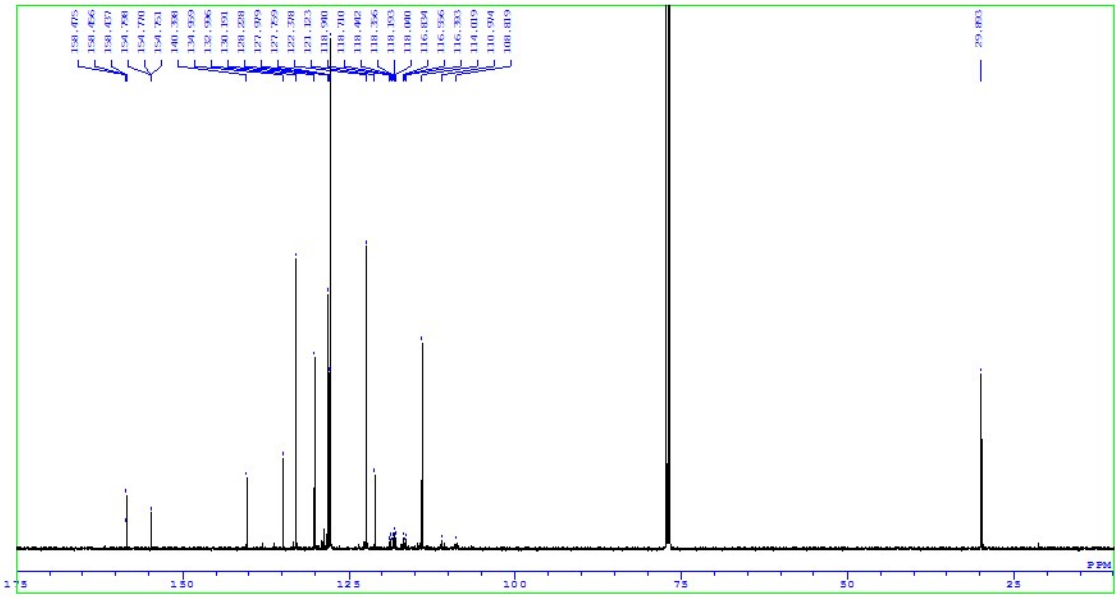
^{19}F NMR of spectrum of **7k**



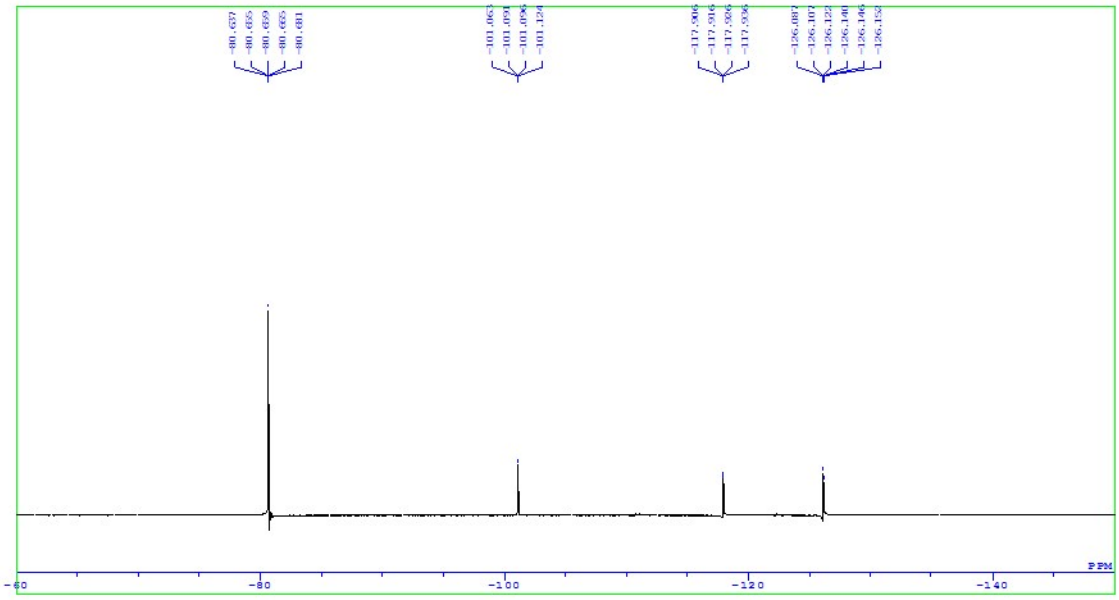
^{1}H NMR of spectrum of **7l**



^{13}C NMR of spectrum of **7l**

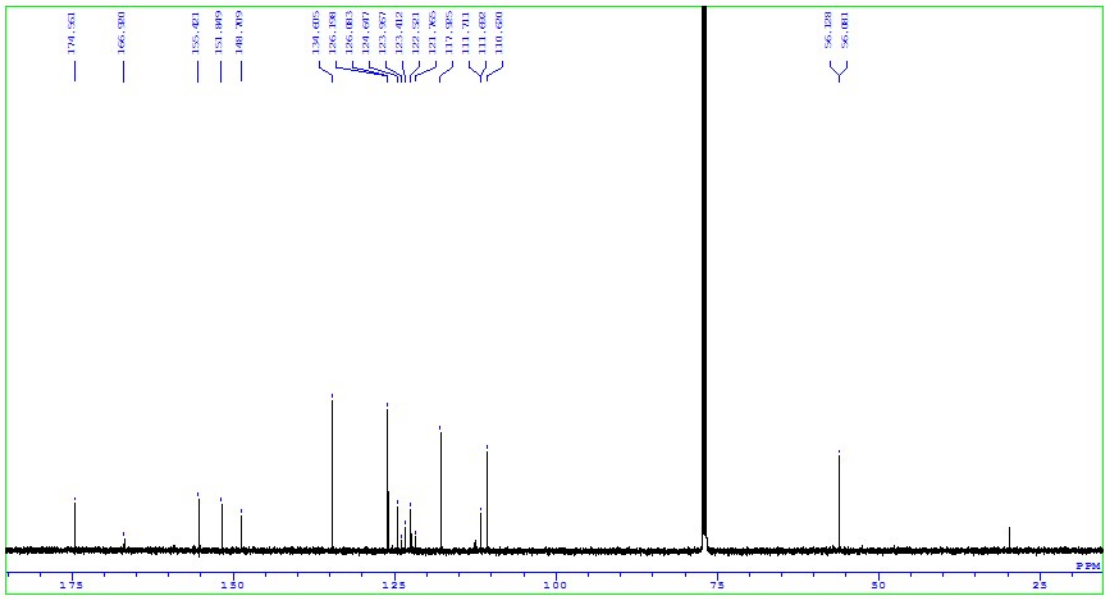


^{19}F NMR of spectrum of **7l**

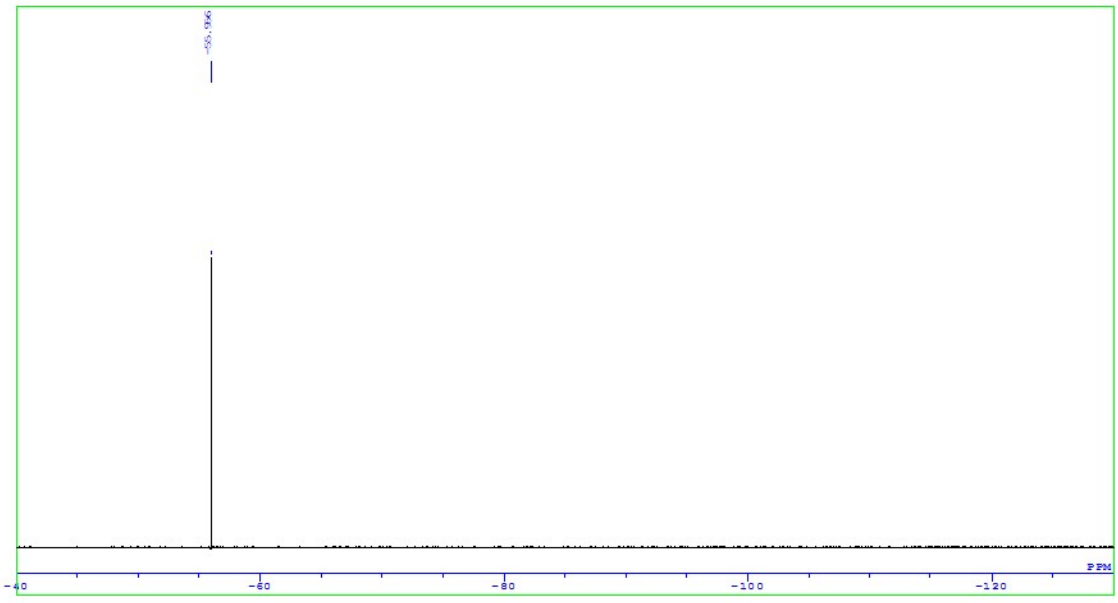


^{1}H NMR of spectrum of **7m**

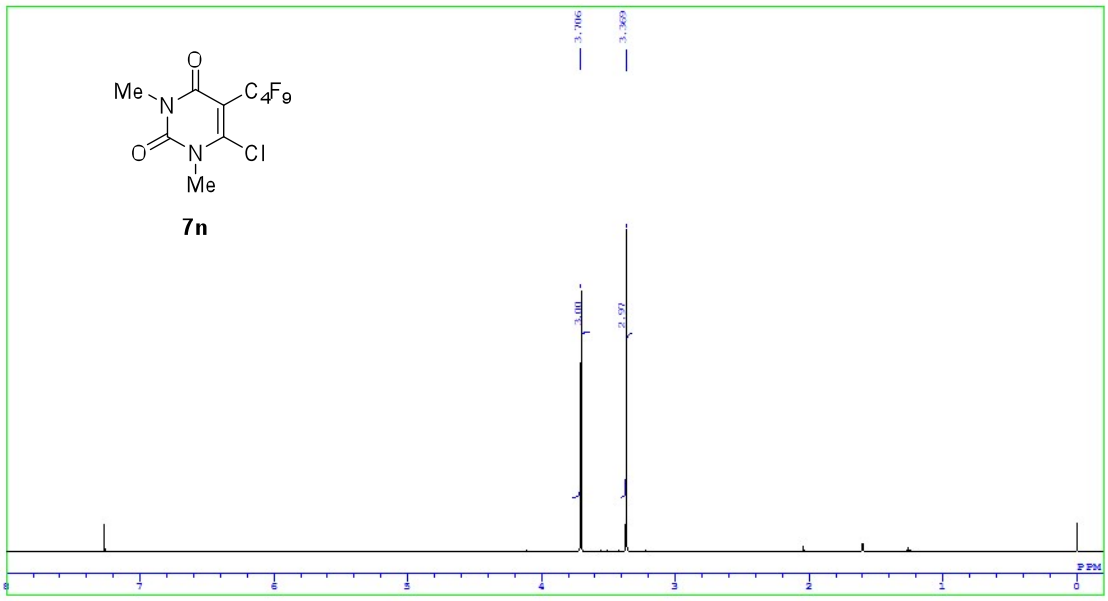
^{13}C NMR of spectrum of **7m**



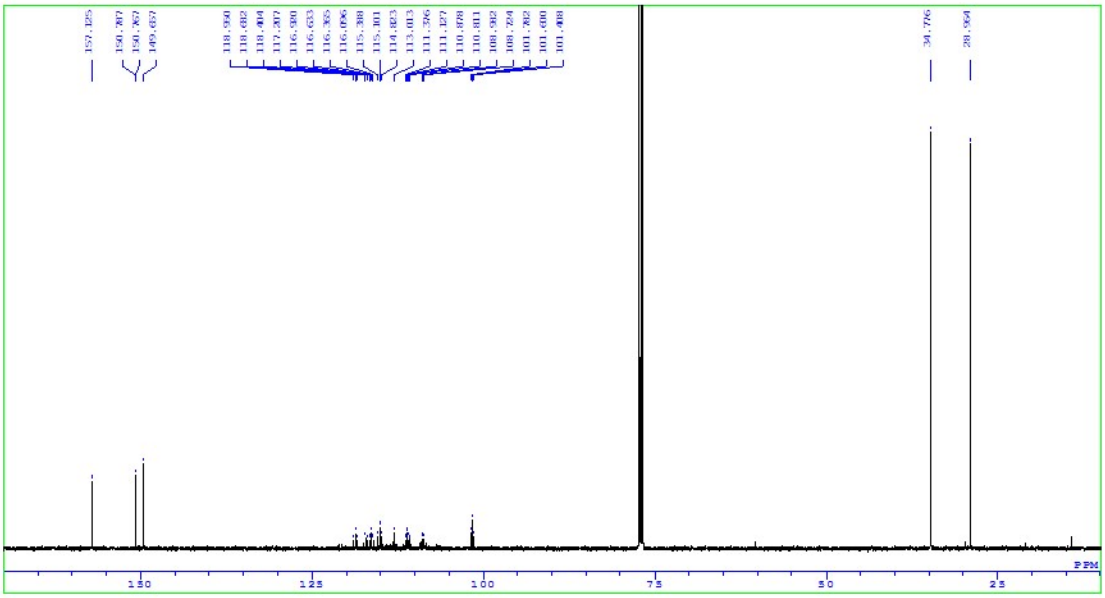
^{19}F NMR of spectrum of **7m**



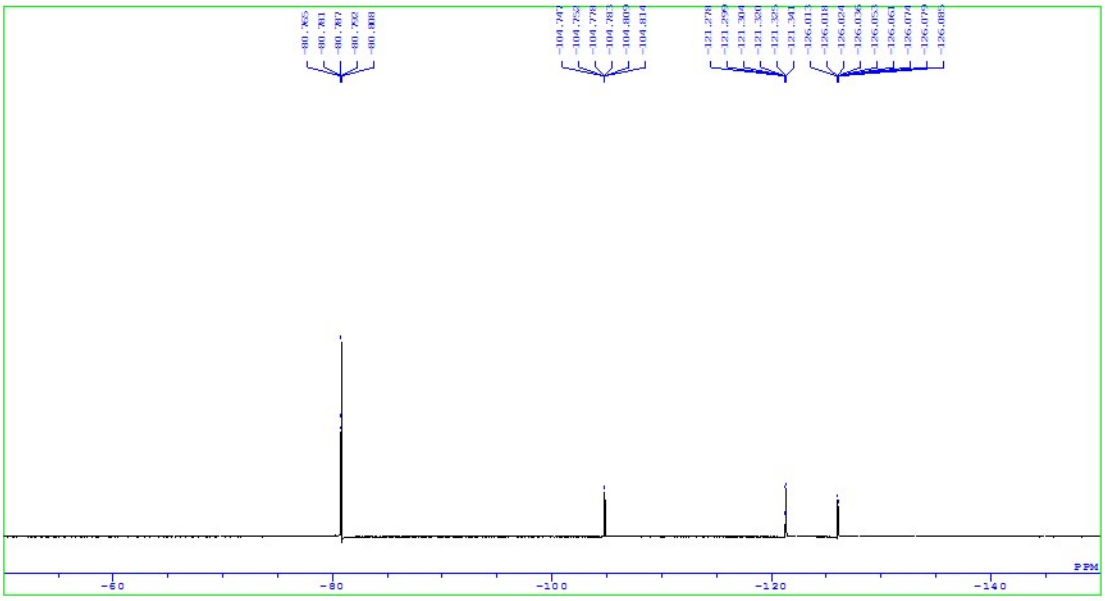
^{1}H NMR of spectrum of **7n**



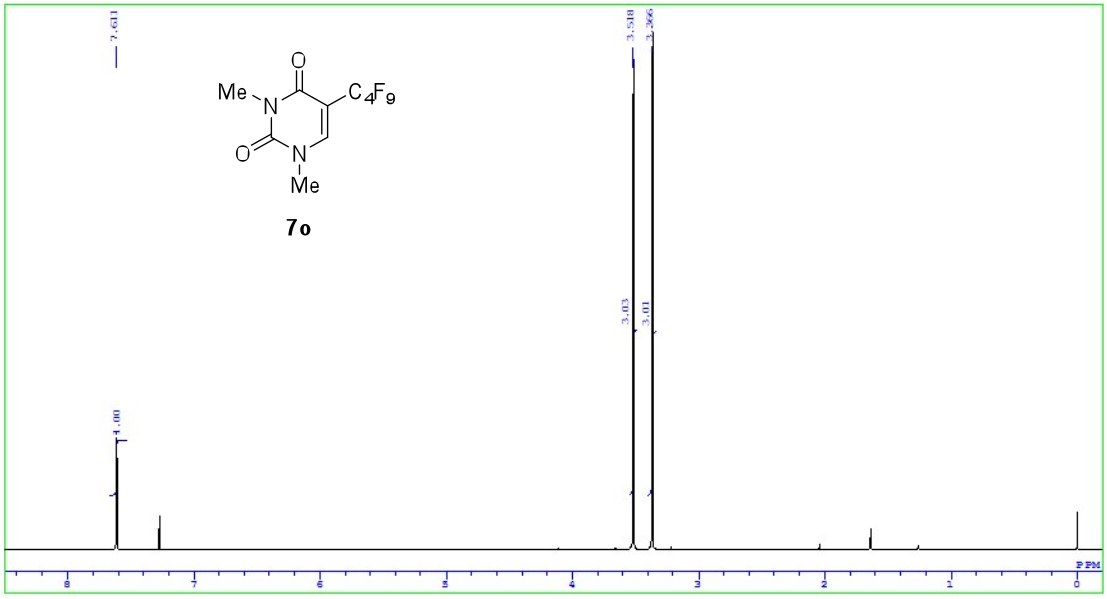
^{13}C NMR of spectrum of **7n**



^{19}F NMR of spectrum of **7n**

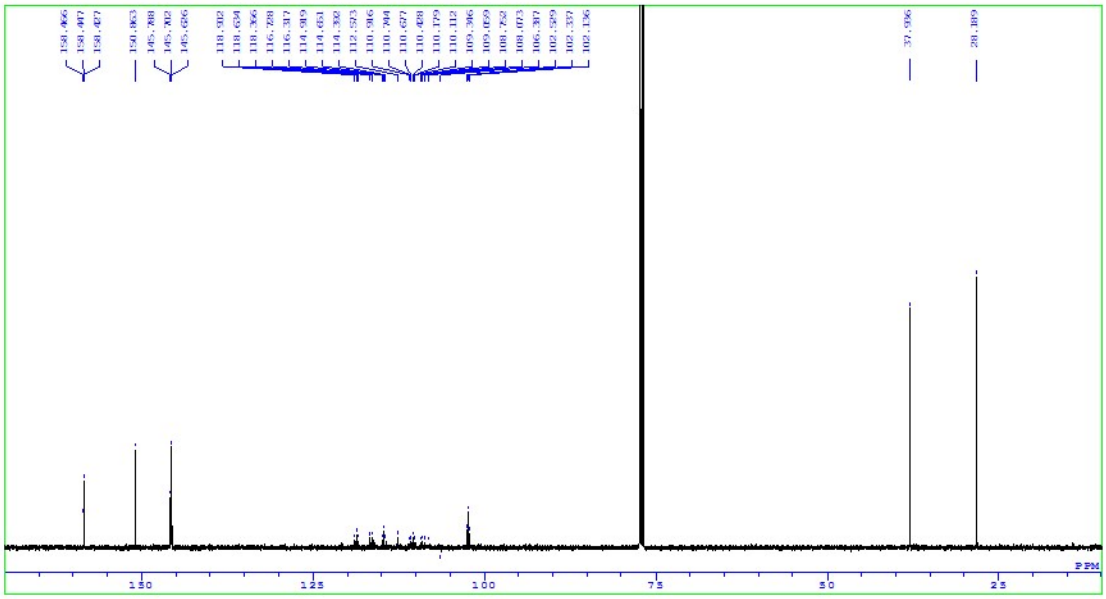


^{1}H NMR of spectrum of **7o**

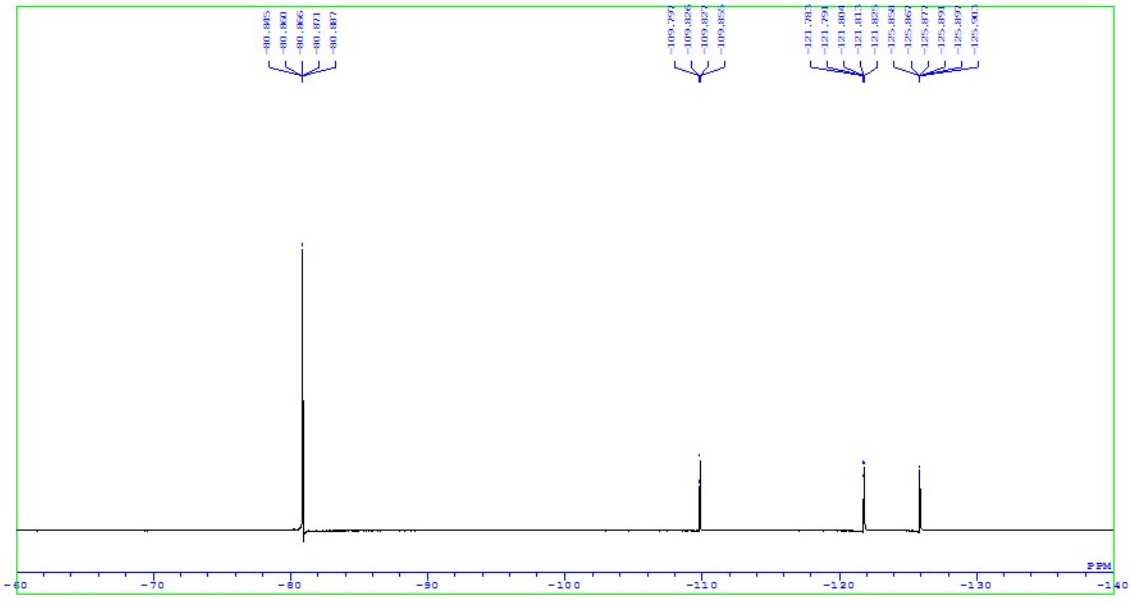


7o

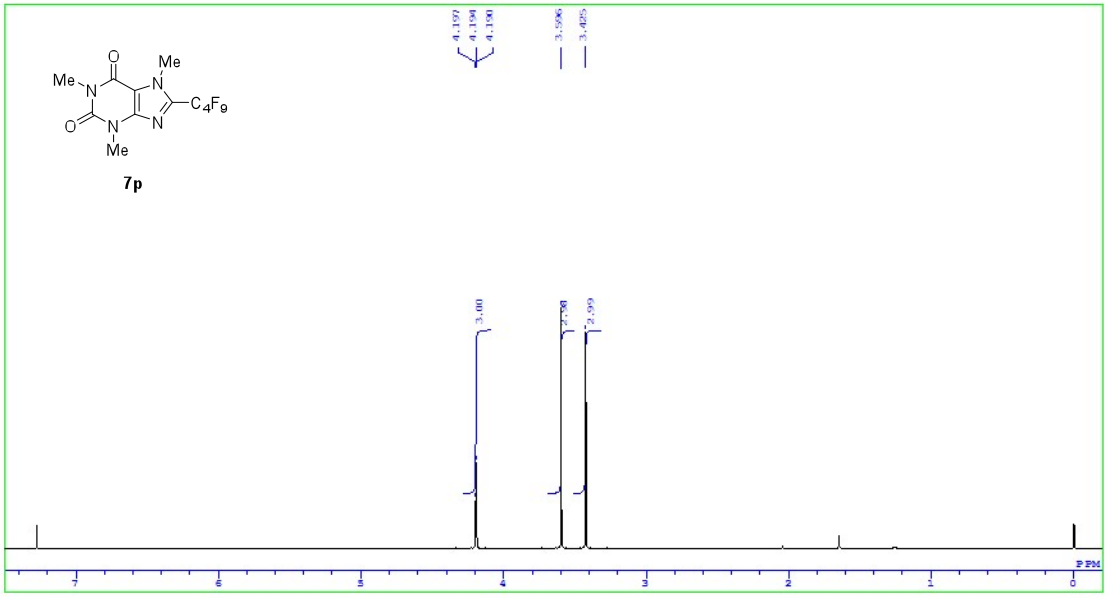
^{13}C NMR of spectrum of **7o**



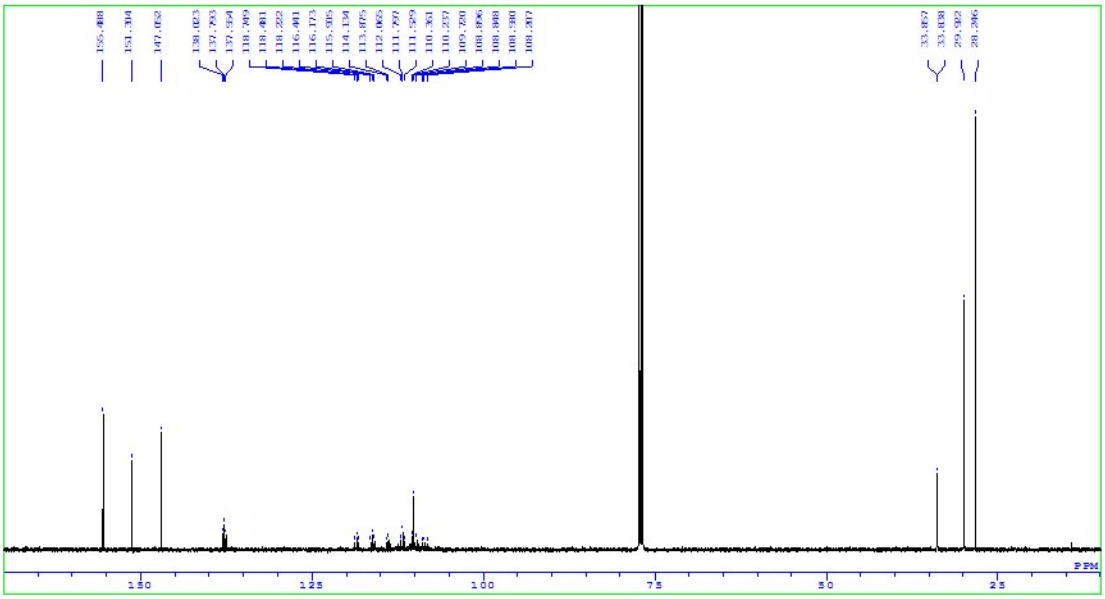
^{19}F NMR of spectrum of **7o**



^{1}H NMR of spectrum of **7p**



^{13}C NMR of spectrum of **7p**



^{19}F NMR of spectrum of **7p**