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Supporting Information

Expedient Synthesis of New Cinnolinediones by Ru-Catalyzed Regioselective Unexpected Deoxygenation-Oxidative Annulation of Propargyl Alcohols with Phthalazinones and Pyridazinones

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Table of Contents

EXPERIMENTAL SECTION

General Consideration

Unless otherwise mentioned, all the reactions were carried out in screw cap reaction tubes. All solvents and reagents were of pure analytical grade. Various ruthenium catalysts were prepared from literature procedure.[1] All palladium salts was bought from the Sigma Aldrich. The products were purified by column chromatography, silica gel (100-200 mesh or 200-420 mesh). A gradient elution using petroleum ether and ethyl acetate was performed based on pre-coated aluminum TLC sheets (silica gel 60F 254).

Analytical information

All isolated compounds were characterized by ^{1}H, ^{13}C and HRMS. Compound **3ae** and **8am** was characterized by single crystal X-ray diffraction (Figure S1 & S2). Copies of the ^{1}H NMR, ^{13}C NMR, NOESY and NOE NMR can be found in this supporting information. All Nuclear Magnetic Resonance Spectra were recorded on 400 MHz and 100 MHz NMR instrument for ^{1}H and ^{13}C NMR respectively. All ^{1}H NMR spectra were reported in units ppm (parts per million), and were measured relative to the signals for residual chloroform (7.26 ppm) and DMSO (2.54 ppm) in the deuterated solvent. All ^{13}C NMR spectra were reported in ppm relative to deuterated chloroform (77.23 ppm) and DMSO (39.52 ppm). Coupling constants (*J*) are reported in Hz; splitting patterns are assigned s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet; br = broad signal. High-resolution mass spectra (HRMS) were performed on TOF-Q analyser.

Optimization Table:

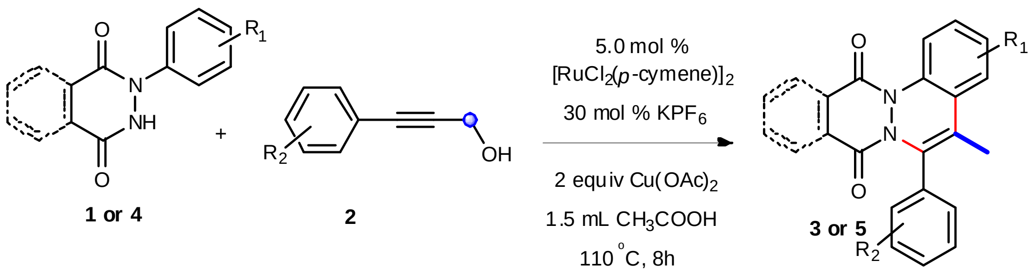
Entry	Ru Catalyst (5 mol %)	Oxidant 2 equiv	Additives (30 mol %)	Solvent 1.5 ml	Yield[a] **3aa**
1	$[RuCl_2(p\text{-cymene})]_2$	-	NaOAc	Toluene	-
2	$[RuCl_2(p\text{-cymene})]_2$	-	NaOAc	Dioxane	-
3	$[RuCl_2(p\text{-cymene})]_2$	-	NaOAc	DCE	-
4	$[RuCl_2(p\text{-cymene})]_2$	-	NaOAc	H_2O	-
5	$[RuCl_2(p\text{-cymene})]_2$	-	NaOAc	MeOH	22
6	$[RuCl_2(p\text{-cymene})]_2$	-	NaOAc	*t*-AmOH	30
7	$[RuCl_2(p\text{-cymene})]_2$	-	NaOAc	Acetic Acid	42
8	$[RuCl_2(p\text{-cymene})]_2$	$Cu(OAc)_2$	NaOAc	Acetic Acid	50
9	$[RuCl_2(p\text{-cymene})]_2$	$Cu(OAc)_2$	KOAc	Acetic Acid	44
10	$[RuCl_2(p\text{-cymene})]_2$	$Cu(OAc)_2$	CsOAc	Acetic Acid	35
11	$[RuCl_2(p\text{-cymene})]_2$	$Cu(OAc)_2$	AgOAc	Acetic Acid	60
12	$[RuCl_2(p\text{-cymene})]_2$	$Cu(OAc)_2$	$AgSbF_6$	Acetic Acid	40
13	$[RuCl_2(p\text{-cymene})]_2$	$Cu(OAc)_2$	KPF_6	Acetic Acid	83
14	$[RuCl_2(p\text{-cymene})]_2$	$CuBr_2$	KPF_6	Acetic Acid	45
15	$[RuCl_2(p\text{-cymene})]_2$	$CuCl_2$	KPF_6	Acetic Acid	22
16	$RuCl_3.XH_2O$	$Cu(OAc)_2$	KPF_6	Acetic Acid	-
17	$RuCl_2(PPh_3)_3$	$Cu(OAc)_2$	KPF_6	Acetic Acid	trace
18	$[Ru(COD)Cl_2]_n$	$Cu(OAc)_2$	KPF_6	Acetic Acid	trace
19	$Ru(DMSO)_4Cl_2$	$Cu(OAc)_2$	KPF_6	Acetic Acid	-
20	-	$Cu(OAc)_2$	-	Acetic Acid	-
21	-	$Cu(OAc)_2$	KPF_6	Acetic Acid	-

Unless otherwise mentioned all the reactions were carried out with **1a** (0.2 mmol), **2a** (0.22 mmol), catalyst (5 mol %), solvent (1.5 mL), additive (30 mol %), oxidant (2 equiv), 110 ^{o}C, 8 h. [a]Isolated yields.

General Synthetic procedure for deoxygenation/oxidative annulation:

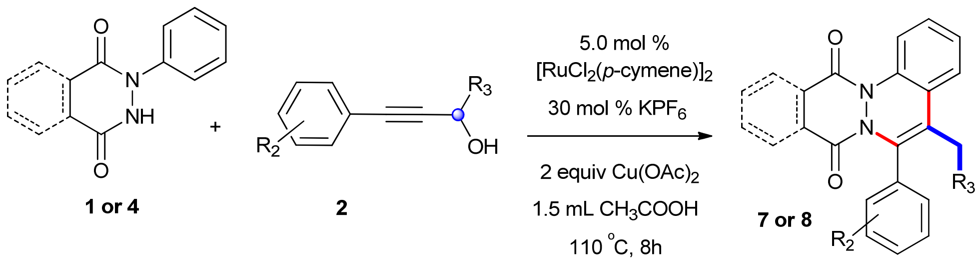
Deoxygenation/oxidative annulation primary propargyl alcohol.

In an oven-dried, vial equipped with stirring bar, were placed 2-phenyl-2,3-dihydrophthalazine-1,4-dione/1-phenyl-1,2-dihydropyridazine-3,6-dione (0.2 mmol), and 3-phenylprop-2-yn-1-ol (primary propargyl alcohol) (0.22 mmol), $[RuCl_2(p\text{-cymene})]_2$ (5 mol %, 0.01mmol), KPF_6 (30 mol %, 0.06 mmol) and copper(II)acetate (0.4 mmol) in acetic acid (1.5 mL). The mixture stirred for 10 min at room temperature, sealed with a Teflon–lined cap, and heated at 110 °C with stirring for 8h. After cooling the ambient temperature, the reaction mixture was diluted with ethyl acetate and filtered through celite and silica gel, and the filtrate was concentrated under reduced pressure. The crude residue was purified through a silica gel column using hexane and ethyl acetate as an eluent.



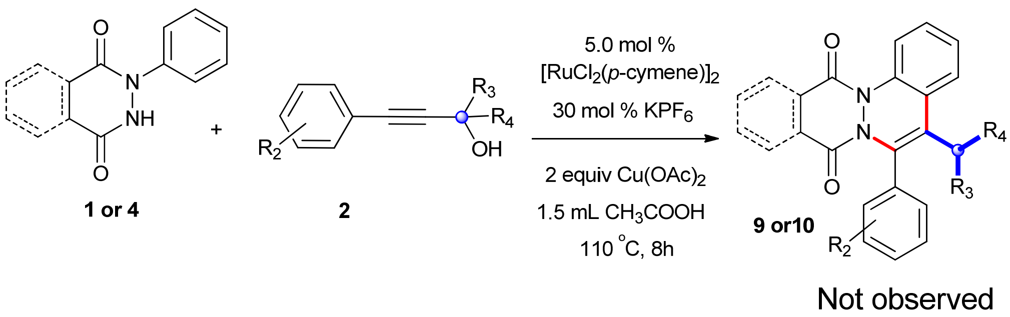
Deoxygenation/oxidative annulation secondary propargyl alcohol.

In an oven-dried, vial equipped with stirring bar, were placed 2-phenyl-2,3-dihydrophthalazine-1,4-dione/1-phenyl-1,2-dihydropyridazine-3,6-dione (0.2 mmol), and secondary propargyl alcohol (0.22 mmol), $[RuCl_2(p\text{-cymene})]_2$ (5 mol %, 0.01mmol), KPF_6 (30 mol %, 0.06 mmol) and copper(II)acetate (0.4 mmol) in acetic acid (1.5 mL). The mixture stirred for 10 min at room temperature, sealed with a Teflon–lined cap, and heated at 110 °C with stirring for 8h. After cooling the ambient temperature, the reaction mixture was diluted with ethyl acetate and filtered through celite and silica gel, and the filtrate was concentrated under reduced pressure. The crude residue was purified through a silica gel column using hexane and ethyl acetate as an eluent.

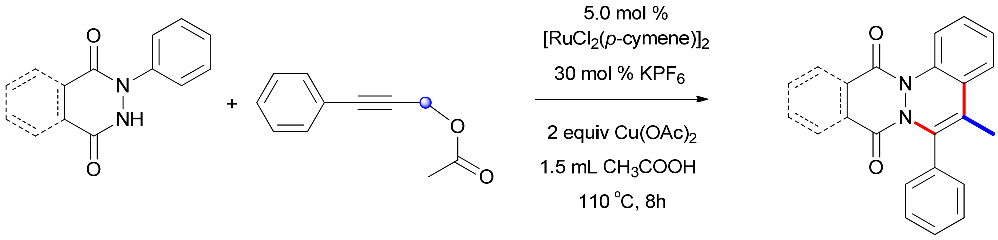


Deoxygenation/oxidative annulation tertiary propargyl alcohol.

In an oven-dried, vial equipped with stirring bar, were placed 2-phenyl-2,3-dihydrophthalazine-1,4-dione/1-phenyl-1,2-dihydropyridazine-3,6-dione (0.2 mmol), and tertiary propargyl alcohol (0.22 mmol), $[RuCl_2(p\text{-cymene})]_2$ (5 mol %, 0.01mmol), KPF_6 (30 mol %, 0.06 mmol) and copper(II)acetate (0.4 mmol) in acetic acid (1.5 mL). The mixture stirred for 10 min at room temperature, sealed with a Teflon–lined cap, and heated at 100 °C with stirring for 8h. After cooling the ambient temperature, the reaction mixture was diluted with ethyl acetate and filtered through celite and silica gel, and the filtrate was concentrated under reduced pressure. The crude residue was purified through a silica gel column using hexane and ethyl acetate, the expected deoxygenation-oxidative annulated product was not observed.

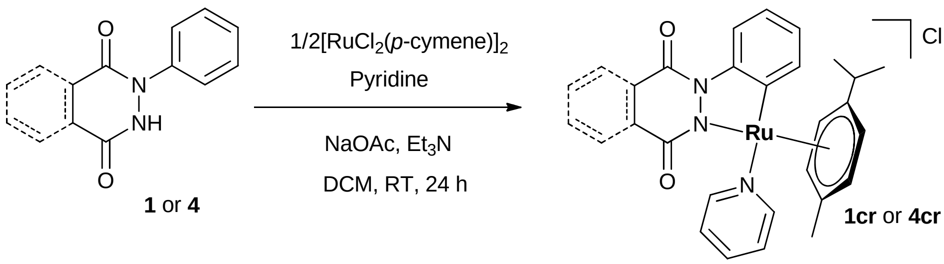


Deoxygenation/oxidative annulation 3-phenylprop-2-yn-1-yl acetate.



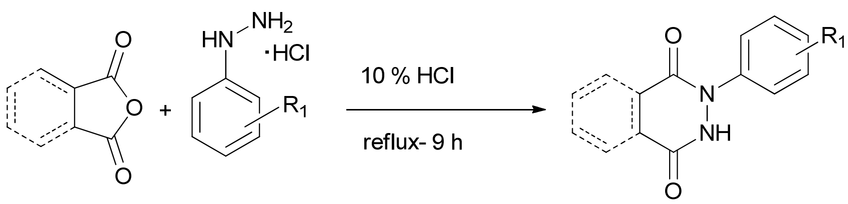
In an oven-dried, vial equipped with stirring bar, were placed 2-phenyl-2,3-dihydrophthalazine-1,4-dione/1-phenyl-1,2-dihydropyridazine-3,6-dione (0.2 mmol), and 3-phenylprop-2-yn-1-yl acetate (0.2 mmol), $[RuCl_2(p\text{-cymene})]_2$ (5 mol %, 0.01mmol), KPF_6 (30 mol %, 0.06 mmol) and copper(II)acetate (0.4 mmol) in acetic acid (1.5 mL). The mixture stirred for 10 min at room temperature, sealed with a Teflon–lined cap, and heated at 110 °C with stirring for 8h. After cooling the ambient temperature, the reaction mixture was diluted with ethyl acetate and filtered through celite and silica gel, and the filtrate was concentrated under reduced pressure. The crude residue was purified through a silica gel column using hexane and ethyl acetate as an eluent.

General Synthetic procedure for the preparation of ruthenacycle



Ruthenacycle complexes were synthesized by reported procedure.[2] Briefly a mixture of pyridine (28.4 mg, 0.36 mmol) was added to a solution of $[RuCl_2(p\text{-cymene})]_2$ (111.2 mg, 0.18 mmol) in DCM (10.0 mL) at RT. After vigorous stirring for 3 h, NaOAc (36.9 mg, 0.45 mmol) and **1a** or **4a** (0.3 mmol) were added to the solution with Et_3N (1.0 mL), and vigorous stirring was continued for 20 h. When the reaction was complete, the solution was transferred to a round-bottom flask. Silica was added to the flask and all volatiles were evaporated under reduced pressure. The crude product was purified by column chromatography on silica gel using DCM/MeOH as a solvent.

General Synthetic procedure for the preparation of phthalazine/pyridazine dione

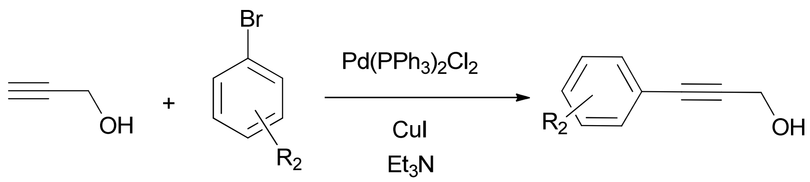


The appropriate phenylhydrazine (1.1equiv) was added in one portion to a stirred mixture of phthalic/malonic anhydride (1.0 equiv) in 10% HCl at room temperature. The mixture was heated to 120

°C for 9 h after it was cooled, the resulting solid was collected by filtration washed with water and recrystallized by using ethanol. Yield (60-80%).[3]

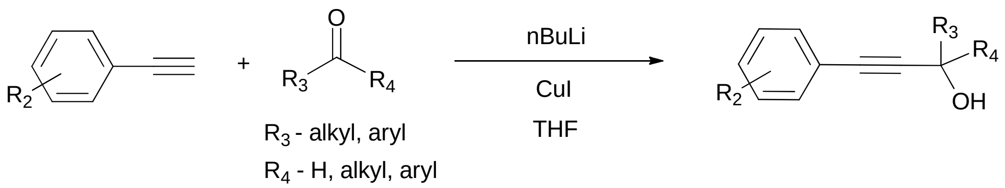
General Synthetic procedure for the preparation propargyl alcohol derivatives

a) Primary propargyl alcohol



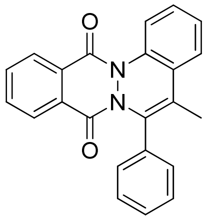
To a round bottom flask was added $Pd(PPh_3)_2Cl_2$ and CuI. The flask was purged with N_2 for 5 minutes, and Et_3N was transferred via cannula under N_2. The aryl halide was then added and the mixture was allowed to stir for 10 minute, and followed by addition of prop-2-yn-1-ol. The reaction mixture was stirred at room temperature or heated as necessary, and the reaction progress monitored by TLC. Upon completion, the crude mixture was filtered through a medium frit, the solid residue washed with Et_3N and ethyl acetate, and the combined organics were concentrated under reduced pressure. Purification via flash column chromatography yielded the desired aryl propargyl alcohols.[4]

b) Secondary and tertiary propargyl alcohol[5]



Under nitrogen atmosphere *n*-BuLi (0.12 mL, 2.5M in hexane) was added into a solution of an alkyne (0.35 mmol) in 3 ml of dry THF at -78 °C . After the mixture was stirred for 1h at the same temperature, an aldehyde or ketone (1 equiv in 4 mL THF) was added and the reaction mixture was stirred for additional 3h in room temperature. After completion of the reaction analyzed by TLC, the solvent was removed in vacuo. The reaction mixture was diluted with EtOAc, and the combined organic layers were washed with brine. After the organic layer was dried with anhydrous Na_2SO_4, the solvent was removed under reduced pressure. The residue was purified by silica gel chromatography or by crystallization with hexane and EtOAc to give propargylic alcohol.

NMR Characterization Data



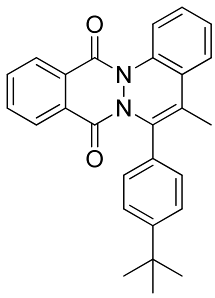
5-methyl-6-phenylphthalazino[2,3-*a*]cinnoline-8,13-dione 3aa

Yellow solid, Yield; 61.5 mg, 83%

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.50 (d, *J* = 8 Hz, 1H), 8.15 (d, *J* = 7.2 Hz, 1H), 8.04 (d, *J* = 8 Hz, 1H), 7.91 (t, *J* = 8 Hz, 1H), 7.83 (t, *J* = 8 Hz, 1H), 7.47 (d, *J* = 8 Hz, 1H), 7.37-7.25 (m, 6H), 2.15 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 157.85, 156.24, 136.30, 135.03, 133.98, 133.68, 129.74, 129.47, 128.92, 128.42, 128.27, 128.19, 127.85, 127.67, 126.24, 124.36, 121.05, 118.13, 14.55.

HRMS $[M + H]^+$ calculated for $C_{23}H_{16}N_2O_2$: 353.1290, found: 353.1285



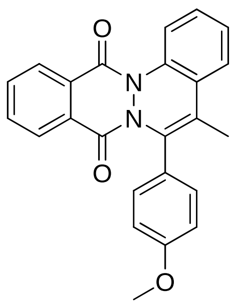
6-(4-(tert-butyl)phenyl)-5-methylphthalazino[2,3-*a*]cinnoline-8,13-dione 3ab

Yellow solid, Yield; 68.7 mg, 80%

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.39 (d, *J* = 8 Hz, 1H), 8.06 (d, *J* = 8 Hz, 1H), 7.93 (d, *J* = 8 Hz, 1H), 7.79 (t, *J* = 8 Hz, 1H), 7.74 (t, *J* = 8 Hz, 1H), 7.35 (d, *J* = 8 Hz, 1H), 7.27-7.05 (m, 6H), 2.05 (s, 3H), 1.24 (s, 12H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 157.92, 156.27, 136.37, 135.08, 133.97, 133.60, 130.86, 129.81, 129.50, 128.54, 128.41, 128.12, 127.86, 127.81, 126.18, 125.08, 124.39, 120.93, 117.96, 34.69, 31.28, 14.68.

HRMS $[M + H]^+$ calculated for $C_{27}H_{24}N_2O_2$: 409.1916, found: 409.1911



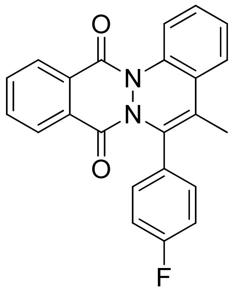
6-(4-methoxyphenyl)-5-methylphthalazino[2,3-*a*]cinnoline-8,13-dione 3ac

Yellow solid, Yield; 62.7 mg, 78%

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.39 (d, *J* = 8 Hz, 1H), 8.07 (d, *J* = 8 Hz, 1H), 7.92 (d, *J* = 8 Hz, 1H), 7.81-7.77 (t, *J* = 8 Hz, 1H), 7.74-7.70 (t, *J* = 8 Hz, 1H), 7.35-7.21 (m, 3H), 7.08 (d, *J* = 8Hz, 2H), 6.80 (d, *J* = 8Hz, 2H), 3.73 (s, 3H), 2.04 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 159.28, 157.90, 156.32, 136.30, 134.91, 133.96, 133.63, 130.19, 129.77, 129.47, 128.39, 128.06, 127.86, 127.81, 126.22, 126.11, 124.30, 120.52, 118.09, 113.68, 55.16, 14.57.

HRMS $[M + Na]^+$ calculated for $C_{24}H_{18}N_2O_3$: 405.1215, found: 405.1210



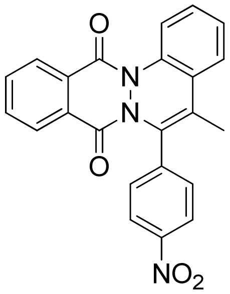
6-(4-fluorophenyl)-5-methylphthalazino[2,3-*a*]cinnoline-8,13-dione 3ad

Yellow solid, Yield; 67.7 mg, 87%

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.39 (d, *J* = 8 Hz, 1H), 8.05 (d, *J* = 8 Hz, 1H), 7.93 (d, *J* = 8 Hz, 1H), 7.81 (t, *J* = 8 Hz, 1H), 7.74 (t, *J* = 8 Hz, 1H), 7.35 (d, *J* = 8 Hz, 1H), 7.27-7.12 (m, 4H), 6.98 (t, *J* = 8 Hz. 2H), 2.02 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 162.0 (d, *J* = 247.0 Hz, C-F coupling), 157.84, 156.23, 136.30, 134.04 (d, *J* = 7 Hz, C-F coupling), 133.80, 133.74 (d, *J* = 8 Hz, C-F coupling), 129.93 (d, *J* = 4Hz, C-F coupling), 129.60, 129.44, 128.44 (d, *J* = 6Hz, C-F coupling), 127.80, 127.45, 126.30, 124.38, 121.35, 118.14, 115.44 (d, *J* = 13 Hz, C-F coupling), 14.53.

HRMS $[M + H]^+$ calculated for $C_{23}H_{15}FN_2O_2$: 371.1196, found: 371.1201



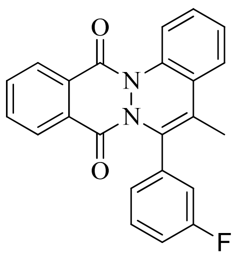
5-methyl-6-(4-nitrophenyl)phthalazino[2,3-*a*]cinnoline-8,13-dione 3ae

Yellow solid, Yield; 76.9 mg, 92%

1H NMR (400 MHz, $CDCl_3$) δ 8.41 (d, *J* = 8 Hz, 1H), 8.32 (d, *J* = 8 Hz, 1H), 8.06 (d, *J* = 8 Hz, 1H), 7.92-7.84 (m, 2H), 7.80 (t, *J* = 8 Hz, 1H), 7.36-7.30 (m, 2H), 7.24-7.18 (m, 2H), 7.00 (d, *J* = 4Hz, 1H), 4.82 (s, 2H), 2.03 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 157.75, 156.22, 147.19, 140.81, 136.36, 134.33, 134.14, 132.54, 129.73, 129.43, 129.21, 129.17, 128.66, 127.87, 126.74, 126.41, 124.64, 123.65, 123.30, 118.11, 14.63.

HRMS $[M + H]^+$ calculated for $C_{23}H_{15}N_3O_4$: 398.1141, found: 398.1129



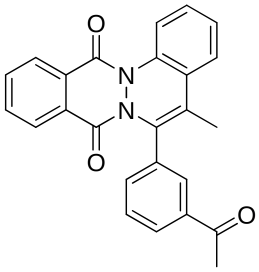
6-(3-fluorophenyl)-5-methylphthalazino[2,3-*a*]cinnoline-8,13-dione 3af

Yellow solid, Yield; 66.2 mg, 85%

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.40 (d, *J* = 8 Hz, 1H), 8.06 (d, *J* = 8 Hz, 1H), 7.94 (d, *J* = 8 Hz, 1H), 7.83-7.79 (t, *J* = 8 Hz, 1H), 7.75-7.71 (t, *J* = 8 Hz, 1H), 7.37-7.20 (m, 4H), 6.97-6.87 (m, 3H), 2.05 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 162.48(d, *J* = 245 Hz, C-F coupling), 157.83, 156.23, 136.35, 136.17 (d, *J* = 8 Hz, C-F coupling), 134.12, 133.85, 133.60, 129.73 (d, *J* = 9 Hz, C-F coupling), 129.49 (d, *J* = 9 Hz, C-F coupling), 128.59, 128.51, 127.85, 127.29, 126.29, 124.69, 124.48, 121.83, 118.09, 116.05(d, *J* = 22 Hz, C-F coupling), 115.32(d, *J* = 21 Hz, C-F coupling), 14.57.

HRMS $[M + H]^+$ calculated for $C_{23}H_{15}FN_2O_2$: 371.1196, found: 371.1211



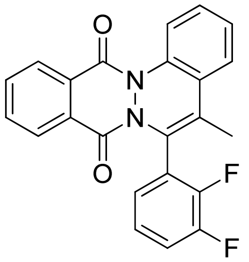
6-(3-acetylphenyl)-5-methylphthalazino[2,3-*a*]cinnoline-8,13-dione 3ag

Yellow solid, Yield; 63.8 mg, 77%

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.40 (d, *J* = 8 Hz, 1H), 8.02 (d, *J* = 8 Hz, 1H), 7.95(d, *J* = 8 Hz, 1H), 7.84-7.77 (m, 3H), 7.73-7.69 (t, *J* = 8 Hz, 1H), 7.40-7.21 (m, 5H), 2.47 (s, 3H), 2.04 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 197.46, 157.83, 156.21, 137.07, 136.34, 134.65, 134.08, 134.00, 133.87, 133.38, 129.49, 128.72, 128.61, 128.55, 128.51, 128.22, 127.76, 127.26, 126.31, 124.42, 121.88, 118.17, 26.59, 14.53.

HRMS $[M + H]^+$ calculated for $C_{25}H_{18}N_2O_3$: 395.1396, found: 395.1401



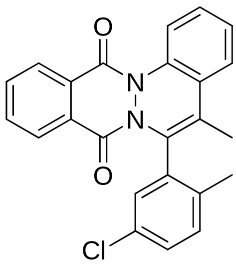
6-(2,3-difluorophenyl)-5-methylphthalazino[2,3-*a*]cinnoline-8,13-dione 3ah

Yellow solid, Yield; 61.2 mg, 75%

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.38 (d, *J* = 8 Hz, 1H), 8.06 (d, *J* = 8 Hz, 1H), 7.94 (d, *J* = 8 Hz, 1H), 7.81 (t, *J* = 8 Hz, 1H), 7.74 (t, *J* = 8 Hz, 1H), 7.38 (d, *J* = 8 Hz, 1H), 7.30 (t, *J* = 8 Hz, 1H), 7.23(t, *J* = 8 Hz, 1H), 7.08-6.95 (m, 3H), 2.02 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 157.70, 155.73, 151.76 (d, *J* = 12 Hz, C-F coupling), 149.28 (d, *J* = 12 Hz, C-F coupling), 136.36, 134.01, 133.84, 129.54, 129.07, 128.88, 128.43, 127.81, 126.98, 126.29, 125.92, 124.44, 123.82, 123.77, 118.53, 117.46 (d, *J* = 18 Hz, C-F coupling), 14.49.

HRMS $[M + H]^+$ calculated for $C_{23}H_{14}F_2N_2O_2$: 389.1102, found: 389.1081



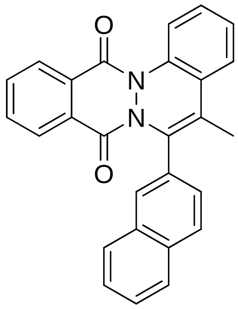
6-(5-chloro-2-methylphenyl)-5-methylphthalazino[2,3-*a*]cinnoline-8,13-dione 3ai

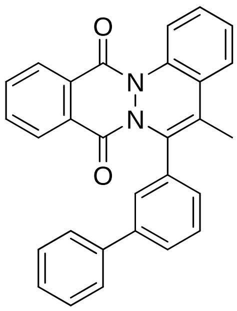
Yellow solid, Yield; 61.4 mg, 73%

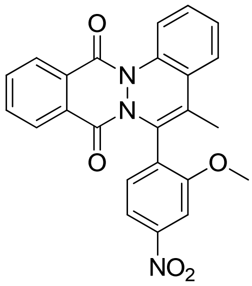
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.37 (d, *J* = 8 Hz, 1H), 8.05 (d, *J* = 8 Hz, 1H), 7.97-7.94 (m, 1H), 7.92 (s, 1H), 7.84-7.83 (m, 1H), 7.81 (t, *J* = 8 Hz, 1H), 7.73 (t, *J* = 8 Hz, 1H), 7.36 (d, *J* = 8 Hz, 1H), 7.29-7.21 (m, 2H), 7.13 (br, 1H), 7.05 (d, *J* = 8 Hz, 1H), 2.09 (s, 3H), 1.88 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 157.93, 155.45, 136.10, 136.01, 134.07, 133.81, 131.37, 131.16, 129.05, 128.62, 128.49, 128.39, 127.86, 127.10, 126.35, 125.71, 124.07, 118.66, 19.36, 14.03.

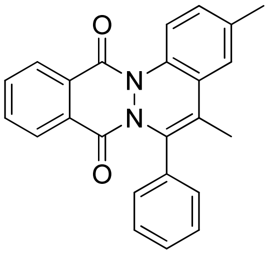
HRMS $[M + H]^+$ calculated for $C_{24}H_{17}ClN_2O_2$: 401.1057, found: 401.1030

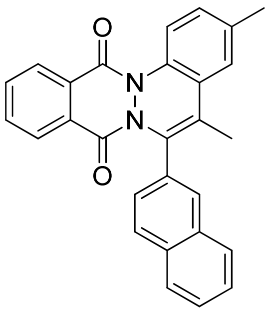
	**5-methyl-6-(naphthalen-2-yl)phthalazino[2,3-*a*]cinnoline-8,13-dione 3aj** Yellow solid, Yield; 64.3 mg, 76% **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.50 (d, *J* = 8 Hz, 1H), 8.09-8.03 (m, 2H), 7.93-7.97 (m, 2H), 7.82-7.76 (m, 4H), 7.47-7.29 (m, 6H), 2.17 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 157.91, 156.29, 136.34, 136.03, 134.95, 134.05, 133.75, 132.93, 131.40, 129.65, 129.50, 128.47, 128.36, 128.22, 127.93, 127.86, 127.83, 127.65, 126.51, 126.36, 126.29, 125.73, 124.44, 121.59, 118.12, 14.68. **HRMS** $[M + H]^+$ calculated for $C_{27}H_{18}N_2O_2$: 403.1447, found: 403.1441

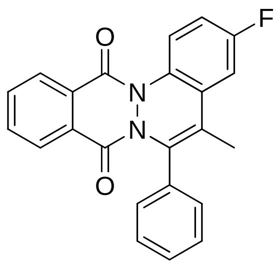
	**6-([1,1'-biphenyl]-3-yl)-5-methylphthalazino[2,3-*a*]cinnoline-8,13-dione 3ak** Yellow solid, Yield; 70.2 mg, 78% **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.40 (d, *J* = 8 Hz, 1H), 8.07 (d, *J* = 8 Hz, 1H), 7.95 (d, *J* = 8 Hz, 1H), 7.81-7.78 (t, *J* = 8 Hz, 1H), 7.74-7.70 (t, *J* = 8 Hz, 1H), 7.45-7.23 (m, 11H), 7.13 (d, *J* = 8 Hz, 1H), 2.01(s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 157.89, 156.33, 141.17, 140.67, 136.36, 134.96, 134.49, 134.02, 133.73, 129.72, 129.49, 128.72, 128.60, 128.48, 128.34, 127.85, 127.74, 127.63, 127.42, 127.22, 127.13, 126.26, 124.41, 121.33, 118.12, 14.69. **HRMS** $[M + H]^+$ calculated for $C_{29}H_{20}N_2O_2$:429.1603, found: 429.1583

	**6-(2-methoxy-4-nitrophenyl)-5-methylphthalazino[2,3-*a*]cinnoline-8,13-dione 3al** Yellow solid, Yield; 62.9 mg, 70% **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.41 (d, *J* = 8 Hz, 1H), 8.05(d, *J* = 8 Hz, 1H), 7.94 (d, *J* = 8 Hz, 1H), 7.88 (d, *J* = 8 Hz, 1H), 7.83-7.79 (t, *J* = 8Hz, 1H), 7.74-7.71 (t, *J* = 8 Hz, 1H), 7.54 (s, 1H), 7.48 (d, *J* = 8 Hz, 1H), 7.40 (d, *J* = 8 Hz, 1H), 7.32-7.28 (t, *J* = 8 Hz, 1H), 7.25-7.21 (t, *J* = 8 Hz, 1H), 3.23 (s, 3H), 2.05 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 157.43, 156.01, 155.87, 148.54, 136.10, 133.83, 133.77, 132.43, 131.08, 129.63, 129.24, 128.84, 128.46, 128.09,

	127.65, 127.48, 126.36, 125.69, 124.44, 123.30, 119.20, 115.74, 105.43, 55.41, 14.79. **HRMS** $[M + H]^+$ calculated for $C_{24}H_{17}N_3O_5$: 428.1246, found: 428.1219

	**3,5-dimethyl-6-phenylphthalazino[2,3-*a*]cinnoline-8,13-dione 3ba** Yellow solid, Yield; 65.5 mg, 85% **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.38 (d, *J* = 8 Hz, 1H), 8.05 (d, *J* = 8 Hz, 1H), 7.84-7.69 (m, 3H), 7.28-7.23 (m, 3H), 7.15-7.14 (m, 3H), 7.07 (d, *J* = 8 Hz, 1H), 2.32 (s, 3H), 2.04 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 156.51, 155.11, 136.48, 136.09, 134.92, 134.54, 133.62, 133.26, 128.94, 128.36, 128.23, 126.67, 124.66, 121.01, 117.39, 21.19, 14.50. **HRMS** $[M + H]^+$ calculated for $C_{24}H_{18}N_2O_2$: 367.1447, found: 367.1473

	**3,5-dimethyl-6-(naphthalen-2-yl)phthalazino[2,3-*a*]cinnoline-8,13-dione 3bj** Yellow solid, Yield; 70.05 mg, 80% **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.41 (d, *J* = 8 Hz, 1H), 8.00 (d, *J* = 8 Hz, 1H), 7.87 (d, *J* = 8 Hz, 1H), 7.82-7.78 (t, *J* = 8 Hz, 1H), 7.75-7.67 (m, 5H), 7.40-7.38 (t, *J* = 4 Hz, 2H), 7.20-7.19 (m, 2H), 7.09 (d, *J* = 8 Hz, 1H), 2.34 (s, 3H), 2.07(s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 157.71, 156.30, 136.04, 134.81, 133.89, 133.68, 132.93, 132.91, 131.53, 129.62, 129.56, 128.95, 128.38, 128.21, 127.88, 127.82, 127.43, 126.46, 126.32, 124.81, 121.58, 117.99, 21.23, 14.68. **HRMS** $[M + Na]^+$ calculated for $C_{28}H_{20}N_2O_2$: 439.1422, found: 417.1417



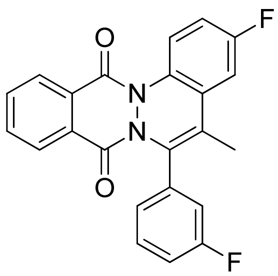
3-fluoro-5-methyl-6-phenylphthalazino[2,3-*a*]cinnoline-8,13-dione 3ca

Yellow solid, Yield; 63.8 mg, 82%

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.38 (d, *J* = 8 Hz, 1H), 8.04 (d, *J* = 8 Hz, 1H), 7.93-7.90 (m, 1H), 7.82 (t, *J* = 8 Hz, 1H), 7.73 (t, *J* = 8 Hz, 1H), 7.26 (br, 3H), 7.15 (d, *J* = 8 Hz, 1H), 7.04 (d, *J* = 8 Hz. 1H), 7.96 (t, *J* = 8 Hz, 1H), 2.01 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 160.44 (d, *J* = 244 Hz, C-F coupling), 157.69, 156.33, 136.25, 134.07, 133.87, 133.58, 132.10, 132.07, 130.03, 129.95, 129.63, 129.32, 128.86, 128.53, 128.44, 128.29, 127.90, 120.22, 120.01 and 119.99 (F coupling), 114.90, 114.67, 111.12 and 110.88 (F coupling), 14.51.

HRMS $[M + H]^+$ calculated for $C_{23}H_{15}FN_2O_2$: 371.1196, found: 371.1121



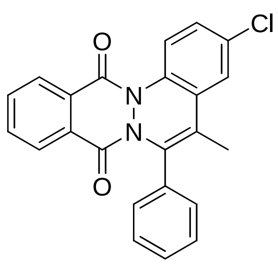
3-fluoro-6-(3-fluorophenyl)-5-methylphthalazino[2,3-*a*]cinnoline-8,13-dione 3cf

Yellow solid, Yield; 69.4 mg, 85%

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.38 (d, *J* = 8 Hz, 1H), 8.05 (d, *J* = 8 Hz, 1H), 7.94 (dd, *J* = 8 Hz, 1H), 7.83-7.79 (t, *J* = 8 Hz, 1H), 7.76-7.72 (t, *J* = 8 Hz, 1H), 7.27-6.85 (m, 6H), 2.02 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 162.69 (d, *J* = 208 Hz, C-F coupling), 160.2 (d, *J* = 207 Hz, C-F coupling), 157.66, 156.28, 135.74, 134.88, 134.17, 134.00, 132.20, 132.17, 129.87, 129.79, 129.65, 129.56, 129.46, 129.33, 128.52, 127.89, 124.67, 120.72, 120.70, 120.21, 120.13, 116.12 and 115.91 (F coupling), 115.68, 115.47, 115.21, 114.98, 111.22 and 110.98 (F coupling), 14.50.

HRMS $[M + H]^+$ calculated for $C_{23}H_{14}F_2N_2O_2$: 389.1102, found: 389.1128



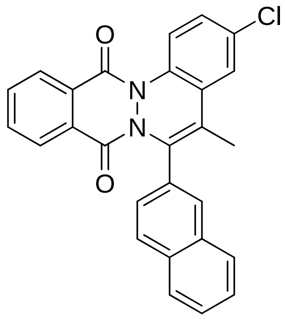
3-chloro-5-methyl-6-phenylphthalazino[2,3-*a*]cinnoline-8,13-dione 3da

Yellow solid, Yield; 65.0 mg, 80%

^{1}H NMR (400 MHz, $CDCl_3$):) δ 8.38 (d, *J* = 8 Hz, 1H), 8.05 (d, *J* = 8 Hz, 1H), 7.89 (d, *J* = 8 Hz, 2H), 7.82-7.78 (t, *J* = 8 Hz, 1H), 7.74-7.70 (t, *J* = 8 Hz, 1H), 7.30-7.13 (m, 7H), 2.02 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 157.79, 156.24, 136.22, 134.69, 134.16, 133.86, 133.60, 131.67, 129.65, 129.48, 129.25, 128.85, 128.53, 128.46, 128.28, 127.98, 127.93, 124.23, 119.92, 119.62, 14.48.

HRMS $[M + H]^+$ calculated for $C_{23}H_{15}ClN_2O_2$: 387.0900, found: 387.0929



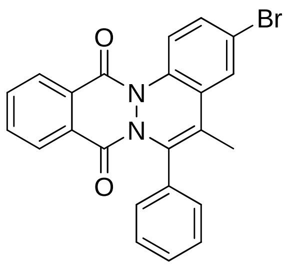
3-chloro-5-methyl-6-(naphthalen-2-yl)phthalazino[2,3-*a*]cinnoline-8,13-dione 3dj

Yellow solid, Yield; 67.0 mg, 73%

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.41 (d, *J* = 8 Hz, 1H), 8.00 (d, *J* = 8 Hz, 1H), 7.97-7.95 (m, 2H), 7.92 (d, *J* = 8 Hz, 1H), 7.85-7.83 (m, 2H), 7.82 (d, *J* = 8 Hz, 1H), 7.72-7.70 (m, 2H), 7.76 (s, 1H), 7.41 (t, *J* = 4 Hz, 1H), 7.33 (s, 1H), 7.23-7.20 (m, 1H), 2.06 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 162.78, 157.85, 156.29, 136.03, 134.74, 134.21, 133.92, 133.02, 132.89, 131.70, 131.36, 131.01,129.47, 129.29, 128.51, 128.23, 128.05, 127.93, 127.85, 126.67, 126.46, 126.08, 125.72, 124.29, 120.42, 119.62, 14.60.

HRMS $[M + H]^+$ calculated for $C_{27}H_{17}ClN_2O_2$: 437.1057, found: 437.1051



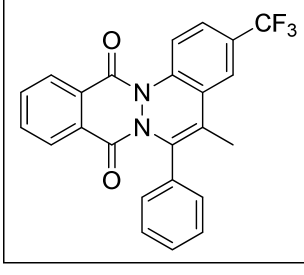
3-bromo-5-methyl-6-phenylphthalazino[2,3-*a*]cinnoline-8,13-dione 3ea

Yellow solid, Yield; 75.1 mg, 83%

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.37 (d, *J* = 8 Hz, 1H), 8.05 (d, *J* = 8 Hz, 1H), 7.82-7.78 (m, 2H), 7.74 (t, *J* = 8 Hz, 1H), 7.45 (s, 1H), 7.35 (d, *J* = 8 Hz, 1H), 7.27-7.26 (m, 3H), 7.14-7.13 (m, 2H), 2.01 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 157.78, 156.21, 136.26, 135.25, 134.16, 133.85, 133.60, 130.91, 129.78, 129.66, 129.26, 128.86, 128.52, 128.47, 128.27, 127.93, 127.17, 119.85, 119.81, 119.43, 14.48.

HRMS $[M + H]^+$ calculated for $C_{23}H_{15}BrN_2O_2$: 431.0395, found: 431.0390



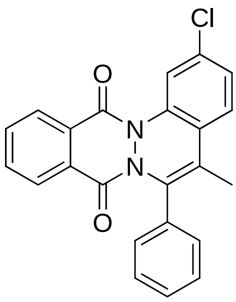
5-methyl-6-phenyl-3-(trifluoromethyl)phthalazino[2,3-*a*]cinnoline-8,13-dione 3fa

Yellow solid, Yield; 65.4 mg, 74%

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.39 (d, *J* = 8 Hz, 1H), 8.06-8.02 (t, *J* = 8 Hz, 2H), 7.82 (d, *J* = 8 Hz, 1H), 7.76-7.72 (t, *J* = 8 Hz, 1H), 7.56 (br s, 1H) 7.50 (d, *J* = 8 Hz, 1H), 7.29-7.15 (m, 5H), 2.07 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 158.14, 136.51, 136.01, 134.42, 133.93, 133.49, 129.71, 129.11, 128.84, 128.63, 128.58, 128.33, 128.02, 125.71, 125.16, 119.96, 118.53, 14.47.

HRMS $[M + H]^+$ calculated for $C_{24}H_{15}F_3N_2O_2$: 421.1164, found: 421.1192



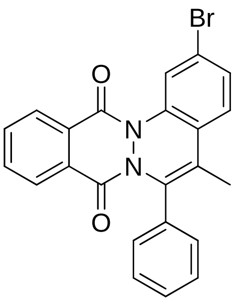
2-chloro-5-methyl-6-phenylphthalazino[2,3-*a*]cinnoline-8,13-dione 3ga

Yellow solid, Yield; 71.5 mg, 88%

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.39 (d, *J* = 8 Hz, 1H), 8.05 (d, *J* = 8 Hz, 1H), 7.97 (s, 1H), 7.83-7.79 (t, *J* = 8 Hz, 1H), 7.75-7.71 (t, *J* = 8 Hz, 1H), 7.30-7.14 (m, 7H), 2.03 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 157.94, 156.18, 137.09, 135.21, 134.29, 133.90, 133.84, 133.69, 129.65, 129.16, 128.84, 128.53, 128.44, 128.26, 127.95, 126.39, 126.22, 125.32, 120.47, 118.40, 14.53.

HRMS $[M + H]^+$ calculated for $C_{23}H_{15}ClN_2O_2$: 387.0900, found: 387.0929



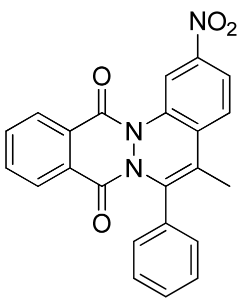
2-bromo-5-methyl-6-phenylphthalazino[2,3-*a*]cinnoline-8,13-dione 3ha

Yellow solid, Yield; 74.2 mg, 82%

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.38 (d, *J* = 8 Hz, 1H), 8.12 (s, 1H), 8.05 (d, *J* = 8 Hz, 1H), 7.83-7.79 (t, *J* = 8 Hz, 1H), 7.75-7.71 (t, *J* = 8 Hz, 1H), 7.34-7.14 (m, 7H), 2.03 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 157.93, 156.17, 137.17, 135.37, 134.29, 133.85, 133.68, 129.65, 129.32, 129.16, 128.83, 128.53, 128.46, 128.26, 127.95, 126.67, 125.53, 121.74, 121.17, 120.50, 14.47.

HRMS $[M + H]^+$ calculated for $C_{23}H_{15}BrN_2O_2$: 431.0395, found: 431.0415



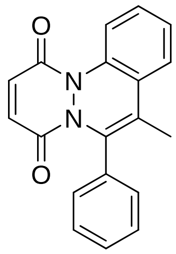
5-methyl-2-nitro-6-phenylphthalazino[2,3-*a*]cinnoline-8,13-dione 3ia

Yellow solid, Yield; 66.8 mg, 80%

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.79(d, *J* = 4 Hz, 1H), 8.42 (d, *J* = 8 Hz, 1H), 8.06 (d, *J* = 8 Hz, 2H), 7.86-7.82 (t, *J* = 8 Hz, 1H), 7.78-7.74 (t, *J* = 8 Hz, 1H), 7.46 (d, *J* = 8 Hz, 1H), 7.32-7.29 (m, 3H), 7.18-7.15 (m, 2H), 2.07 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 158.00, 156.24, 146.87, 138.59, 136.79, 134.59, 134.21, 133.76, 133.14, 129.56, 128.97, 128.77, 128.44, 128.08, 124.75, 121.20, 119.39, 113.89, 14.56.

HRMS $[M + H]^+$ calculated for $C_{23}H_{15}N_3O_4$: 398.1141, found: 398.1168



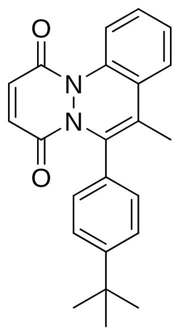
7-methyl-6-phenylpyridazino[1,2-*a*]cinnoline-1,4-dione 5aa

Red solid, Yield; 54.0 mg, 85%

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08 (d, *J* = 8 Hz, 1H), 7.37-7.23 (m, 6H), 7.19 (d, *J* = 8 Hz, 1H), 6.99 (d, *J* = 8 Hz, 1H), 6.75 (d, *J* = 12 Hz, 1H), 2.01 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 156.70, 155.05, 135.58, 135.35, 134.94, 134.64, 133.46, 128.92, 128.44, 128.34, 128.27, 126.87, 126.66, 124.33, 121.03, 117.52, 14.50.

HRMS $[M + H]^+$ calculated for $C_{19}H_{14}N_2O_2$: 303.1134, found:303.1128



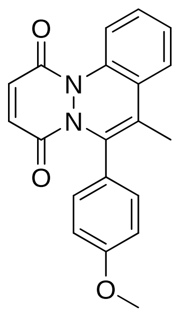
6-(4-(tert-butyl)phenyl)-7-methylpyridazino[1,2-*a*]cinnoline-1,4-dione 5ab

Red solid, Yield; 62.5 mg, 83%

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 (d, *J* = 8 Hz, 1H), 7.36-7.30 (m, 3H), 7.26-7.18 (m, 2H), 7.09 (d, *J* = 8 Hz, 1H), 6.99 (d, *J* = 12 Hz, 1H), 6.76 (d, *J* = 12 Hz, 1H), 2.01 (s, 3H), 1.26 (s, 12H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 156.80, 155.11, 151.29, 135.62, 135.38, 134.84, 134.75, 130.30, 128.55, 128.17, 127.08, 126.61, 125.16, 124.33, 120.83, 117.42, 31.29, 14.63.

HRMS $[M + Na]^+$ calculated for $C_{23}H_{22}N_2O_2$: 381.1579, found: 381.1573



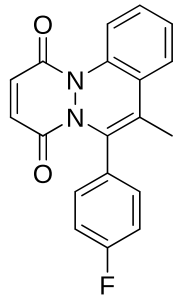
6-(4-methoxyphenyl)-7-methylpyridazino[1,2-*a*]cinnoline-1,4-dione 5ac

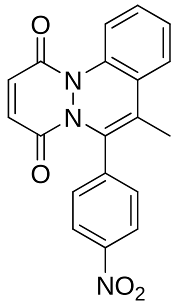
Red solid, Yield; 57.3 mg, 82%

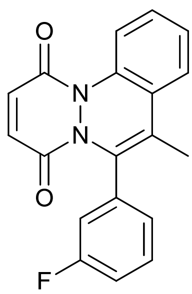
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 (d, *J* = 8 Hz, 1H), 7.35 (d, *J* = 8 Hz, 1H), 7.27-7.20 (m, 2H), 7.11 (d, *J* = 8 Hz, 1H), 6.99 (d, *J* = 12 Hz, 1H), 6.85 (d, *J* = 8 Hz, 1H), 6.75 (d, *J* = 12 Hz, 1H), 3.75 (s, 3H), 2.00 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 159.47, 156.75, 155.13, 135.62, 135.33, 134.83, 134.60, 130.24, 128.12, 127.06, 126.61, 125.59, 124.25, 120.56, 117.49, 113.75, 55.23, 14.48.

	HRMS $[M + H]^+$ calculated for $C_{20}H_{16}N_2O_3$: 333.1239, found: 333.1209

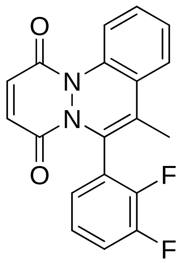
	**6-(4-fluorophenyl)-7-methylpyridazino[1,2-*a*]cinnoline-1,4-dione 5ad** Red solid, Yield; 57.2 mg, 85% **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.07 (d, *J* = 8 Hz, 1H), 7.36 (d, *J* = 8 Hz, 1H), 7.29 (m, 7H), 6.74 (d, *J* = 8 Hz, 1H), 1.99 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 162.37 (d, *J* = 247 Hz, C-F coupling), 156.66, 155.00, 135.60, 135.29, 135.05, 133.64, 130.83 and 130.74 (F coupling), 129.43, 129.40, 128.48, 126.71 and 126.66 (F coupling), 124.34, 121.35, 117.53, 115.59 and 115.37 (F coupling), 14.48. **HRMS** $[M + H]^+$ calculated for $C_{19}H_{13}FN_2O_2$: 321.1039, found: 321.1011

	**7-methyl-6-(4-nitrophenyl)pyridazino[1,2-*a*]cinnoline-1,4-dione 5ae** Red solid, Yield; 68.6 mg, 94% **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.20 (d, *J* = 8 Hz, 2H), 8.11 (d, *J* = 8 Hz, 1H), 7.40-7.26 (m, 5H), 7.04 (d, *J* = 12 Hz, 1H), 6.76 (d, *J* = 8 Hz, 1H), 2.03 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 156.53, 154.84, 147.34, 140.28, 135.70, 135.52, 135.01, 132.12, 129.79, 129.21, 126.82, 125.99, 124.58, 123.64, 123.08, 117.48, 14.54. **HRMS** $[M + H]^+$ calculated for $C_{19}H_{13}N_3O_4$: 348.0984, found: 348.0101

	**6-(3-fluorophenyl)-7-methylpyridazino[1,2-*a*]cinnoline-1,4-dione 5af** Red solid, Yield; 53.9mg, 80% **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.07 (d, *J* = 8 Hz, 1H), 7.37 (d, *J* = 8 Hz, 1H), 7.31-7.21 (m, 3H), 7.00-6.88 (m, 4H), 6.75 (d, *J* = 8 Hz, 1H), 2.01 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 161.50 (d, *J* = 246 Hz), 156.63, 154.97, 135.66, 135.64, 135.56, 135.24 and 135.14 (F coupling), 133.25, 133.23, 129.86 and 129.77 (F coupling), 128.64, 126.69, 126.53, 124.72, 124.69 and 124.43 (F coupling), 121.73, 117.49, 116.11 (d, *J* = 22 Hz), 115.46 (d, *J* = 21

Hz), 14.50.

HRMS [M + H]$^+$ calculated for $C_{19}H_{13}FN_2O_2$: 321.1039, found: 321.1022



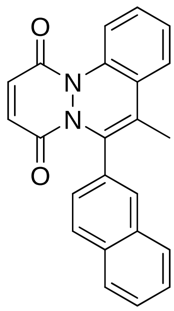
6-(2,3-difluorophenyl)-7-methylpyridazino[1,2-*a*]cinnoline-1,4-dione 5ah

Red solid, Yield; 54.7 mg, 77%

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08 (d, *J* = 8 Hz, 1H), 7.39 (d, *J* = 8 Hz, 1H), 7.33 (t, *J* = 8 Hz, 1H), 7.26 (t, *J* = 8 Hz, 1H), 7.12-6.97 (m, 4H), 6.76 (d, *J* = 8 Hz, 1H), 2.01 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 156.55, 154.58, 151.77, 149.31 and 149.08 (F coupling), 146.61 and 146.48 (F coupling), 135.64, 135.35, 134.73, 128.95, 127.83, 126.71 and 126.06 (F coupling), 124.41, 123.98, 123.93, 123.91, 123.86, 123.66, 123.18 and 123.07 (F coupling), 117.91, 117.72 and 117.55 (F coupling), 14.51.

HRMS [M + H]$^+$ calculated for $C_{19}H_{12}F_2N_2O_2$: 339.0945, found: 339.0955



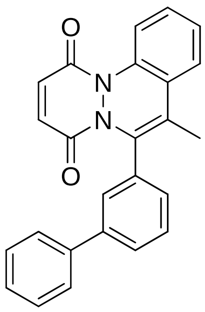
7-methyl-6-(naphthalen-2-yl)pyridazino[1,2-*a*]cinnoline-1,4-dione 5aj

Red solid, Yield; 59.2 mg, 80%

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.11 (d, *J* = 8 Hz, 1H), 7.79-7.74 (m, 3H), 7.67 (s, 1H), 7.44-7.24 (m, 6H), 7.03 (d, *J* = 12 Hz, 1H), 6.75 (d, *J* = 8 Hz, 1H), 2.05 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 156.75, 155.08, 135.63, 135.35, 135.05, 134.59, 133.00, 132.90, 130.87, 128.42, 128.23, 128.00, 127.84, 126.87, 126.71, 126.66, 126.49, 126.28, 124.39, 121.53, 117.52, 14.62.

HRMS [M + Na]$^+$ calculated for $C_{23}H_{16}N_2O_2$: 375.1109, found: 353.1104



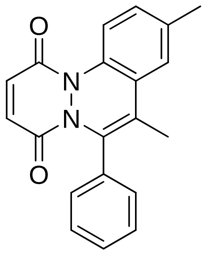
6-([1,1'-biphenyl]-3-yl)-7-methylpyridazino[1,2-*a*]cinnoline-1,4-dione 5ak

Red solid, Yield; 59.6 mg, 75%

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01 (d, *J* = 8 Hz, 1H), 7.51(d, *J* = 8 Hz, 3H), 7.41-7.16 (m, 9H), 7.00 (d, *J* = 8 Hz, 1H), 6.76 (d, *J* = 8 Hz, 1H), 2.06 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 156.72, 155.08, 141.28, 140.61, 135.66, 135.33, 135.04, 134.56, 134.01, 128.81, 128.67, 128.41, 127.86, 127.63, 127.55, 127.25, 126.83, 126.67, 124.37, 121.28, 117.50, 14.62.

HRMS $[M + H]^+$ calculated for $C_{25}H_{18}N_2O_2$: 379.1447, found: 379.1119



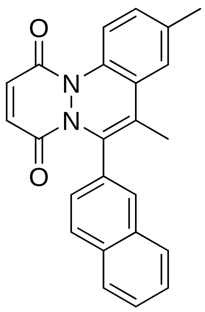
7,9-dimethyl-6-phenylpyridazino[1,2-*a*]cinnoline-1,4-dione 5ba

Red solid, Yield; 53.9 mg, 81%

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 (d, *J* = 8 Hz, 1H), 7.33-7.26 (m, 3H), 7.18-7.15 (m, 2H), 7.08 (d, *J* = 8 Hz, 1H), 6.98 (d, *J* = 12 Hz, 1H), 6.73 (d, *J* = 12 Hz, 1H), 2.32 (s, 3H), 1.99 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 156.51, 155.11, 136.48, 135.09, 134.92, 134.54, 133.62, 133.26, 128.94, 128.36, 128.23, 126.67, 124.66, 121.01, 117.39, 21.19, 14.50.

HRMS $[M + Na]^+$ calculated for $C_{20}H_{16}N_2O_2$: 339.1109, found: 339.1104



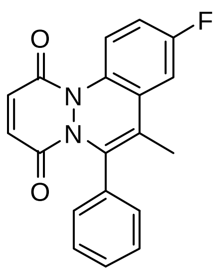
7,9-dimethyl-6-(naphthalen-2-yl)pyridazino[1,2-*a*]cinnoline-1,4-dione 5bj

Red solid, Yield; 60.1 mg, 78%

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02 (d, *J* = 8 Hz, 1H), 7.78-7.76 (m, 3H), 7.66 (s, 1H), 7.43-7.41 (m, 2H), 7.25 (d, *J* = 8 Hz, 1H), 7.18 (s, 1H), 7.11 (d, *J* = 8 Hz, 1H), 7.02 (d, *J* = 8 Hz, 1H), 6.73 (d, *J* = 8 Hz, 1H), 2.34 (s, 3H), 2.03 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 156.57, 155.14, 136.54, 135.09, 135.04, 134.44, 133.28, 132.98, 132.90, 131.01, 129.02, 128.38, 128.22, 127.95, 127.84, 126.65, 126.62, 126.45, 126.34, 124.73, 121.53, 117.39, 21.24, 14.63.

HRMS $[M + H]^+$ calculated for $C_{24}H_{18}N_2O_2$: 367.1447, found: 367.1441



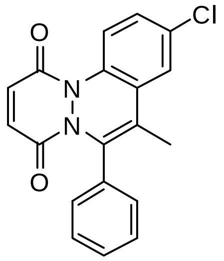
9-fluoro-7-methyl-6-phenylpyridazino[1,2-*a*]cinnoline-1,4-dione 5ca

Red solid, Yield; 50.5 mg, 75%

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08 (br m, 1H), 7.34-7.28 (m, 3H), 7.17 (d, *J* = 8 Hz, 2H), 7.03 (d, *J* = 8 Hz, 1H), 6.98-6.93 (m, 2H), 6.74 (d, *J* = 8 Hz, 1H), 1.97 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 160.57 (d, *J* = 245 Hz, C-F coupling), 156.45, 155.10, 135.91, 135.11 (d, *J* = 35 Hz, C-F coupling), 133.12, 131.53, 129.33, 129.25, 128.87, 128.67, 128.34, 120.01, 119.73 and 119.64 (F coupling), 114.86 (d, *J* = 23 Hz, C-F coupling), 110.90 (d, *J* = 24 Hz, C-F coupling), 14.43.

HRMS $[M + H]^+$ calculated for $C_{19}H_{13}FN_2O_2$: 321.1039, found: 321.1011



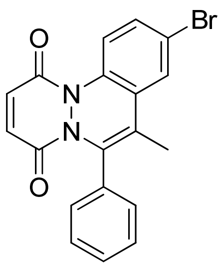
9-chloro-7-methyl-6-phenylpyridazino[1,2-*a*]cinnoline-1,4-dione 5da

Red solid, Yield; 54.4 mg, 77%

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 (d, *J* = 8 Hz, 1H), 7.34-7.28 (m, 4H), 7.23-7.15 (m, 3H), 6.98 (d, *J* = 8 Hz, 1H), 6.75 (d, *J* = 8 Hz, 1H), 1.98 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 156.56, 155.00, 135.81, 135.46, 134.87, 134.00, 133.09, 132.10, 128.85, 128.69, 128.36, 128.05, 124.18, 119.94, 119.03, 14.45.

HRMS $[M + H]^+$ calculated for $C_{19}H_{13}ClN_2O_2$: 337.0744, found: 337.0723



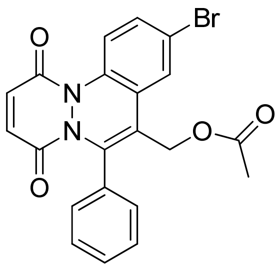
9-bromo-7-methyl-6-phenylpyridazino[1,2-*a*]cinnoline-1,4-dione 5ea

Red solid, Yield; 64 mg, 80%

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (d, *J* = 8 Hz, 1H), 7.45-7.15 (m, 7H), 6.98 (d, *J* = 8 Hz, 1H), 6.76 (d, *J* = 8 Hz, 1H), 1.98 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 156.56, 154.99, 135.81, 135.48, 134.87, 134.52, 133.06, 130.99, 128.98, 128.85, 128.70, 128.36, 127.14, 119.89, 119.86, 119.24, 14.46.

HRMS $[M + H]^+$ calculated for $C_{19}H_{13}BrN_2O_2$: 381.0239, found: 381.0233



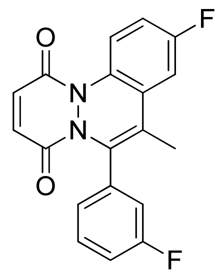
(9-bromo-1,4-dioxo-6-phenyl-1,4-dihydropyridazino[1,2-*a*]cinnolin-7-yl)methyl acetate 6ea

Red solid, Yield; 9.2 mg, 10%

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 (d, *J* = 8 Hz, 1H), 7.43-7.16 (m, 7H), 7.02 (d, *J* = 8 Hz, 1H), 6.77 (d, *J* = 12 Hz, 1H), 4.76 (s, 2H), 2.02 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 170.51, 156.27, 155.39, 141.21, 135.51, 135.25, 134.58, 131.46, 131.39, 129.69, 128.92, 128.62, 128.60, 127.00, 120.20, 119.89, 117.96, 59.91, 20.92.

HRMS $[M + Na]^+$ calculated for $C_{21}H_{15}BrN_2O_4$: 461.0113, found: 461.0129



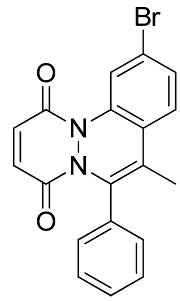
9-fluoro-6-(3-fluorophenyl)-7-methylpyridazino[1,2-*a*]cinnoline-1,4-dione 5cf

Red solid, Yield; 62.6 mg, 88%

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09 (dd, *J* = 8 Hz, 1H), 7.32-7.27 (m, 1H), 7.05-6.87 (m, 6H), 6.76 (d, *J* = 8 Hz, 1H), 1.98 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 162.69 (d, *J* = 208 Hz, C-F coupling), 160.23 (d, *J* = 207 Hz, C-F coupling), 156.66, 156.28, 135.74 (d, *J* = 6 Hz, C-F coupling), 134.88, 134.17, 134.00, 132.20, 132.17, 129.87, 129.79, 129.65, 129.56, 129.46 and 129.33 (F coupling), 128.52, 127.89, 124.67, 120.72, 120.70, 120.21 and 120.13 (F coupling) 116.12, 115.91, 115.68, 115.47 and 115.21 (F coupling), 114.98, 111.59 (d, J= 25 Hz, C-F coupling), 14.50.

HRMS $[M + H]^+$ calculated for $C_{19}H_{12}F_2N_2O_2$: 339.0945, found: 339.0924



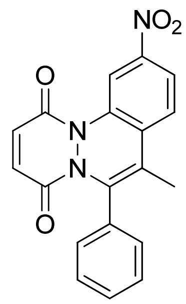
10-bromo-7-methyl-6-phenylpyridazino[1,2-*a*]cinnoline-1,4-dione 5ha

Red solid, Yield; 62.3 mg, 78%

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.26 (d, *J* = 8 Hz, 1H), 7.37-7.15 (m, 7H), 6.99 (d, *J* = 12 Hz, 1H), 6.76 (d, *J* = 12 Hz, 1H), 2.06 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 156.68, 154.89, 136.41, 135.63, 135.01, 134.78, 133.17, 129.75, 128.84, 128.61, 128.33, 125.89, 125.48, 121.85, 120.61, 120.47, 14.40.

HRMS $[M + H]^+$ calculated for $C_{19}H_{13}BrN_2O_2$: 381.0239, found: 381.0211



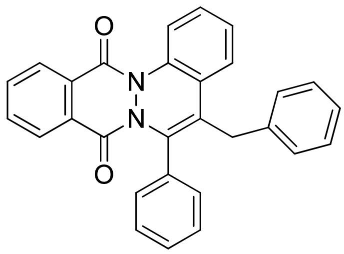
7-methyl-10-nitro-6-phenylpyridazino[1,2-*a*]cinnoline-1,4-dione 5ia

Red solid, Yield; 55.5 mg, 76%

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.93 (s, 1H), 8.09 (d, *J* = 8 Hz, 1H), 7.47 (d, *J* = 8 Hz, 1H), 7.35-7.18 (m, 5H), 7.04 (d, *J* = 8 Hz, 1H), 6.80 (d, *J* = 8 Hz, 1H), 2.03 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 156.61, 154.86, 146.79, 138.14, 136.02, 135.91, 134.92, 132.89, 132.59, 129.11, 128.76, 128.51, 124.77, 121.52, 119.41, 113.35, 14.51.

HRMS $[M + H]^+$ calculated for $C_{19}H_{13}N_3O_4$: 348.0984, found: 348.1011



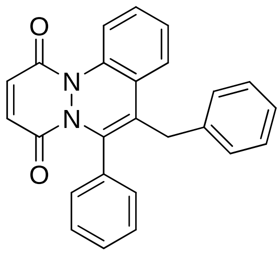
5-benzyl-6-phenylphthalazino[2,3-*a*]cinnoline-8,13-dione 7al

Yellow solid, Yield; 63.0 mg, 70%

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.41 (d, *J* = 8 Hz, 1H), 8.07 (d, *J* = 8 Hz, 1H), 7.93 (d, *J* = 8 Hz, 1H), 7.83-7.79 (t, *J* = 8 Hz, 1H), 7.75-7.71 (t, *J* = 8 Hz, 1H), 7.23-7.11 (m, 12H), 7.04-7.00 (t, *J* = 8 Hz, 1H), 3.83 (s, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 157.78, 156.44, 139.36, 137.20, 136.76, 134.02, 133.86, 133.79, 129.68, 129.54, 128.74, 128.56, 128.48, 128.33, 128.04, 127.90, 126.36, 126.33, 126.15, 125.33, 123.01, 118.26, 33.97.

HRMS $[M + H]^+$ calculated for $C_{29}H_{20}N_2O_2$: 429.1603, found: 429.1588



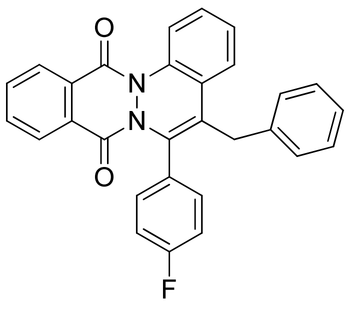
7-benzyl-6-phenylpyridazino[1,2-*a*]cinnoline-1,4-dione 8al

Red solid, yield; 59.6 mg, 75%

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08 (d, *J* = 8 Hz, 1H), 7.26 (m, 3H), 7.23-7.20 (m, 4H), 7.17-7.00 (m, 8H), 6.78 (d, *J* = 12 Hz, 1H), 3.79 (s, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 156.62, 155.25, 139.11, 136.72, 136.06, 135.31, 135.19, 133.33, 128.76, 128.49, 128.42, 127.97, 126.59, 126.44, 125.58, 125.33, 123.01, 117.62, 33.88.

HRMS $[M + H]^+$ calculated for $C_{25}H_{18}N_2O_2$: 379.1447, found: 379.1459



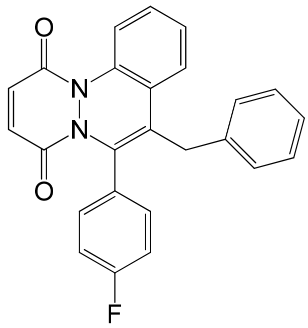
5-benzyl-6-(4-fluorophenyl)phthalazino[2,3-*a*]cinnoline-8,13-dione 7am

Yellow solid, Yield; 61.0 mg, 65%

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.41 (d, *J* = 8 Hz, 1H), 8.08 (d, *J* = 8 Hz, 1H), 7.93 (d, *J* = 8 Hz, 1H), 7.84-7.80 (t, *J* = 8 Hz, 1H), 7.77-7.73 (t, *J* = 8 Hz, 1H), 7.24-7.13 (m, 9H), 7.05-7.01 (t, *J* = 8 Hz, 1H), 6.91-6.87 (t, *J* = 8 Hz, 2H), 3.79 (s, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 157.77, 156.42, 139.14, 136.75, 136.15, 134.13 and 133.92 (F coupling), 130.29, 129.79, 129.54, 129.51, 128.82, 128.54, 128.47, 127.95, 127.85, 126.48, 126.23 and 126.18 (F coupling), 125.34, 123.33, 118.26, 115.65 and 115.43 (F, coupling), 33.97.

HRMS $[M + H]^+$ calculated for $C_{29}H_{19}FN_2O_2$: 447.1509, found: 447.1524



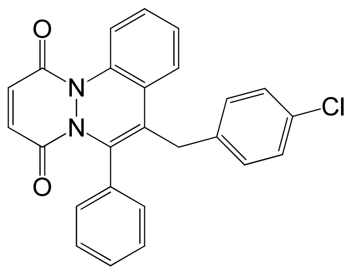
7-benzyl-6-(4-fluorophenyl)pyridazino[1,2-*a*]cinnoline-1,4-dione 8am

Red solid, Yield; 56.7 mg, 68%

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 (d, *J* = 8 Hz, 1H), 7.24-7.13 (m, 7H), 7.10-7.00 (m, 4H), 6.96-6.92 (t, *J* = 8 Hz, 2H), 6.77 (d, *J* = 8 Hz, 1H), 3.76 (s, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 162.58 (d, *J* = 248 Hz, C-F coupling), 156.59, 155.20, 138.88, 136.08, 135.70, 135.31, 135.23, 130.45 and 130.37 (F coupling), 129.29, 129.26, 128.83, 128.54, 127.88, 126.65, 126.54, 125.45 and 125.33 (F coupling), 123.38, 117.63, 115.71, 115.60 (d, *J* = 22 Hz, C-F coupling), 33.87.

HRMS $[M + H]^+$ calculated for $C_{25}H_{17}FN_2O_2$: 397.1352, found: 397.1377



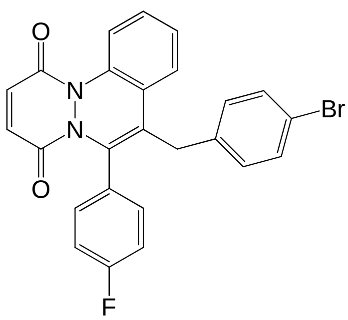
7-(4-chlorobenzyl)-6-phenylpyridazino[1,2-*a*]cinnoline-1,4-dione 8an

Red solid, Yield; 58.9 mg, 68%

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 (d, *J* = 8 Hz, 1H), 7.27-7.26 (m, 3H), 7.22-7.11 (m, 5H), 7.09 (d, *J* = 8 Hz, 2H), 7.03-7.00 (m, 3H), 6.77 (d, *J* = 8 Hz, 1H), 3.74 (s, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 156.58, 155.24, 137.58, 137.00, 136.08, 135.29, 135.26, 133.18, 132.27, 129.28, 128.89, 128.55, 128.49, 128.44, 126.64, 125.32, 125.09, 122.52, 117.77, 33.26.

HRMS $[M + H]^+$ calculated for $C_{25}H_{17}ClN_2O_2$; 413.1057, found: 413.1081



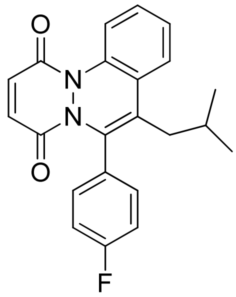
7-(4-bromobenzyl)-6-(4-fluorophenyl)pyridazino[1,2-*a*]cinnoline-1,4-dione 8ao

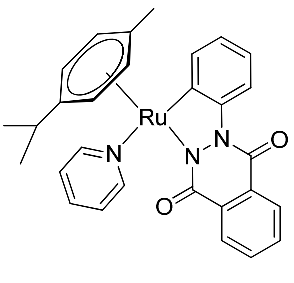
Red solid, yield; 66.8 mg, 67%

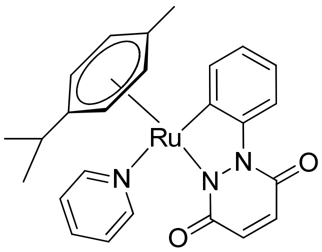
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 (d, *J* = 8 Hz, 1H), 7.33 (d, *J* = 8 Hz, 2H), 7.24-7.22 (m, 1H), 7.16-6.93 (m, 9H), 6.77 (d, *J* = 8 Hz, 1H), 3.69 (s, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 162.34 (d, *J* = 147 Hz, C-F coupling), 156.54, 155.19, 137.90, 136.10 and 136.02 (F coupling), 135.38 and 135.21 (F coupling), 131.92, 130.40, 130.32, 129.57, 128.71, 126.71, 125.17, 125.08, 122.80, 120.42, 117.78, 115.70 (d, *J* = 22 Hz, C-F coupling), 33.33.

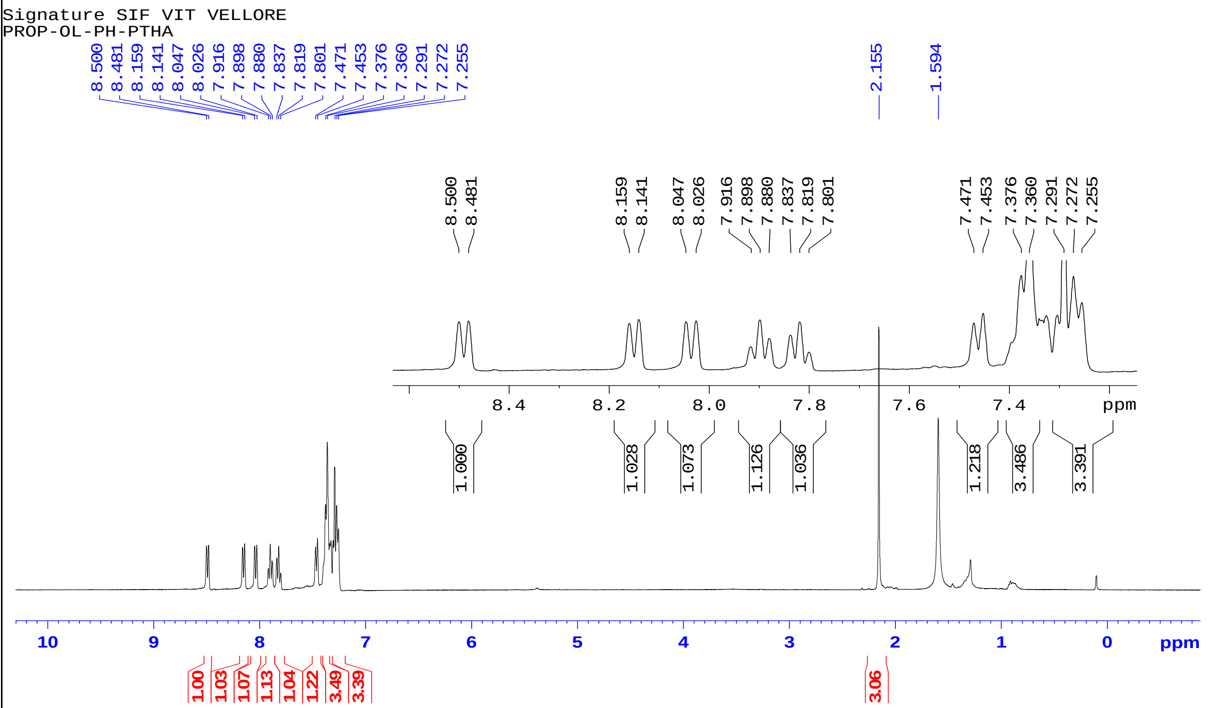
	HRMS [M + H]$^+$ calculated for $C_{25}H_{16}BrFN_2O_2$:475.0457,found: 475.0481

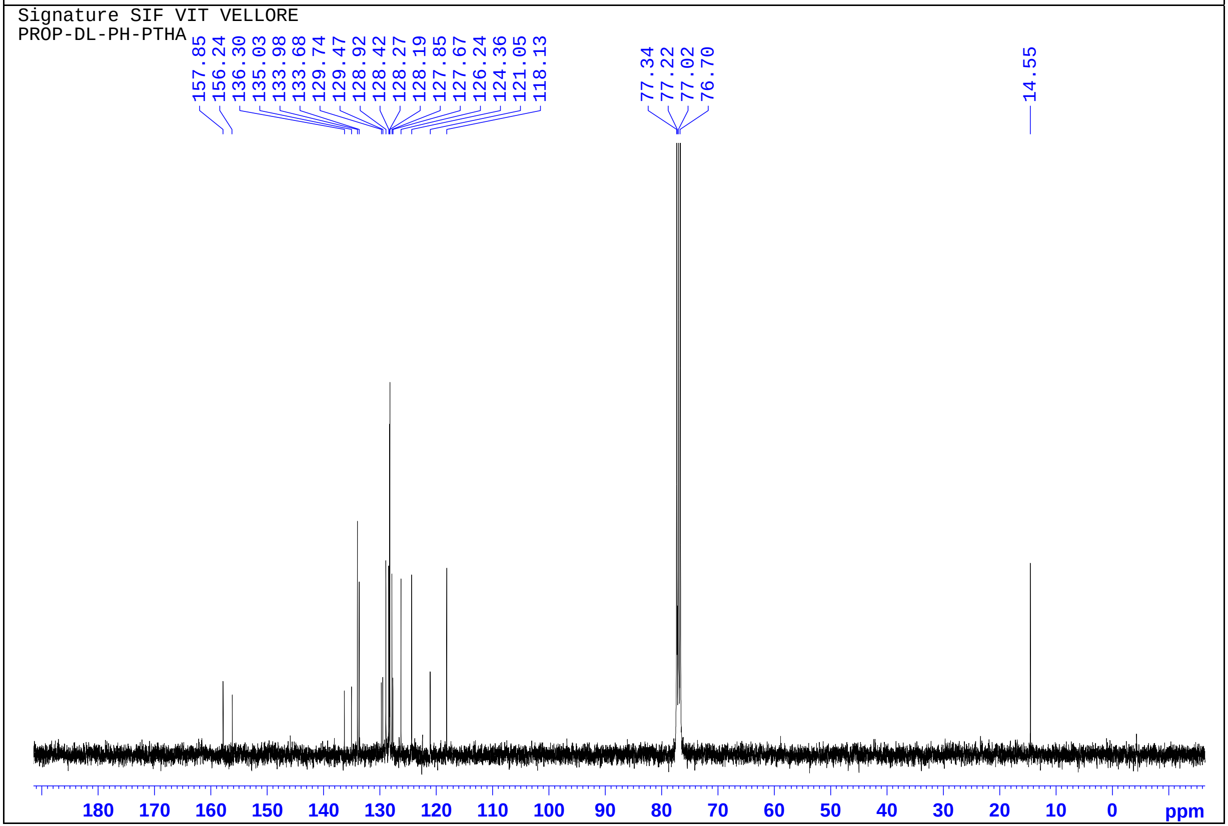
	**6-(4-fluorophenyl)-7-isobutylpyridazino[1,2-*a*]cinnoline-1,4-dione 8ap** Red solid, Yield; 58.6 mg, 77% **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.06 (d, *J* = 8 Hz, 1H), 7.36 (d, *J* = 8 Hz, 1H), 7.27-7.22 (m, 2H), 7.16-7.13 (m, 2H), 7.02-6.96 (m, 3H), 6.72 (d, *J* = 12 Hz, 1H), 2.37 (d, 8 Hz, 2H), 1.63-1.56 (m, 1H), 0.59 (d, *J* = 8 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 162.36 (d, *J* = 241 Hz, C-F coupling), 156.58, 154.87, 136.32, 135.46, 135.09 and 134.91 (F coupling), 131.42, 131.34, 129.33, 128.38, 126.60, 125.23 and 125.14 (F coupling), 124.59, 117.89, 115.48 (d, *J* = 22 Hz, C-F coupling), 35.41, 27.36, 22.21. **HRMS** [M + H]$^+$ calculated for $C_{22}H_{19}FN_2O_2$: 363.1509, found:363.1488

	**Cycloruthenated complex 1cr** Orange yellow solid, yield; 68% **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.81 (d, *J* = 8 Hz, 2H), 8.61 (d, *J* = 8 Hz, 1H), 8.29 (d, *J* = 8 Hz, 2H), 8.04 (d, *J* = 8 Hz, 1H), 7.69-7.65 (t, *J* = 8 Hz, 1H), 7.60-7.57 (t, *J* = 6 Hz, 1H), 7.44-7.41 (t, *J* = 6 Hz, 1H), 7.00-6.95 (m, 4H), 6.01 (d, *J* = 8 Hz, 1H), 5.88 (d, *J* = 8 Hz,1H), 5.66 (d, *J* = 8 Hz, 1H), 4.80 (d, *J* = 8 Hz, 1H), 2.10-2.06 (m, 1H), 1.46 (s, 3H), 0.80 (d, *J* = 8Hz, 3H), 0.73 (d, *J* = 8 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 162.74, 160.24, 159.06, 154.87, 148.89, 138.15, 136.61, 132.13, 130.79, 130.02, 128.98, 128.83, 127.05, 126.39, 124.68, 124.39, 123.56, 118.93, 104.08, 97.73, 94.12, 94.04, 89.63, 79.68, 30.87, 22.95, 22.13, 18.00. **ESI-MS** m/z calculated for $C_{29}H_{28}N_3O_2Ru$ [M + H]$^+$: 552.1225, found: 552.1060. m/z calculated for $C_{29}H_{28}N_3O_2Ru$ [(M + H) -Pyridine]$^+$: 473.0803, found: 473.0637

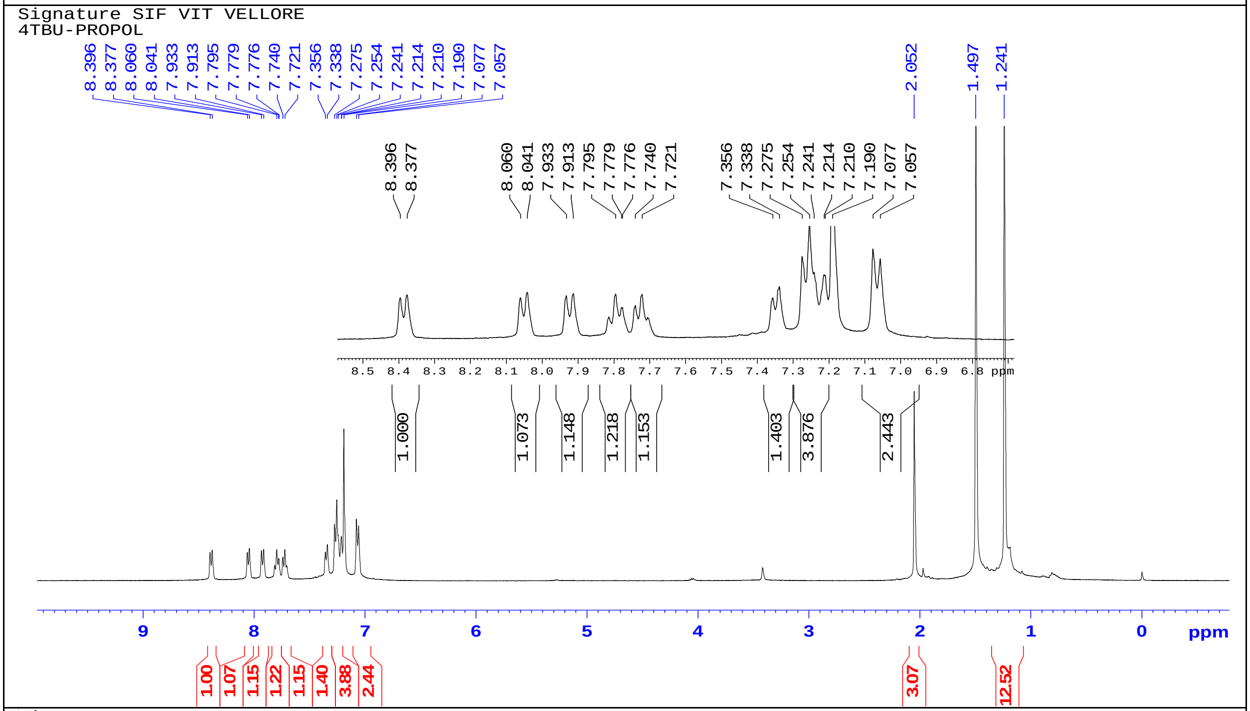
	**Cycloruthenated complex 4cr** Orange yellow solid, yield; 73% **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.74 (d, *J* = 4 Hz, 2H), 8.60 (d, *J* = 8 Hz, 1H), 8.01 (d, *J* = 8 Hz, 1H), 7.48-7.45 (t, *J* = 8 Hz, 1H), 7.01-6.98 (m, 3H), 6.95-6.92 (t, *J* = 8 Hz, 1H), 6.77 (d, *J* = 8 Hz, 1H), 6.61 (d, *J* = 8 Hz, 1H), 5.91 (d, *J* = 5.7 Hz, 1H), 5.84 (d, *J* = 6.4 Hz, 1H), 5.63 (d, *J* = 5.6 Hz, 1H), 4.81 (d, *J* = 5.6 Hz, 1H), 2.11-2.03 (m, 1H), 1.45 (s, 3H), 0.83 (d, *J* = 8 Hz, 3H), 0.77 (d, *J* = 8 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 163.69, 160.38, 159.37, 154.89, 149.00, 138.15, 136.74, 132.52, 131.74, 125.16, 124.44, 123.60, 118.52, 103.92, 98.56, 94.12, 94.05, 89.78, 79.99, 30.83, 22.89, 22.03, 17.76. **ESI-MS** m/z calculated for $C_{25}H_{25}N_3O_2Ru$ [M + H]$^+$: 502.1069, found: 502.0994 m/z calculated for $C_{25}H_{25}N_3O_2Ru$ [(M + H) -Pyridine]$^+$: 423.0647, found: 423.0581.

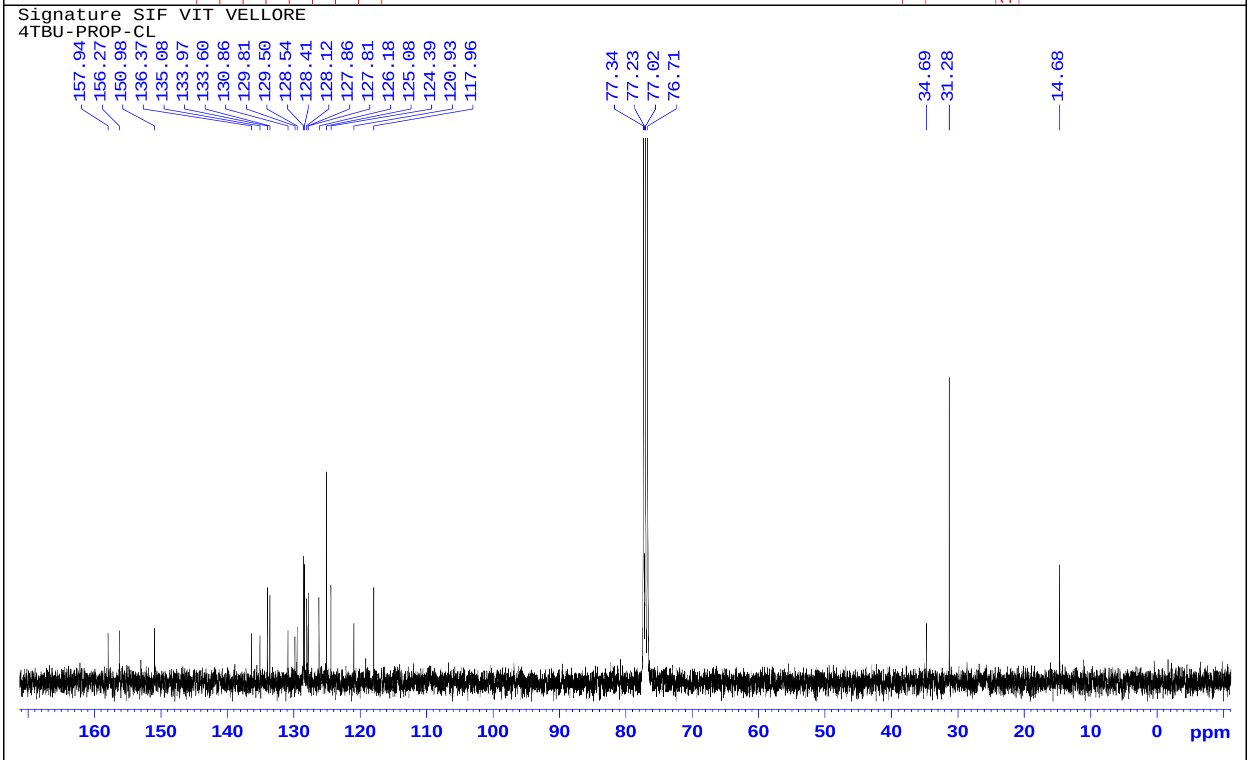
[1]H NMR and [13]C NMR of **3aa**



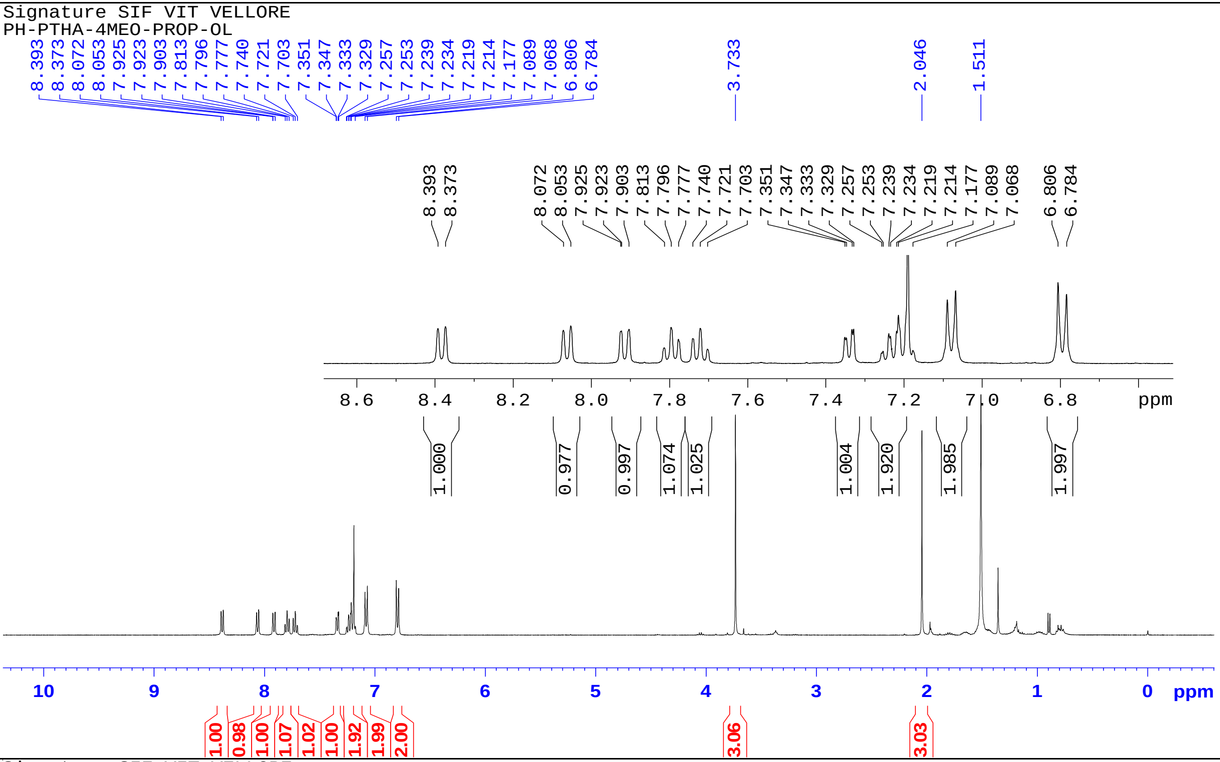


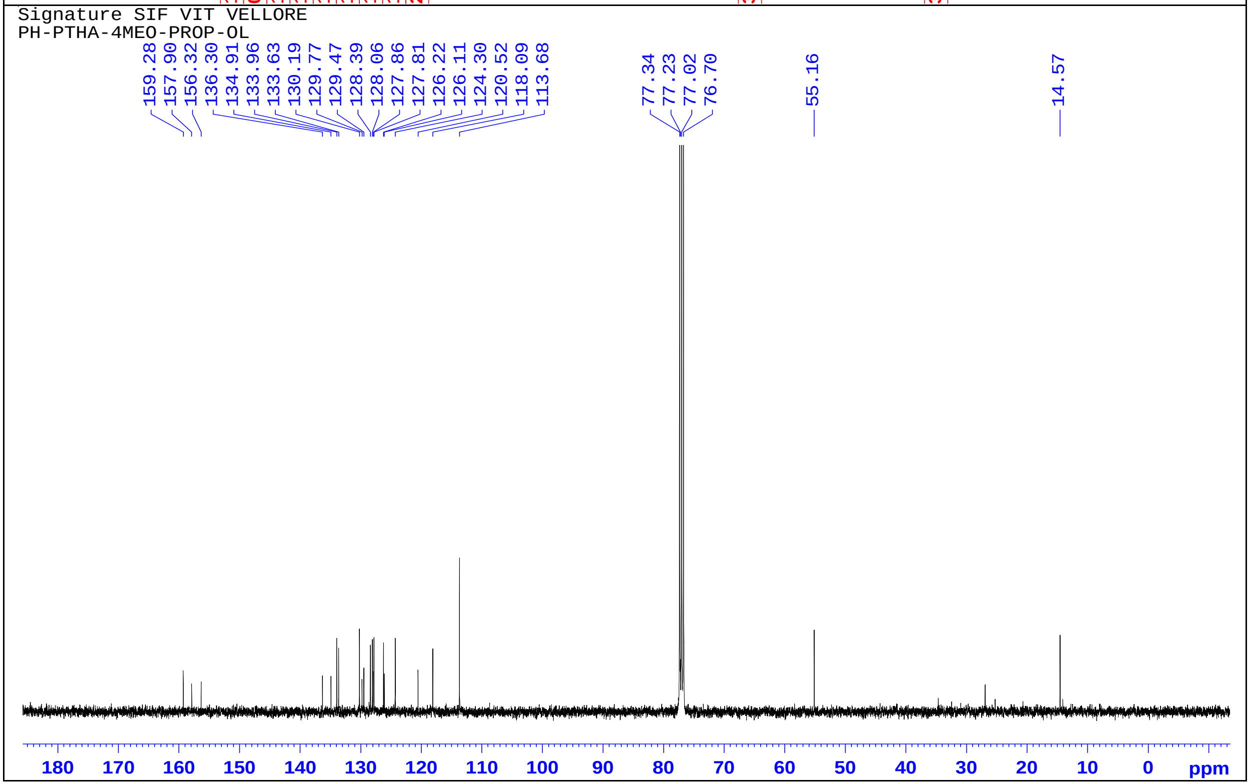
[1]H NMR and [13]C NMR of **3ab**



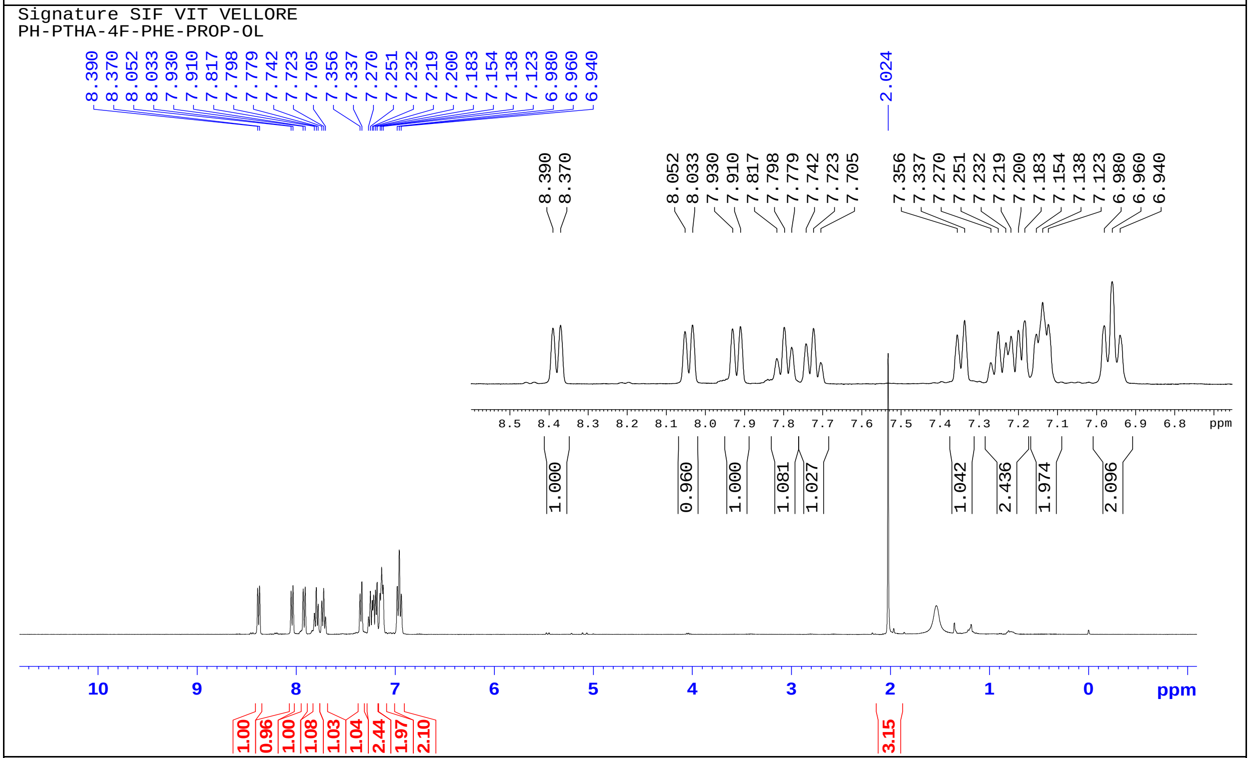


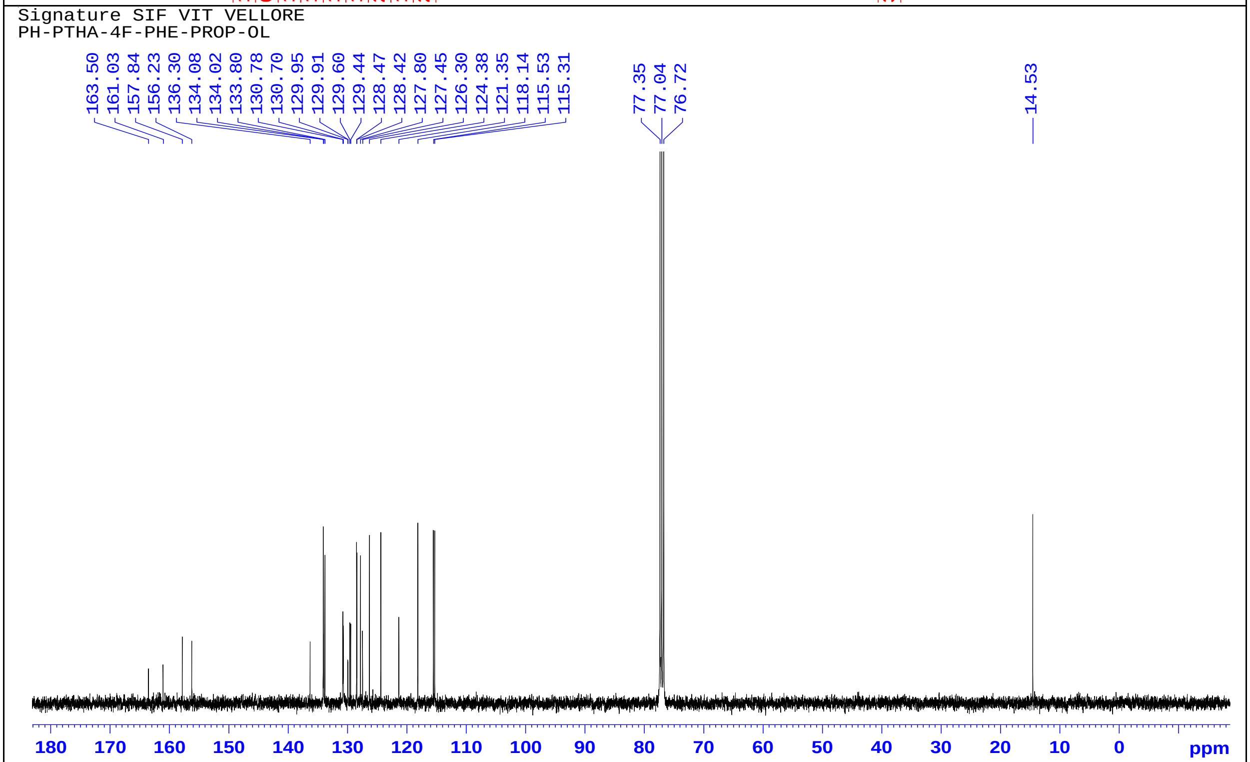
[1]H NMR and [13]C NMR of **3ac**



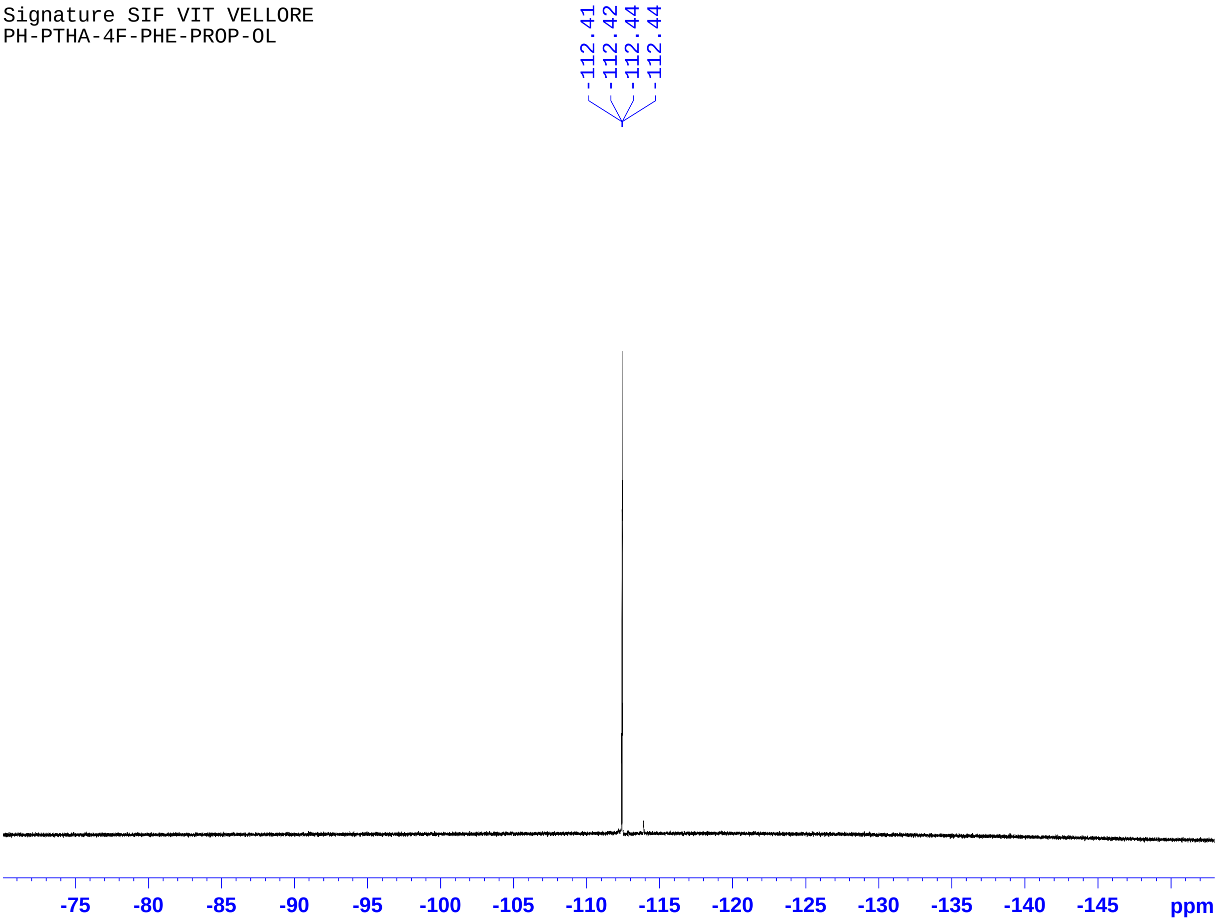


^{1}H NMR and ^{13}C NMR of **3ad**

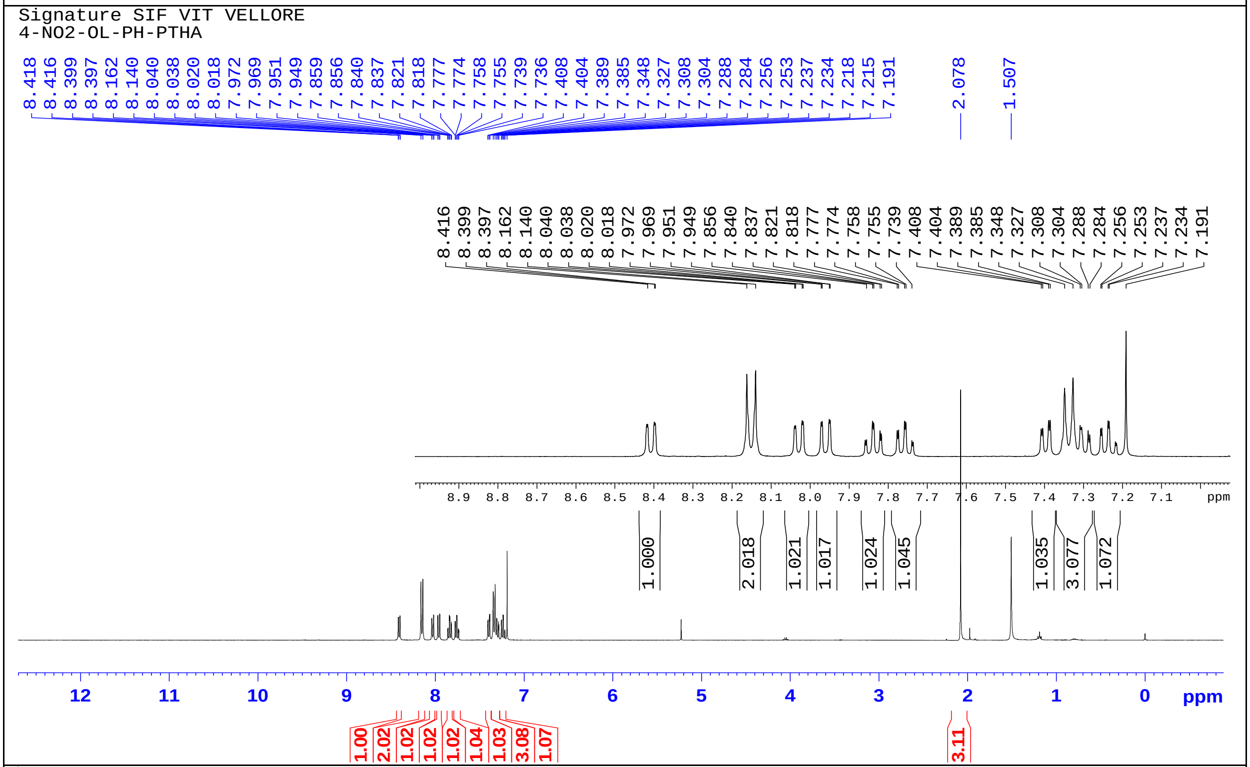


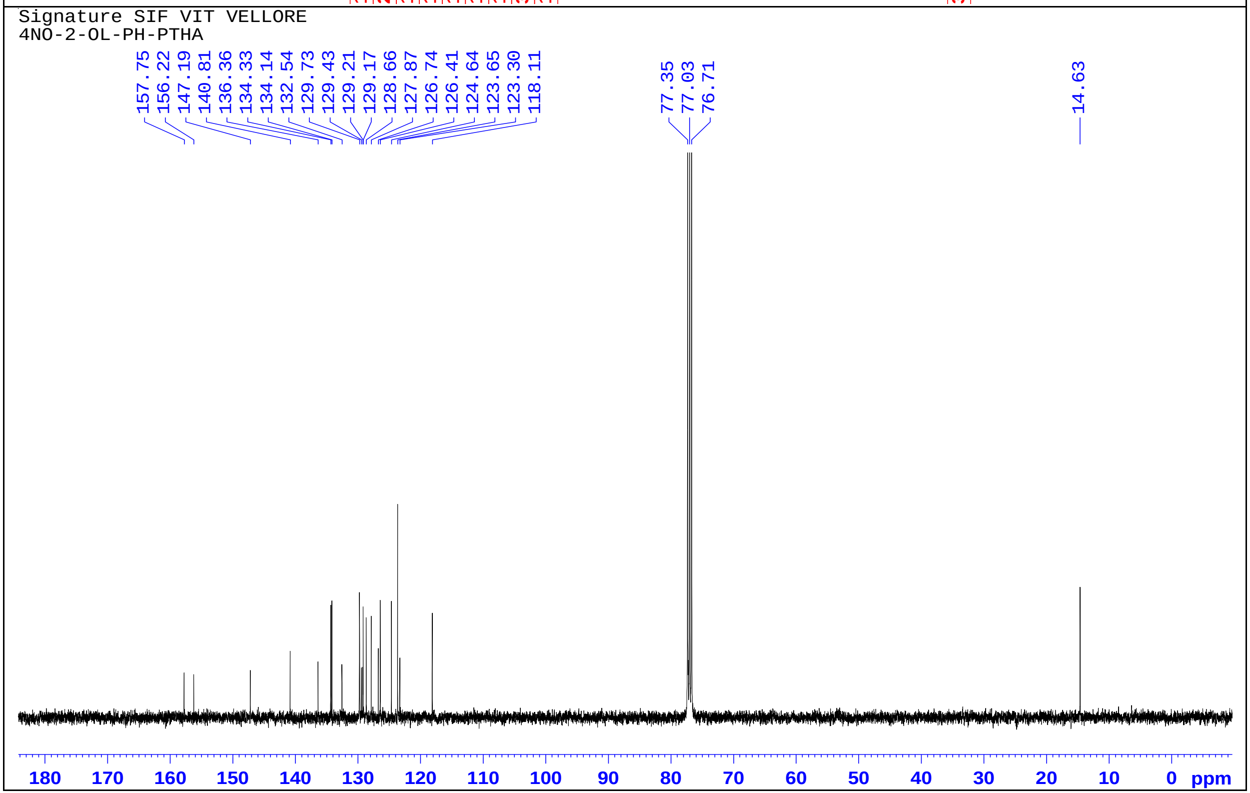


[19]F NMR of **3ad**

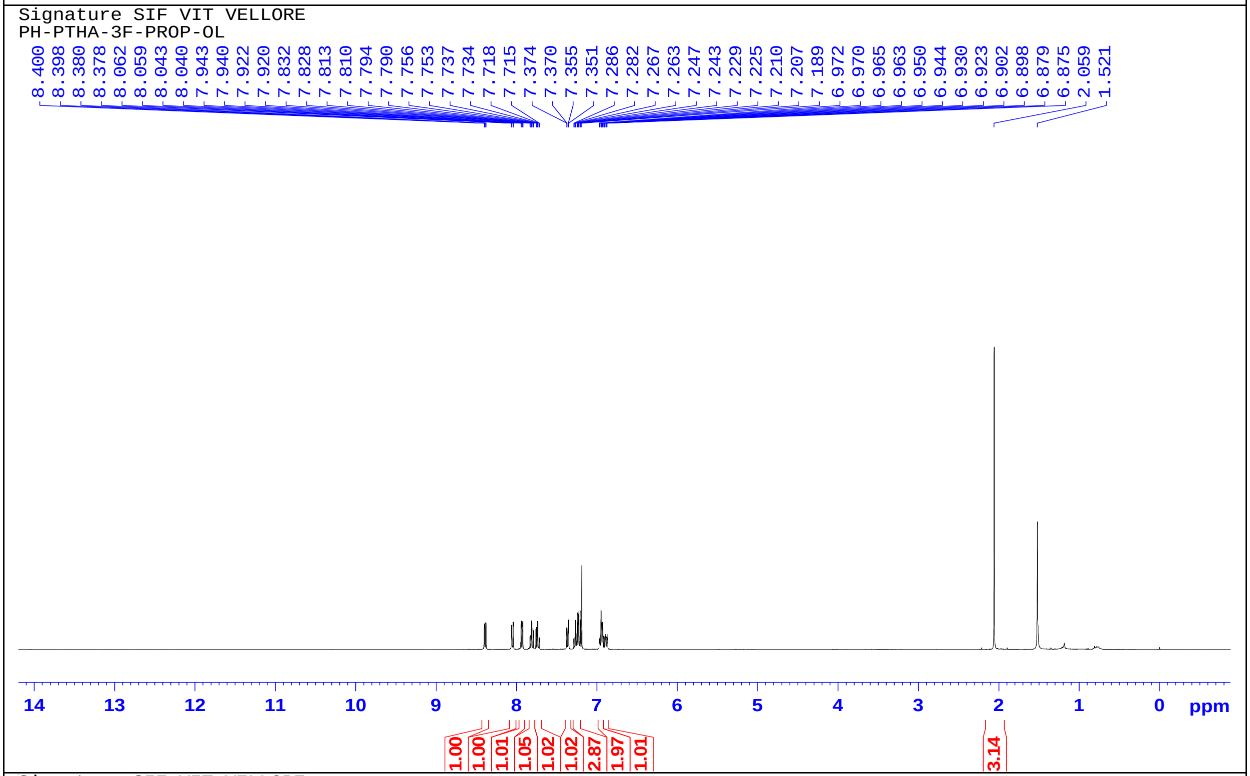


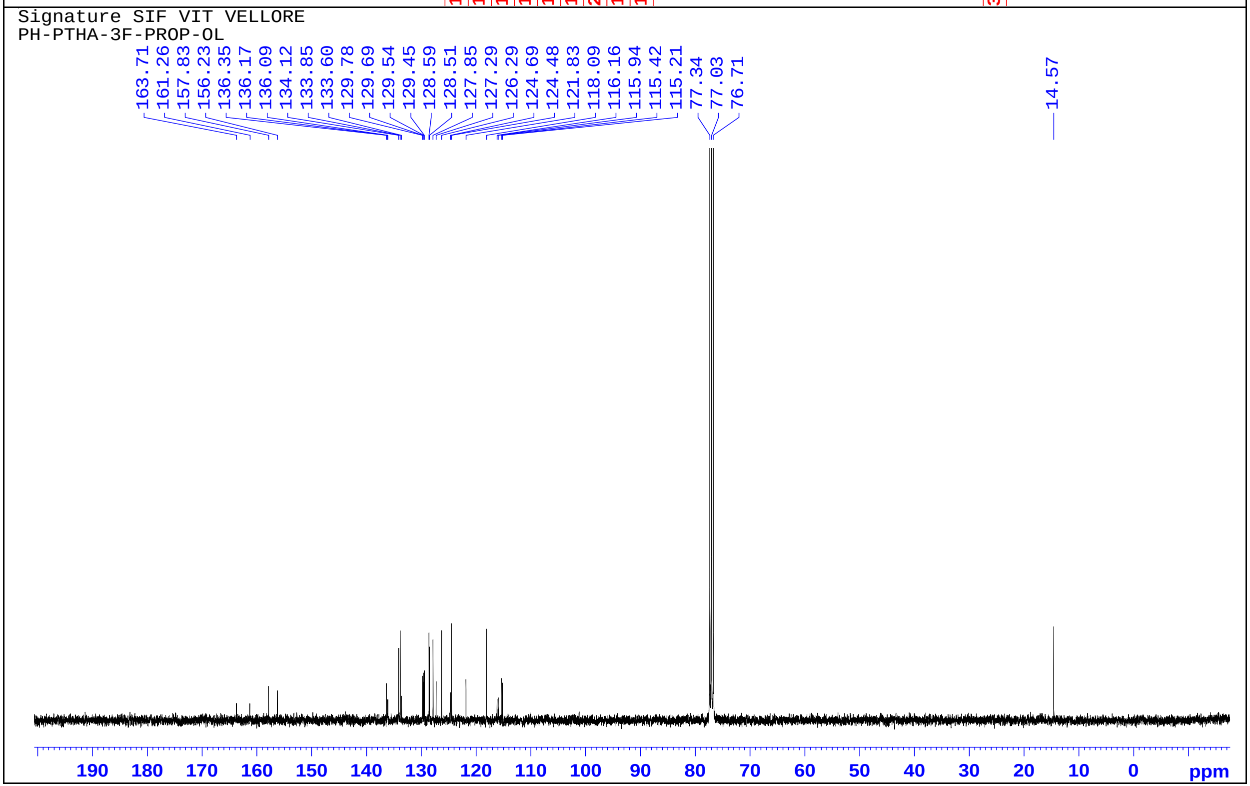
^{1}H NMR and ^{13}C NMR of **3ae**



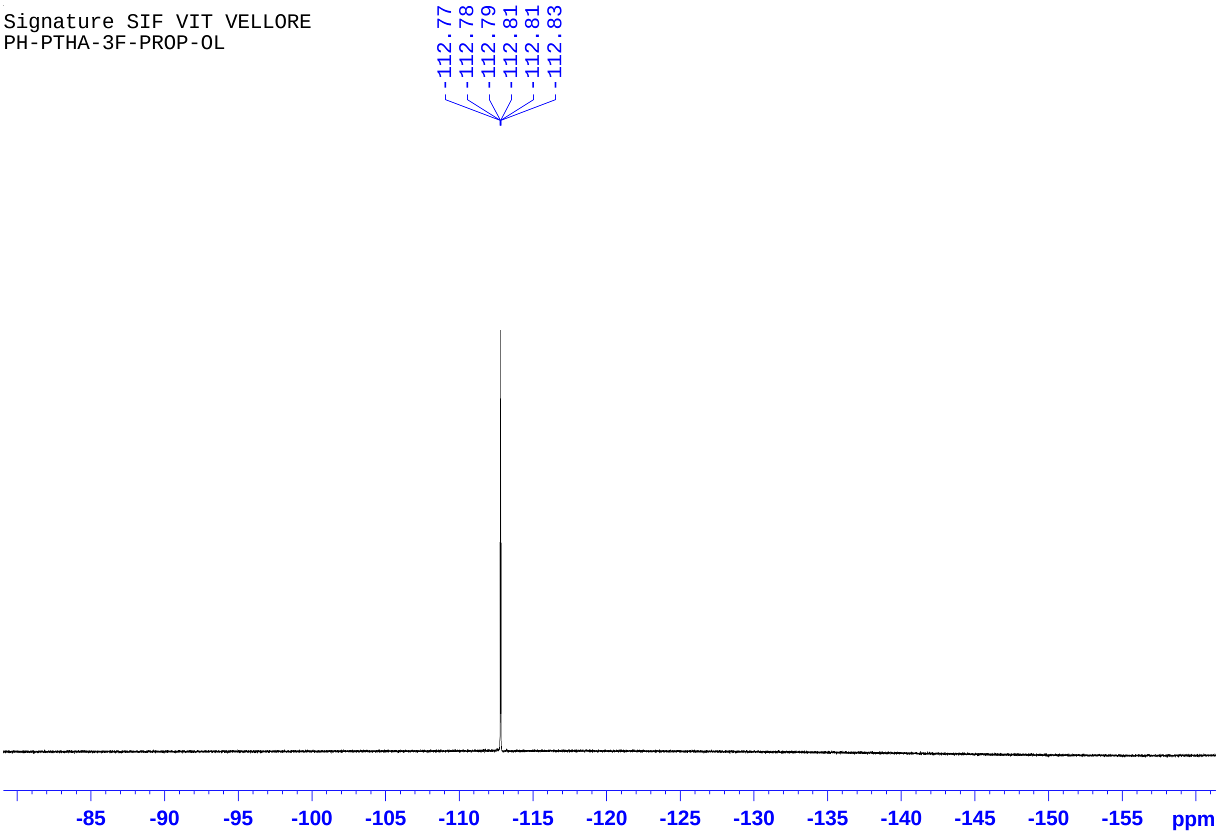


^{1}H NMR and ^{13}C NMR of **3af**

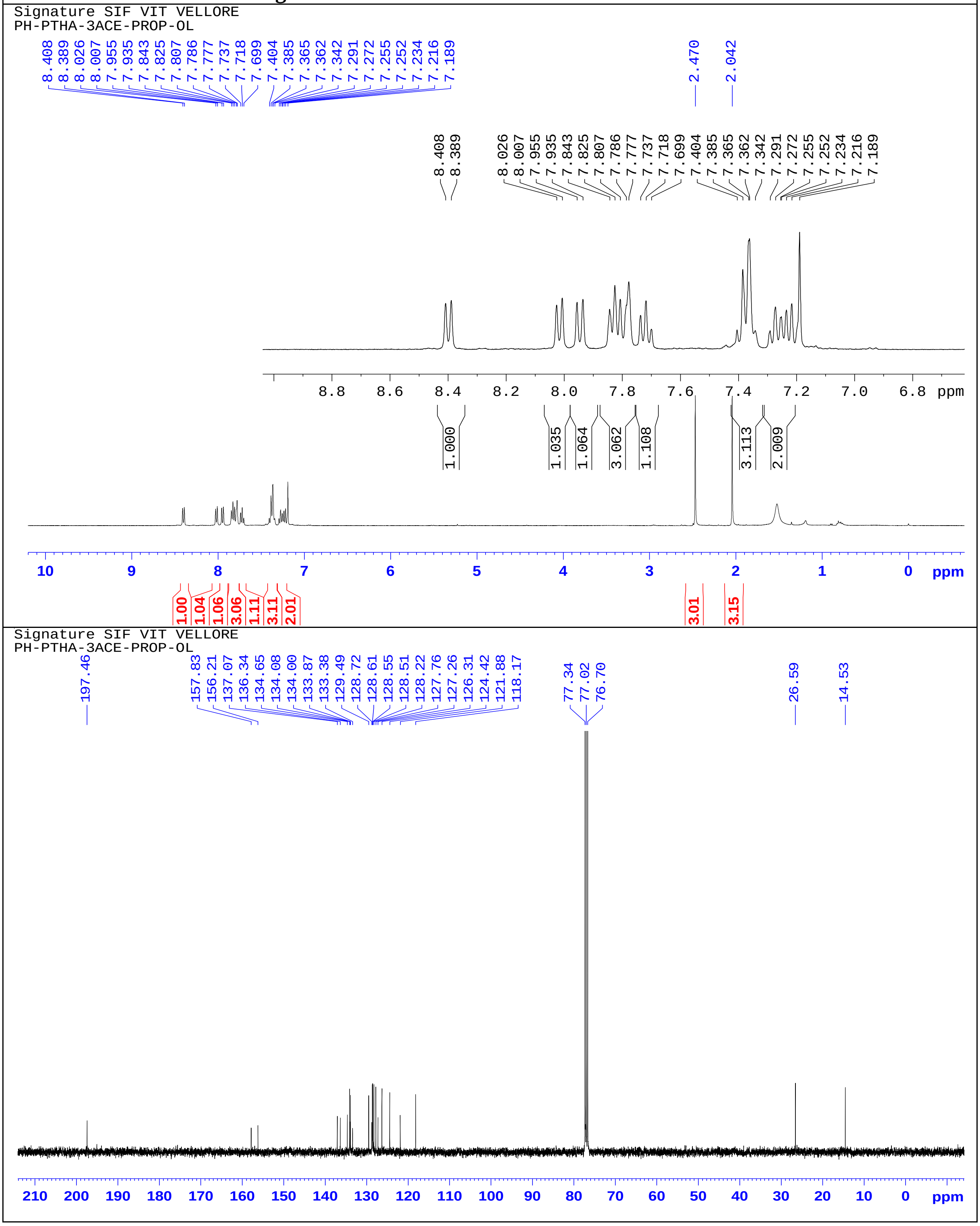




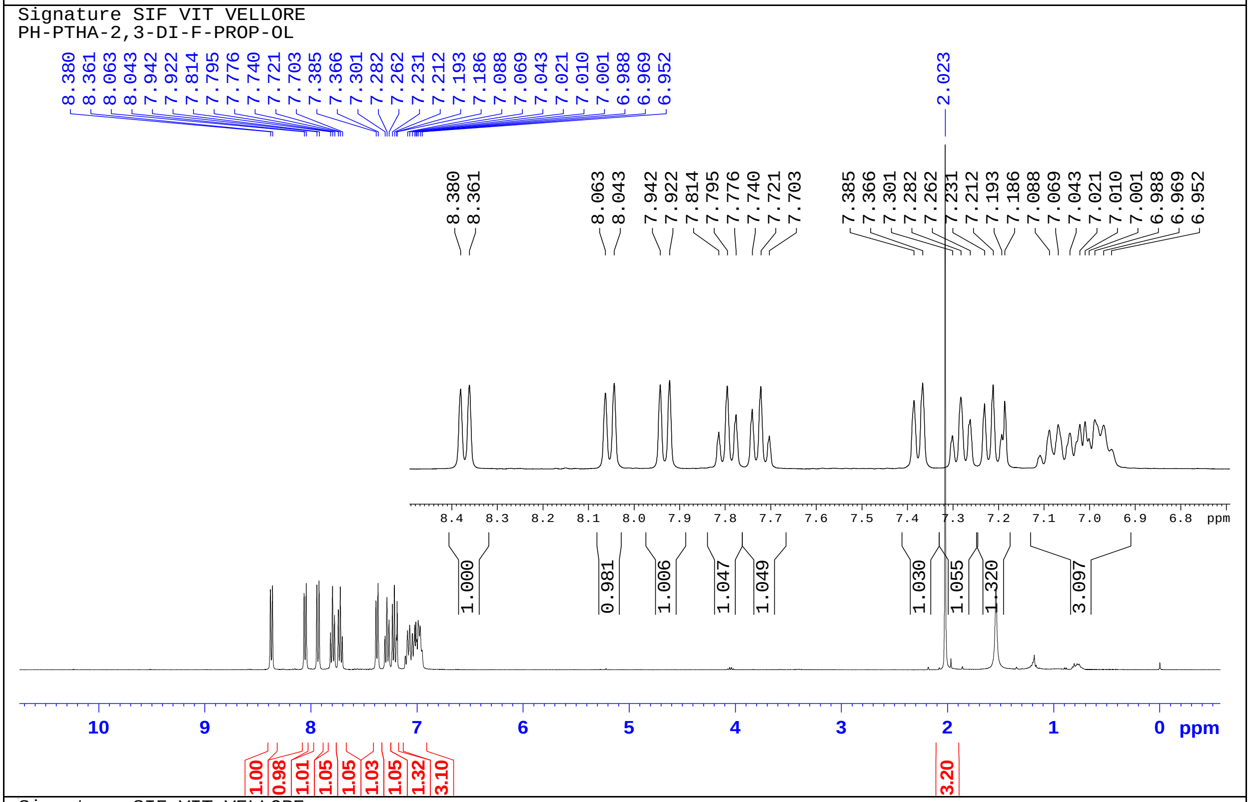
^{19}F NMR of **3af**

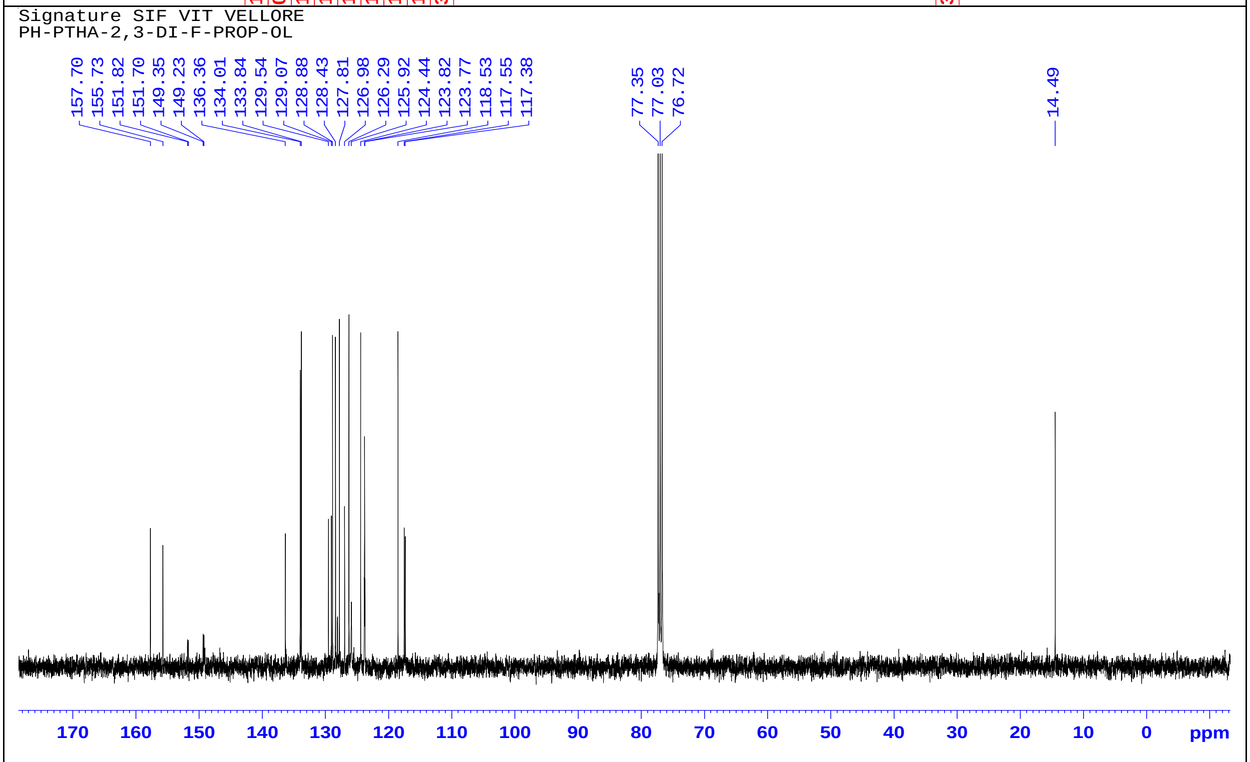


^{1}H NMR and ^{13}C NMR of **3ag**

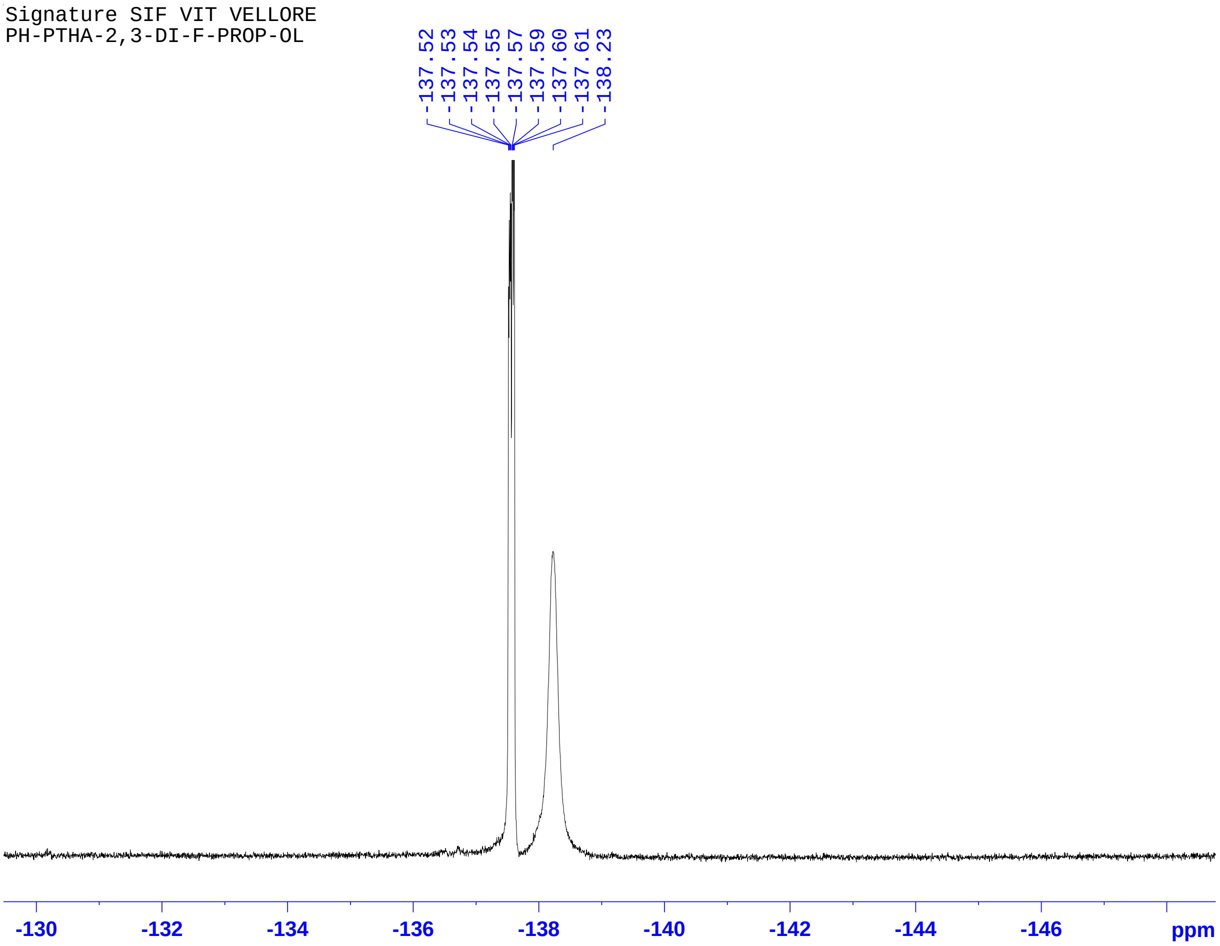


[1]H NMR and [13]C NMR of **3ah**

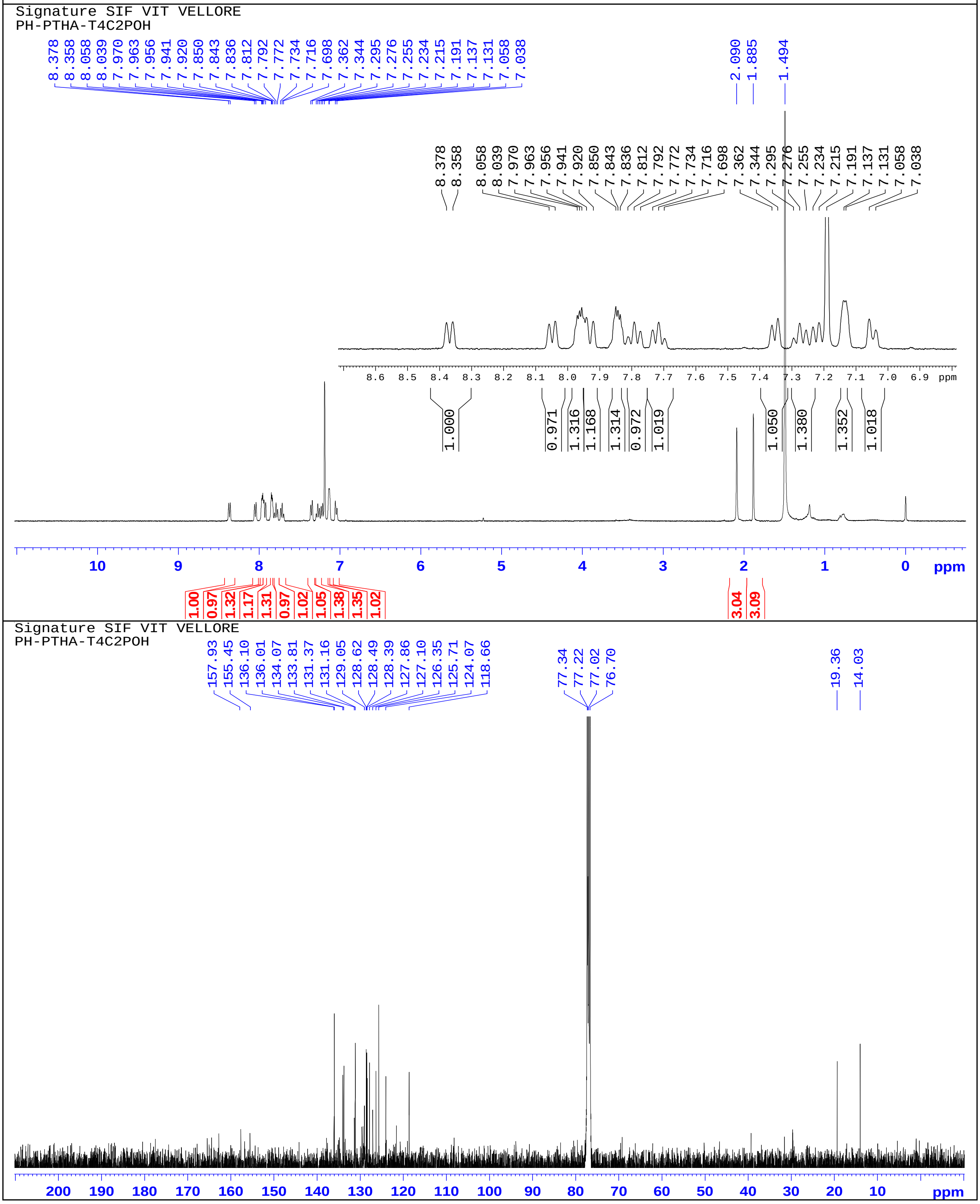




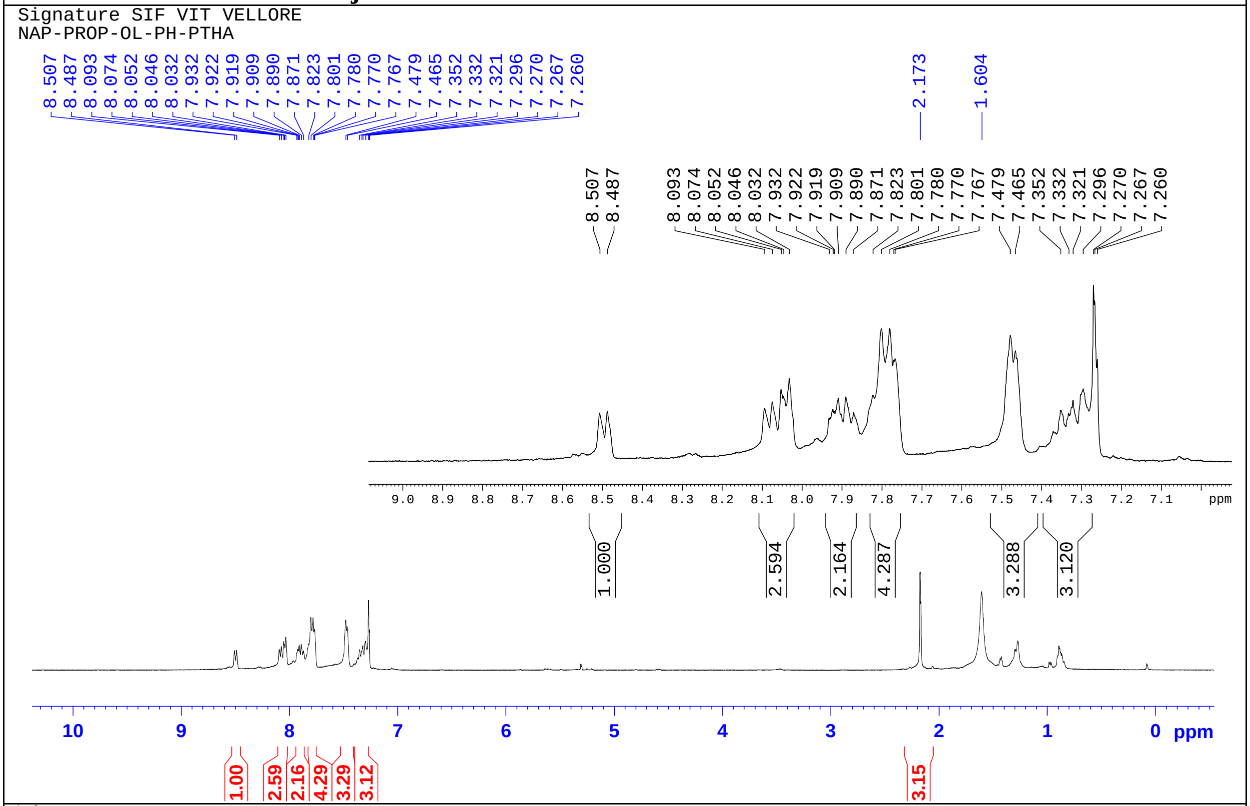
^{19}F NMR of **3ah**

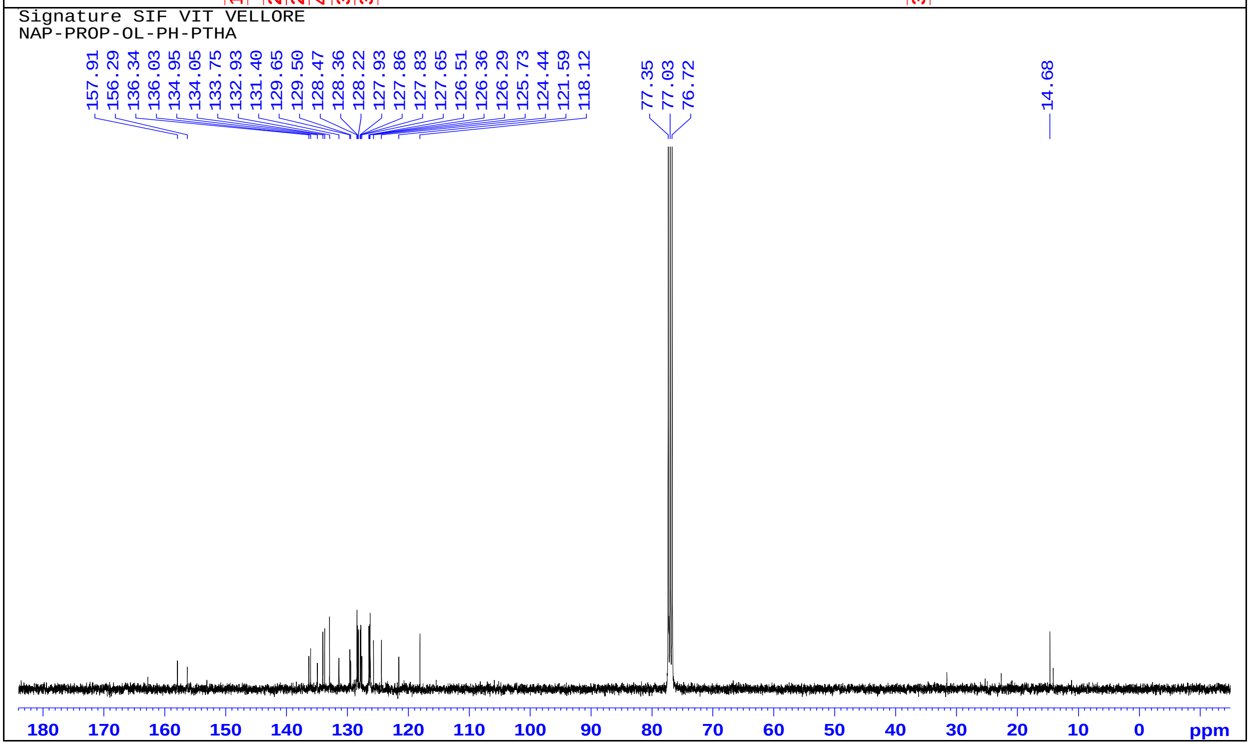


[1]H NMR and [13]C NMR of **3ai**

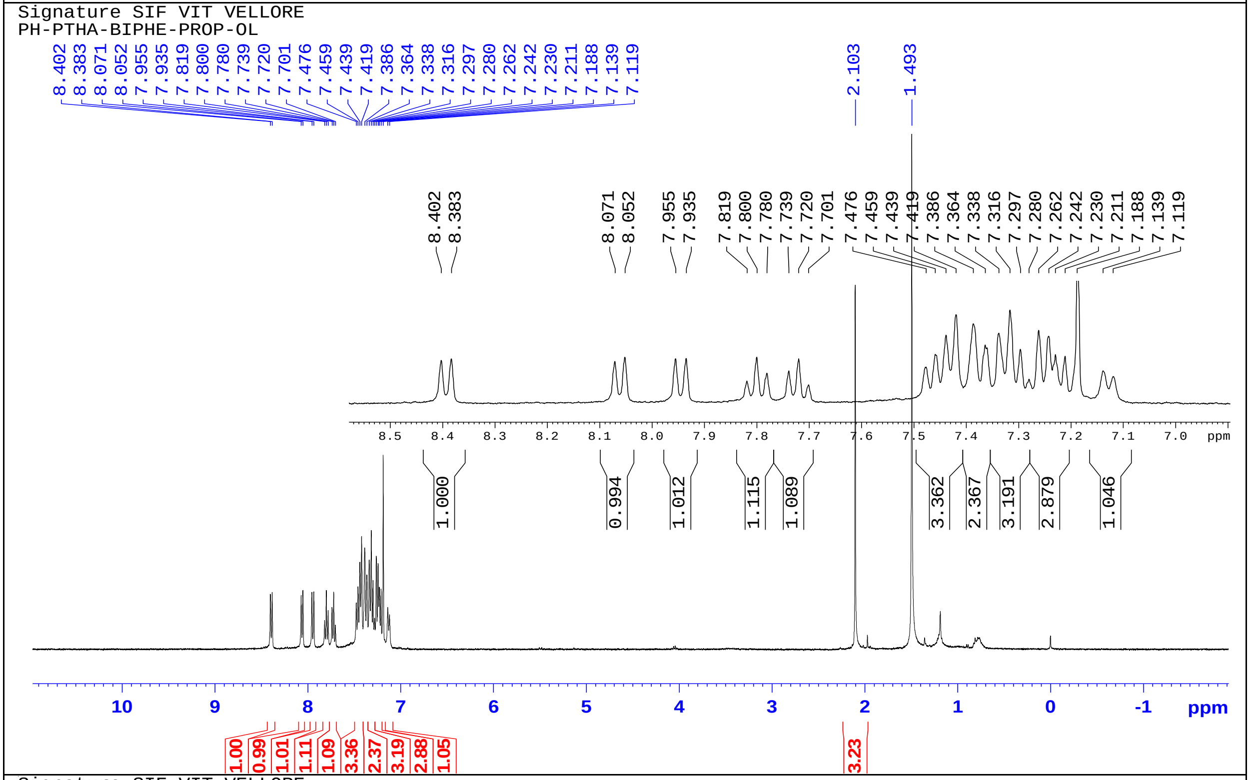


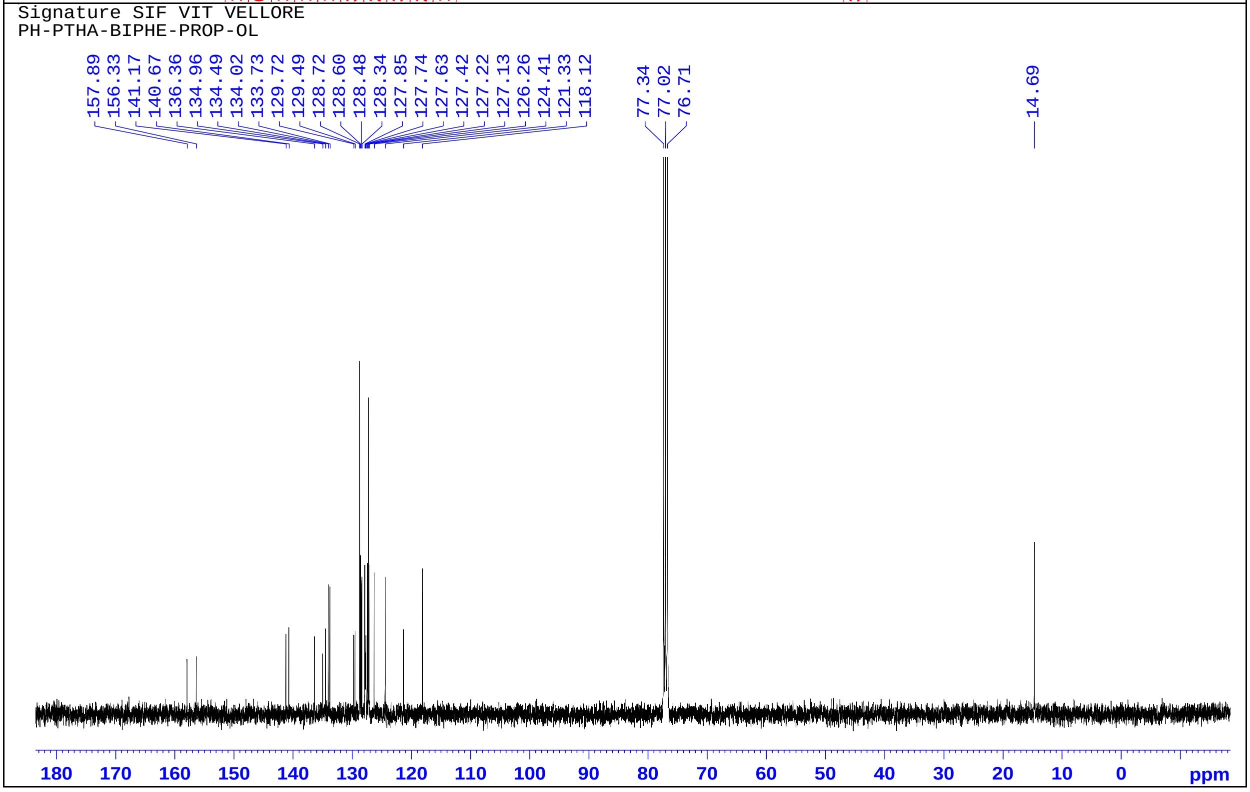
^{1}H NMR and ^{13}C NMR of **3aj**



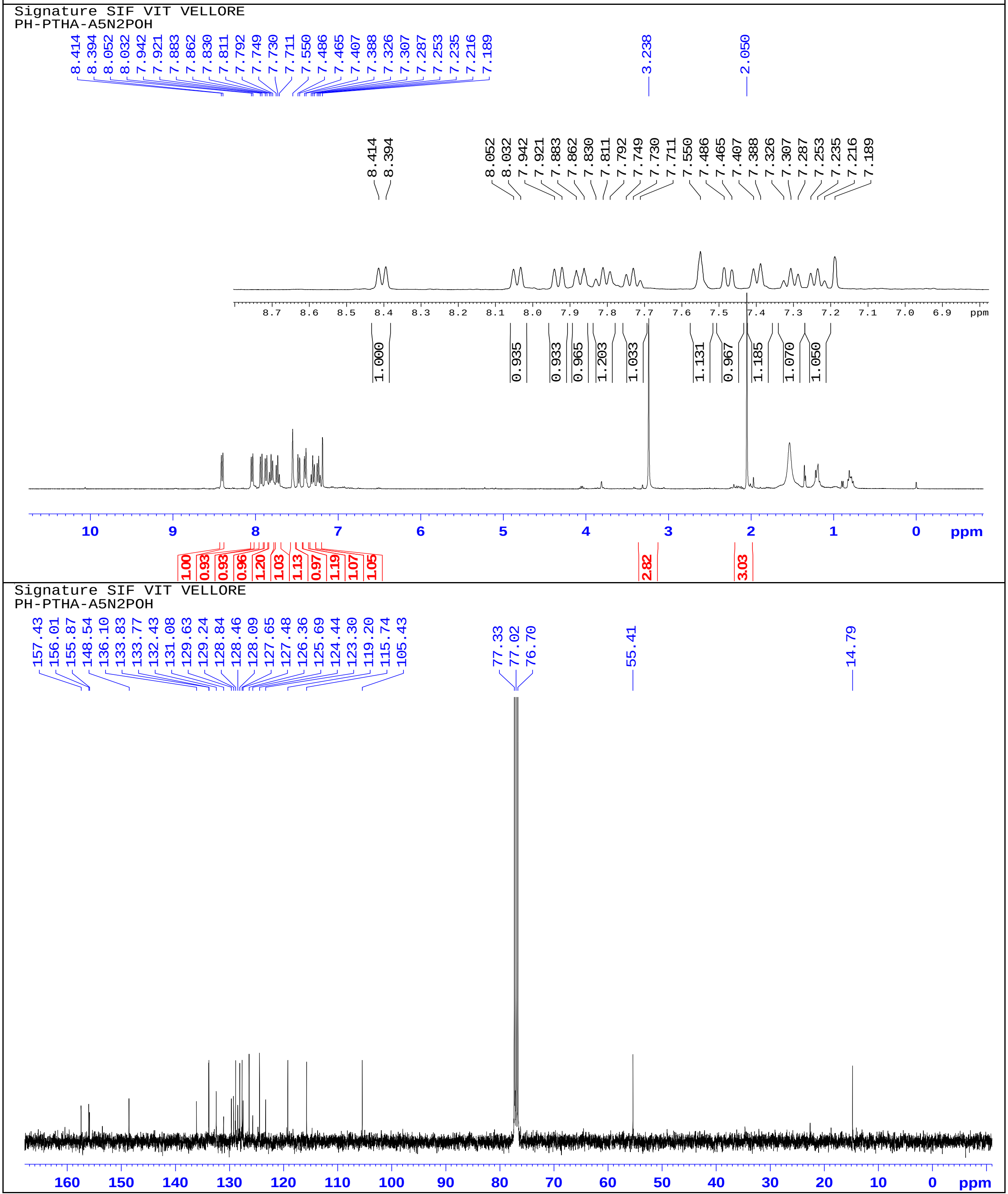


[1]H NMR and [13]C NMR of **3ak**

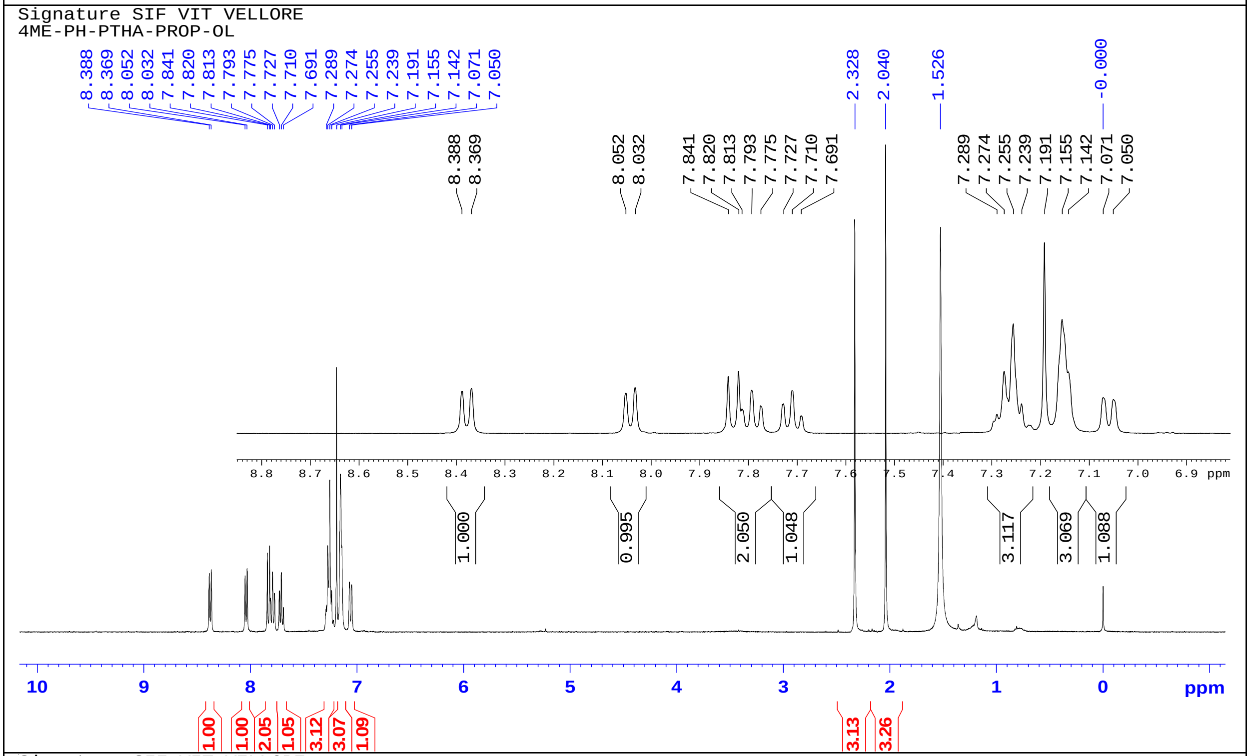


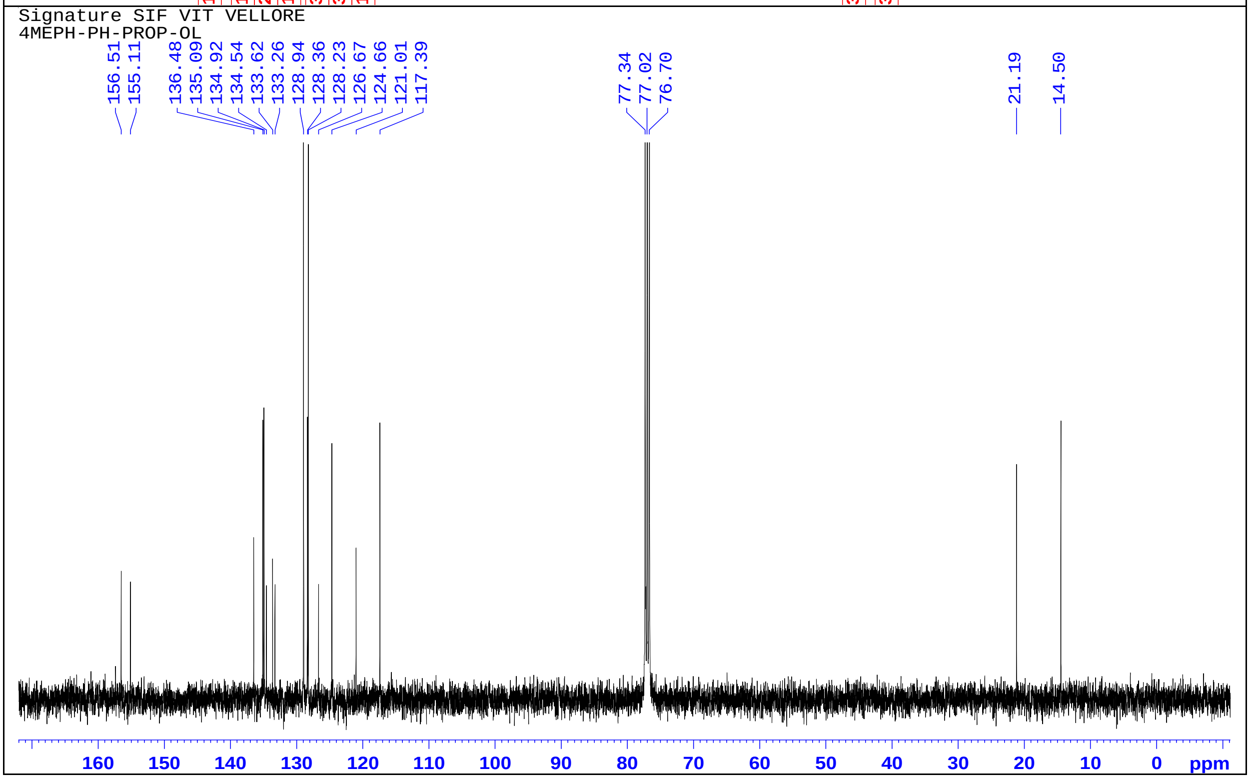


^{1}H NMR and ^{13}C NMR of **3al**

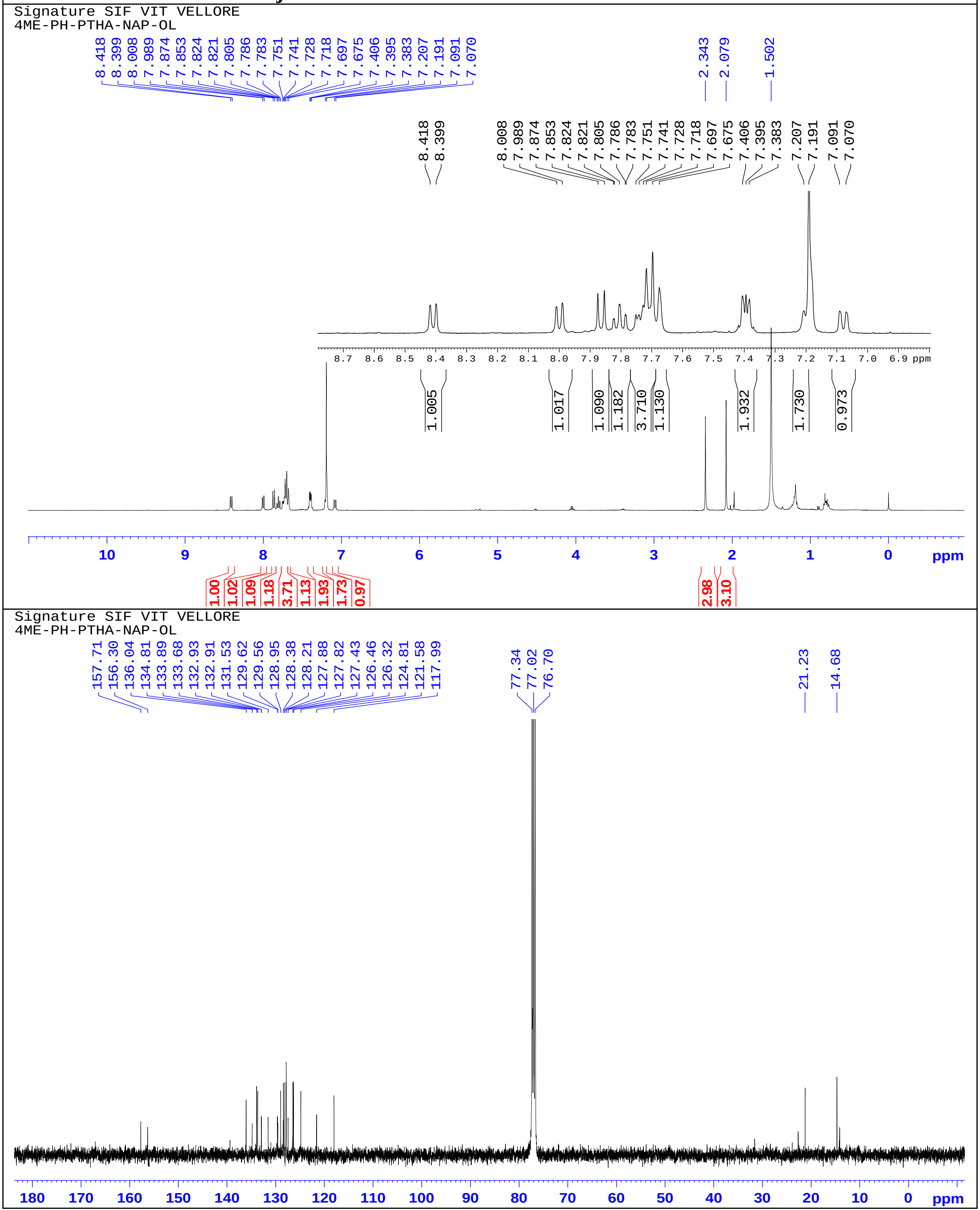


[1] H NMR and [13] C NMR of **3ba**

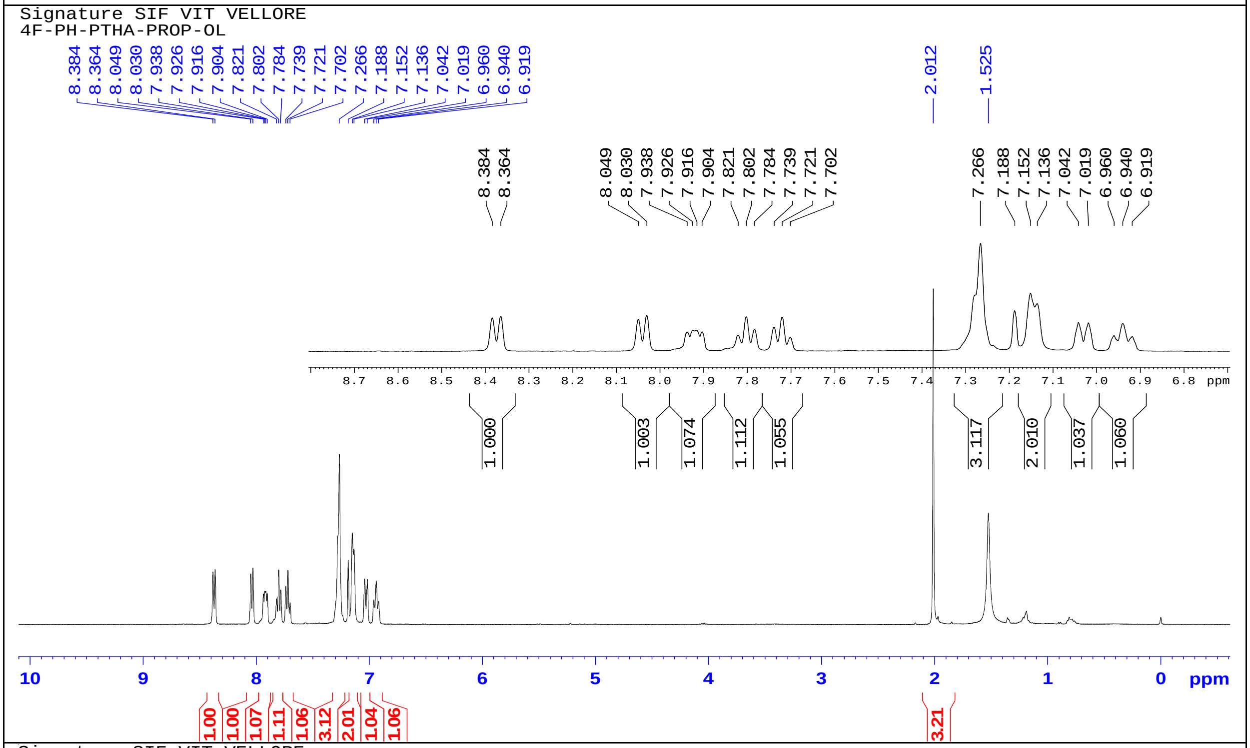


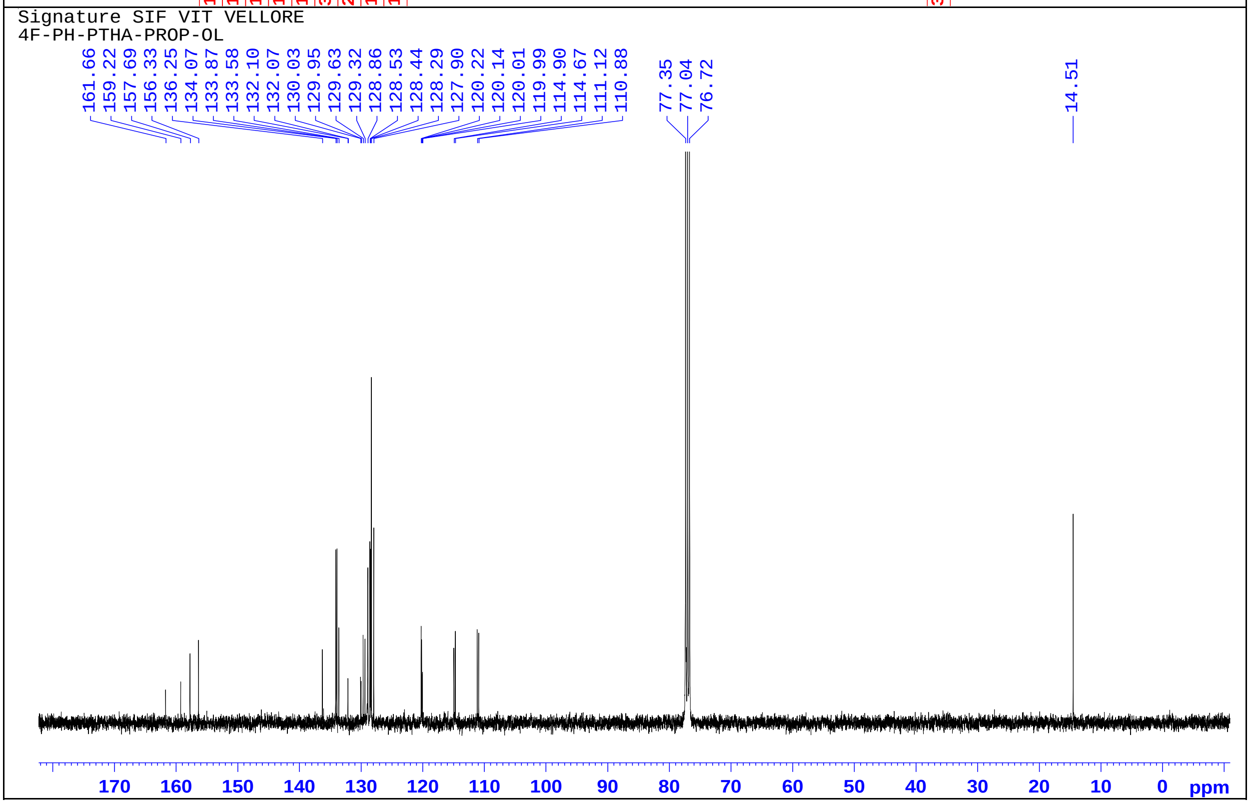


[1]H NMR and [13]C NMR of **3bj**

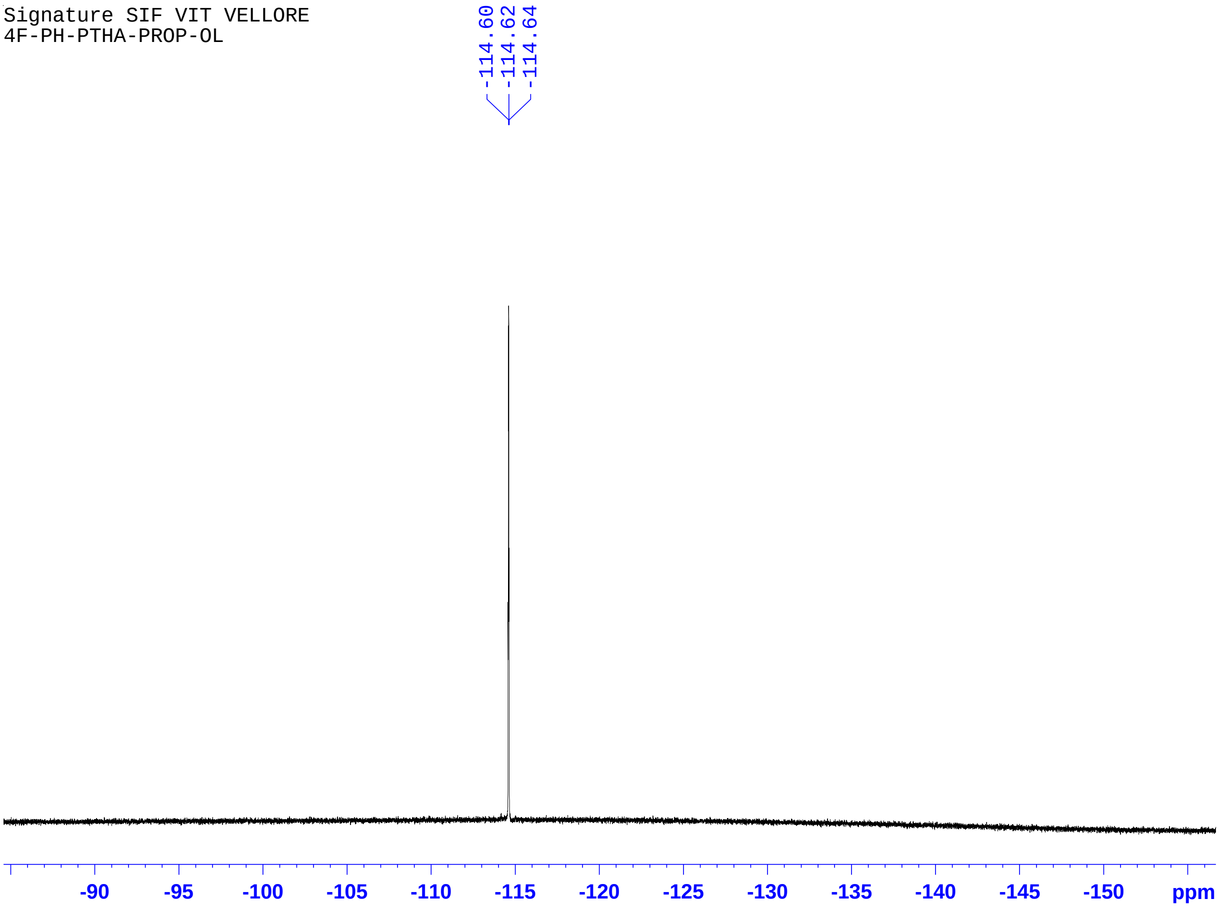


^{1}H NMR and ^{13}C NMR of **3ca**

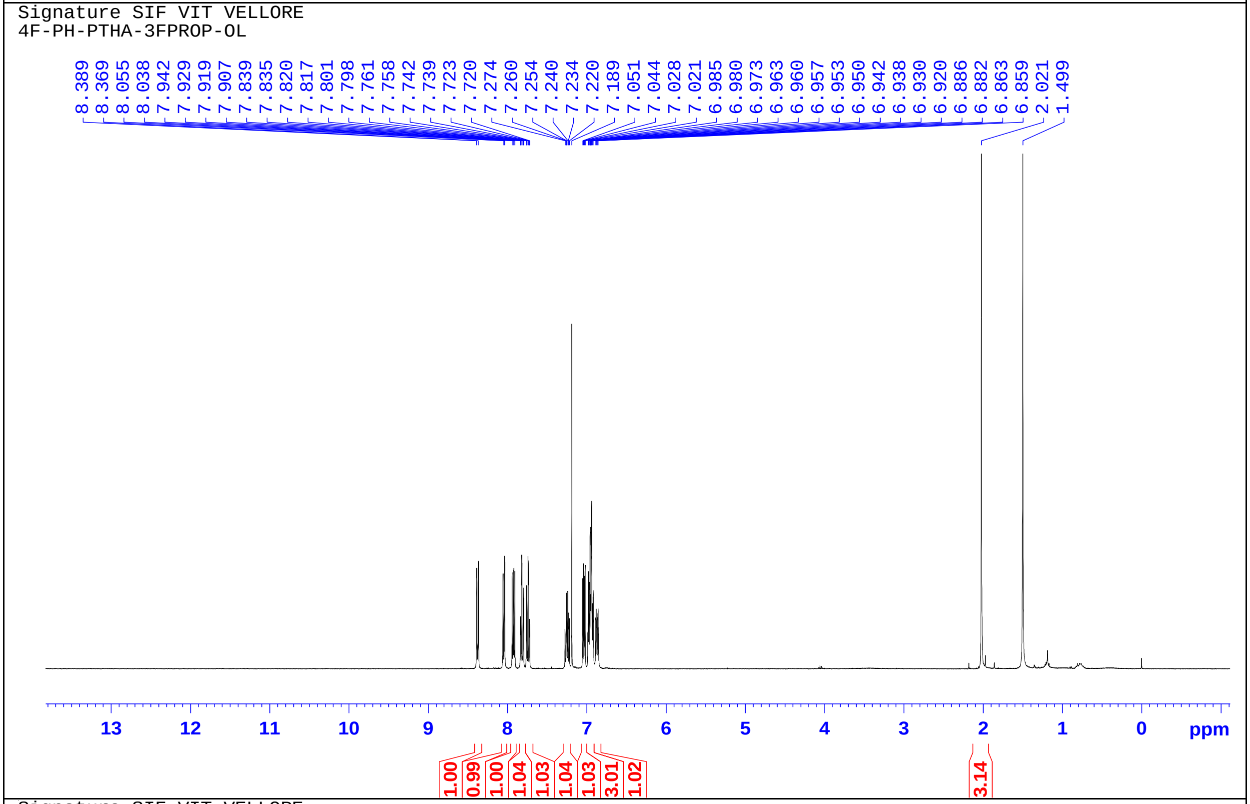


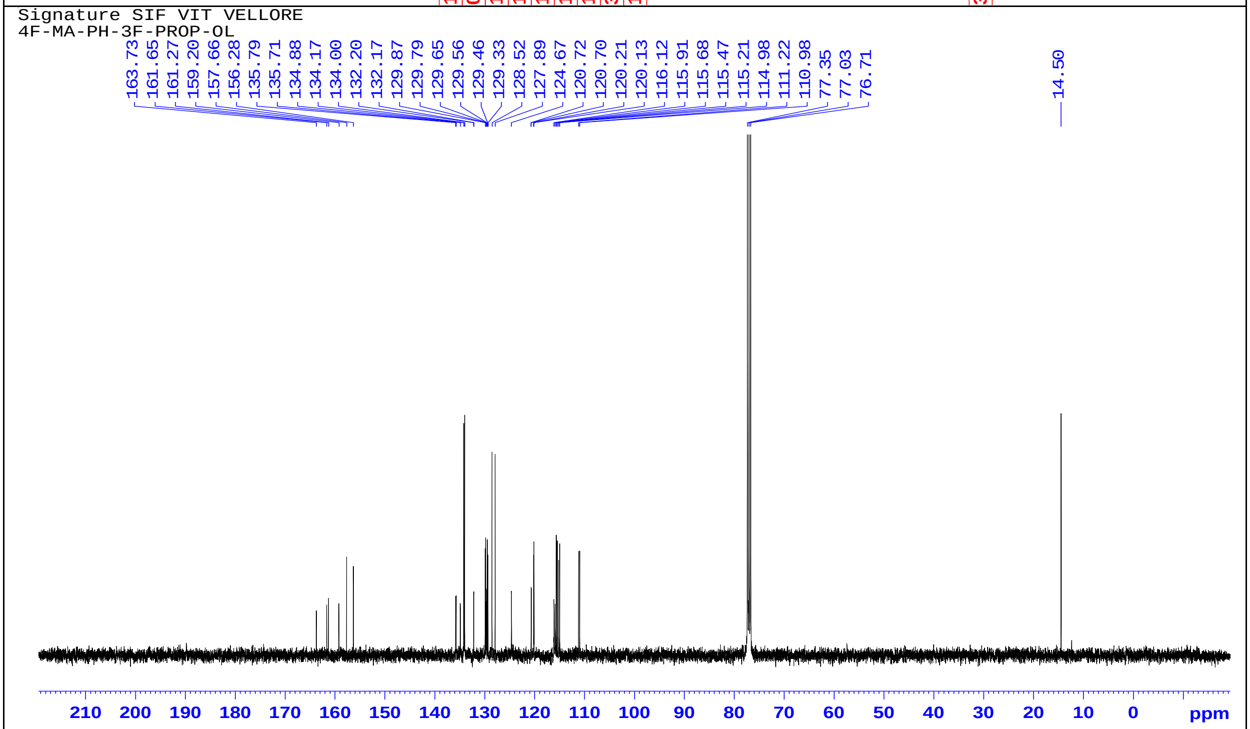


^{19}F NMR of **3ca**

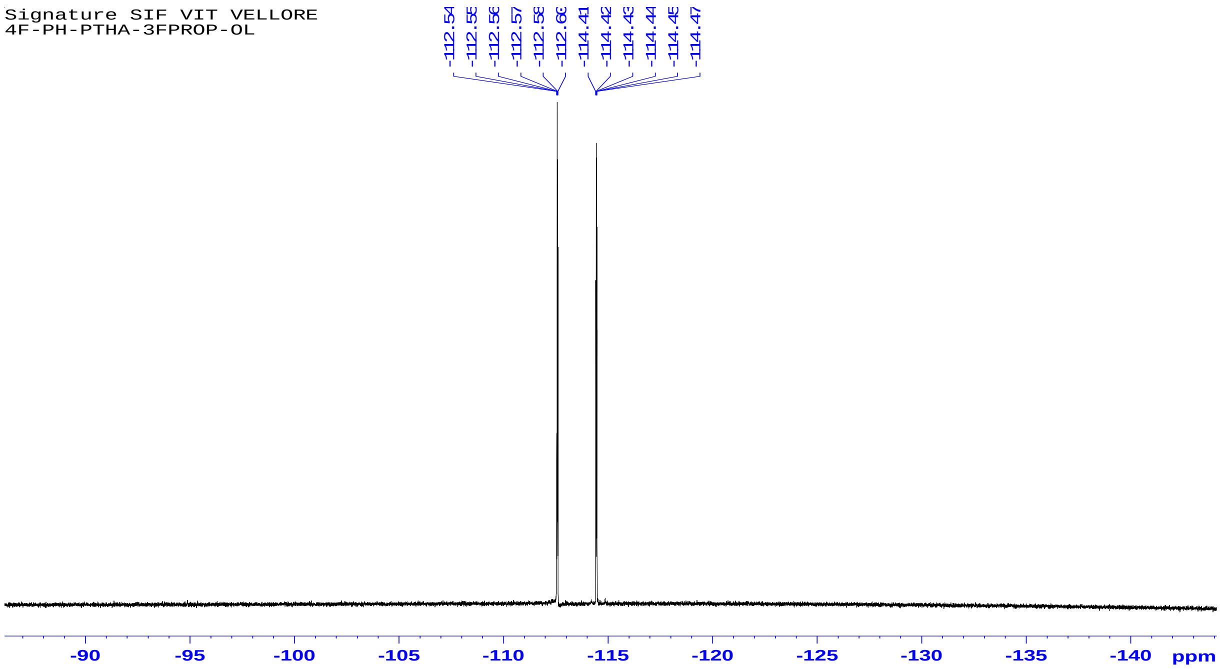


[1]H NMR and [13]C NMR of **3cf**

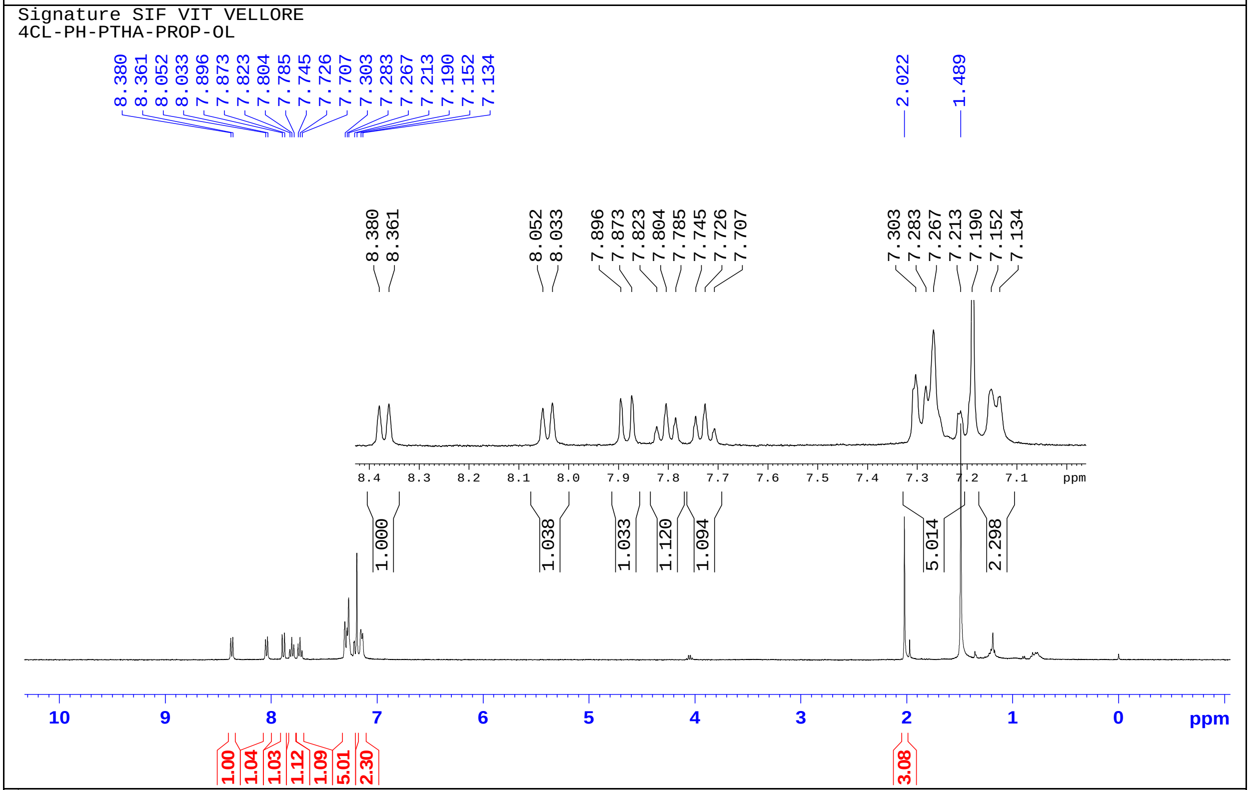


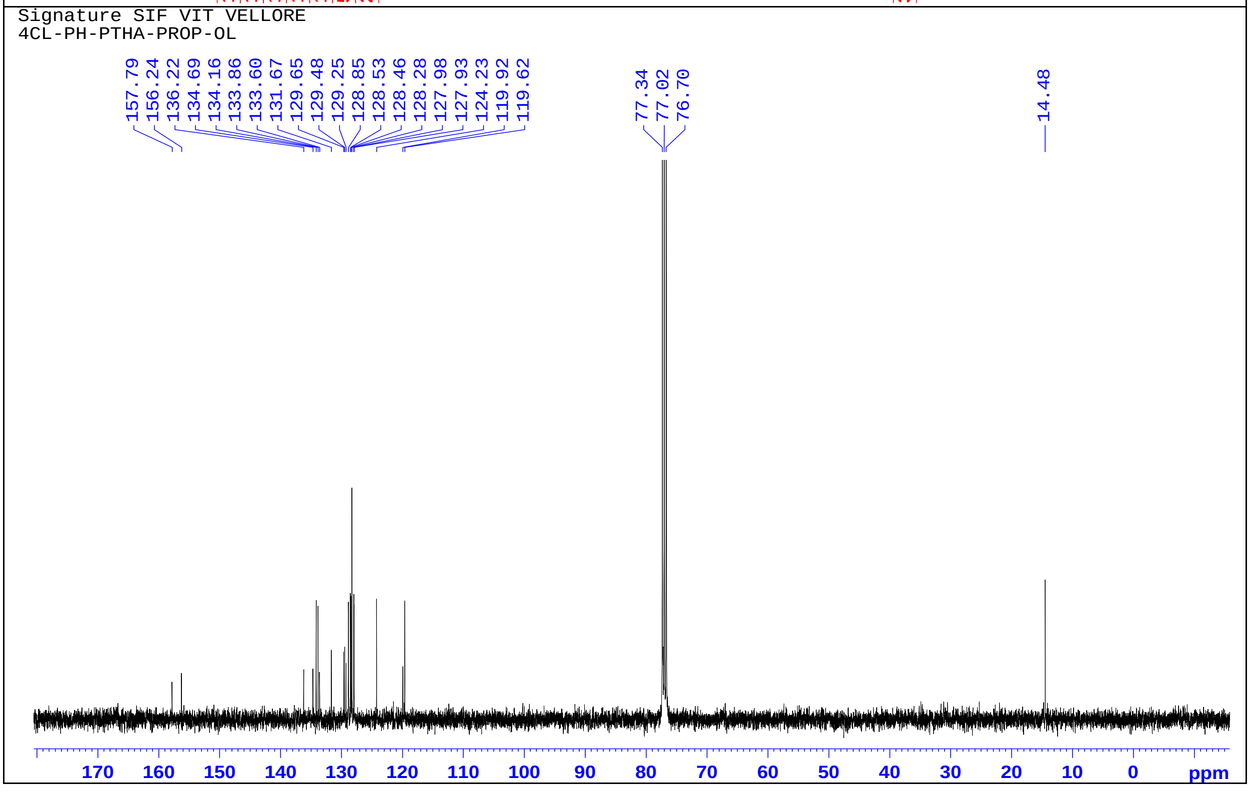


^{19}F NMR of **3cf**

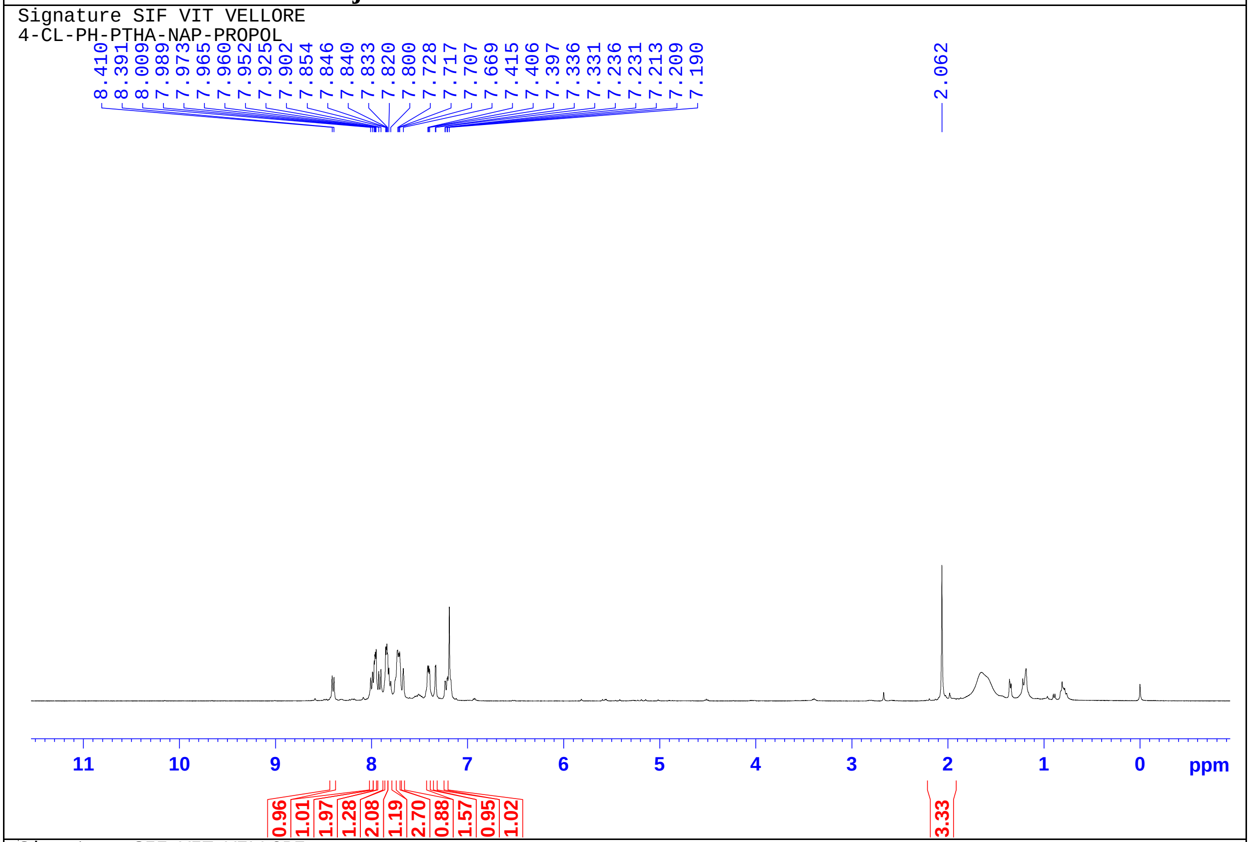


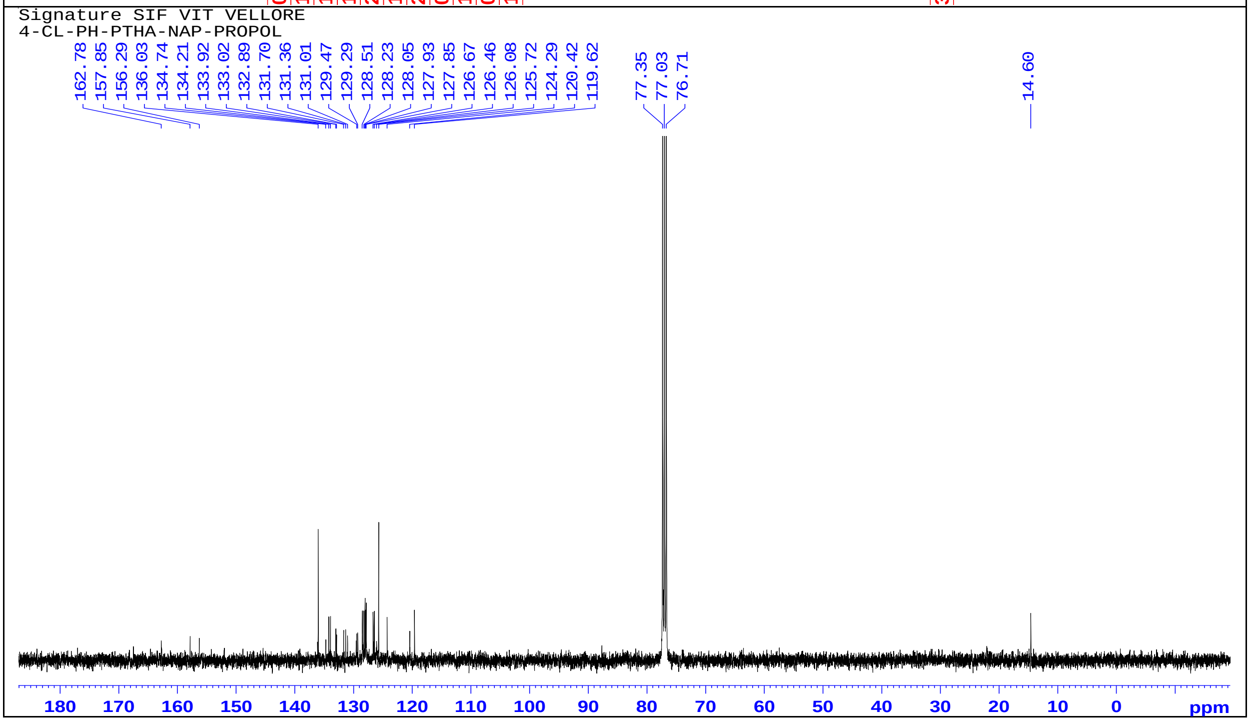
[1]H NMR and [13]C NMR of **3da**



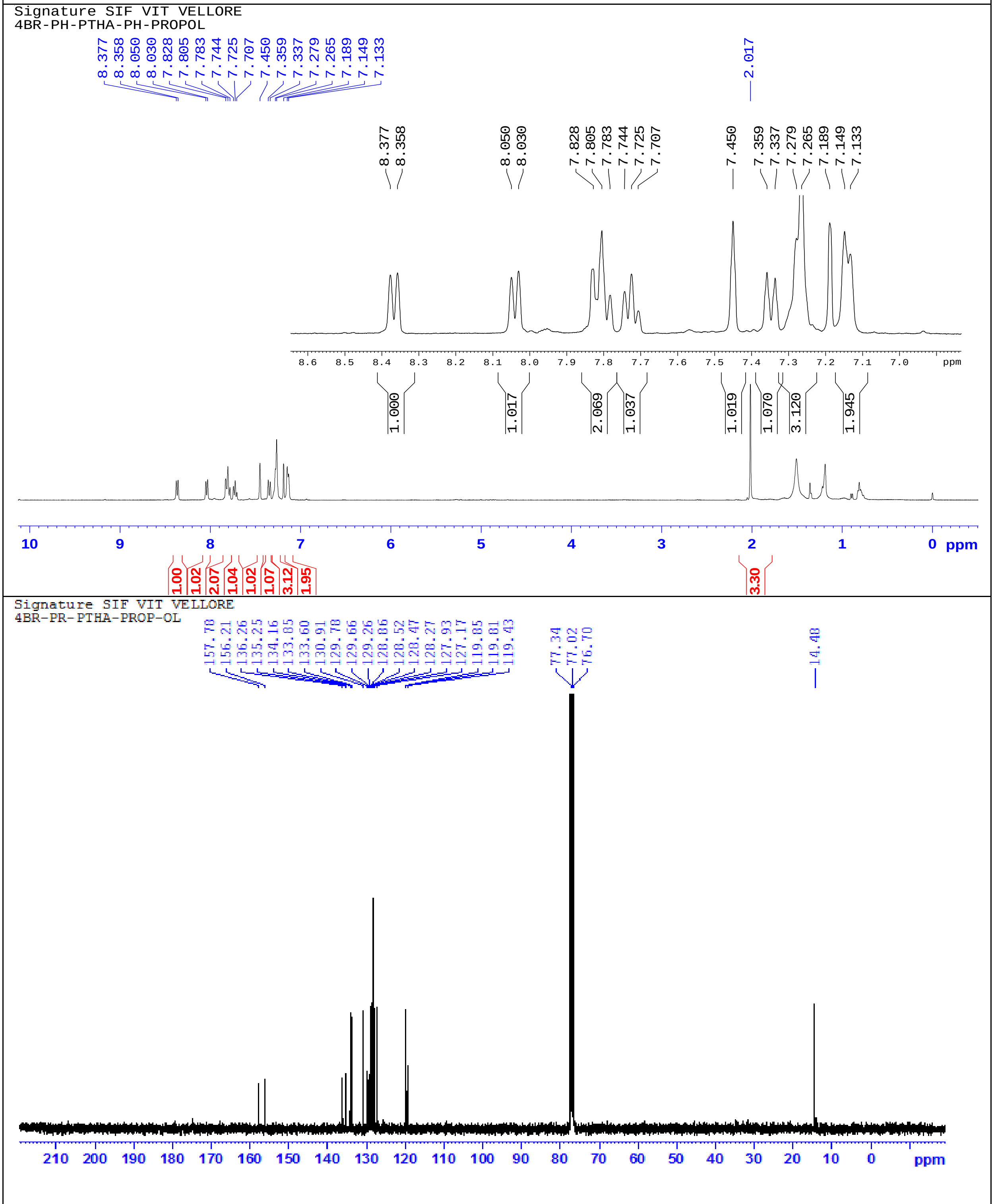


[1]H NMR and [13]C NMR of **3dj**

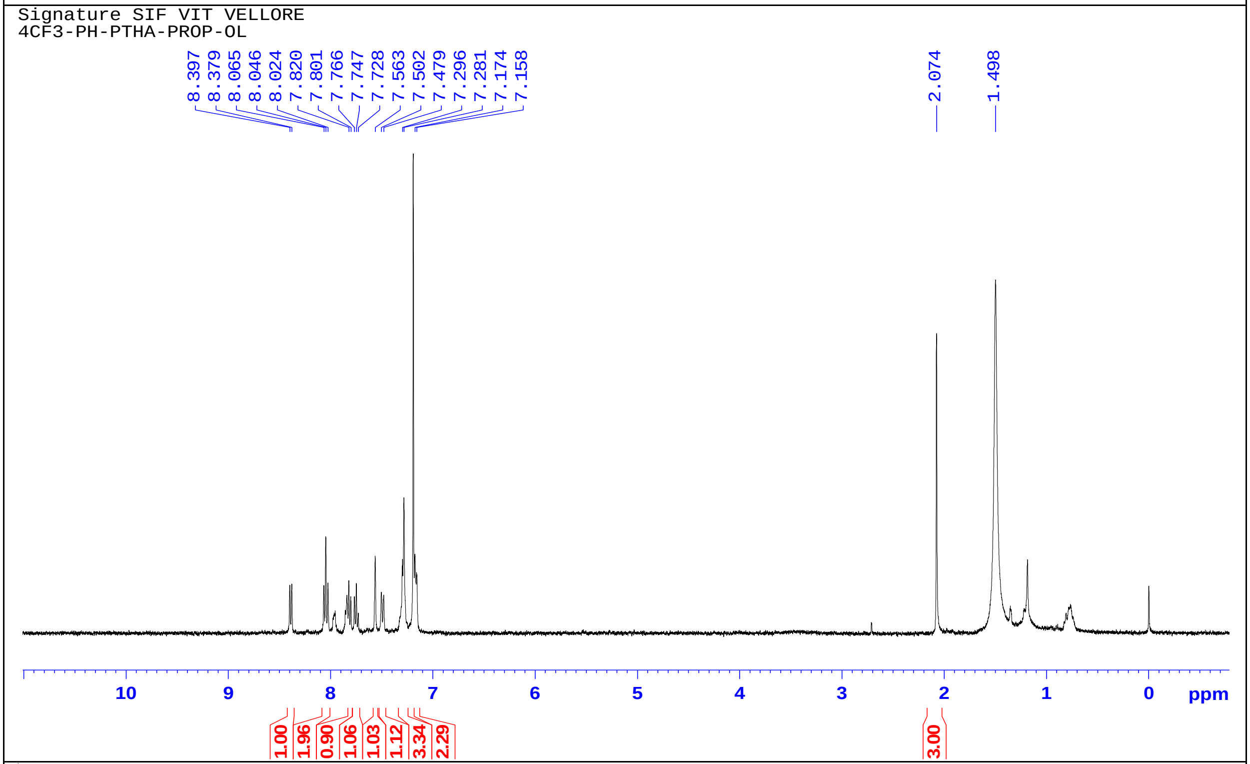


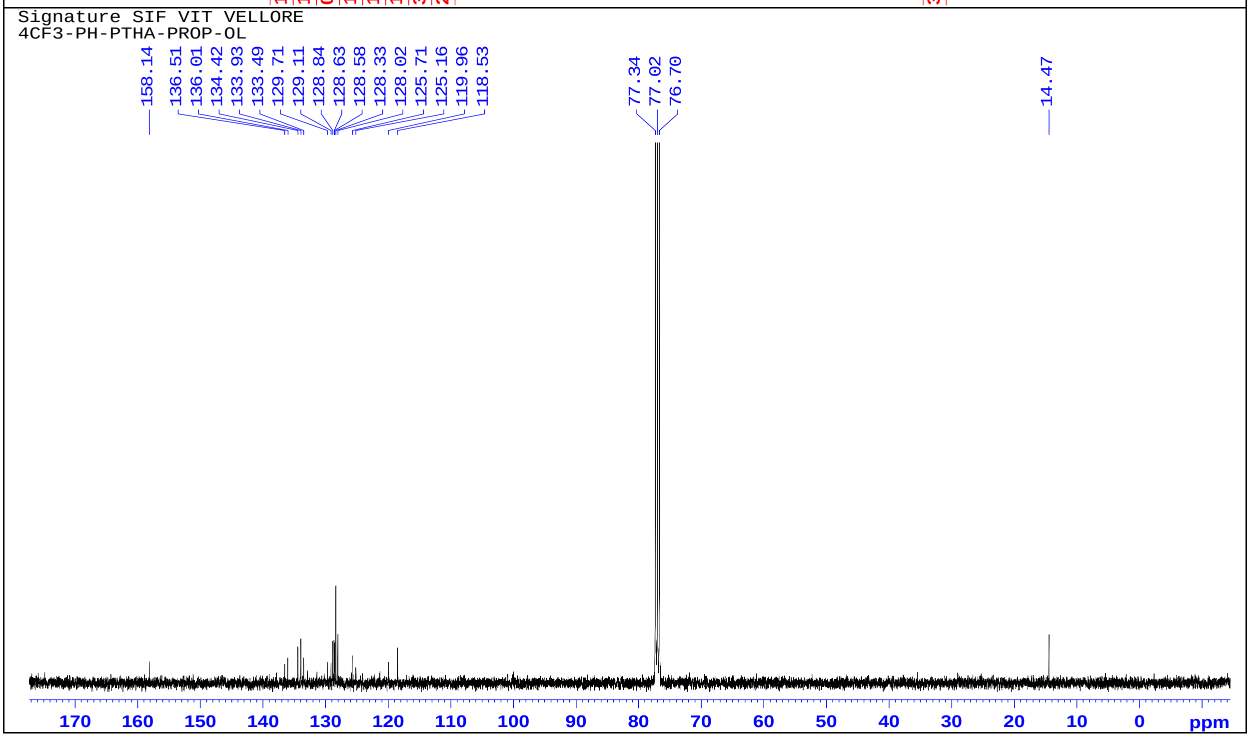


^{1}H NMR and ^{13}C NMR of **3ea**

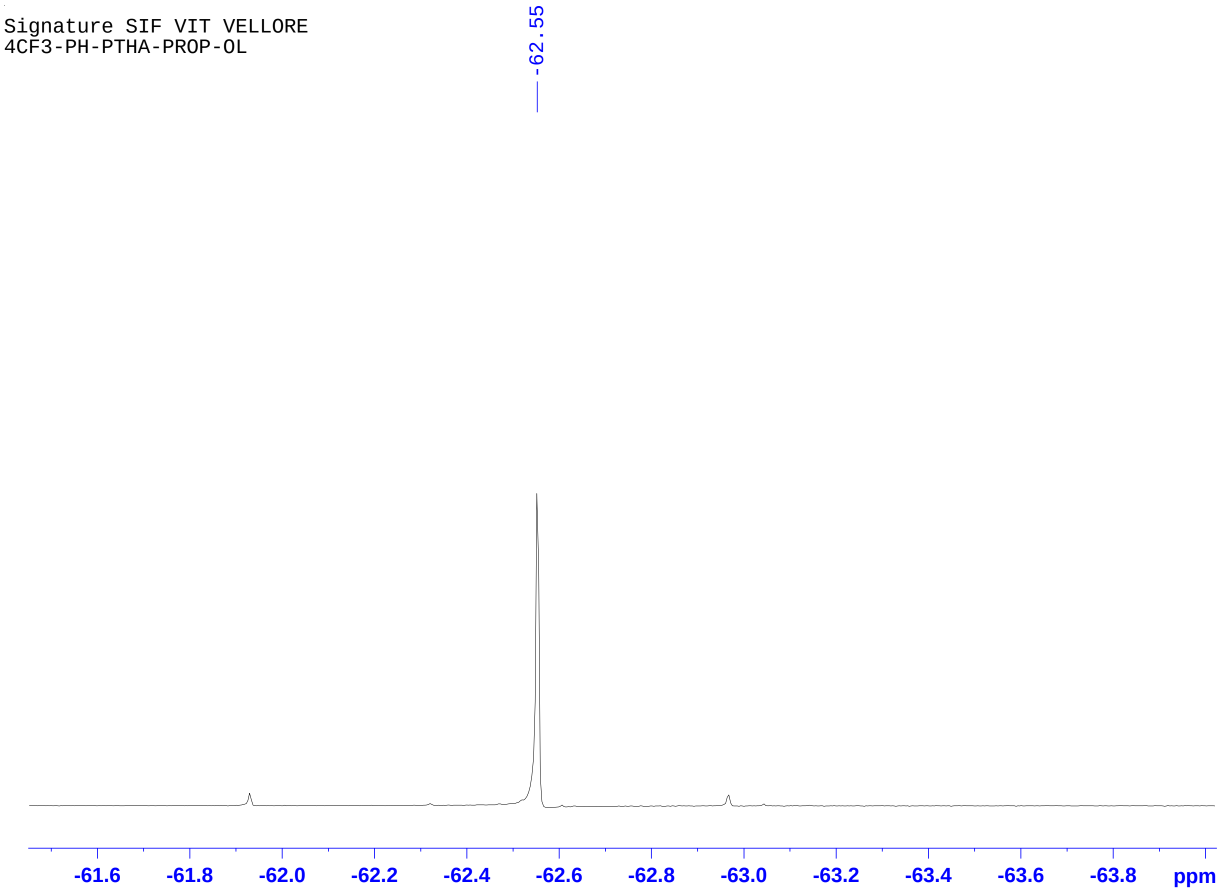


[1]H NMR and [13]C NMR of **3fa**

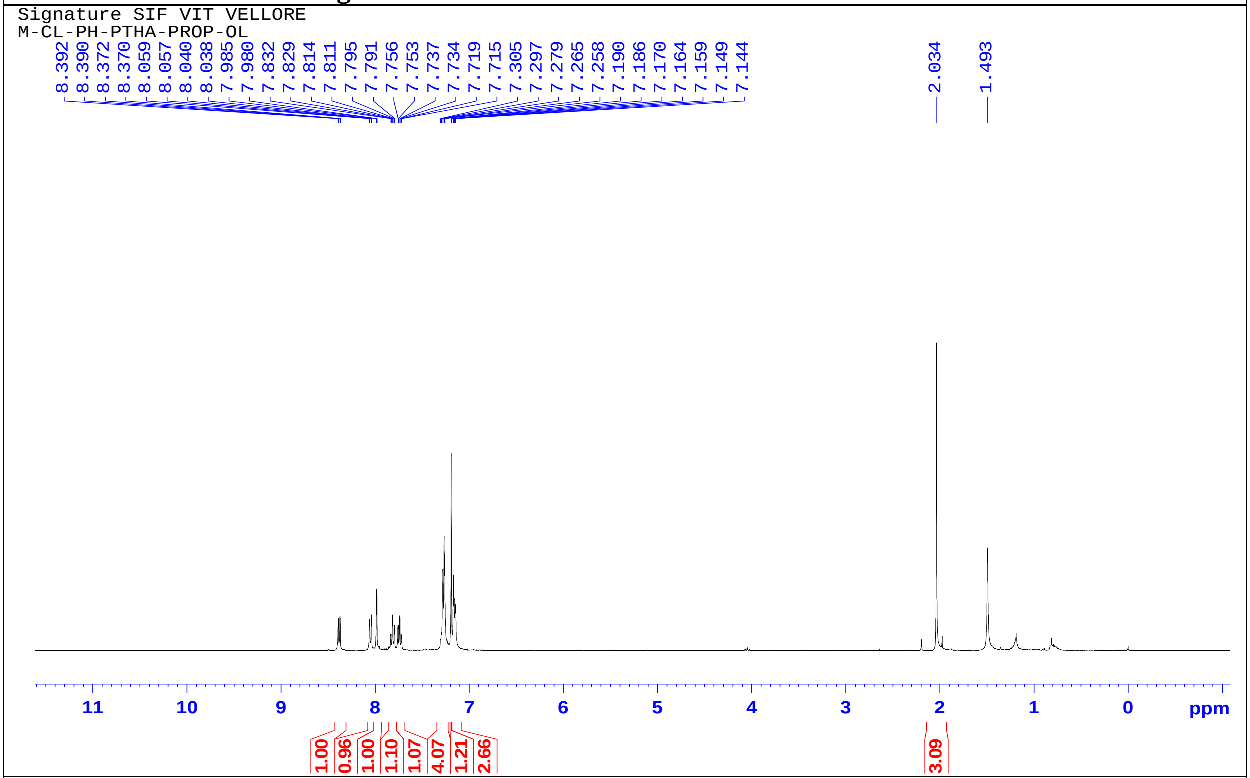


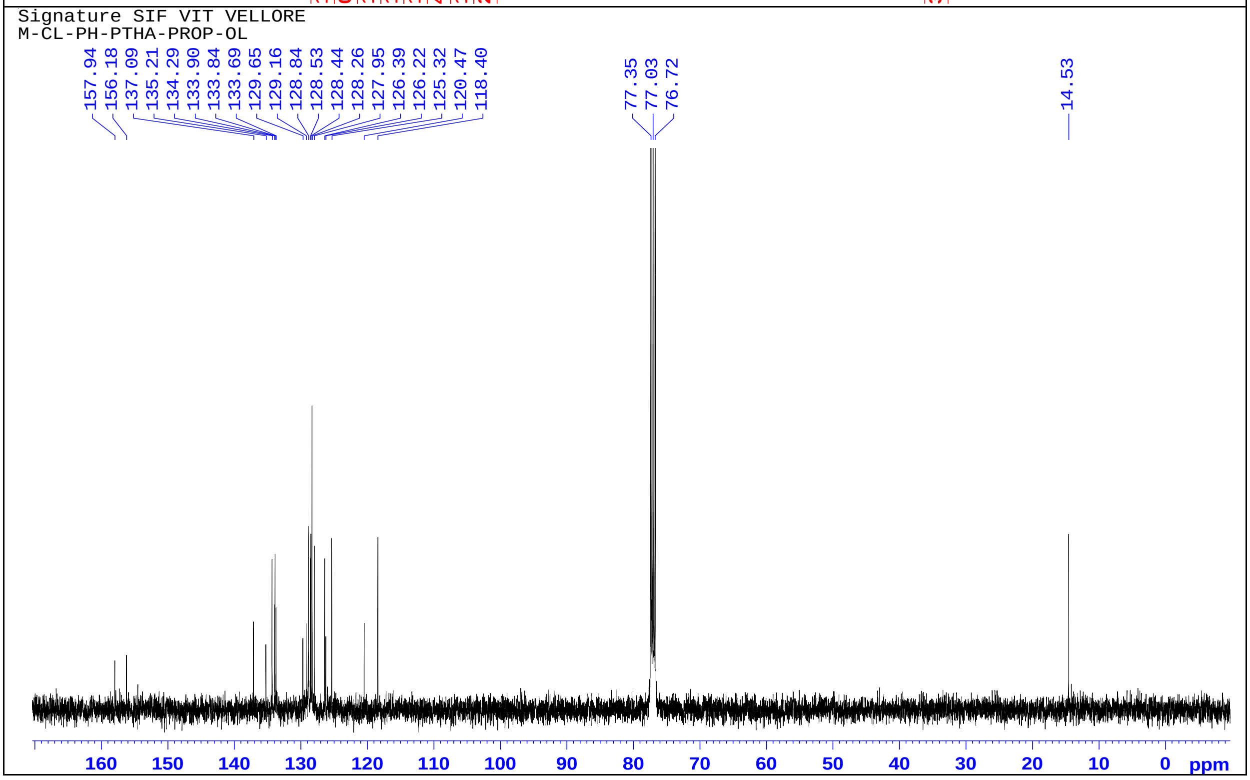


^{19}F NMR of **3fa**

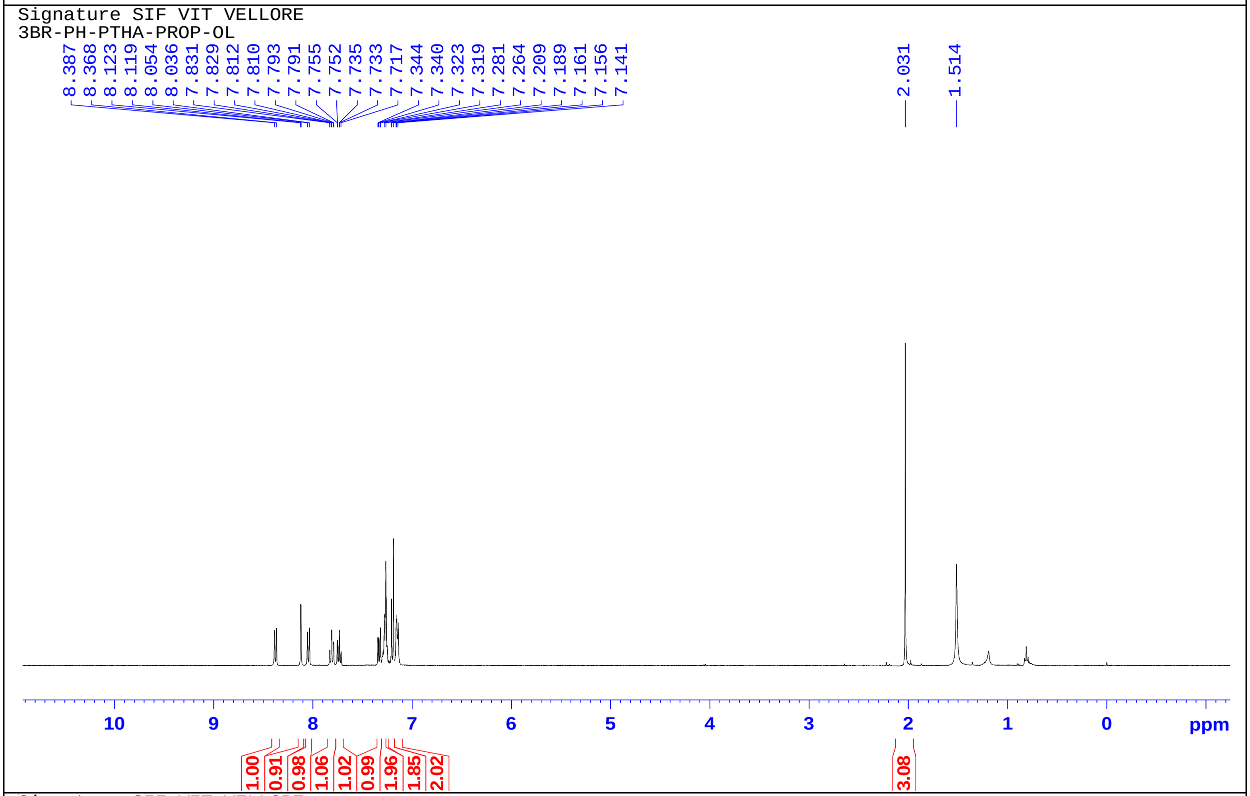


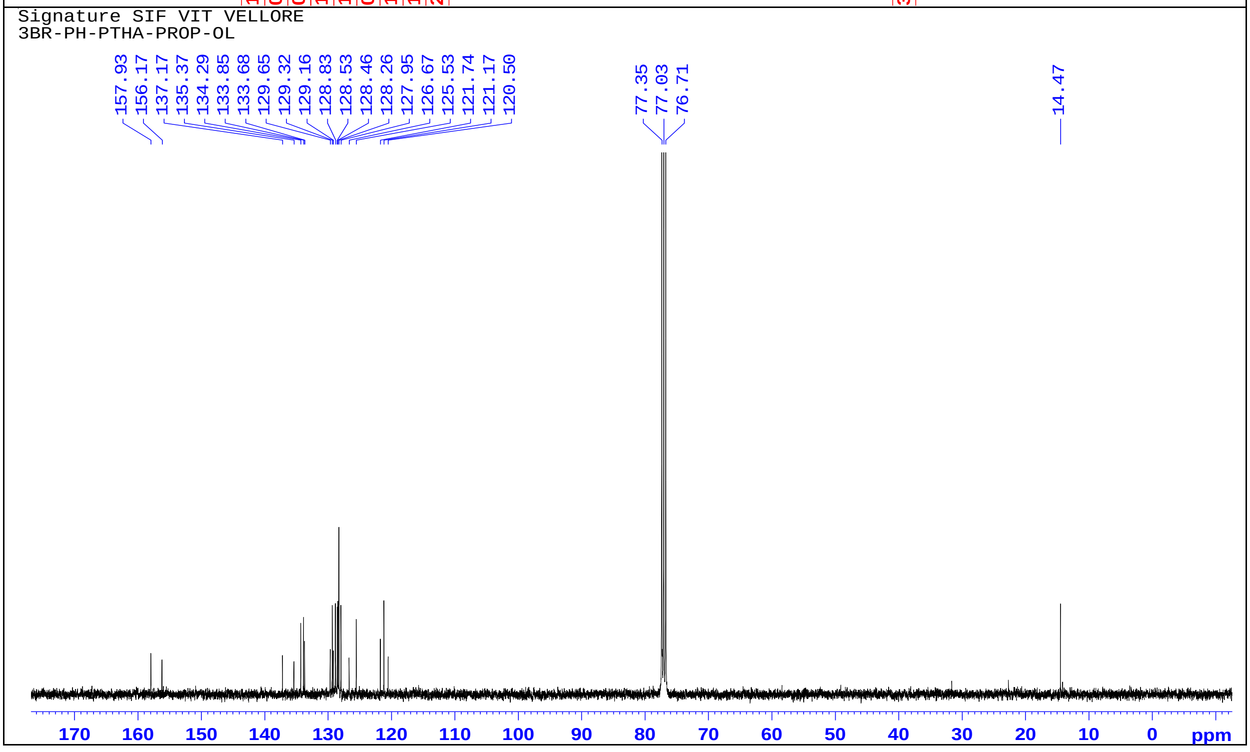
[1]H NMR and [13]C NMR of **3ga**



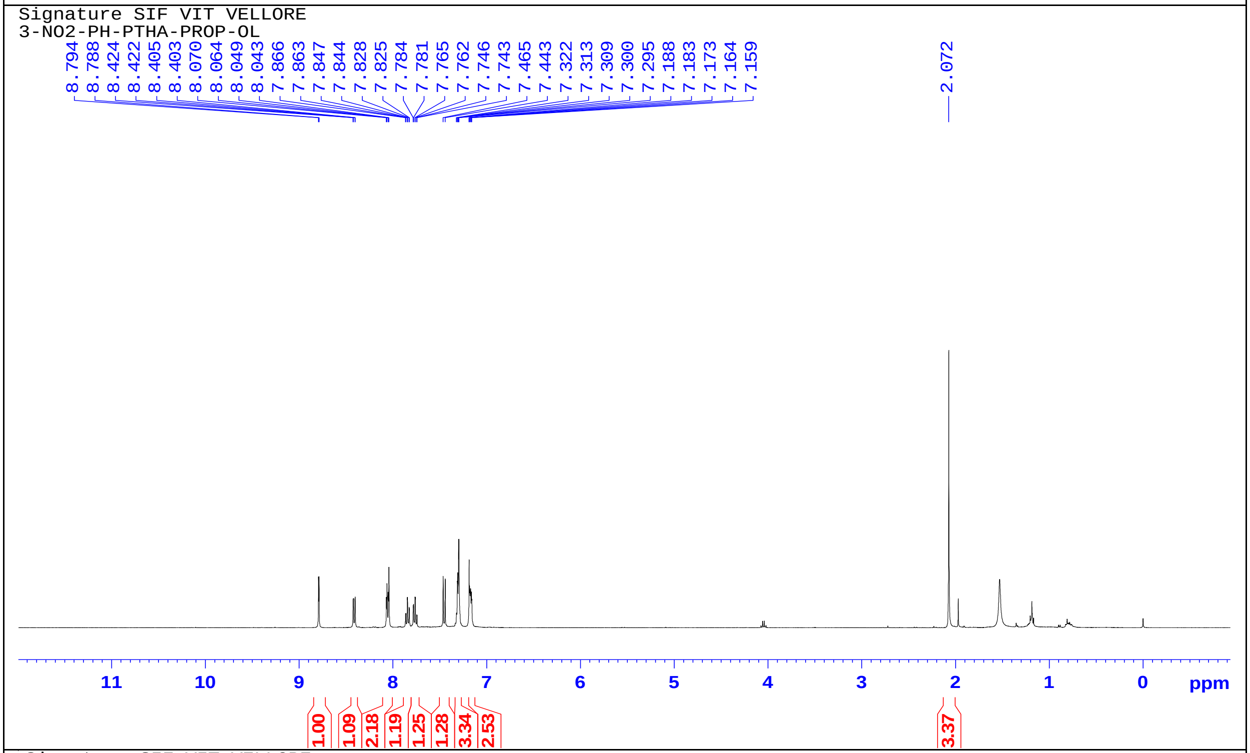


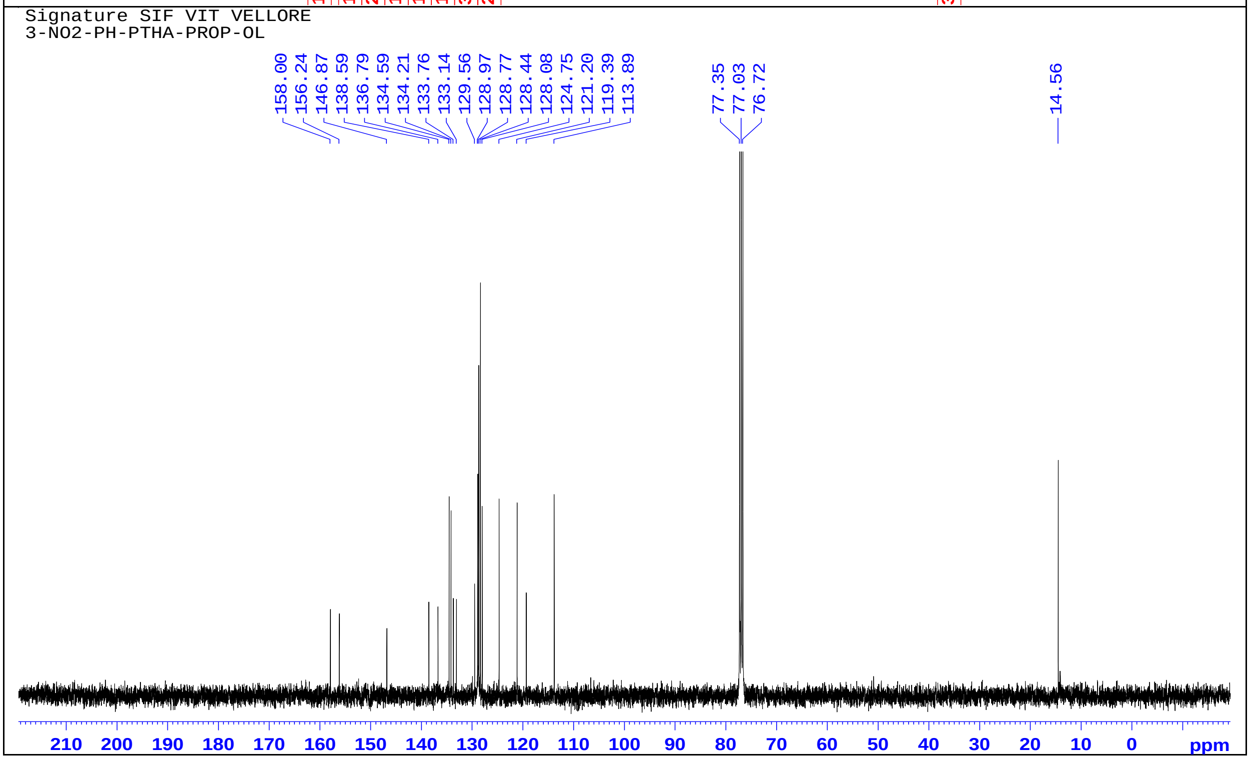
^{1}H NMR and ^{13}C NMR of **3ha**



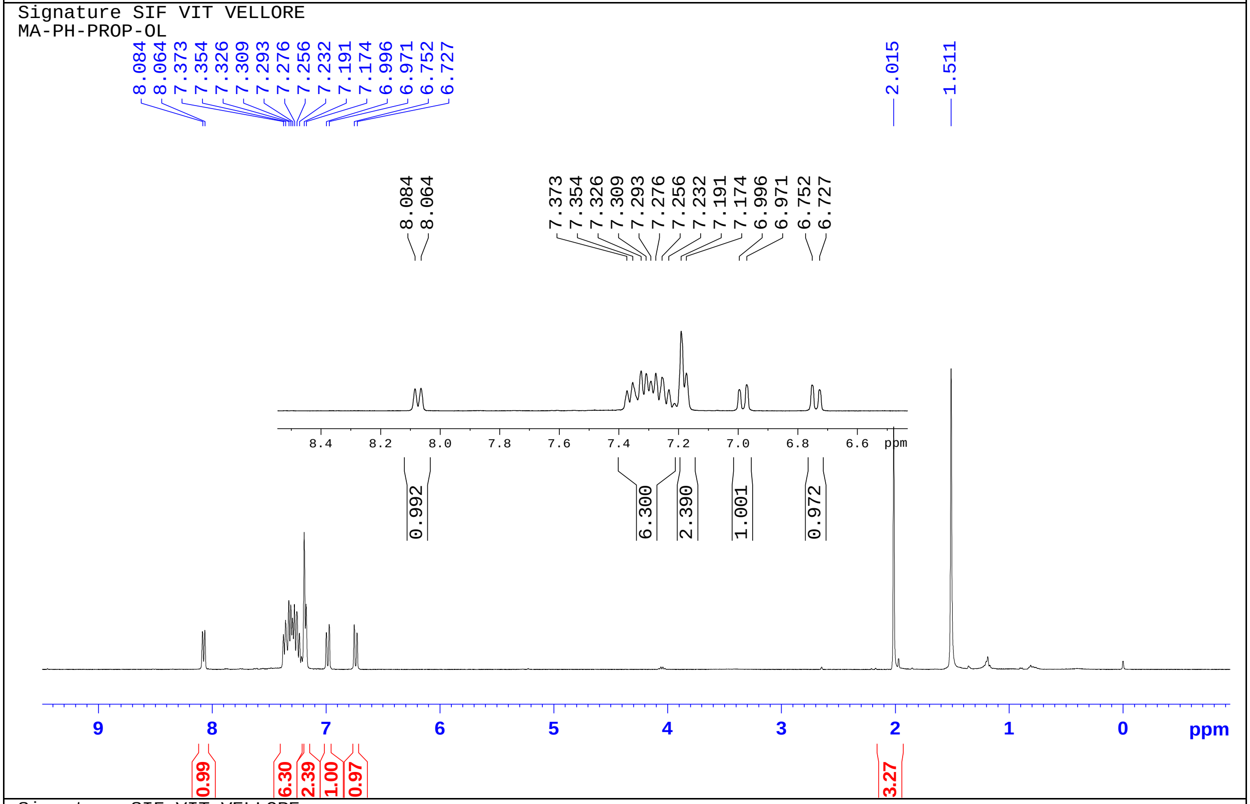


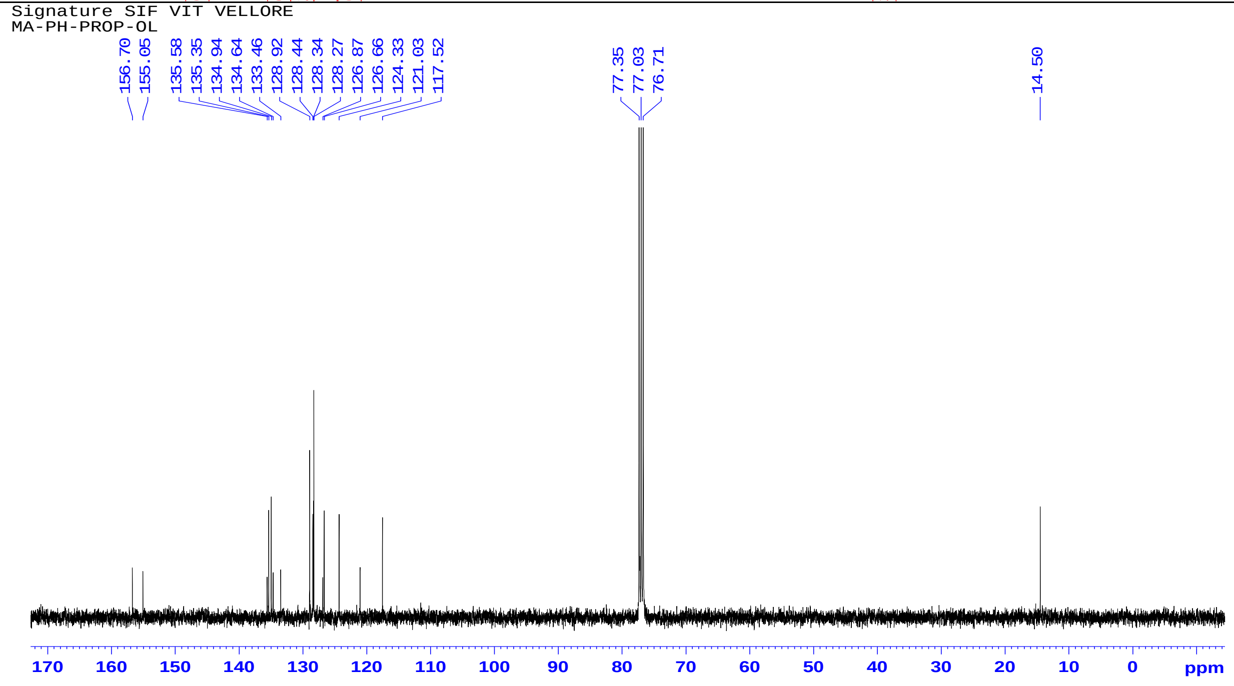
^{1}H NMR and ^{13}C NMR of **3ia**



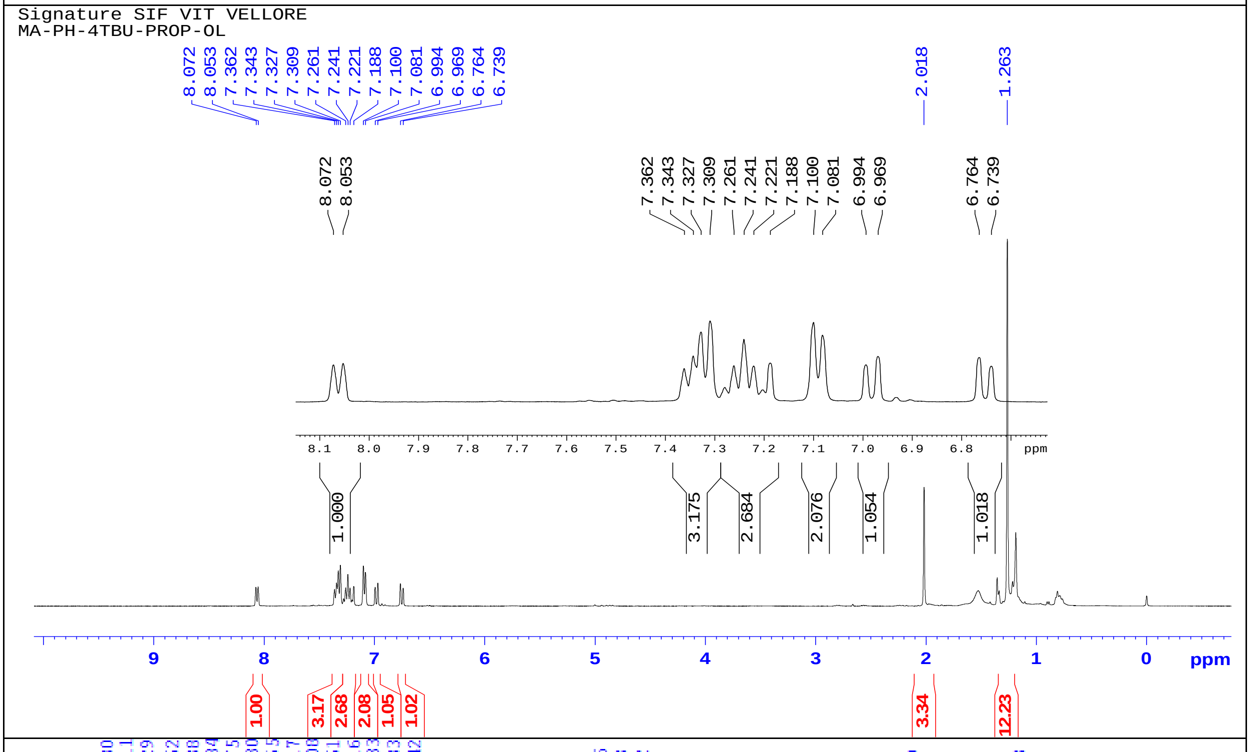


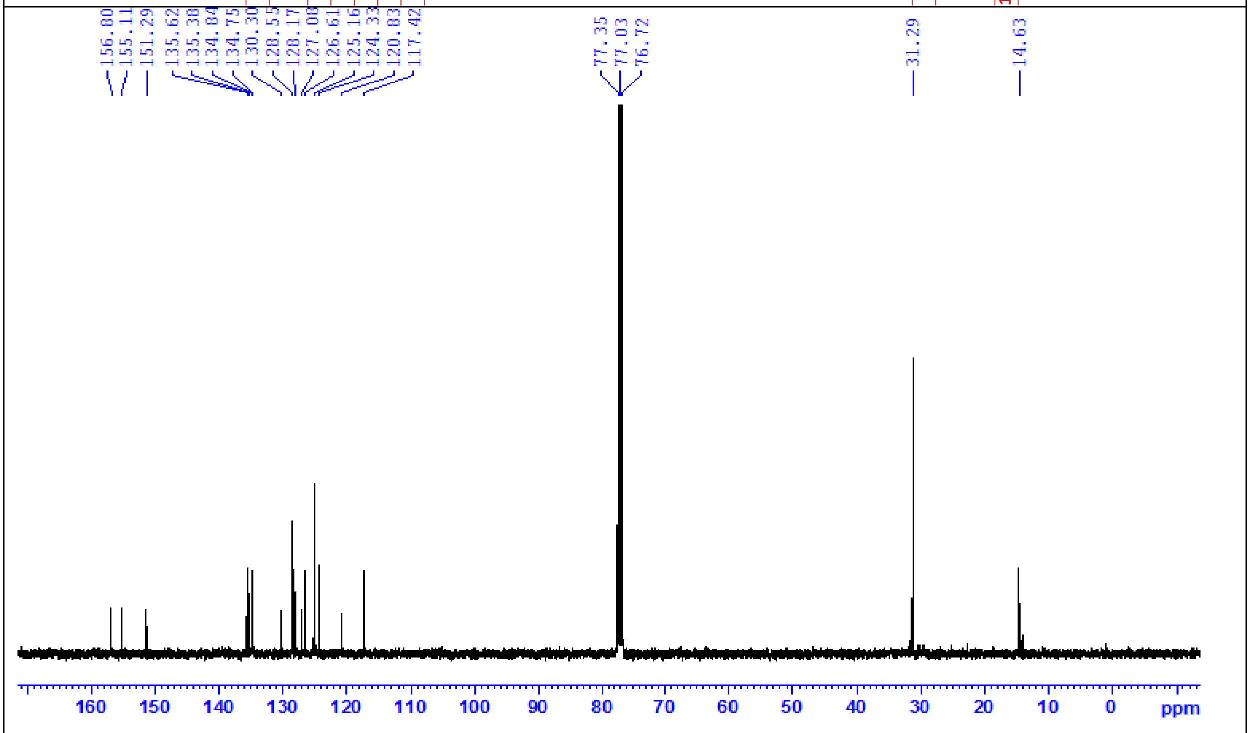
^{1}H NMR and ^{13}C NMR of **5aa**



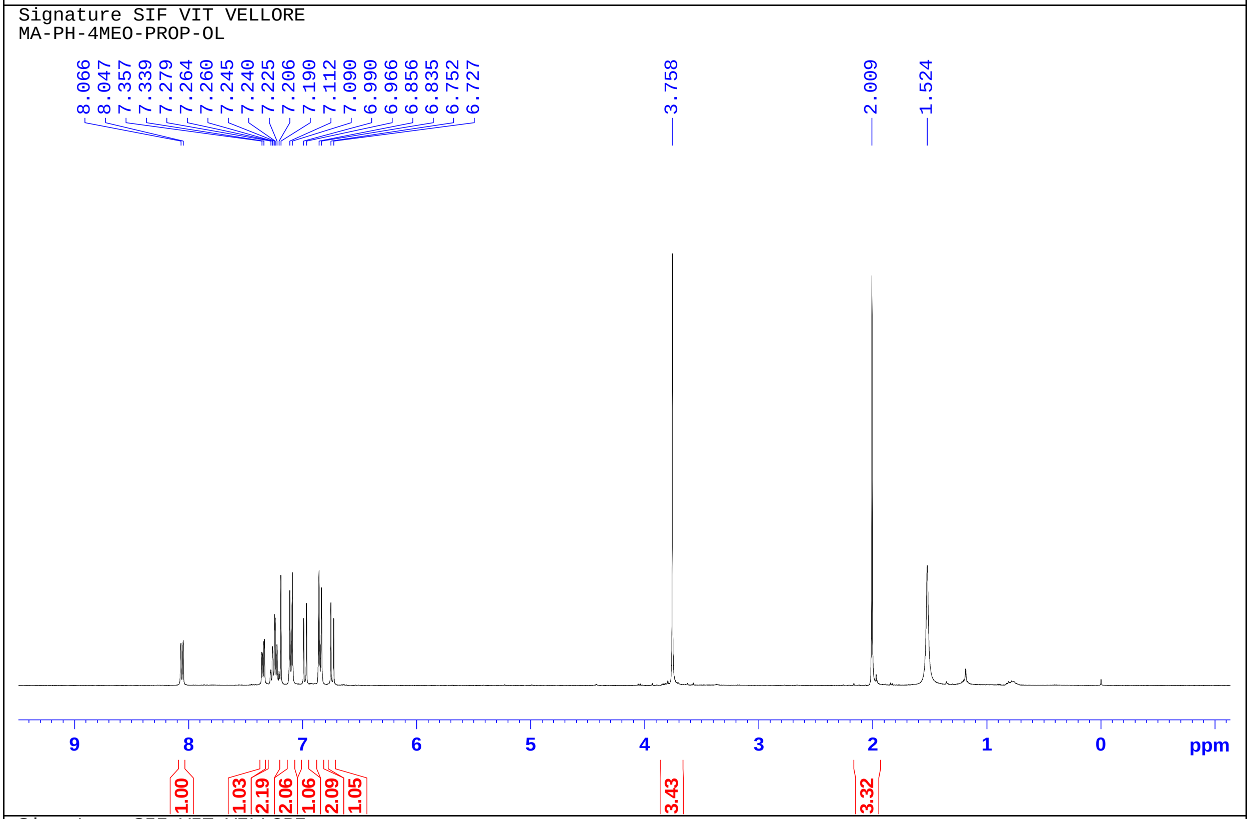


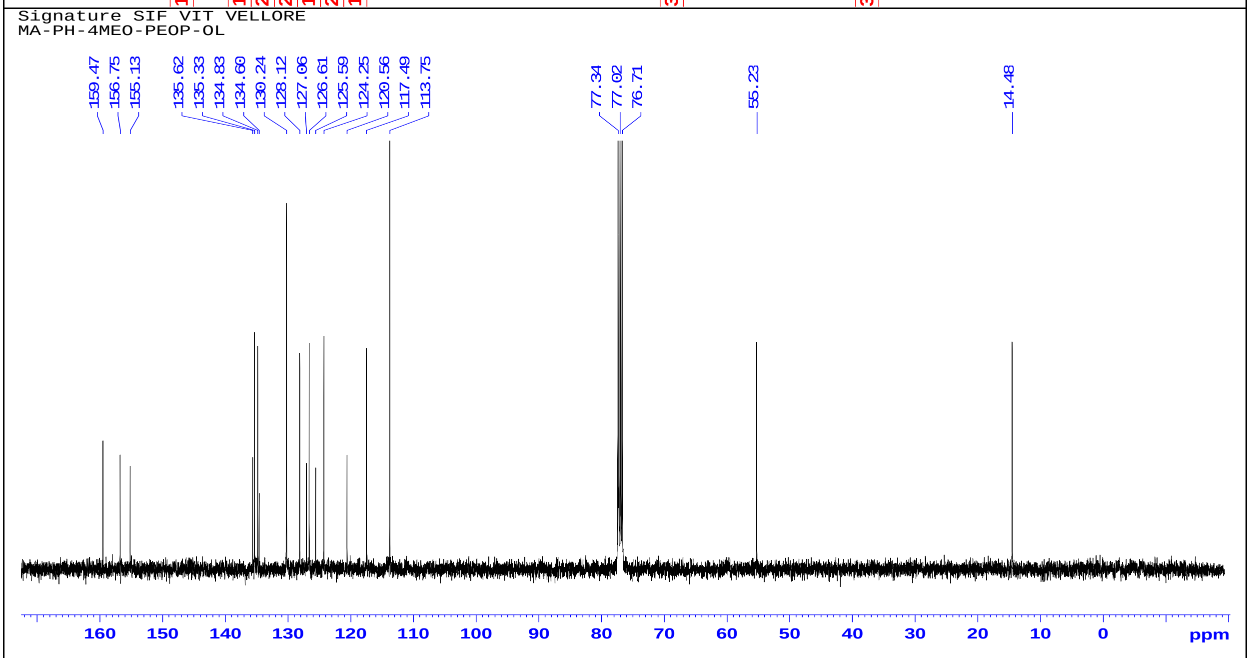
[1]H NMR and [13]C NMR of **5ab**



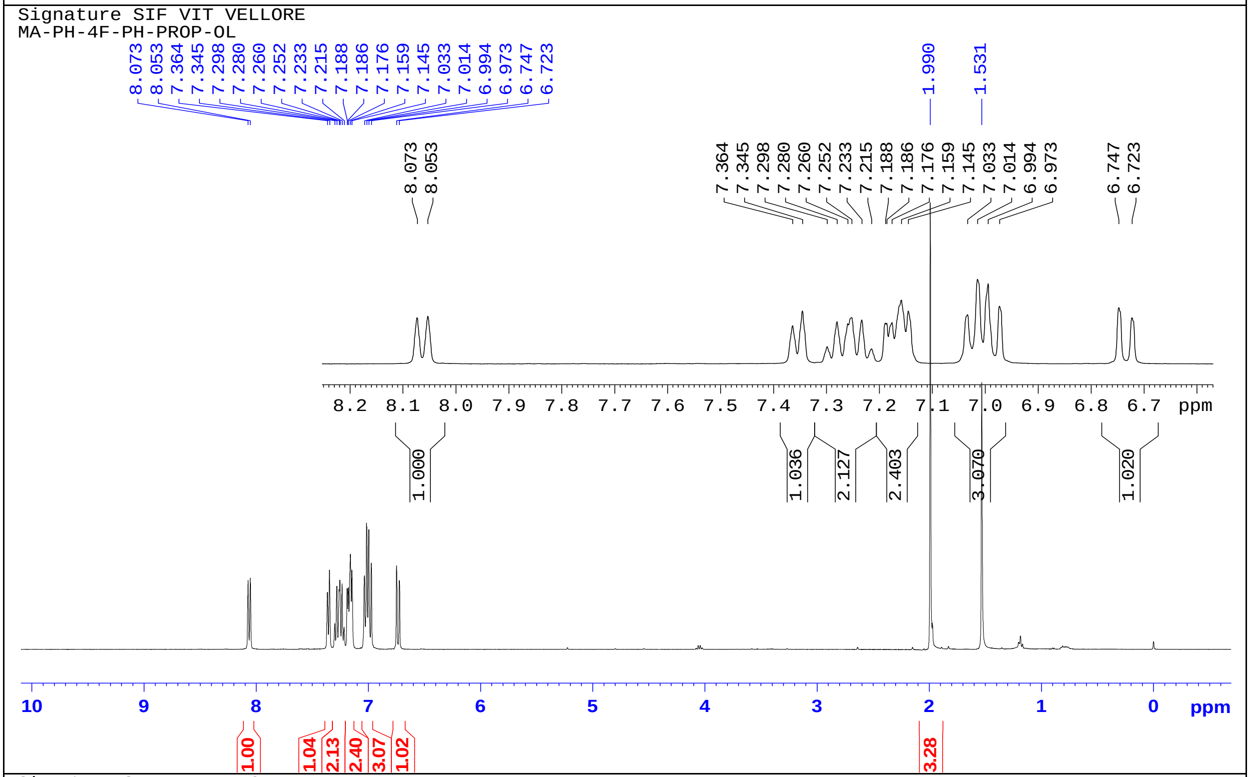


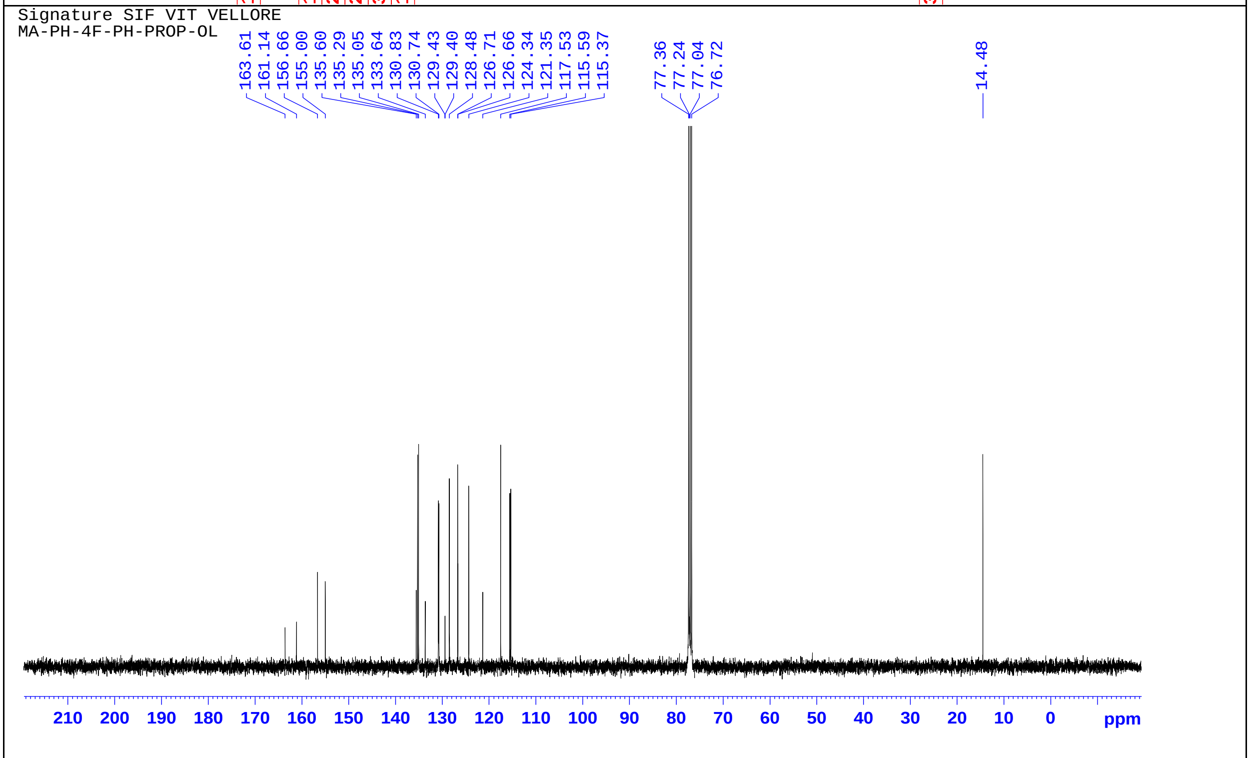
^{1}H NMR and ^{13}C NMR of **5ac**



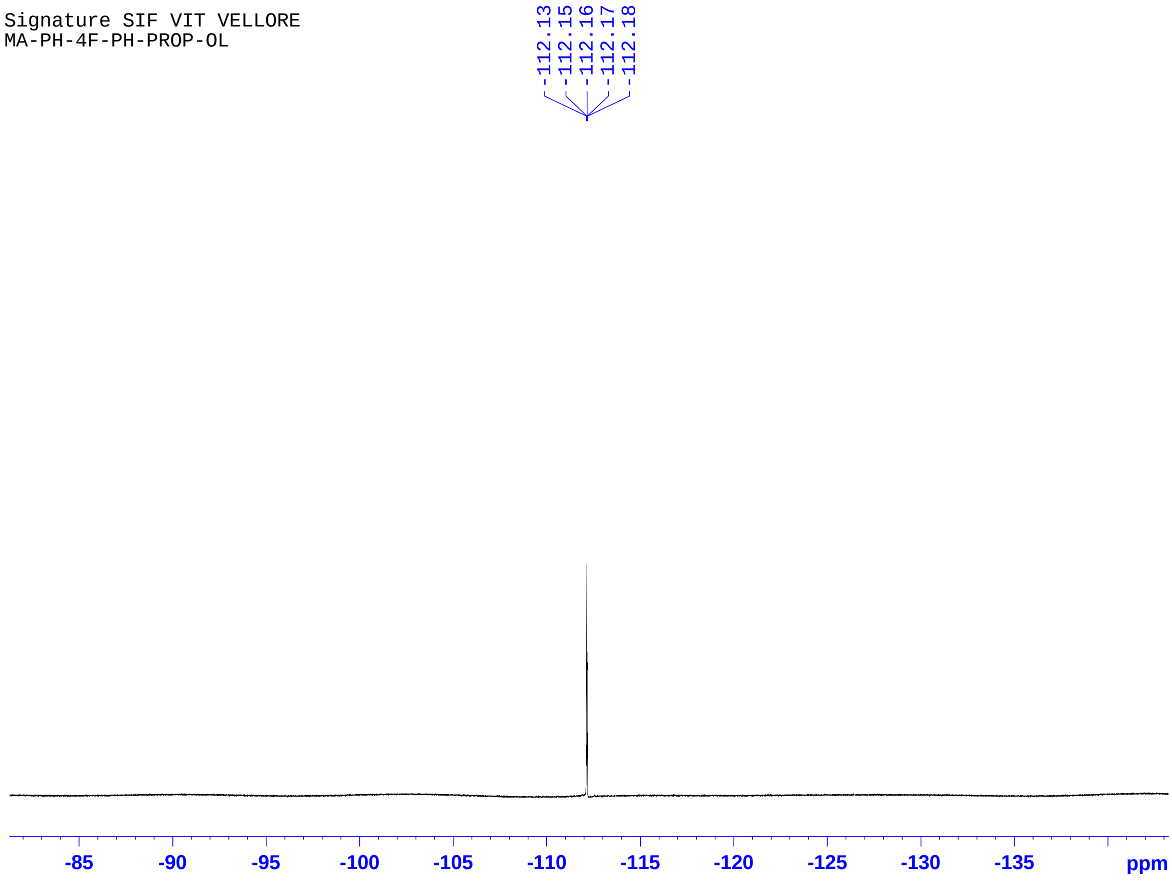


[1]H NMR and [13]C NMR of **5ad**

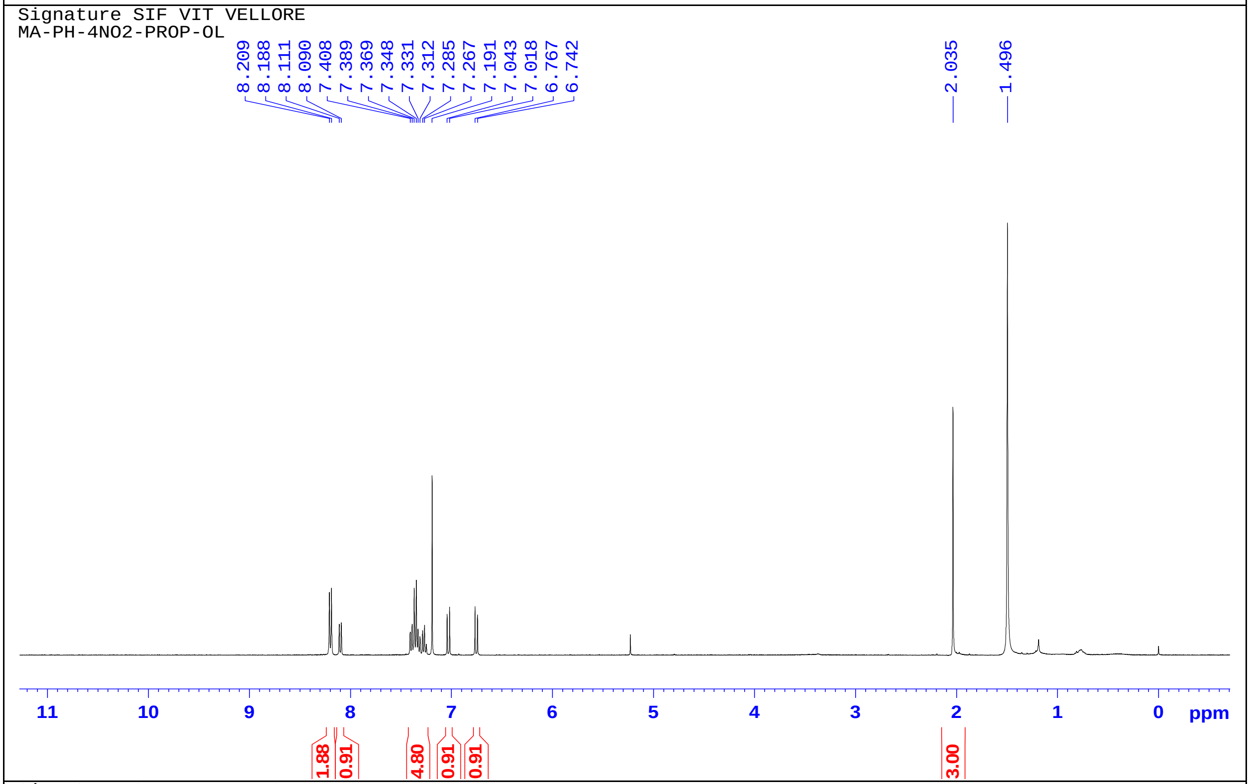


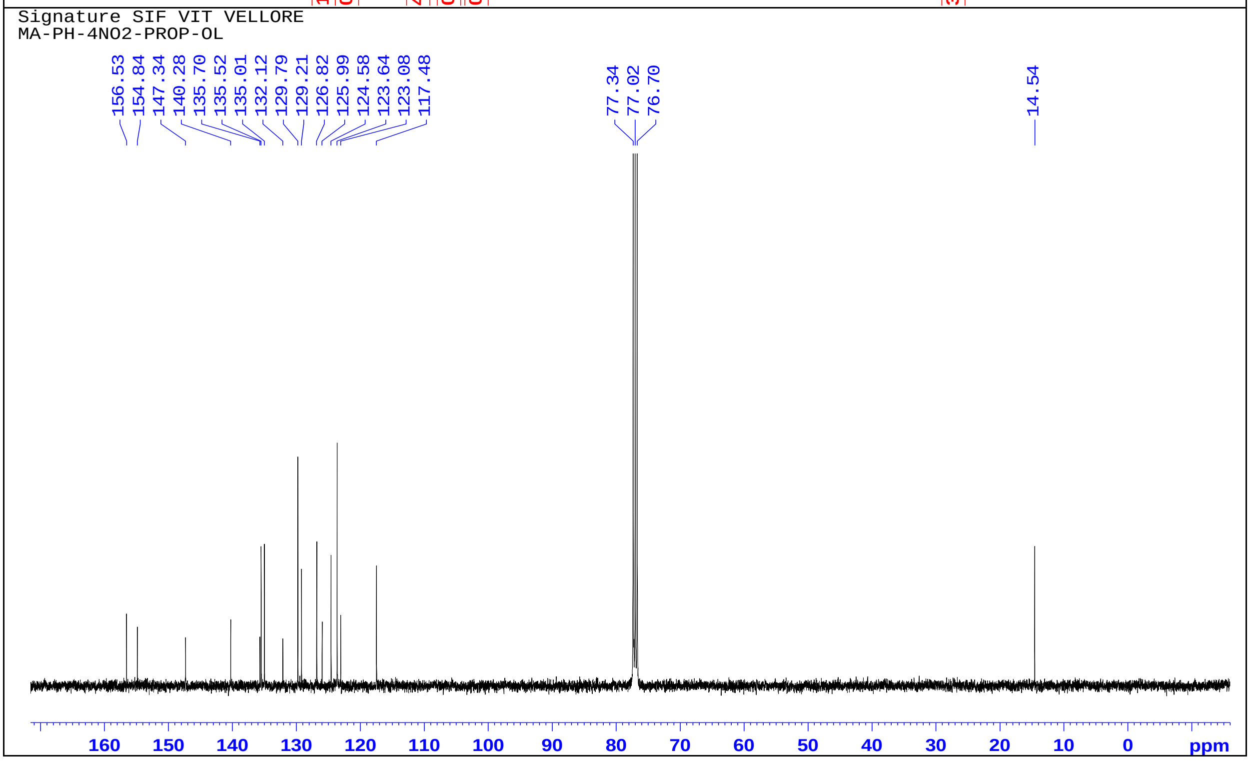


^{19}F NMR of **5ad**

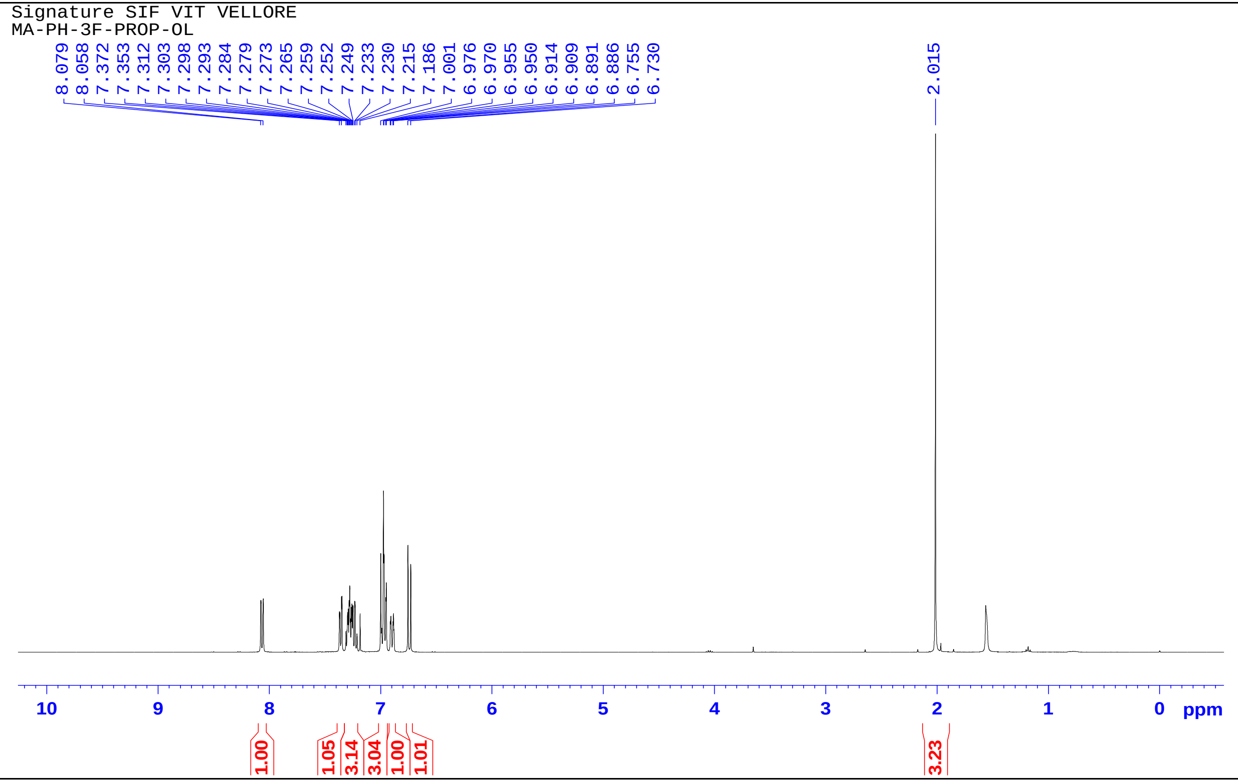


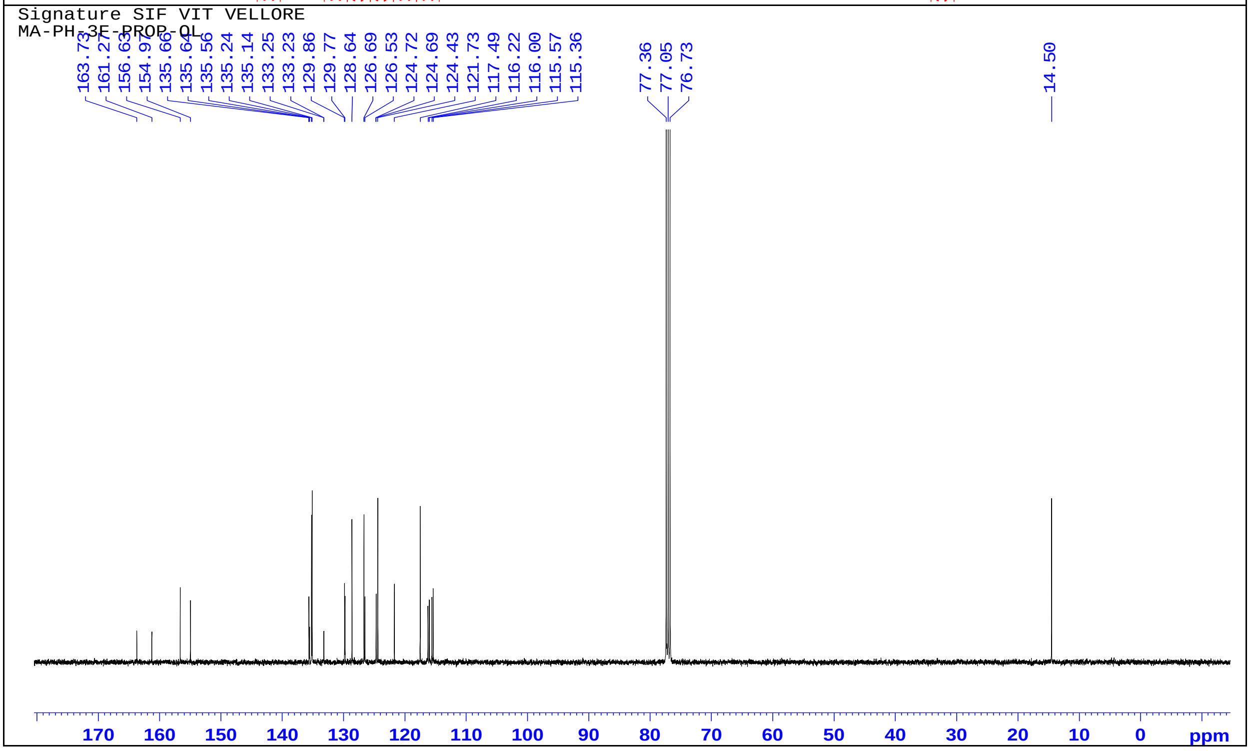
^{1}H NMR and ^{13}C NMR of **5ae**



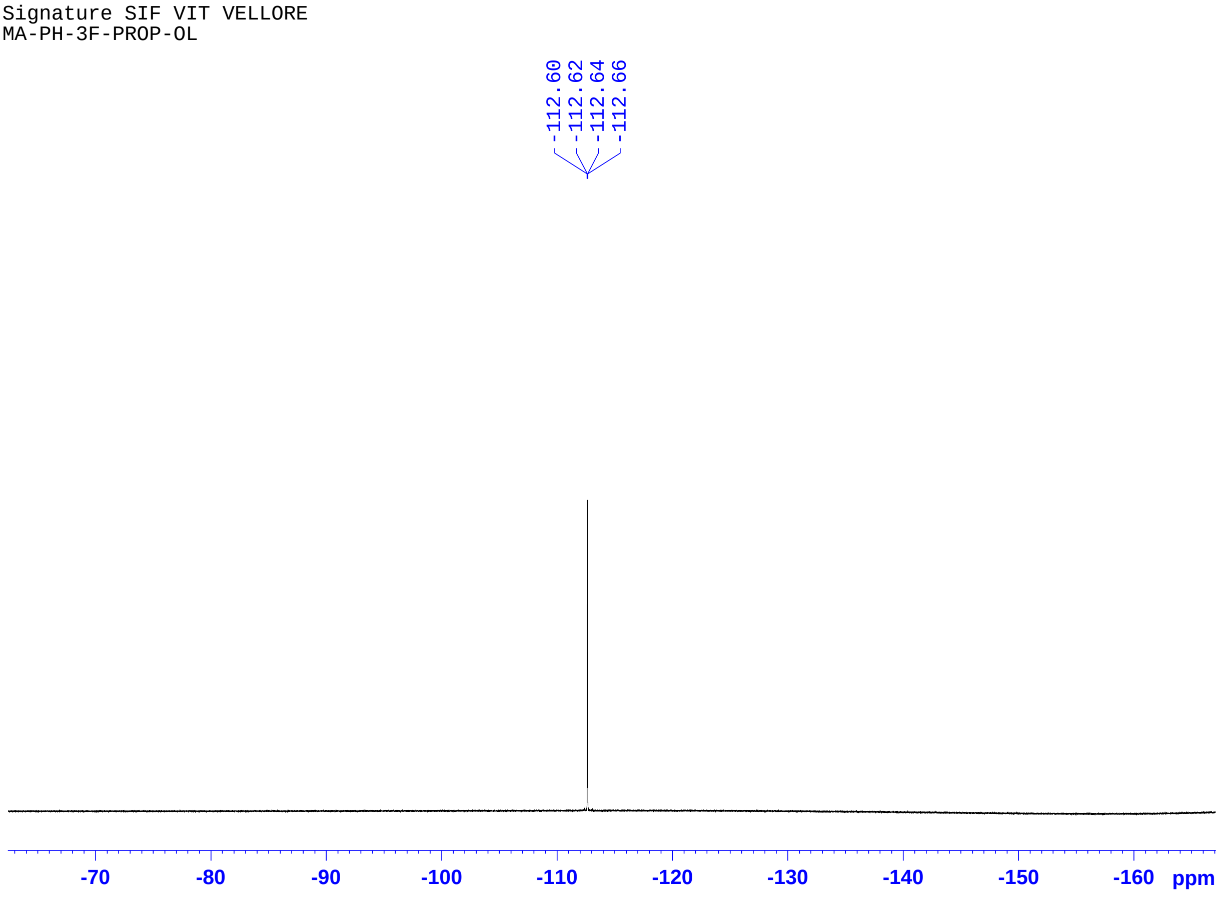


^{1}H NMR and ^{13}C NMR of **5af**

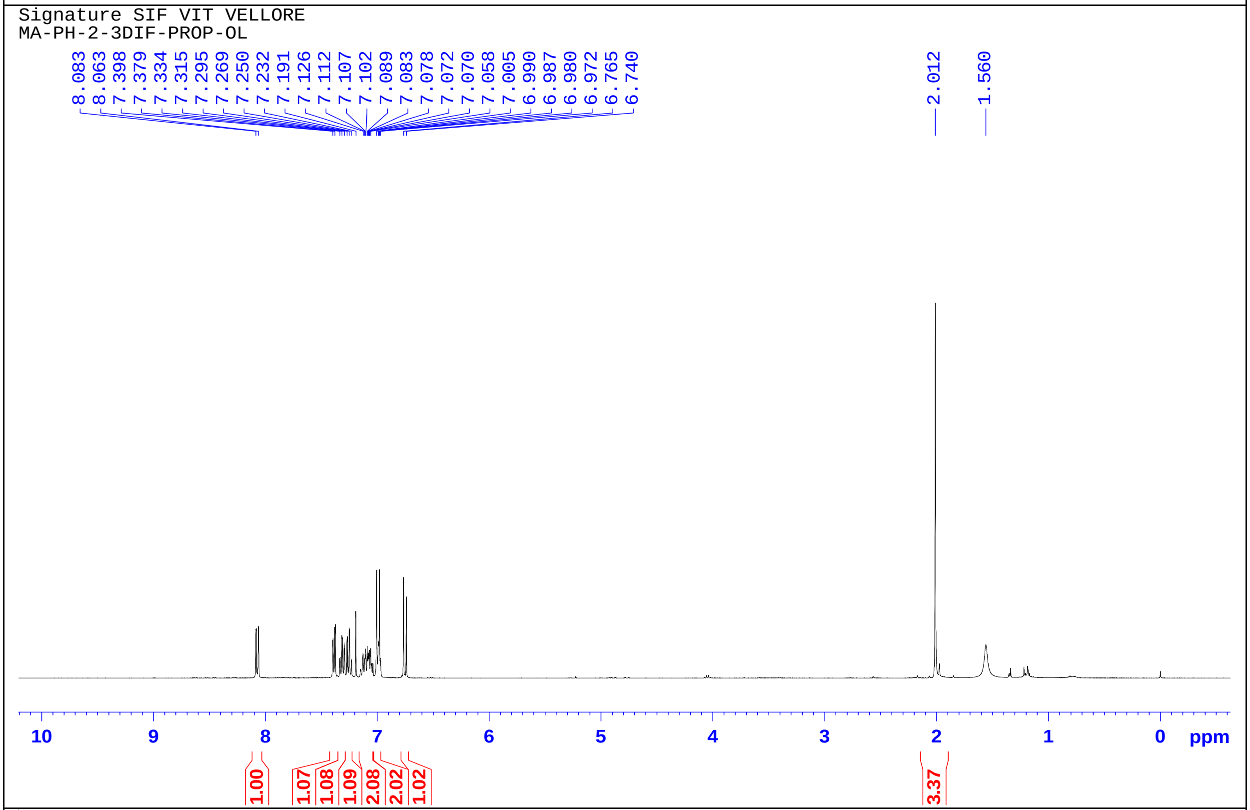


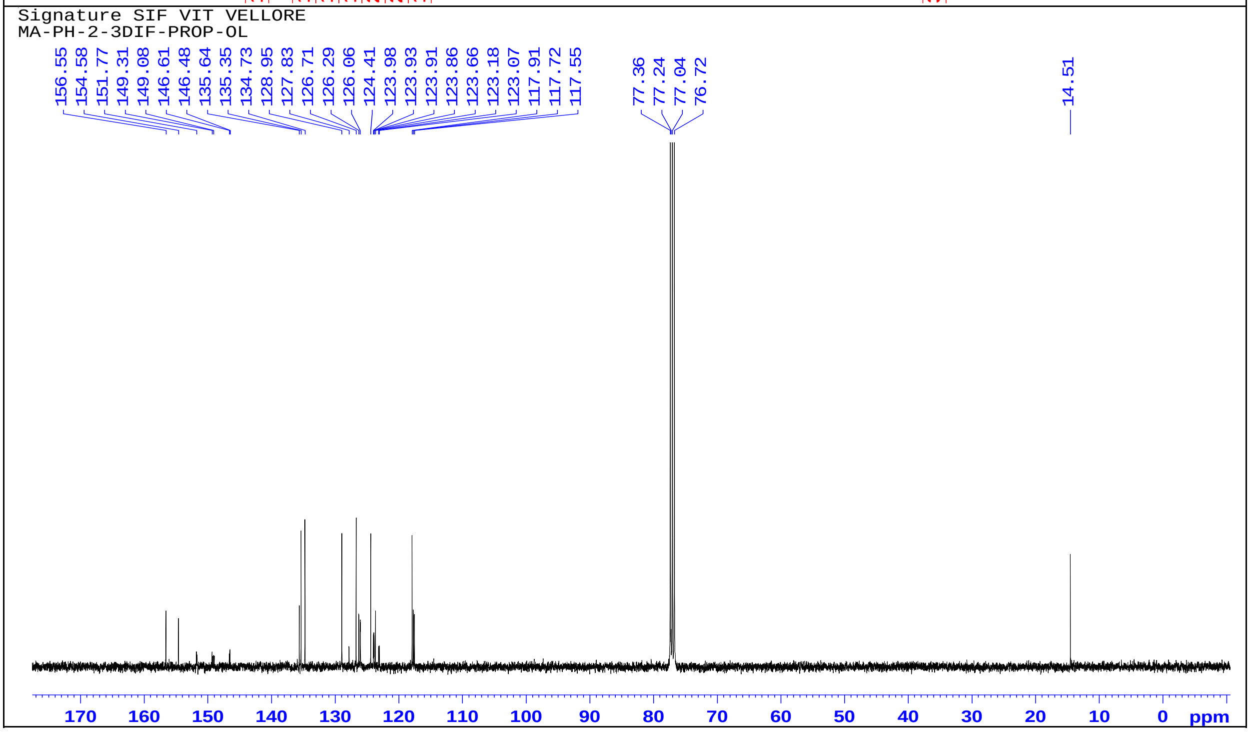


^{19}F NMR of **5af**

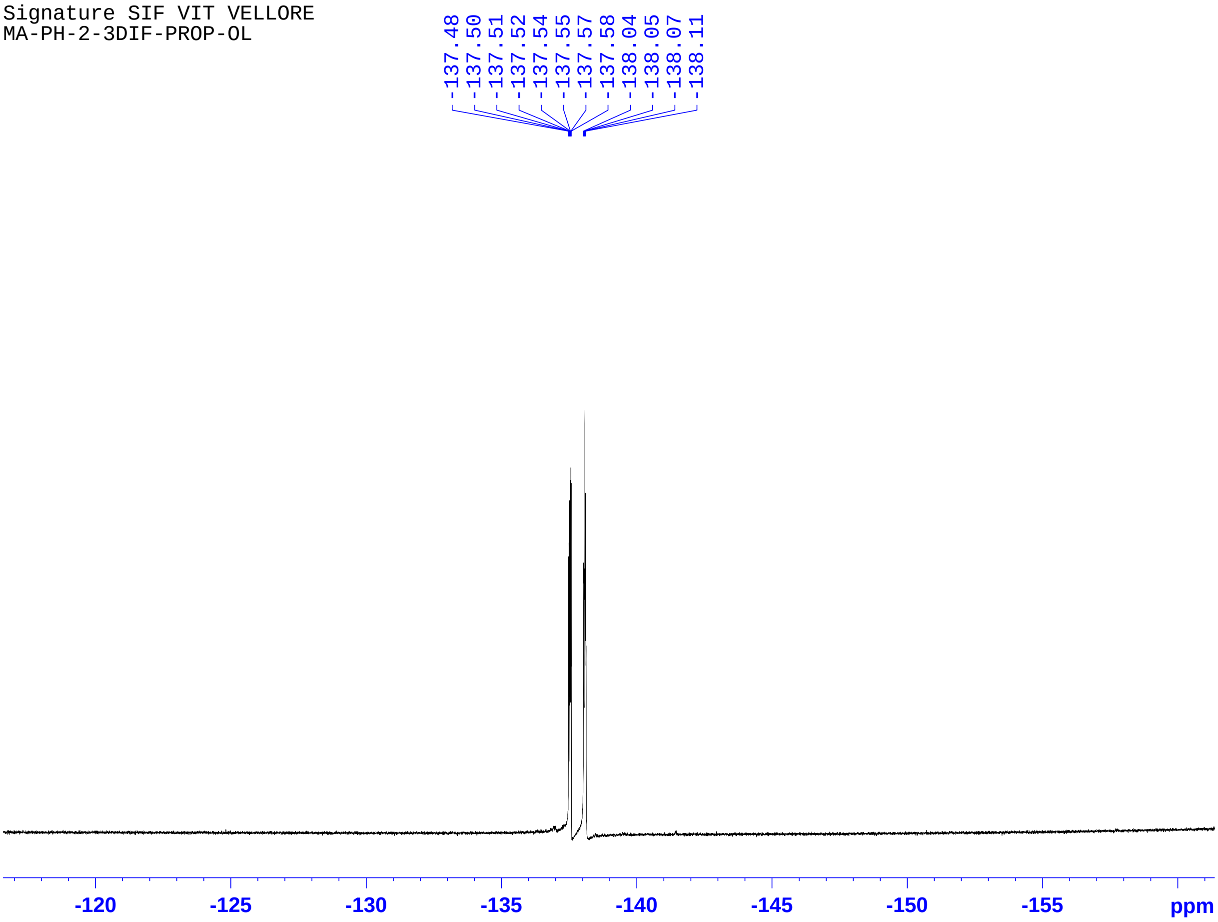


[1]H NMR and [13]C NMR of **5ah**

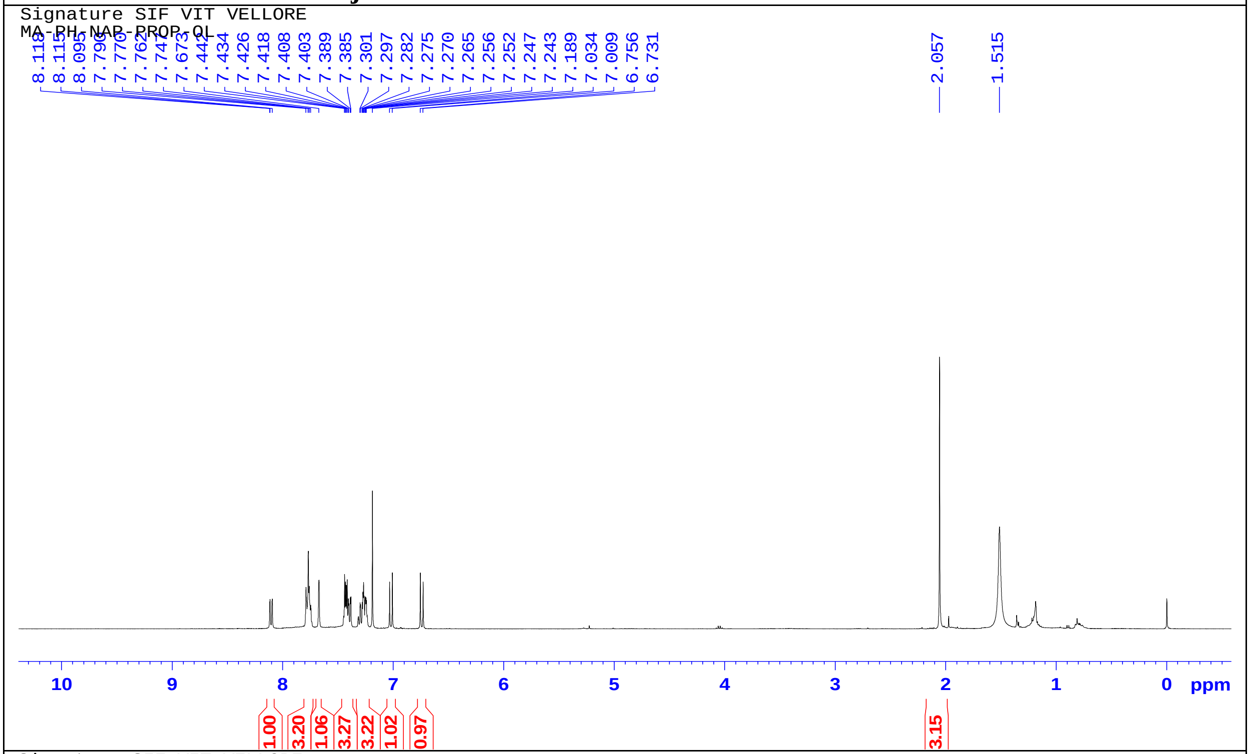


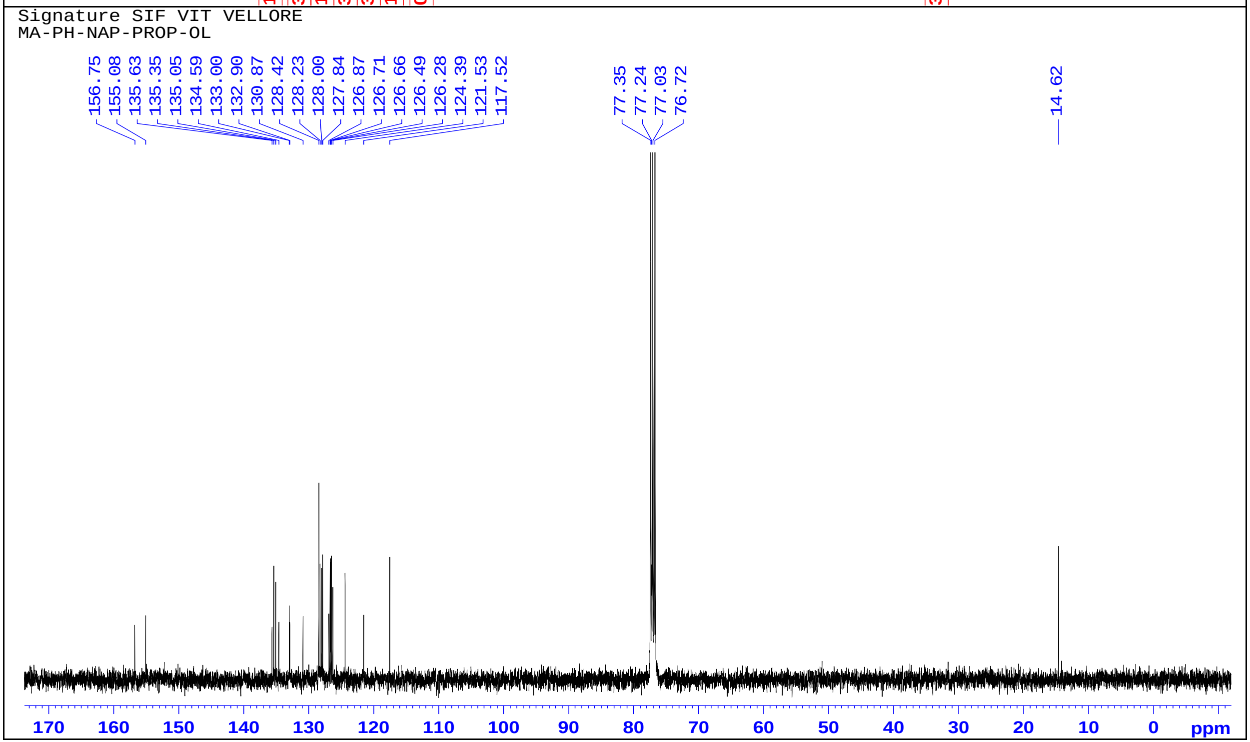


^{19}F NMR of **5ah**

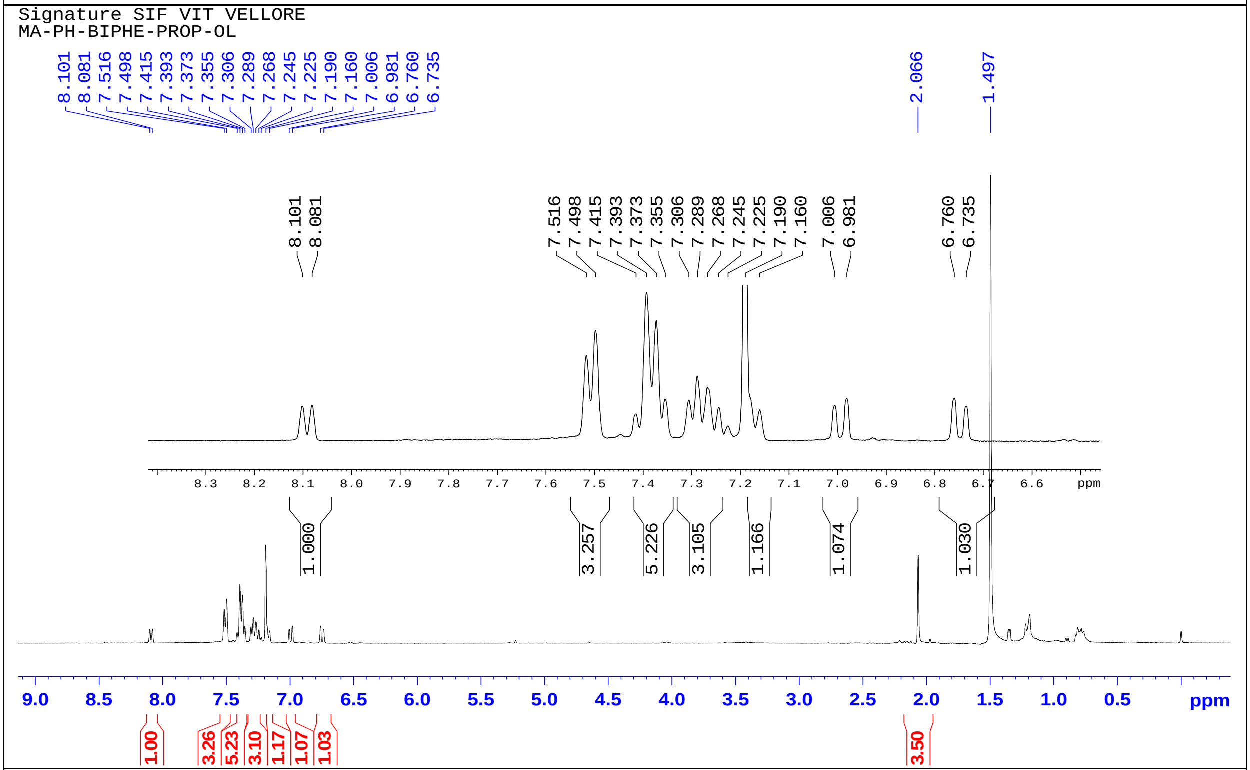


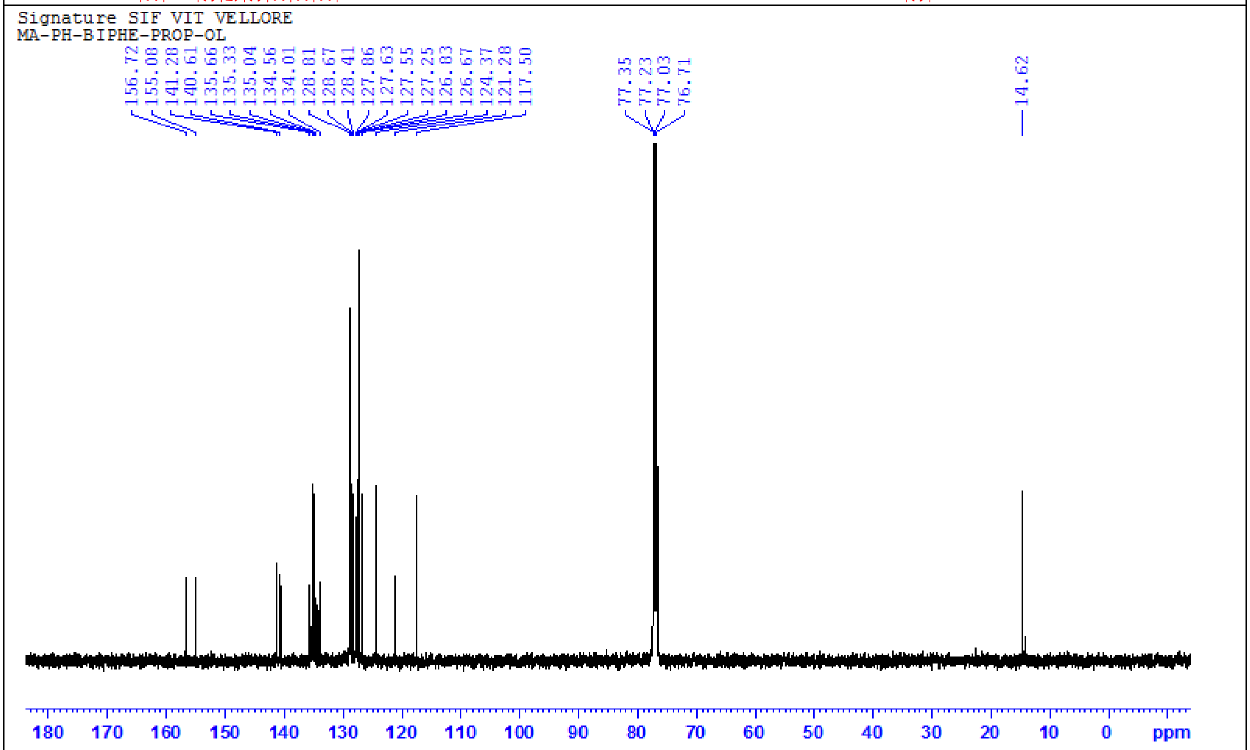
^{1}H NMR and ^{13}C NMR of **5aj**



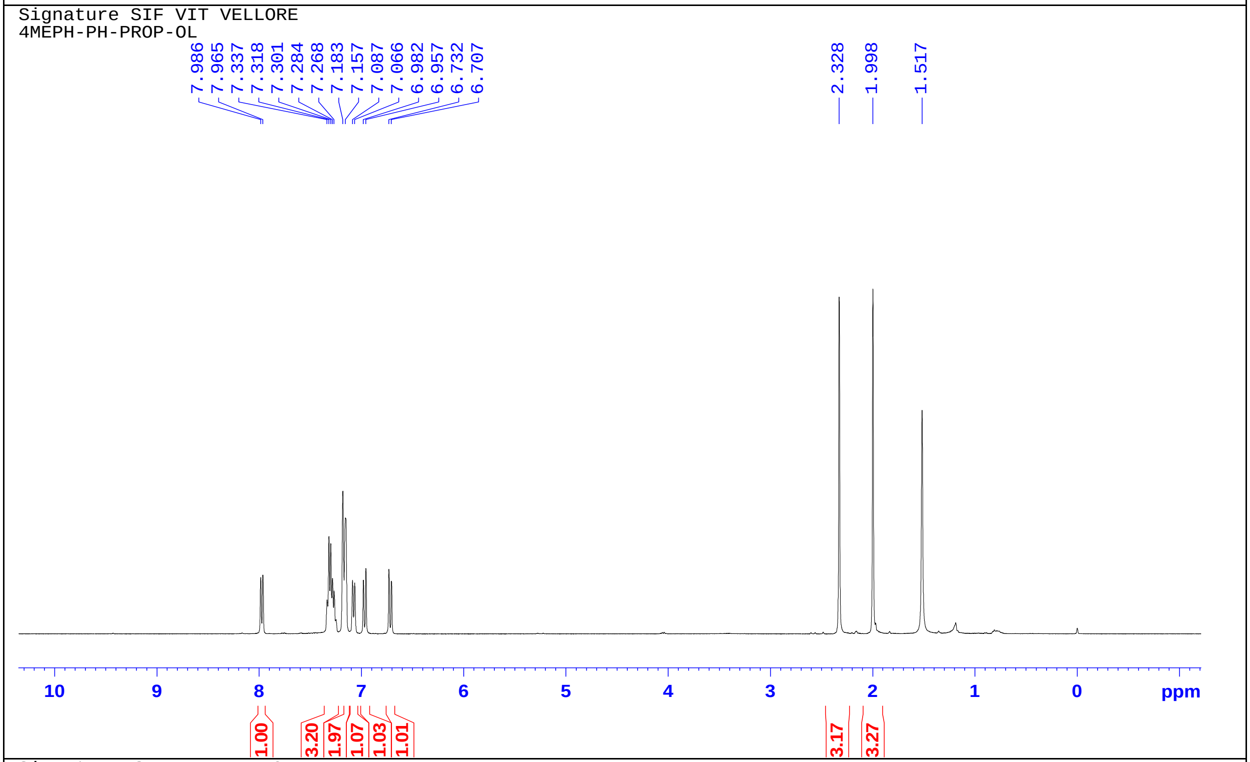


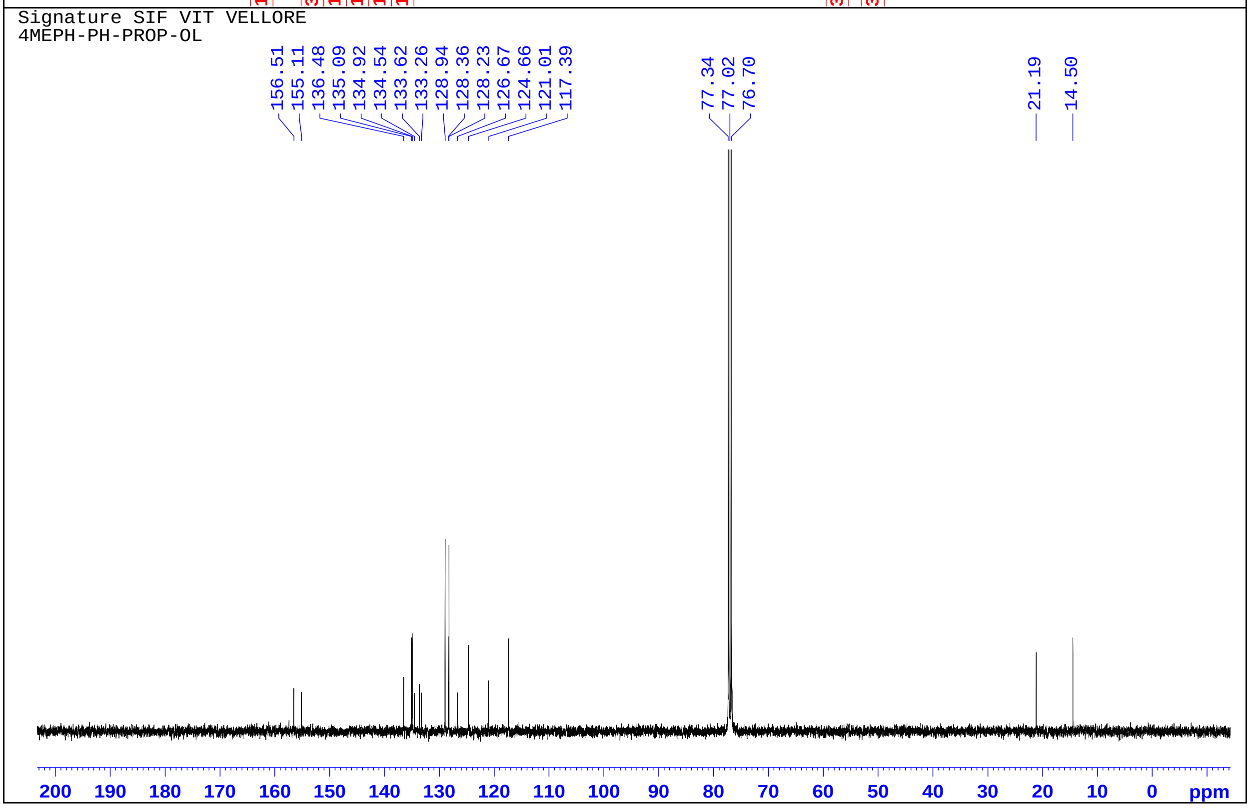
^{1}H NMR and ^{13}C NMR of **5ak**



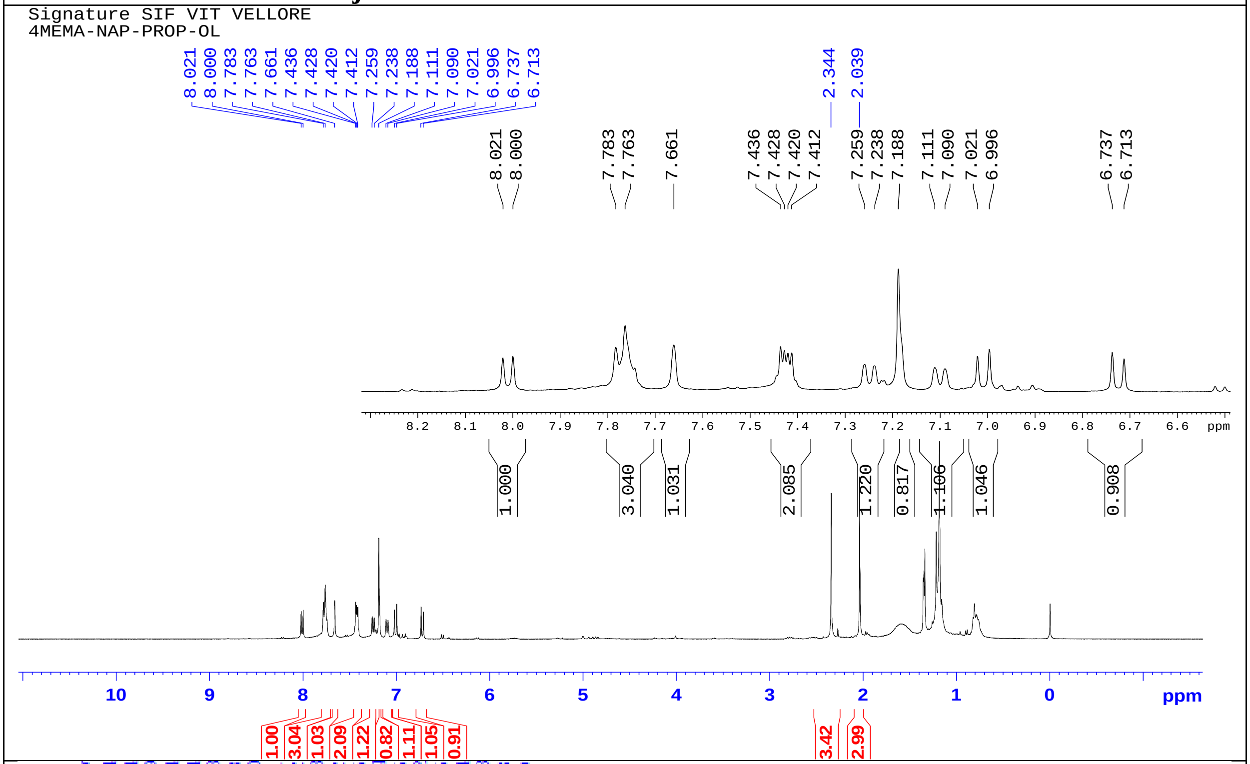


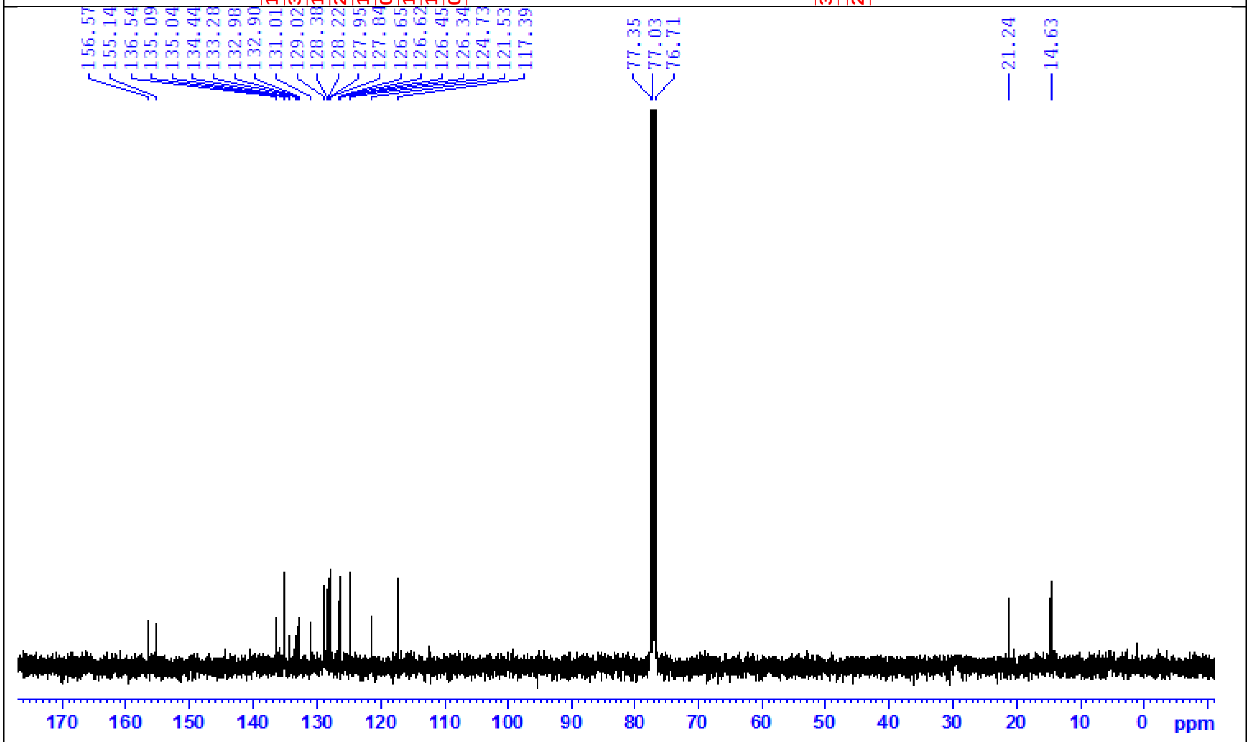
^{1}H NMR and ^{13}C NMR of **5ba**



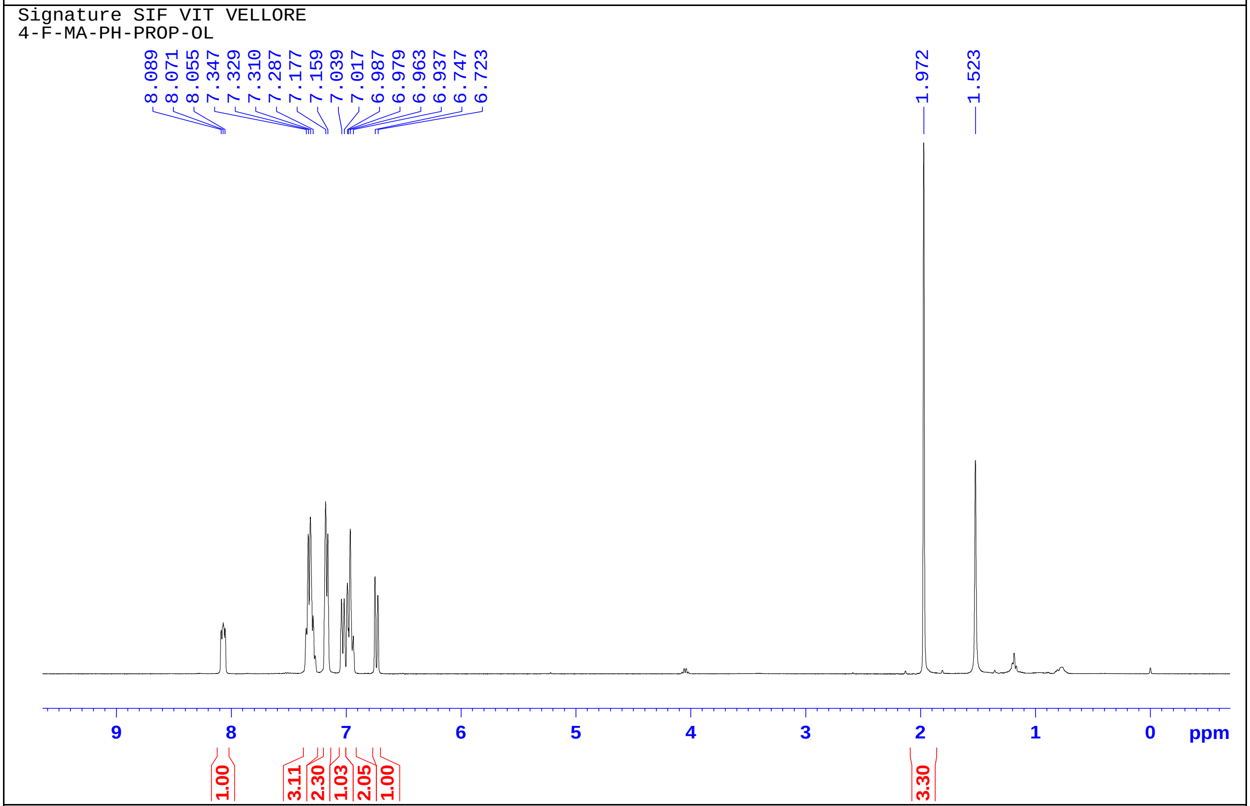


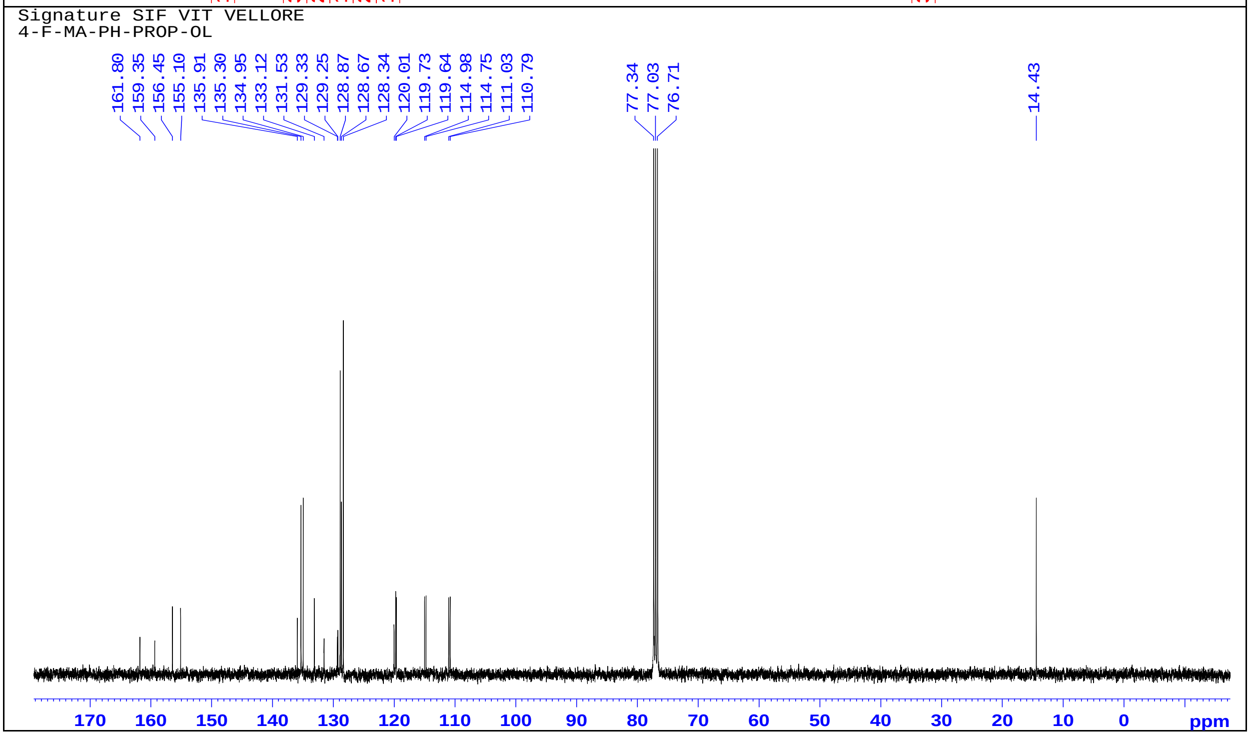
^{1}H NMR and ^{13}C NMR of **5bj**



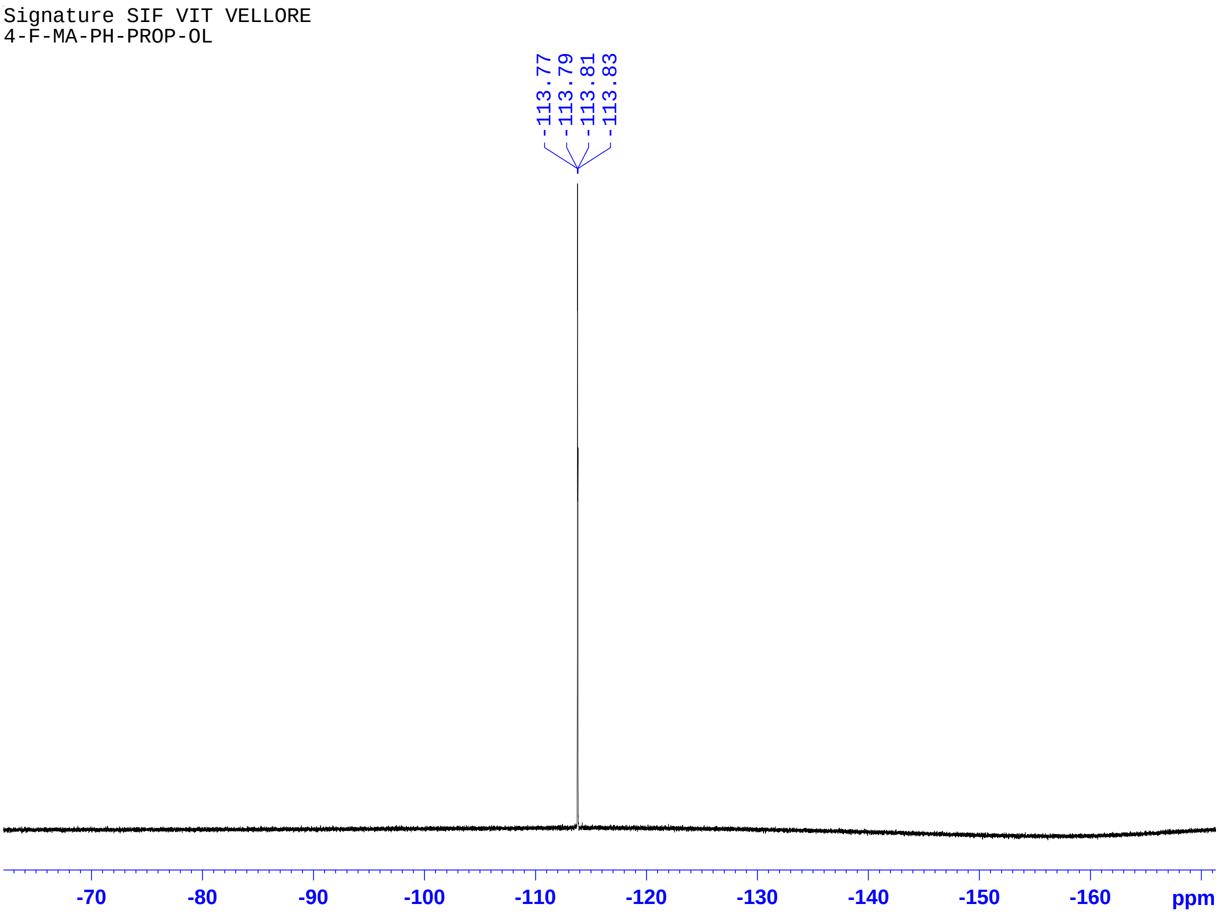


[1]H NMR and [13]C NMR of **5ca**

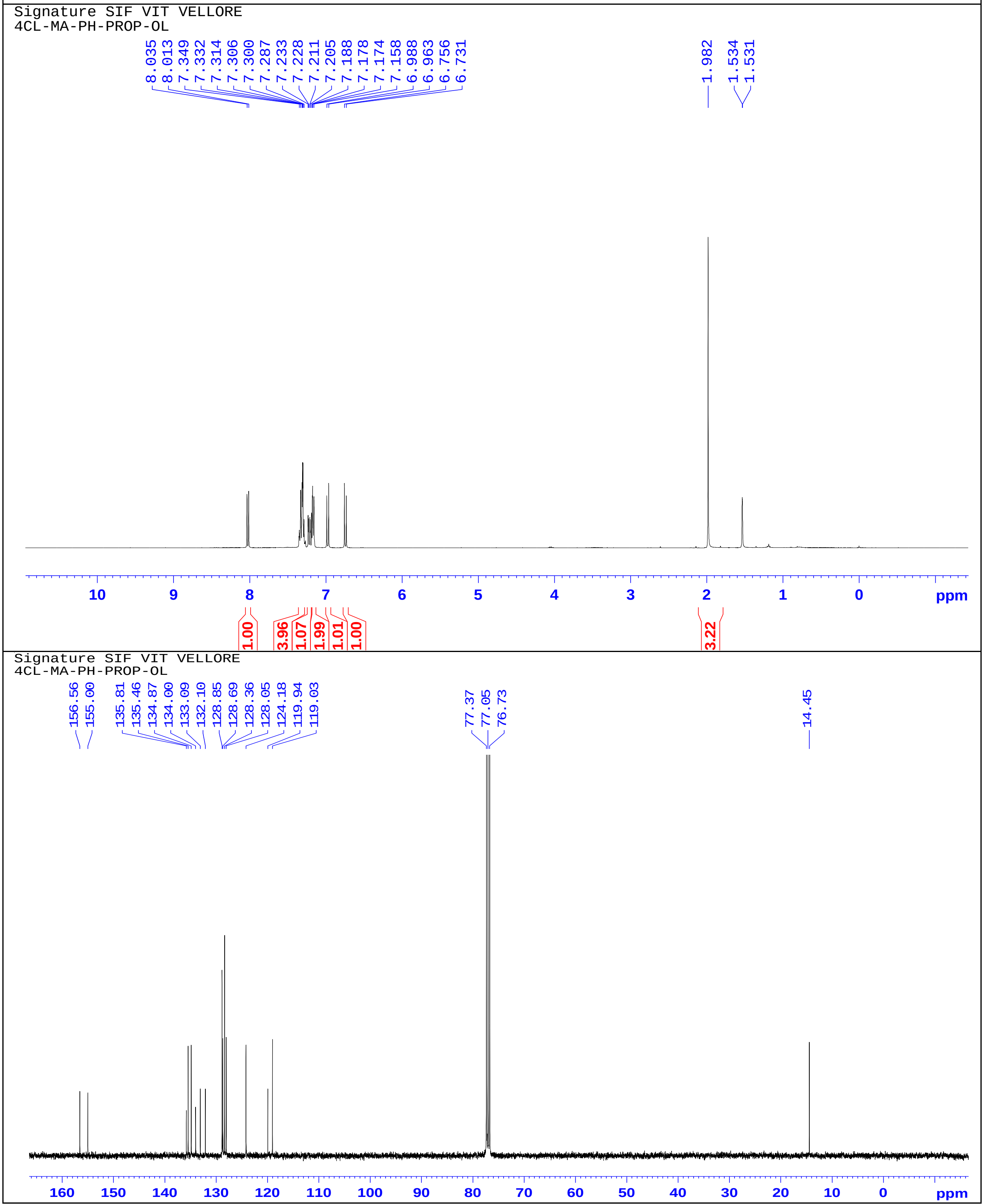




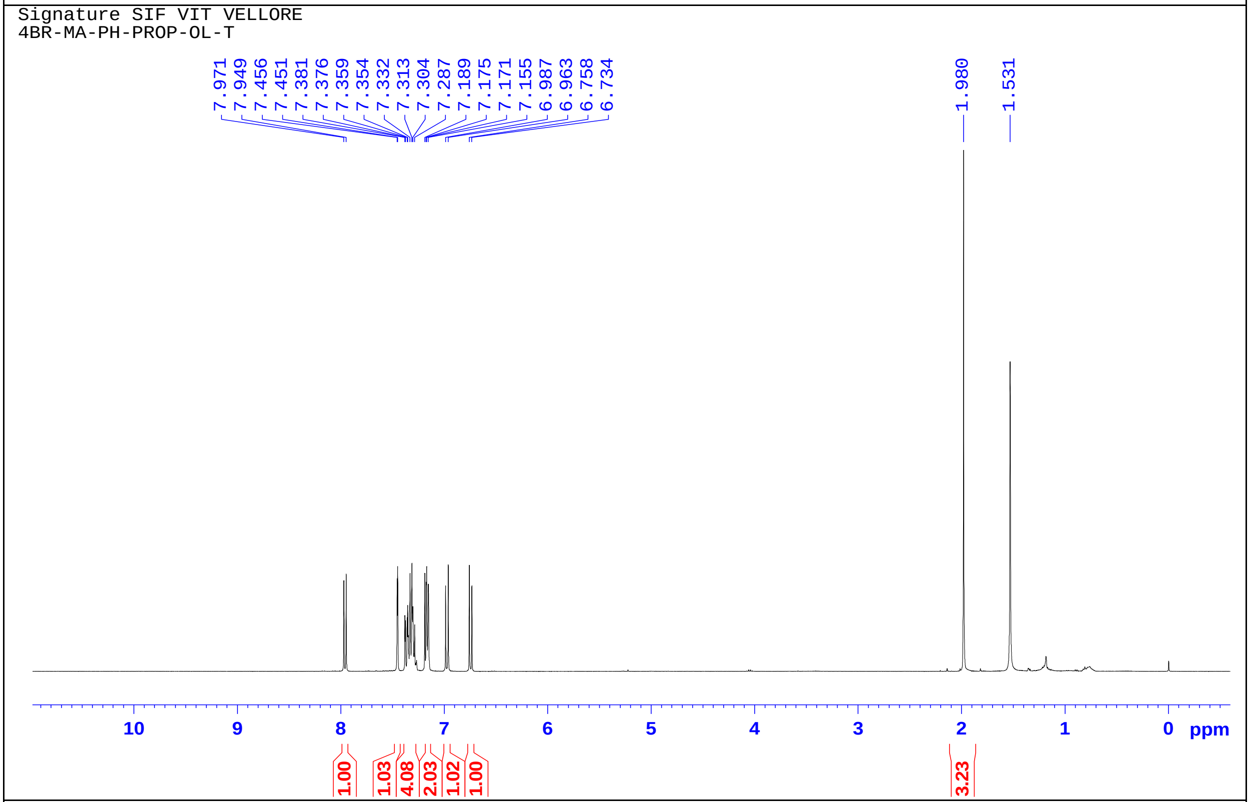
^{19}F NMR of **5ca**

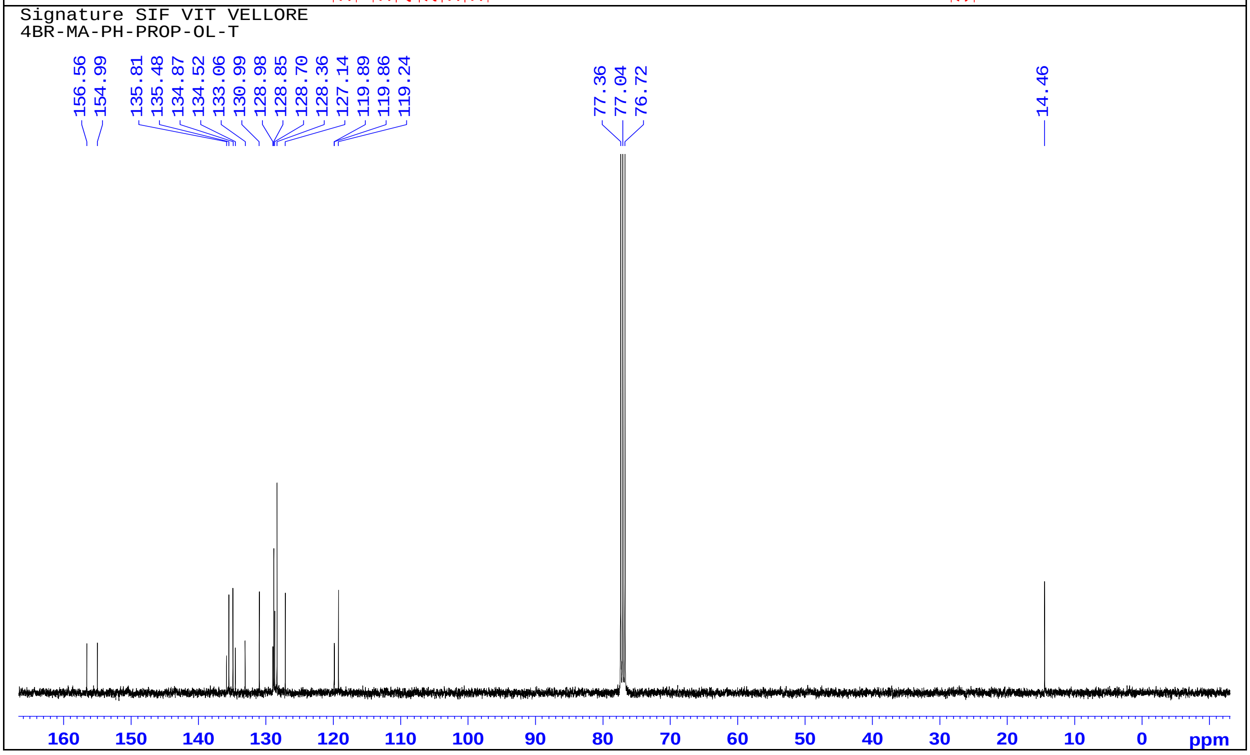


[1]H NMR and [13]C NMR of **5da**

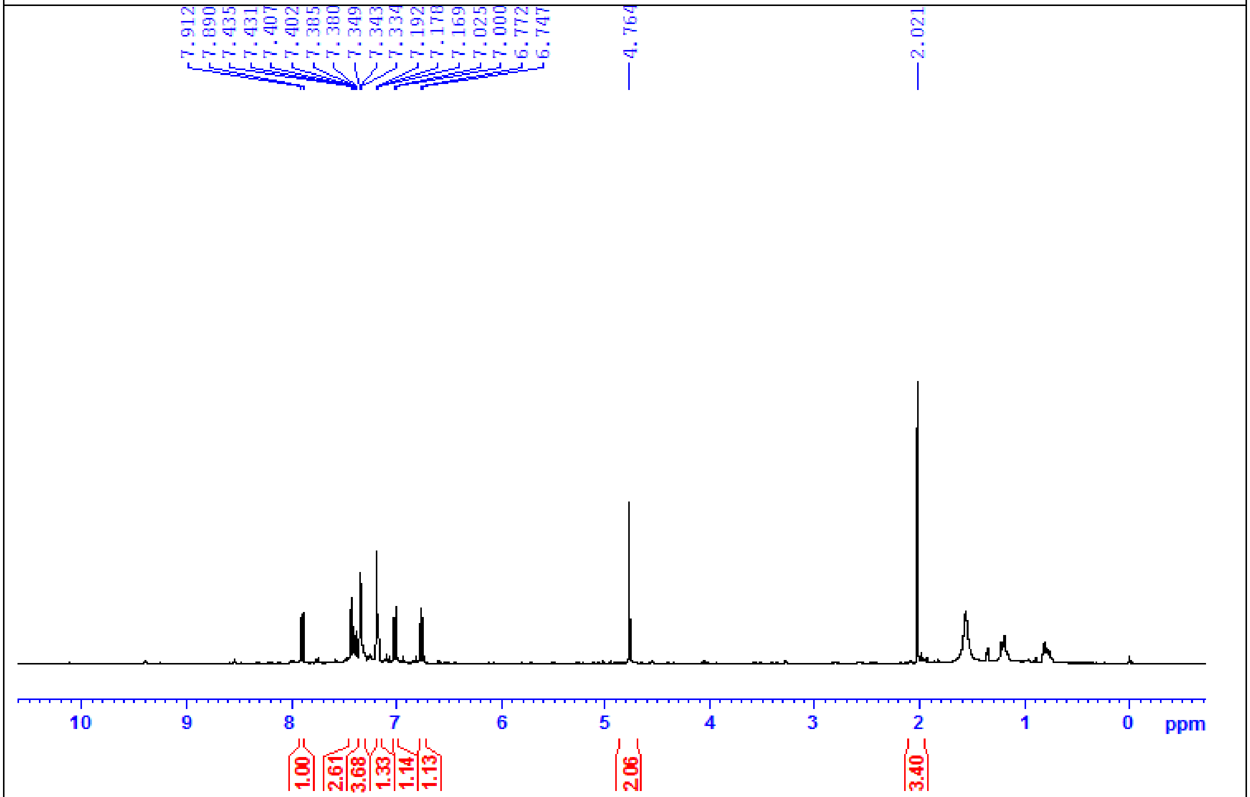


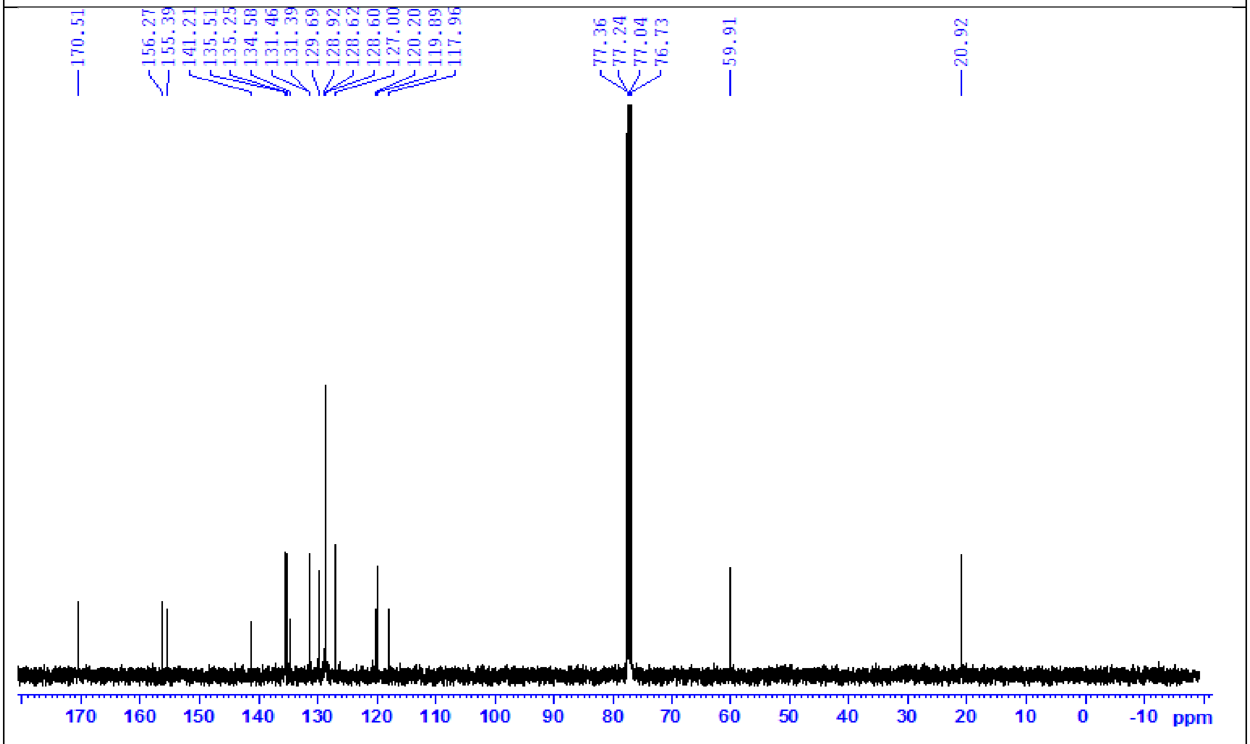
[1]H NMR and [13]C NMR of **5ea**



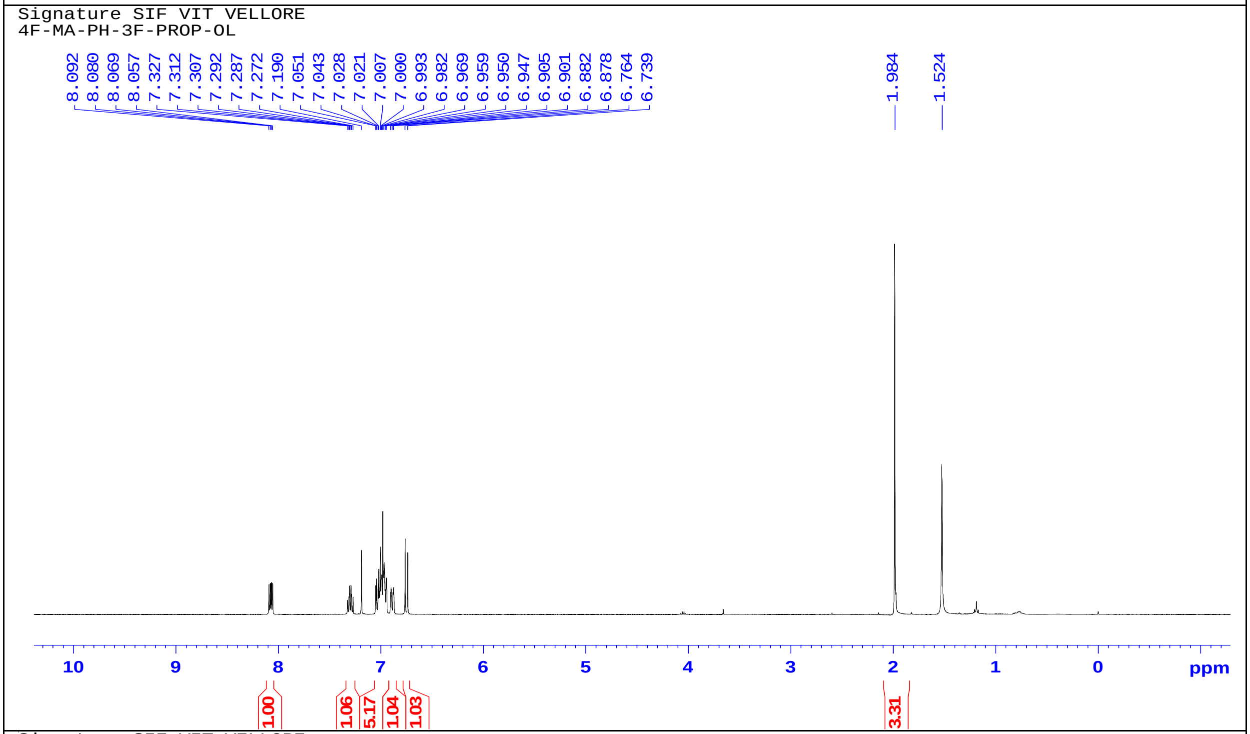


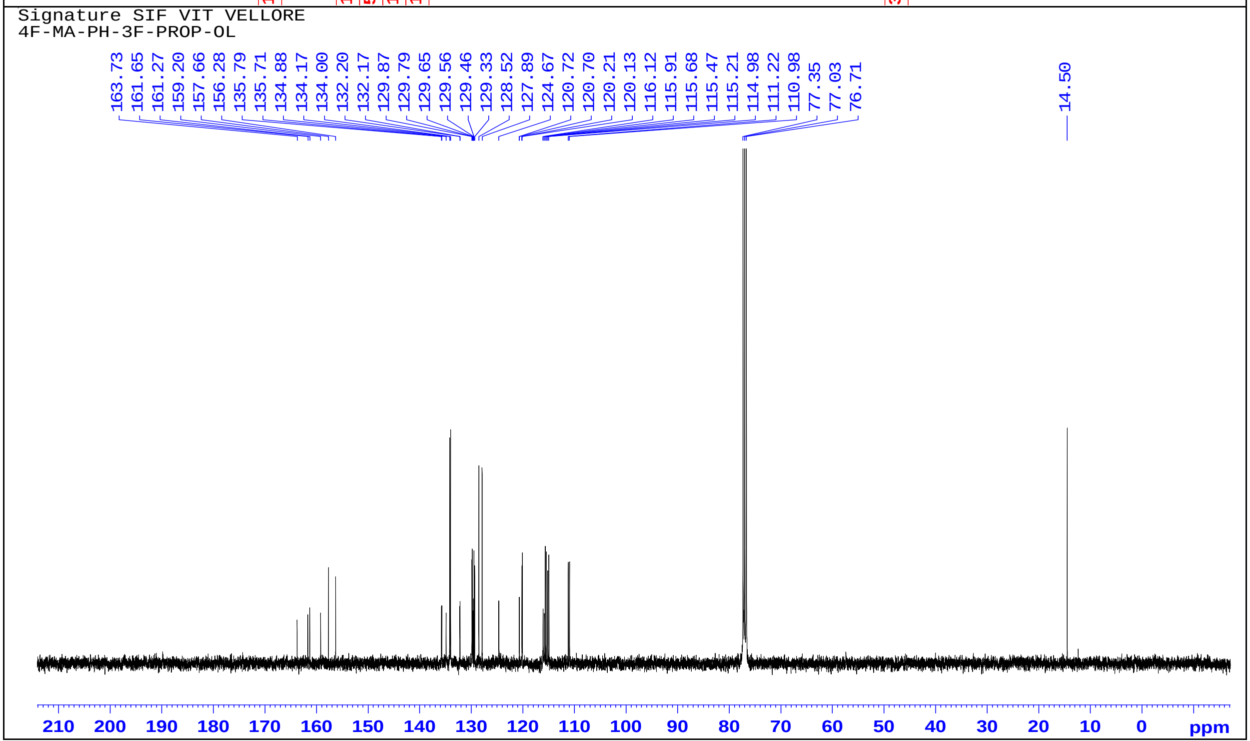
[1]H NMR and [13]C NMR of **6ea**



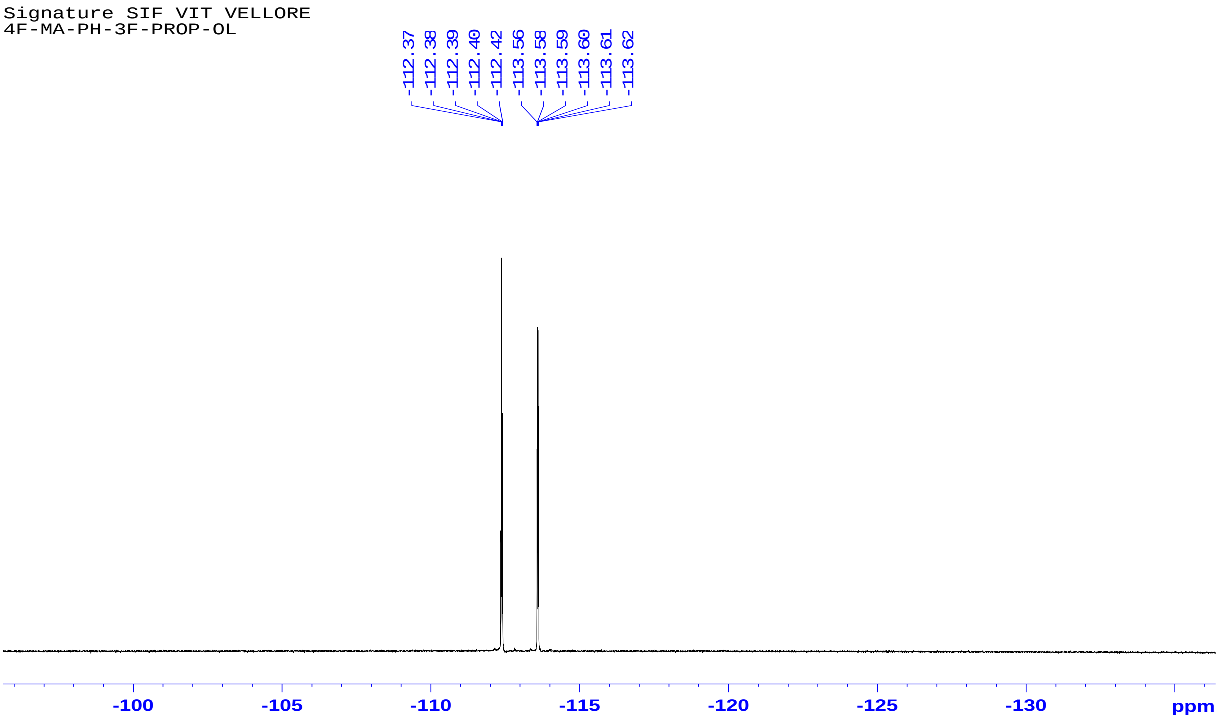


[1]H NMR and [13]C NMR of **5cf**

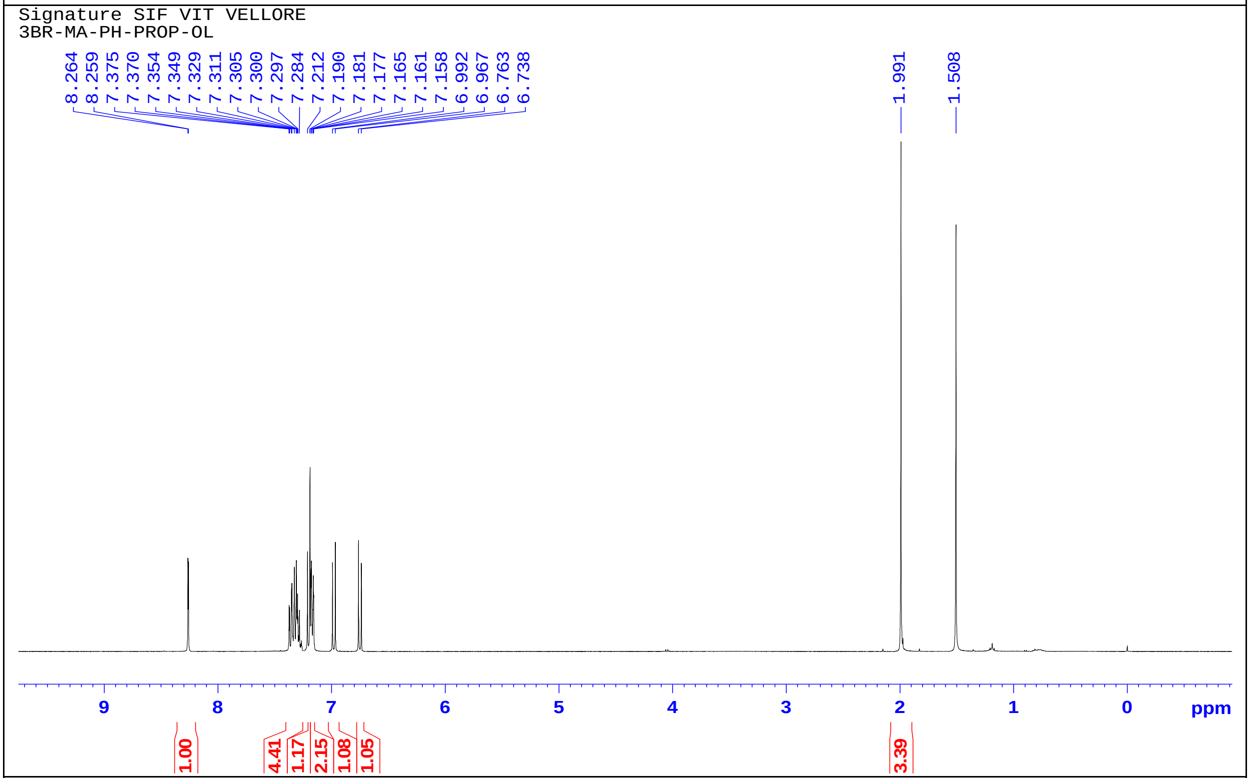


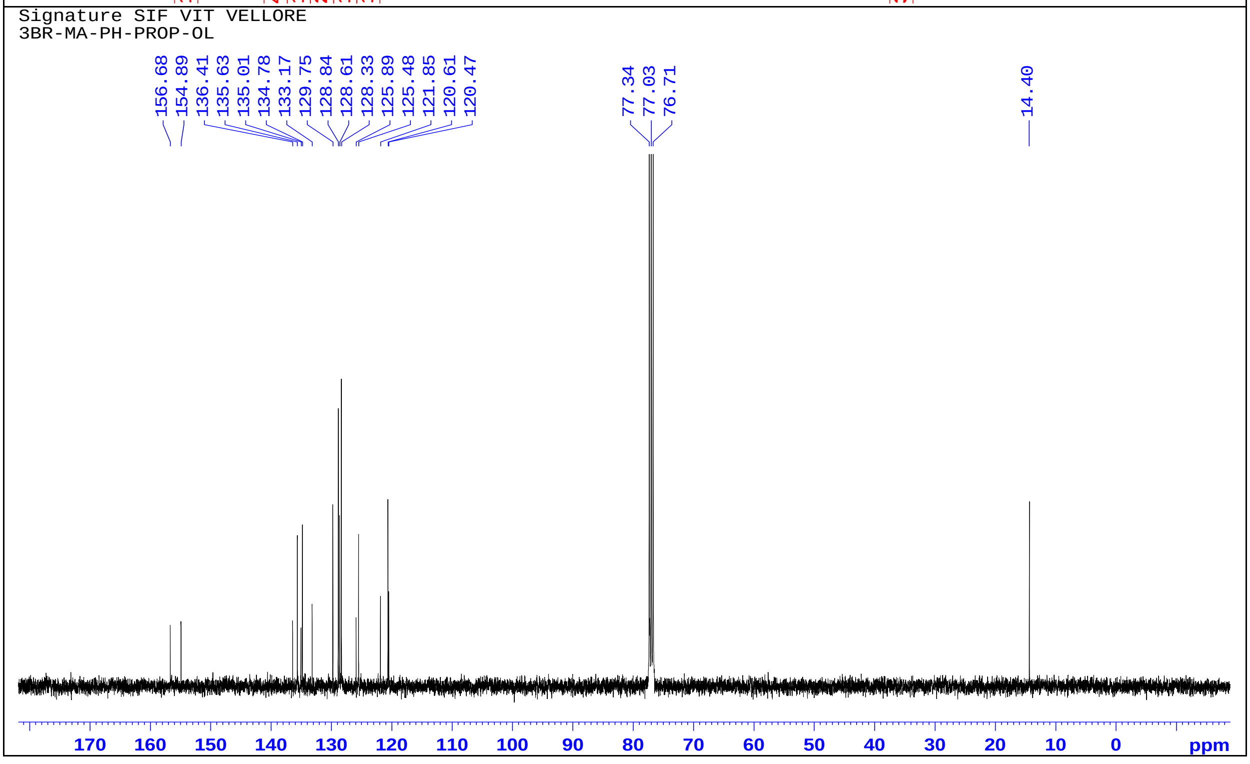


^{19}F NMR of **5cf**

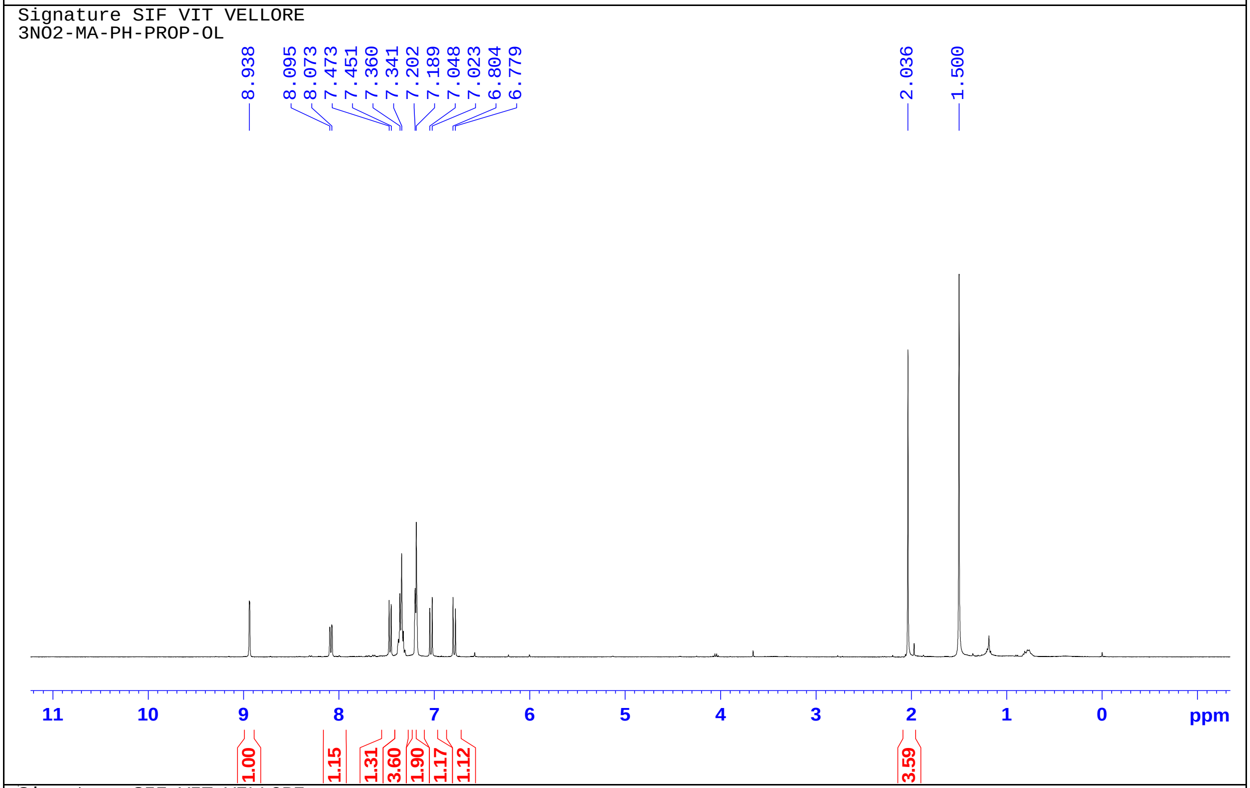


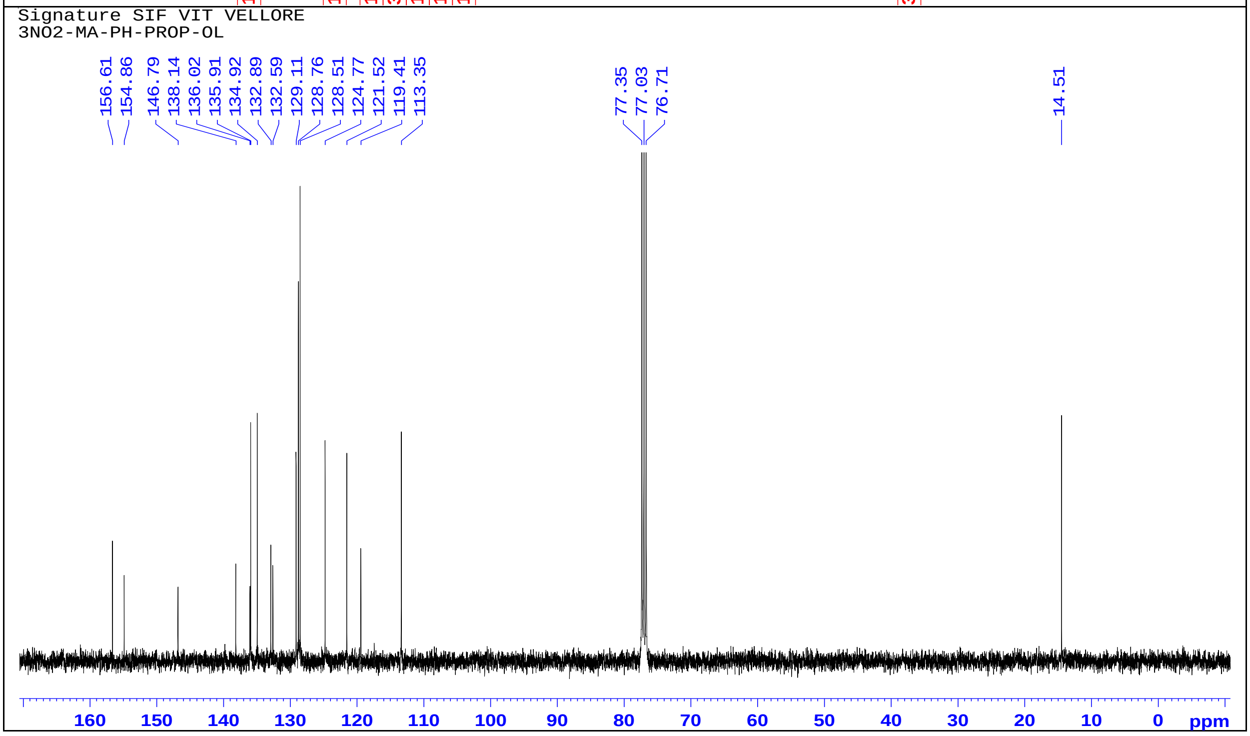
[1]H NMR and [13]C NMR of **5ha**



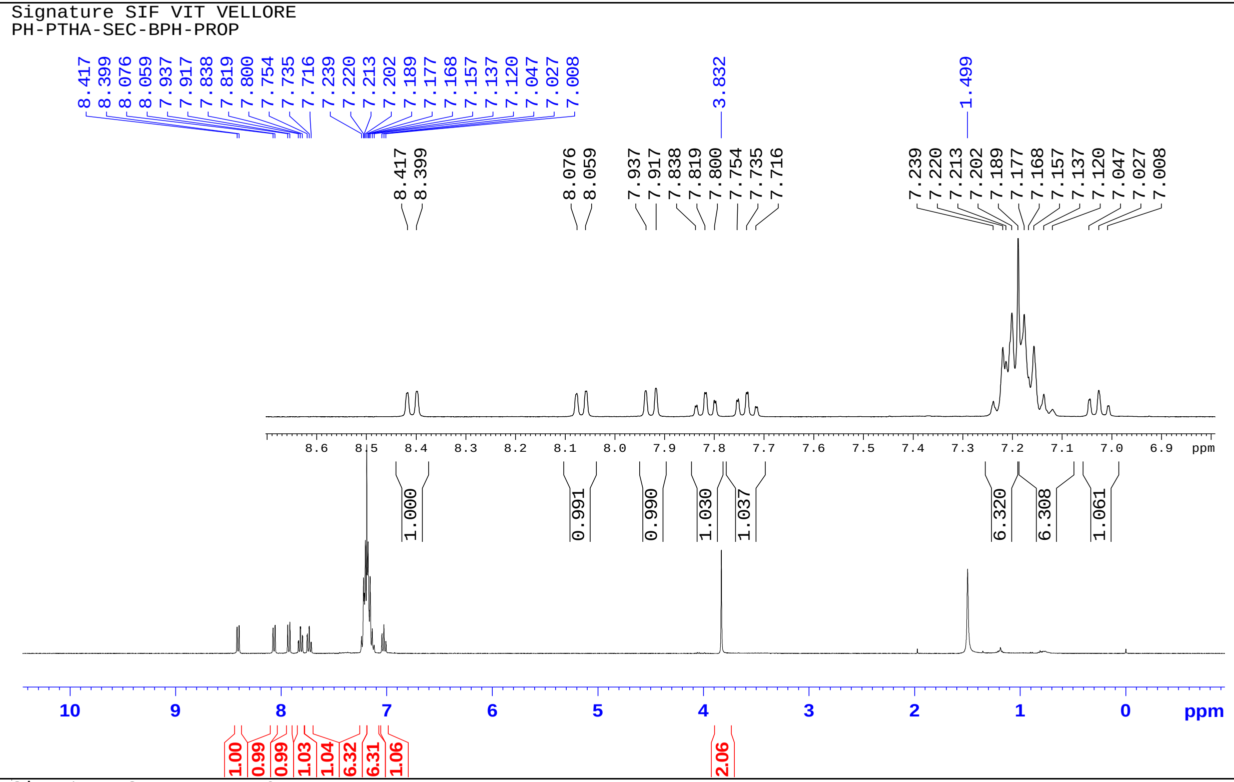


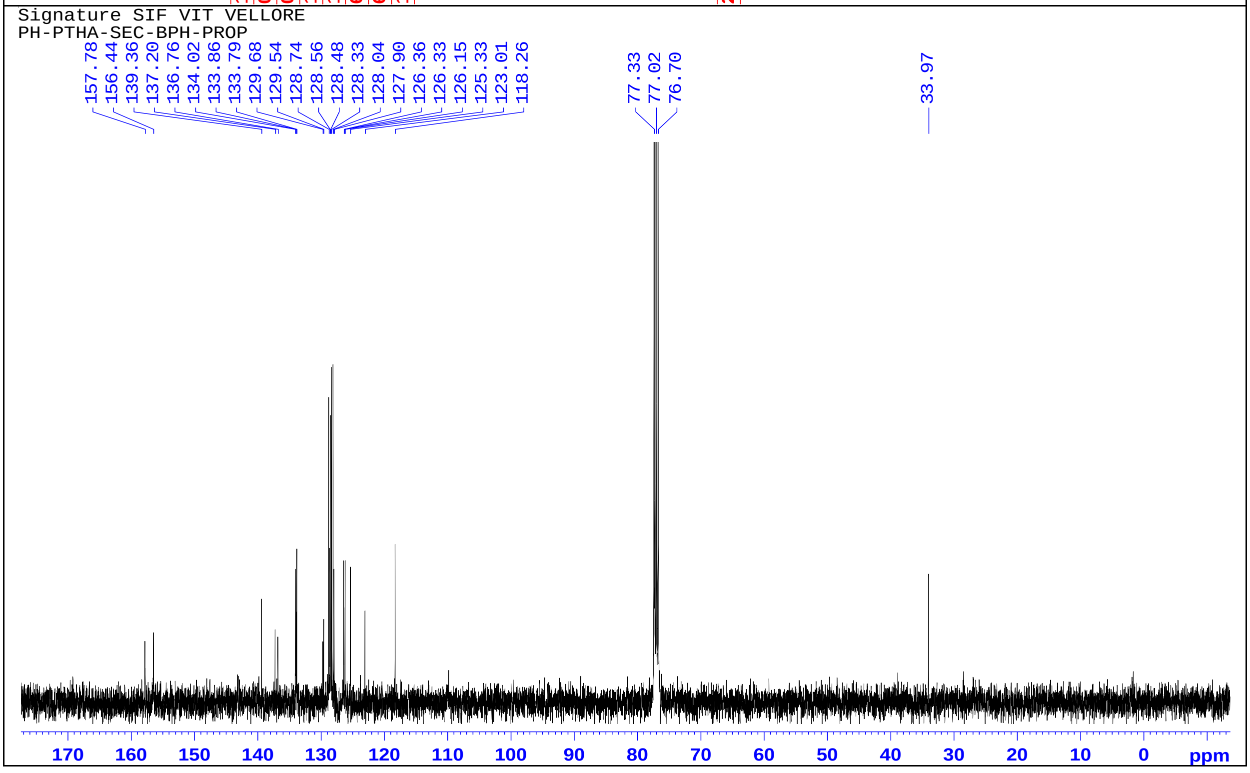
^{1}H NMR and ^{13}C NMR of **5ia**



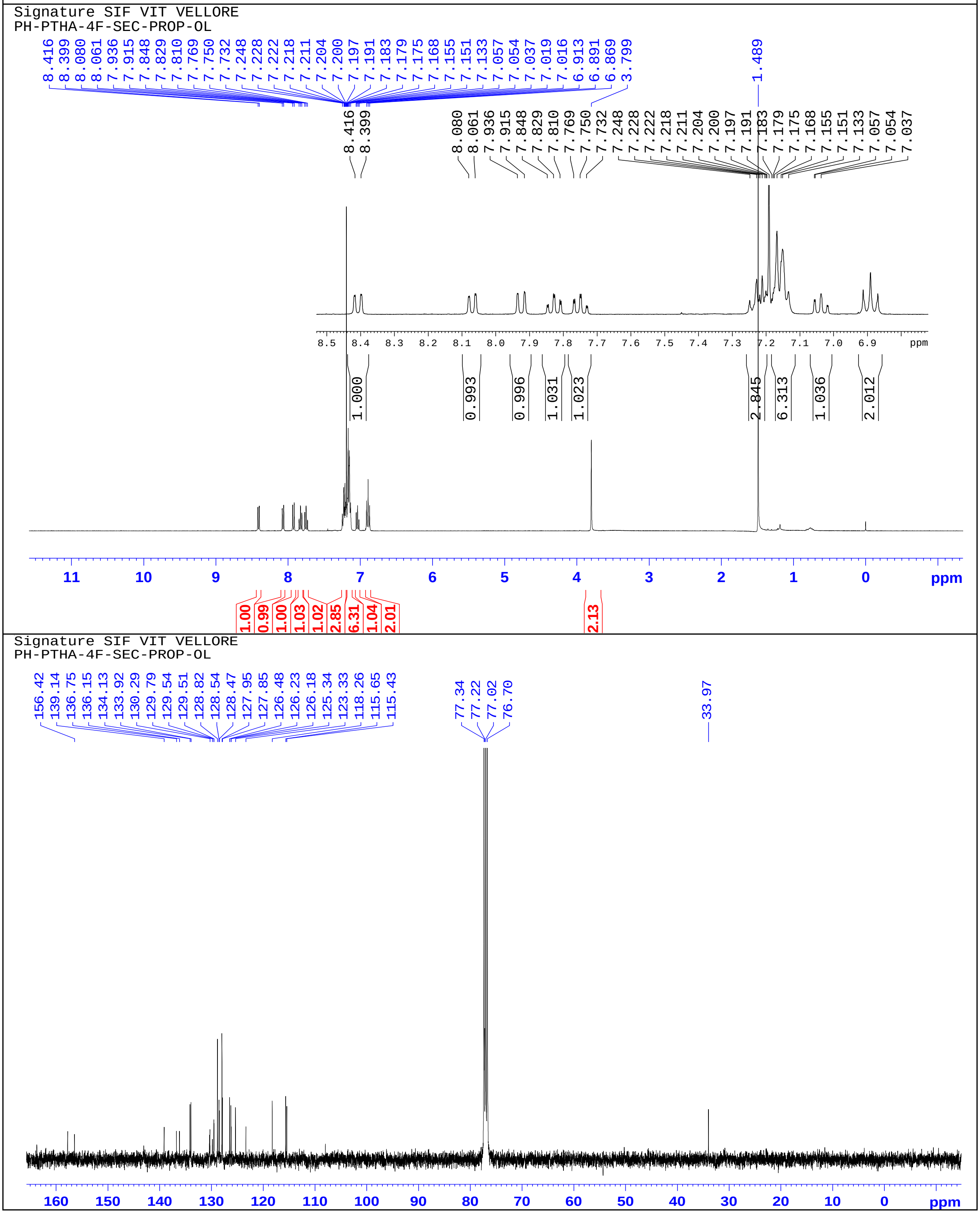


^{1}H NMR and ^{13}C NMR of **7al**

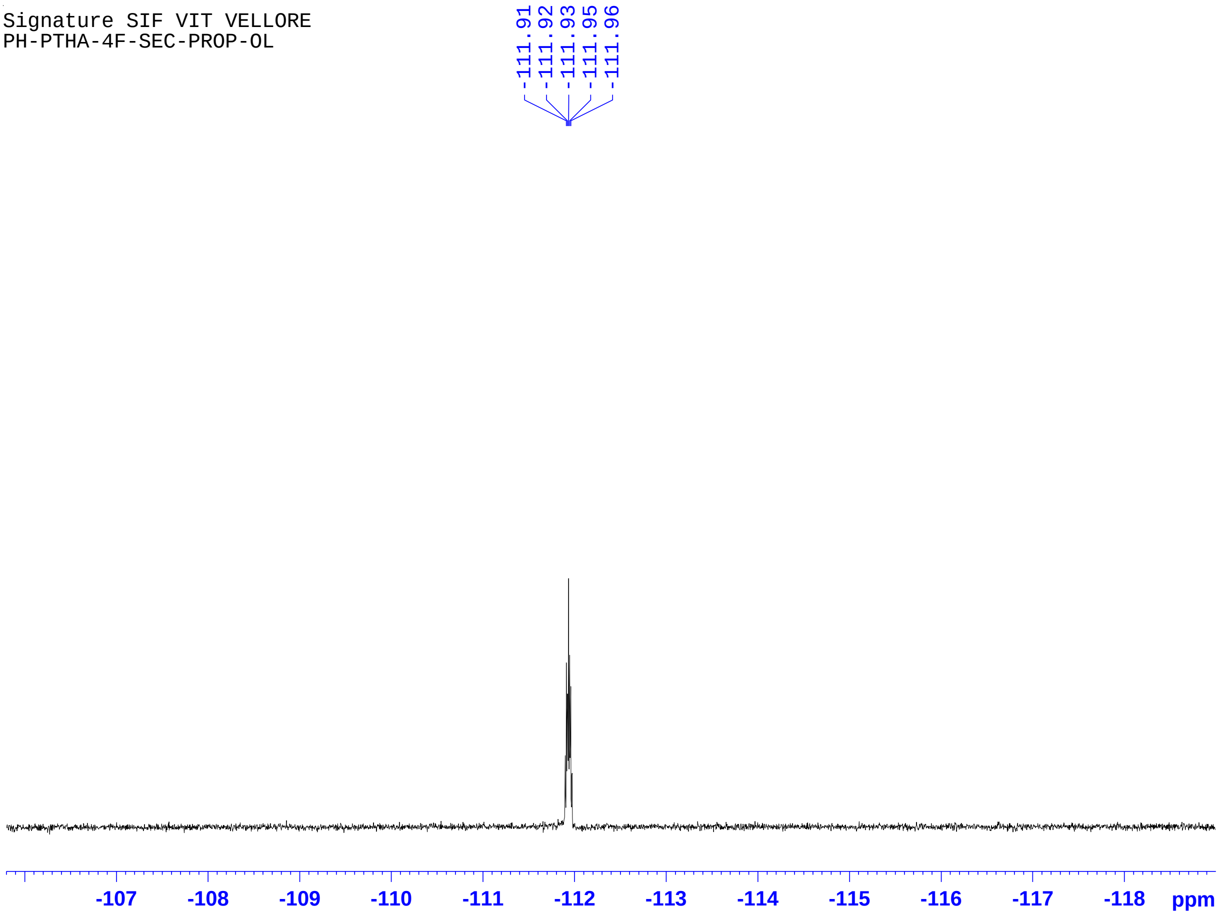




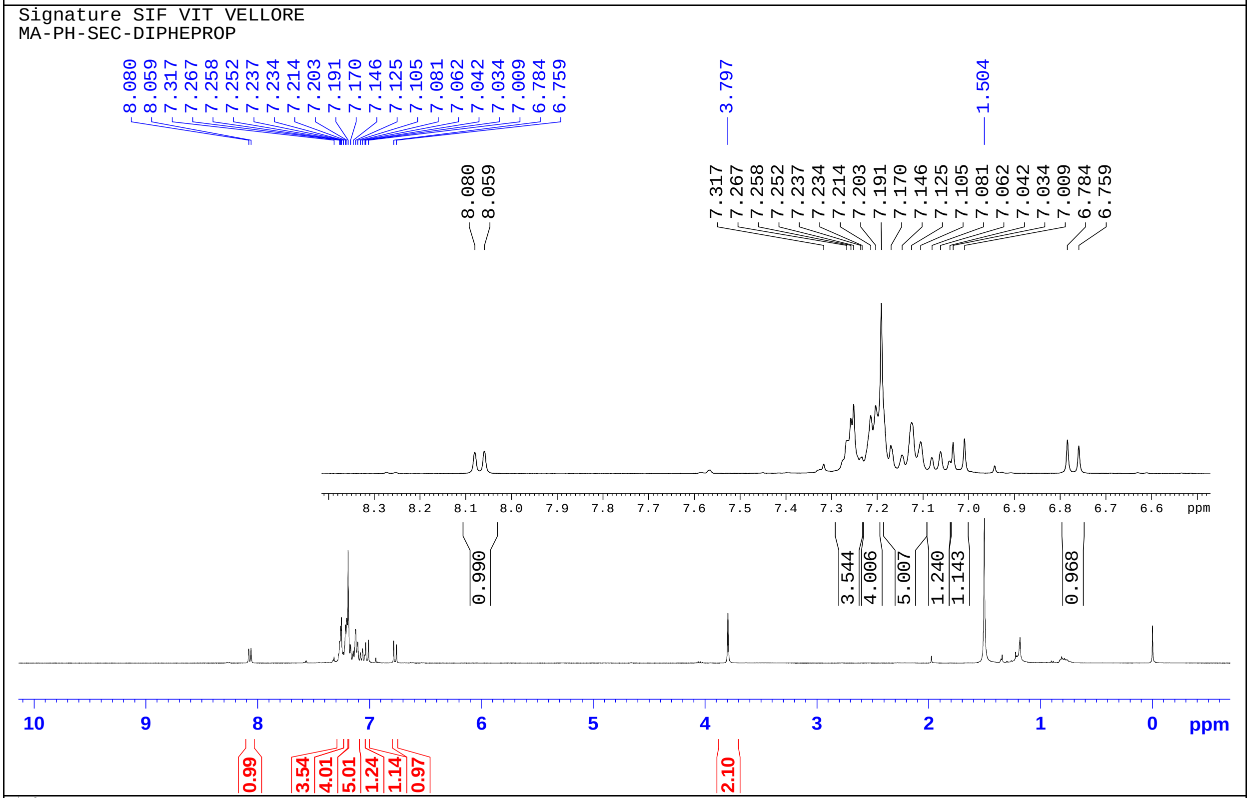
^{1}H NMR and ^{13}C NMR of **7am**

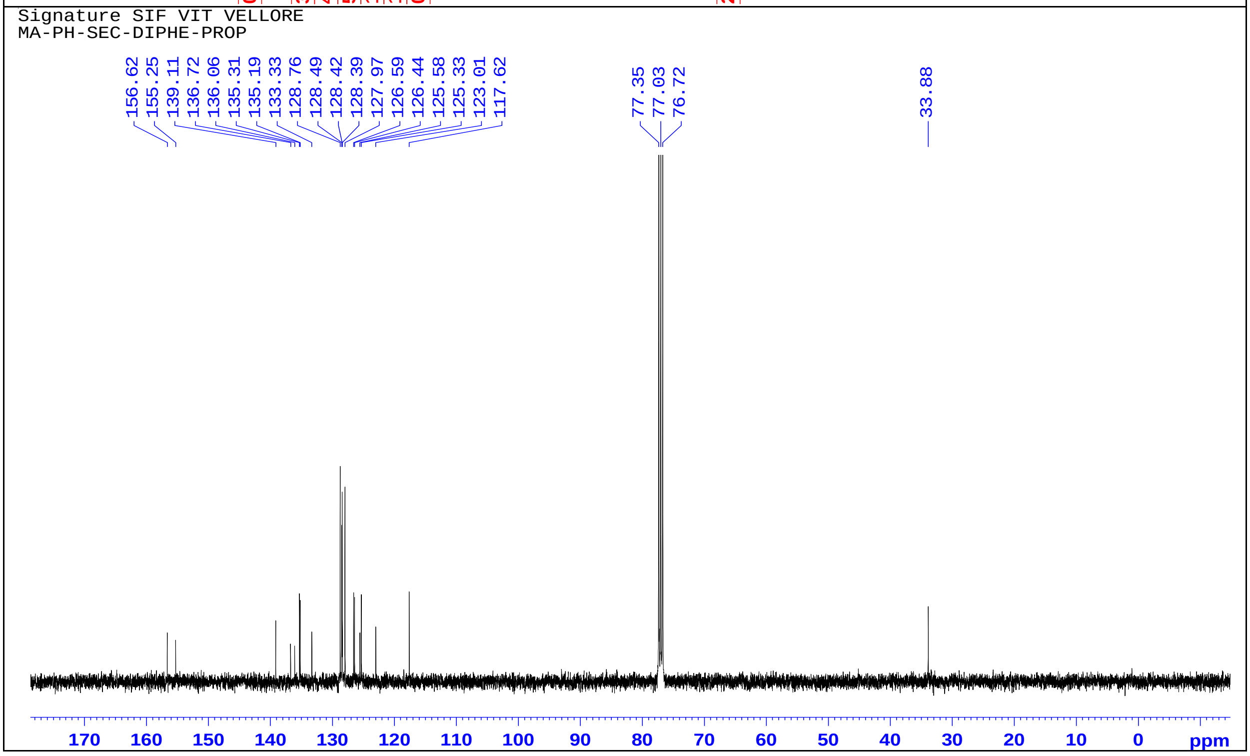


^{19}F NMR of **7am**

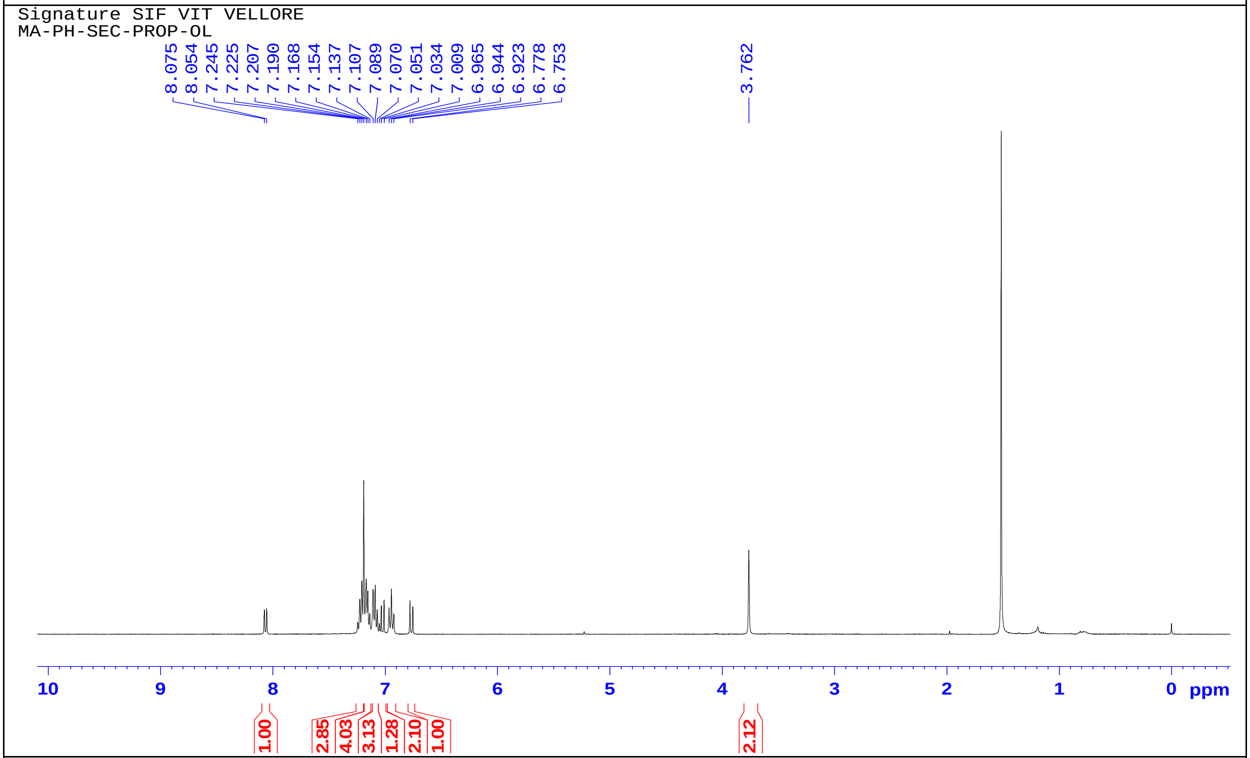


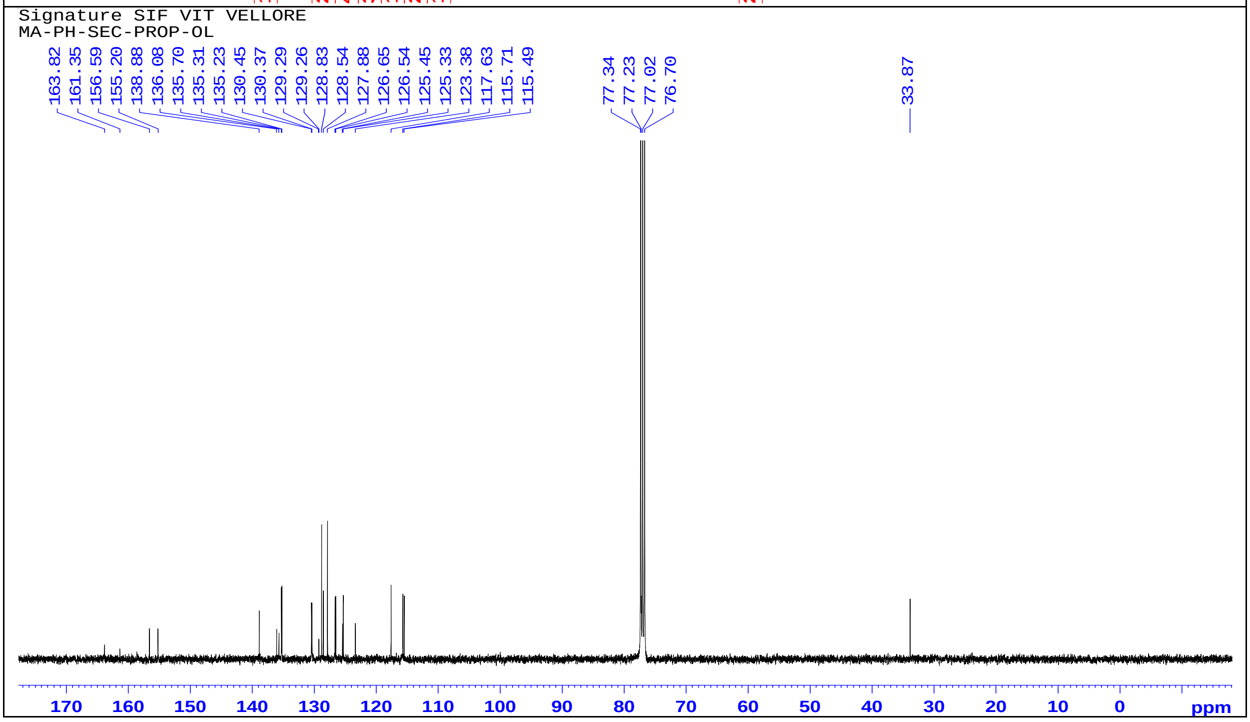
[1]H NMR and [13]C NMR of **8al**



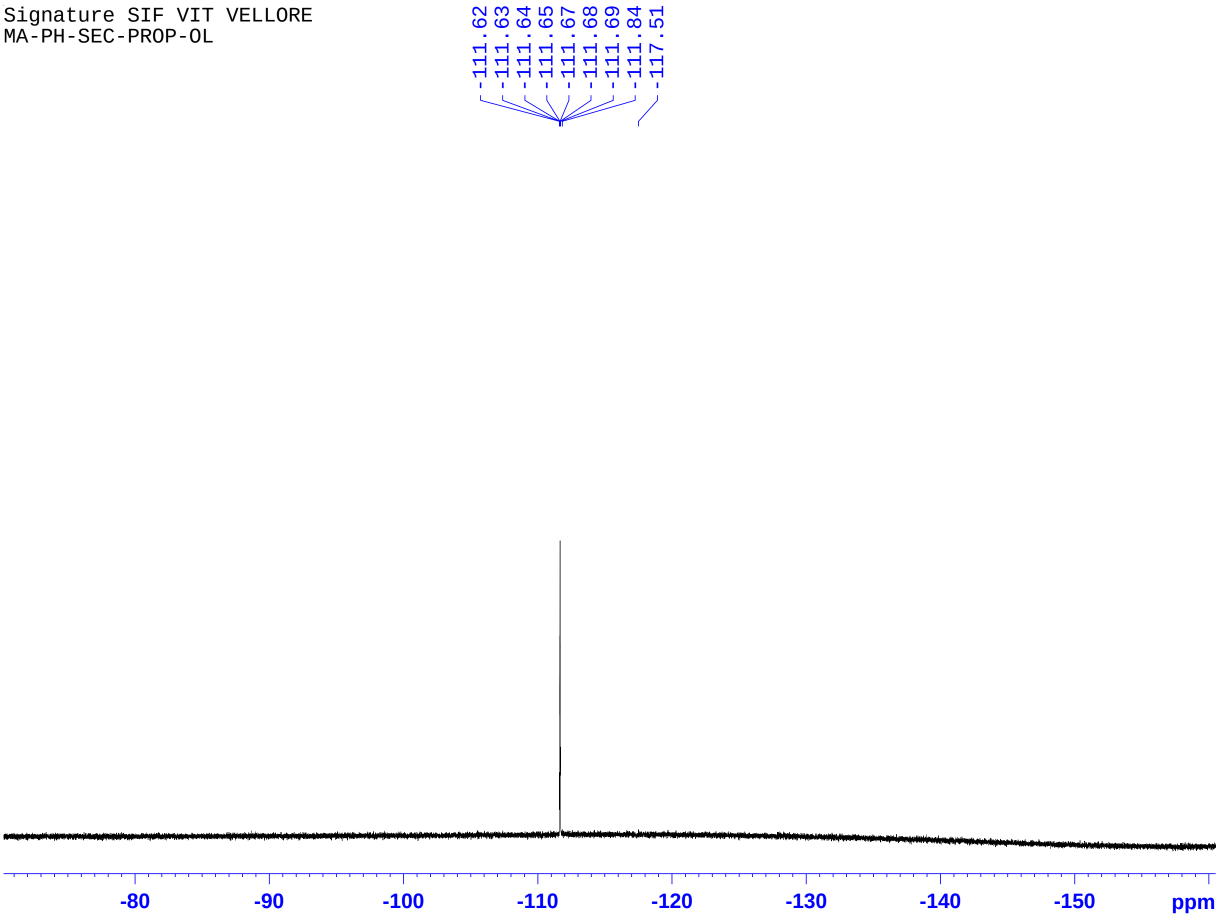


^{1}H NMR and ^{13}C NMR of **8am**

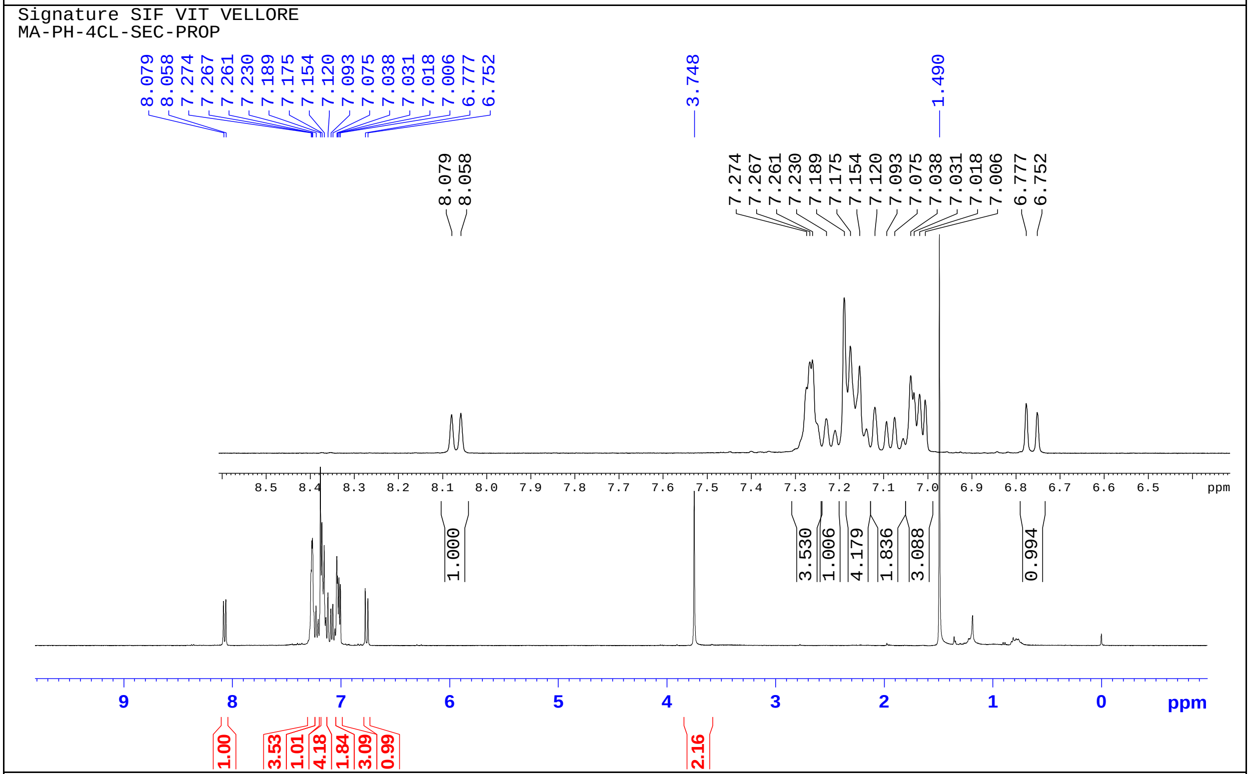


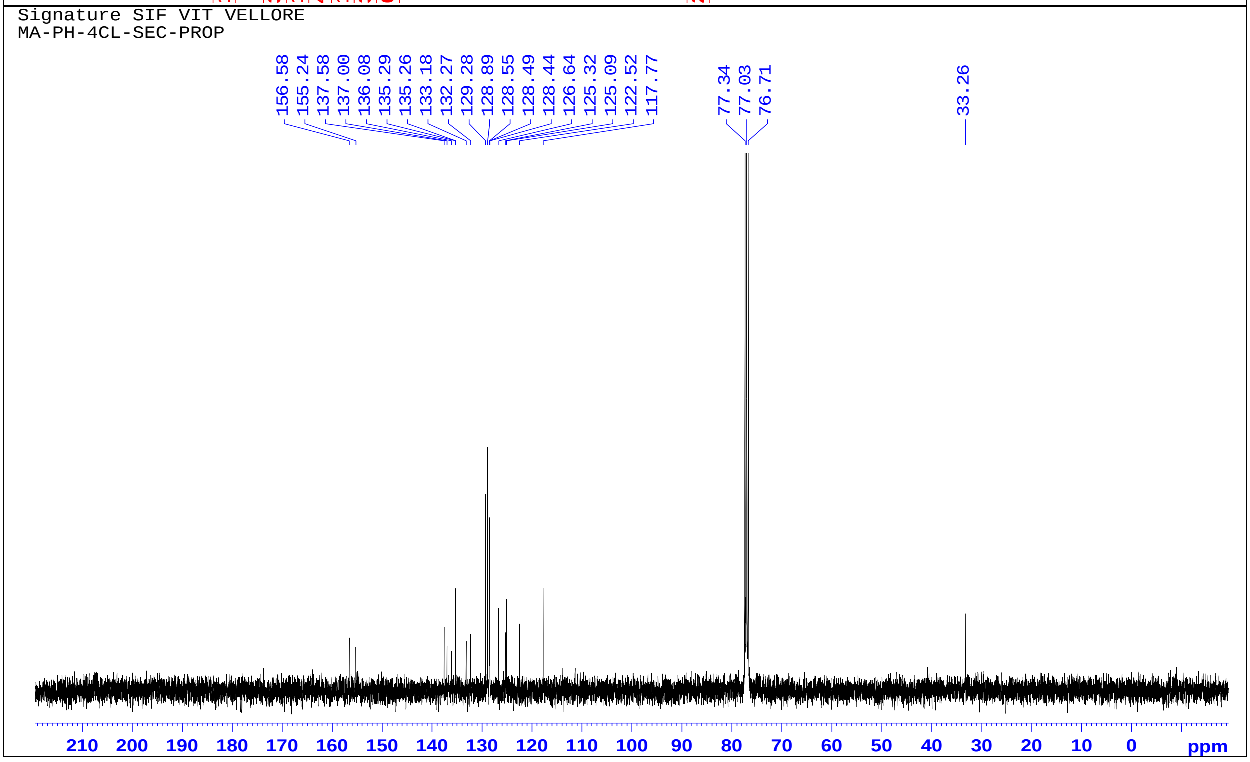


^{19}F NMR of **8am**

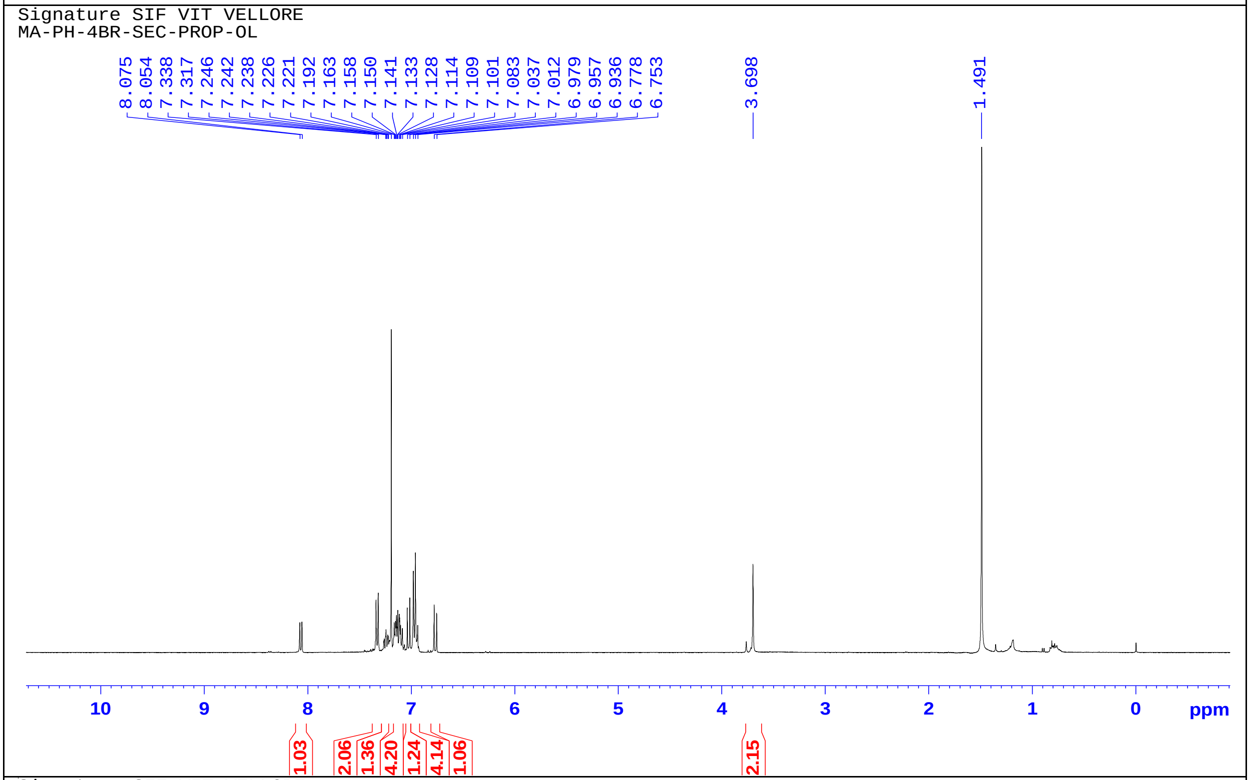


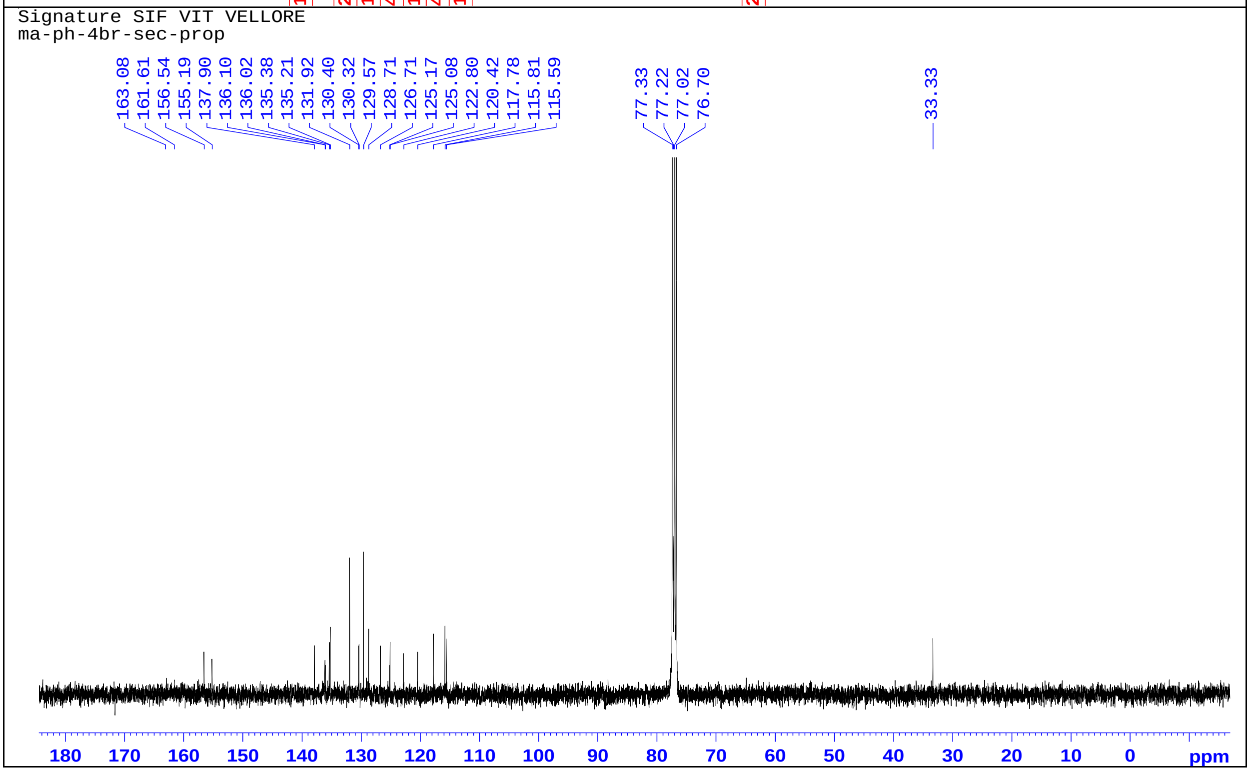
[1]H NMR and [13]C NMR of **8an**



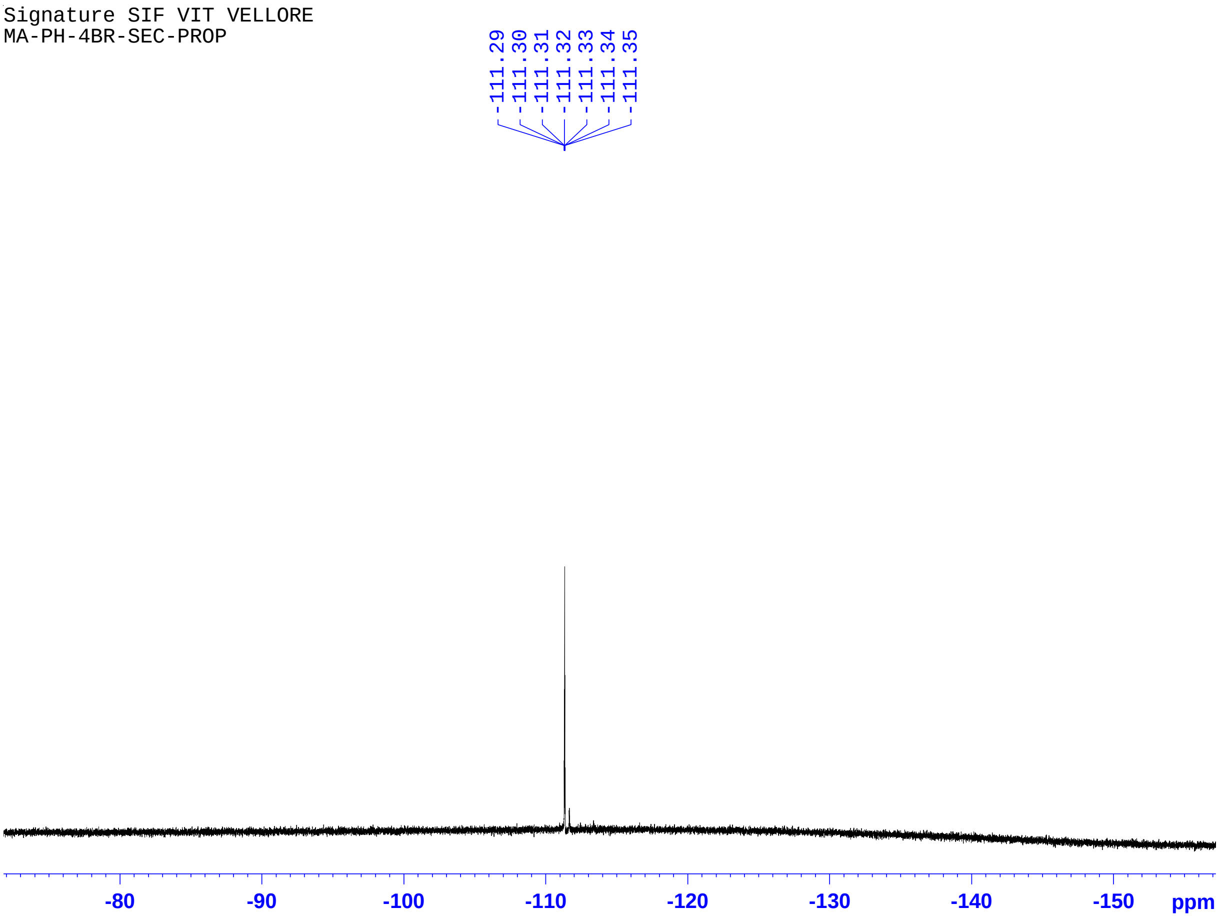


[1]H NMR and [13]C NMR of **8ao**

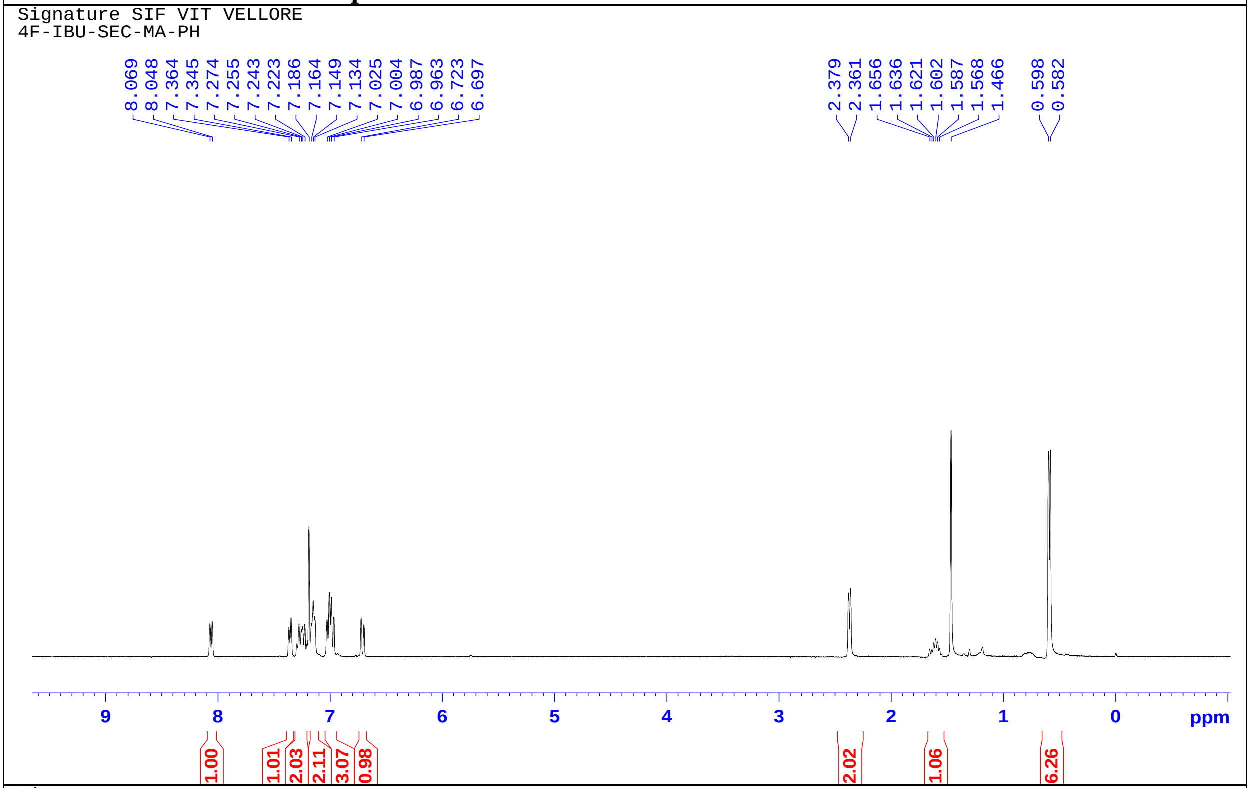


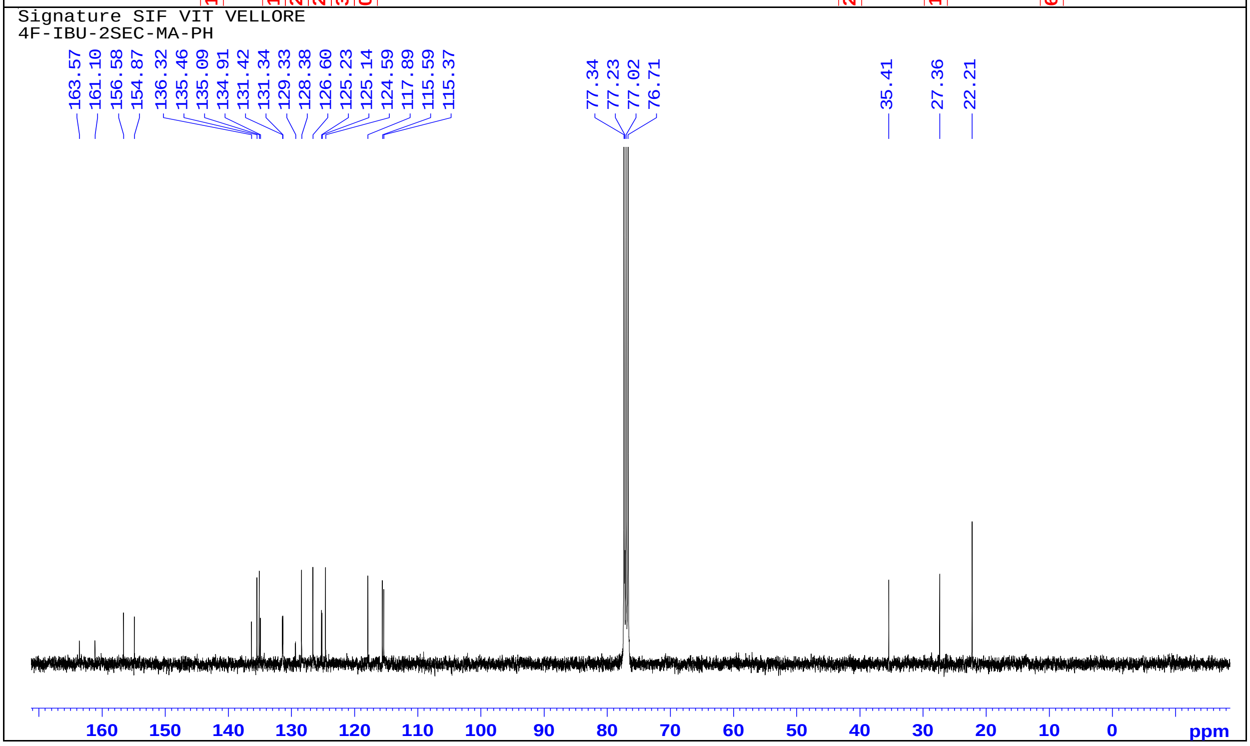


^{19}F NMR of **8ao**

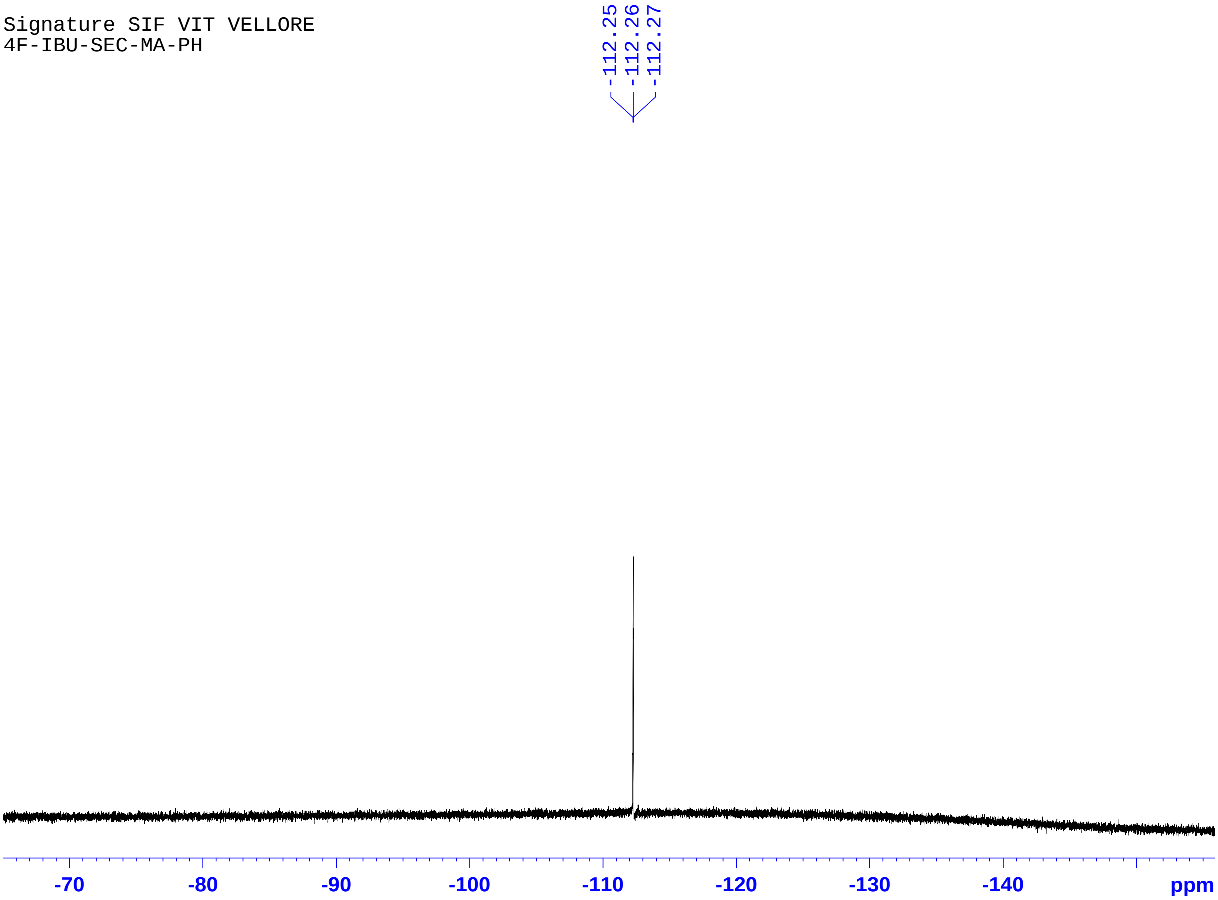


^{1}H NMR and ^{13}C NMR of **8ap**

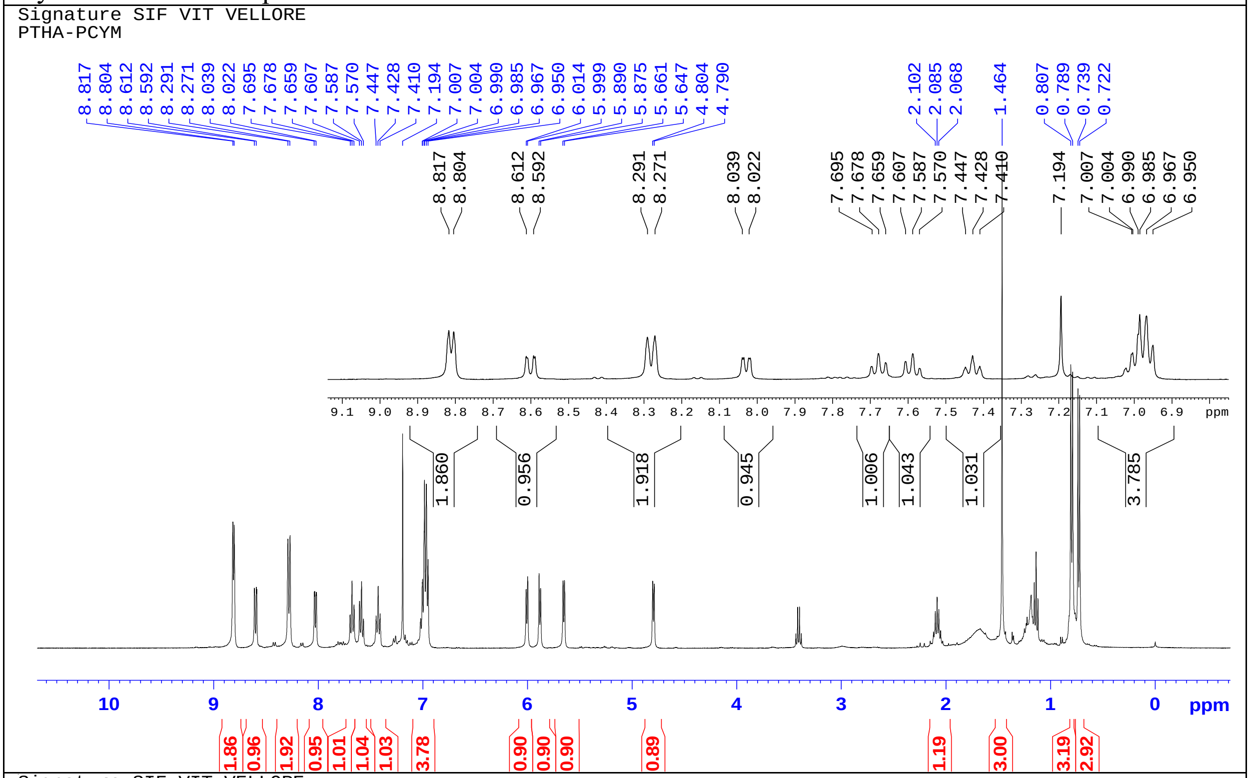


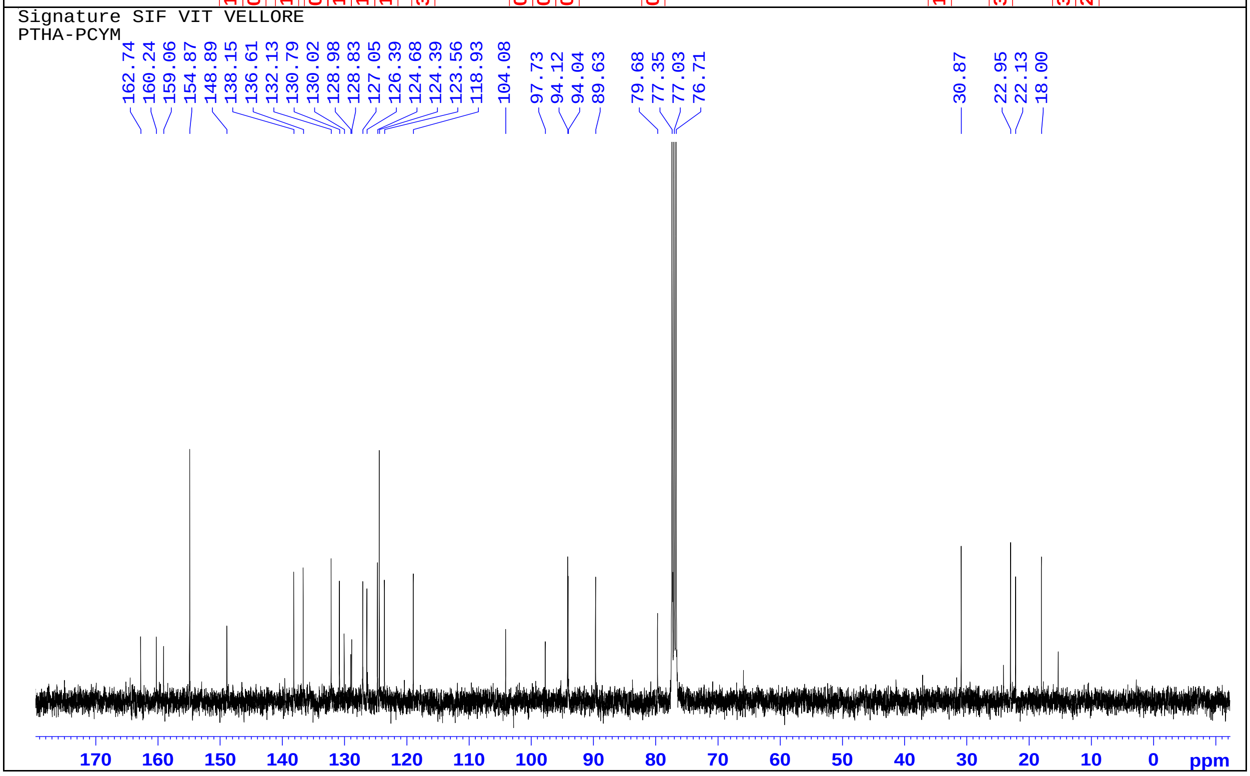


[19]F NMR of **8ap**

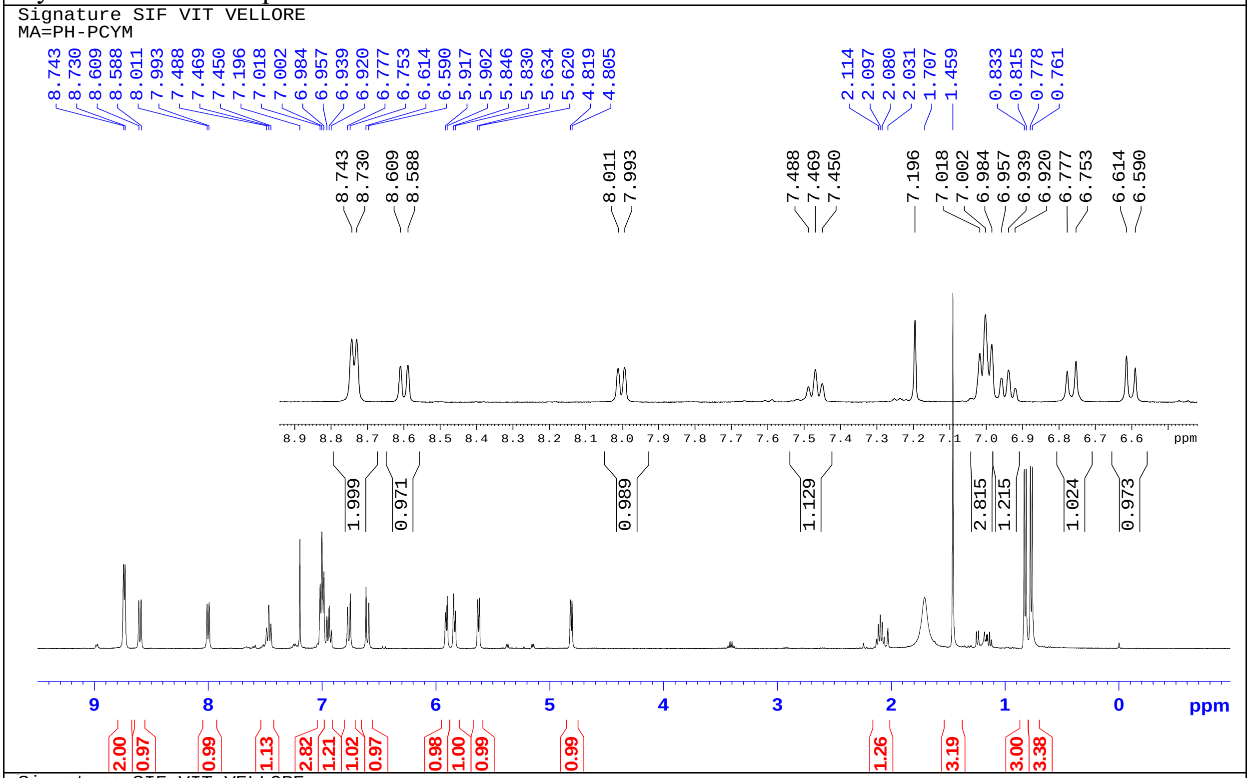


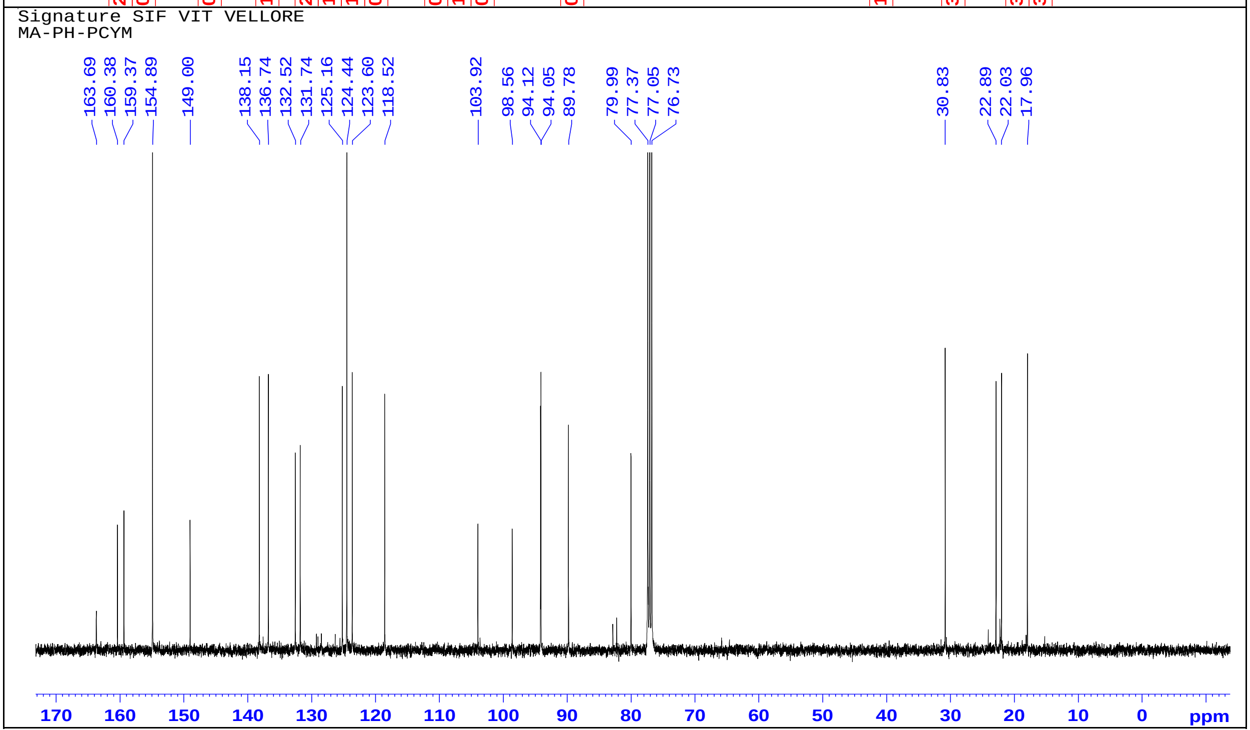
Cycloruthenated complex **1cr**



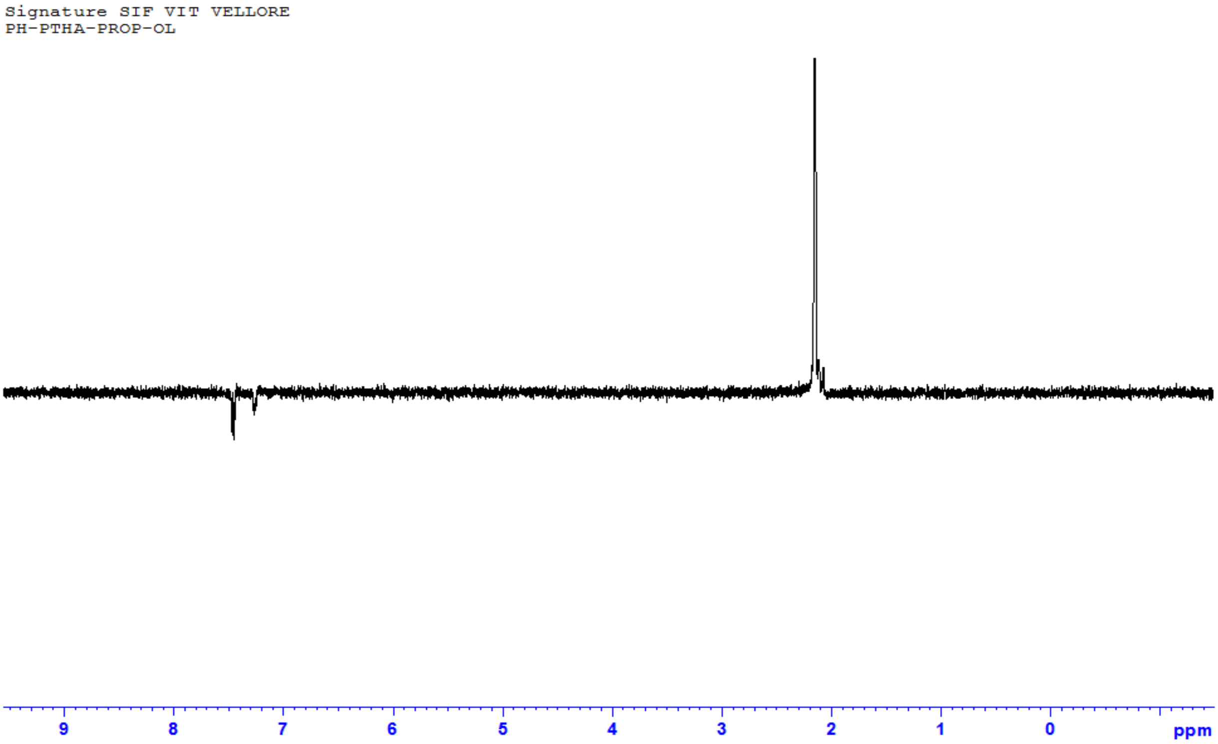


Cycloruthenated complex **4cr**

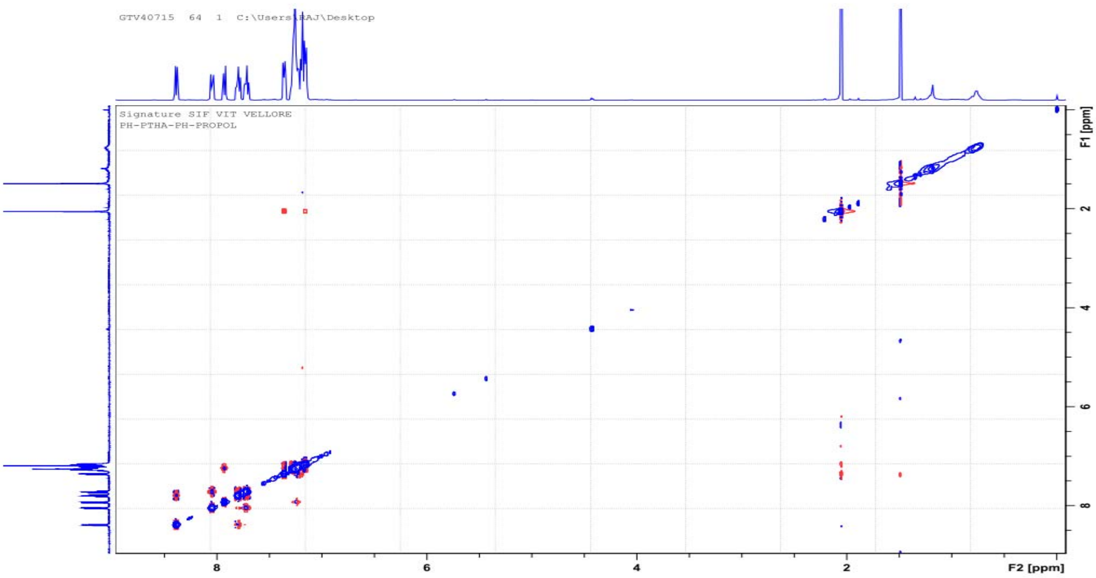




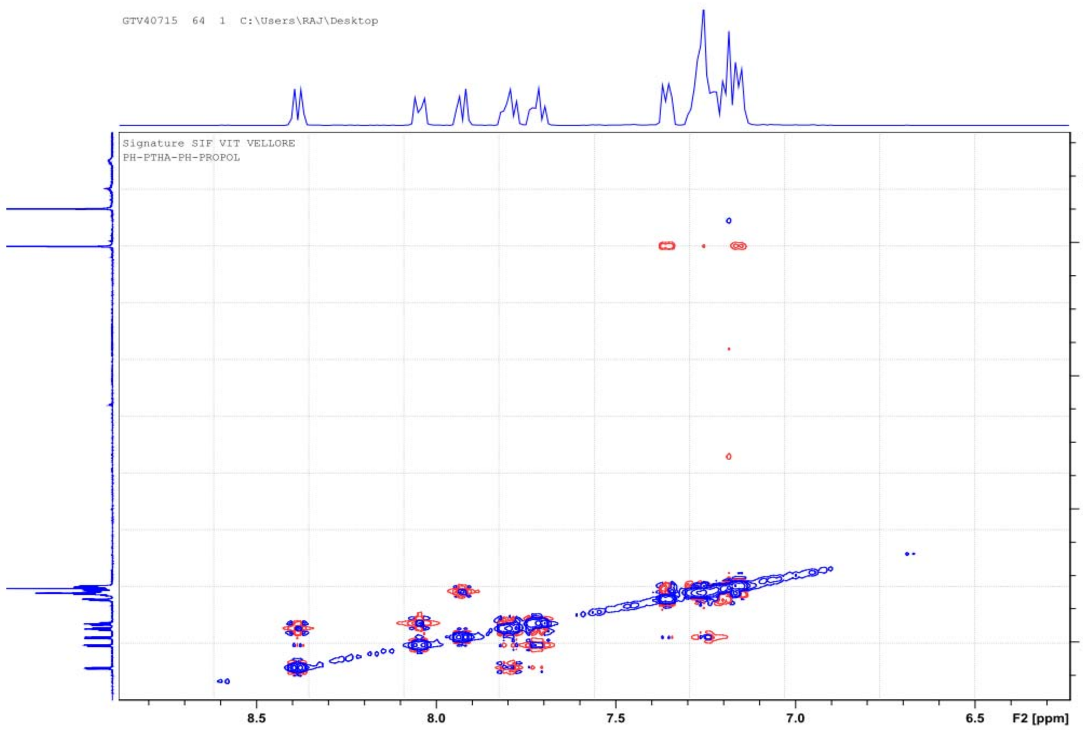
NOE Spectrum of **3aa**



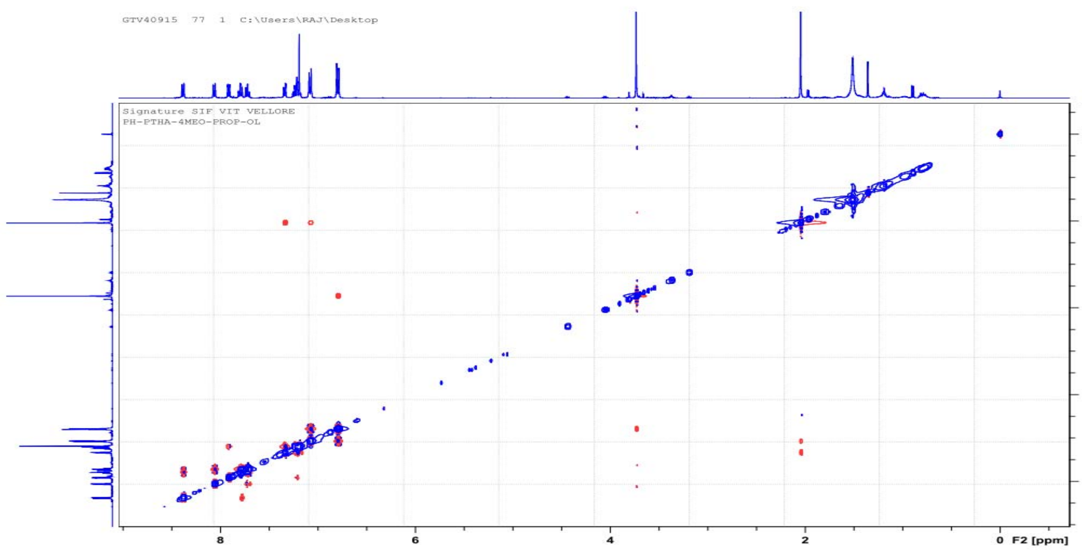
NOESY Spectrum of **3aa**



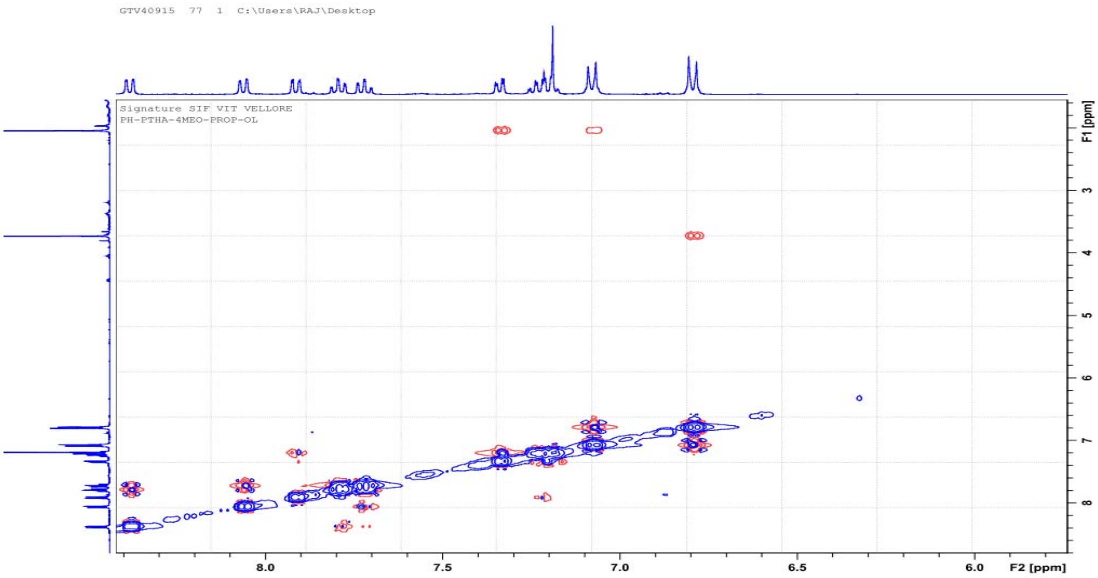
NOESY Expanded Spectrum of **3aa**



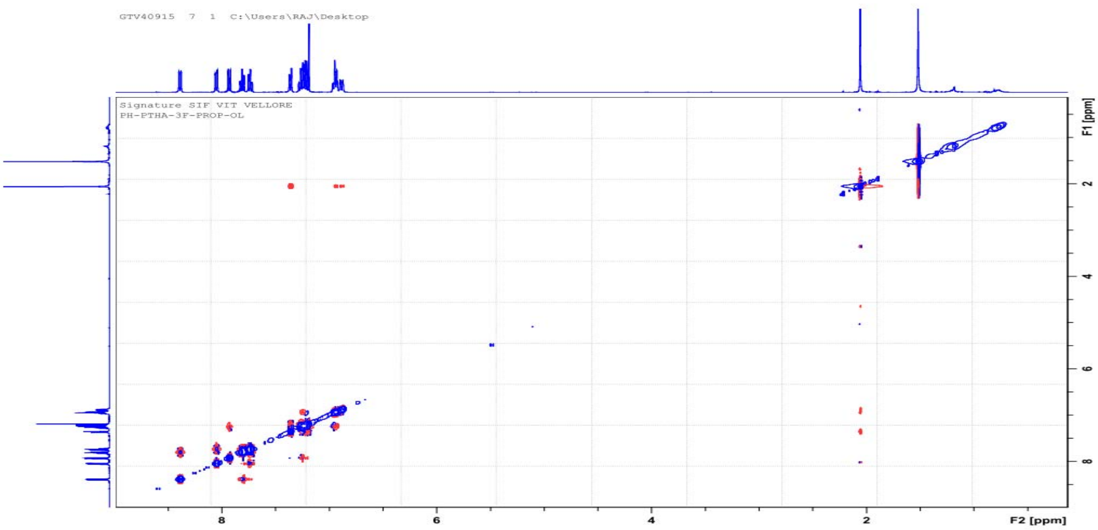
NOESY Spectrum of **3ac**



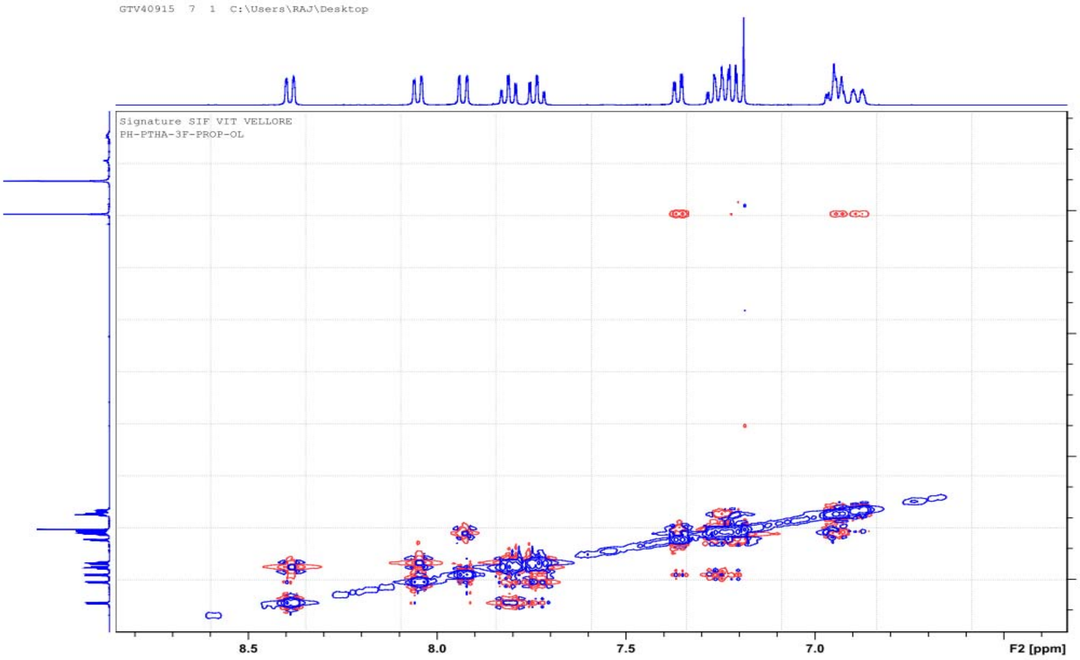
NOESY Expanded Spectrum of **3ac**



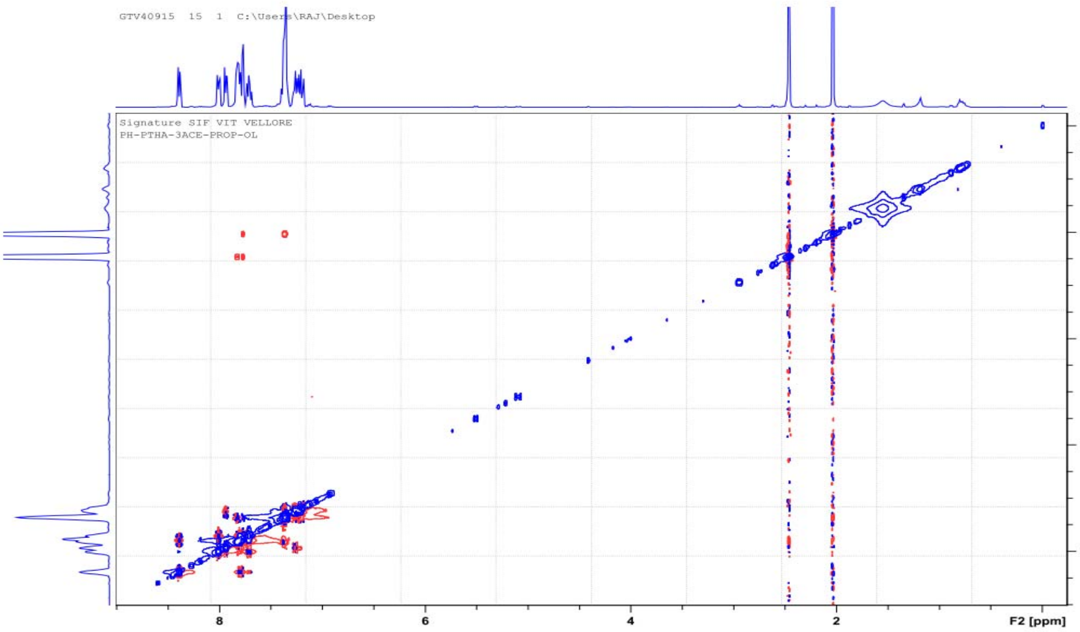
NOESY Spectrum of **3af**



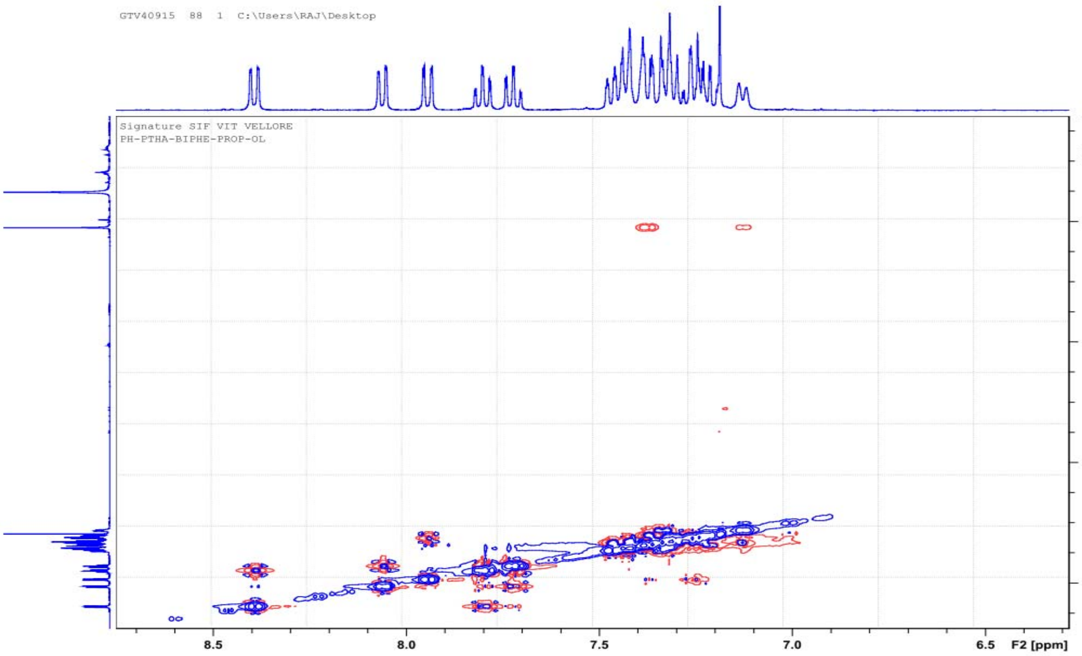
NOESY Expanded Spectrum of **3af**



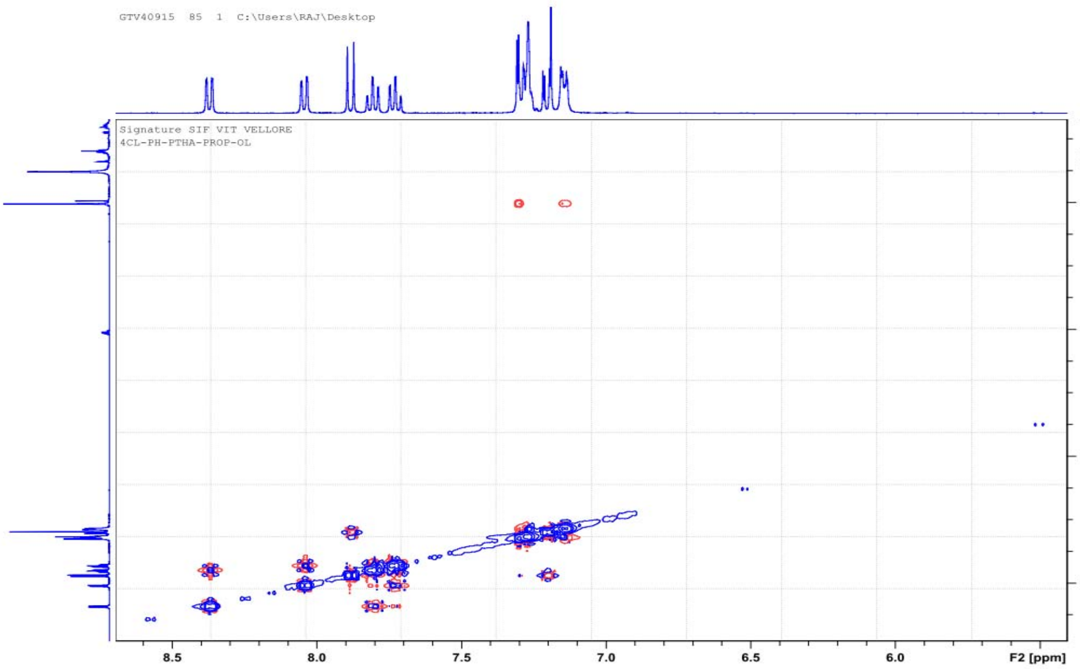
NOESY Spectrum of **3ag**



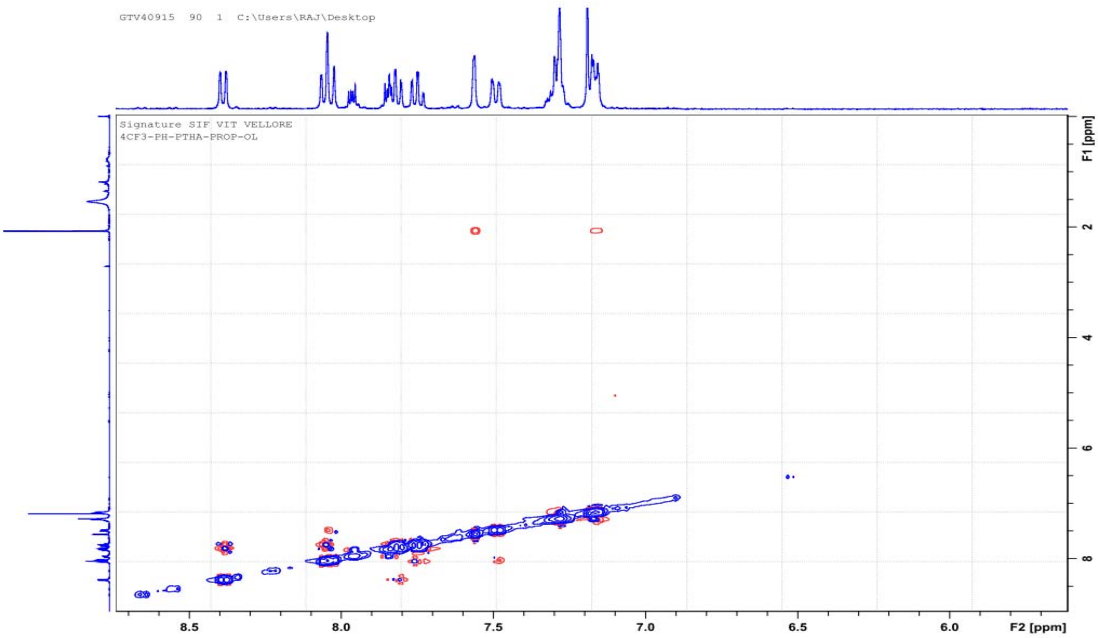
NOESY Spectrum of **3ak**



NOESY Spectrum of **3da**

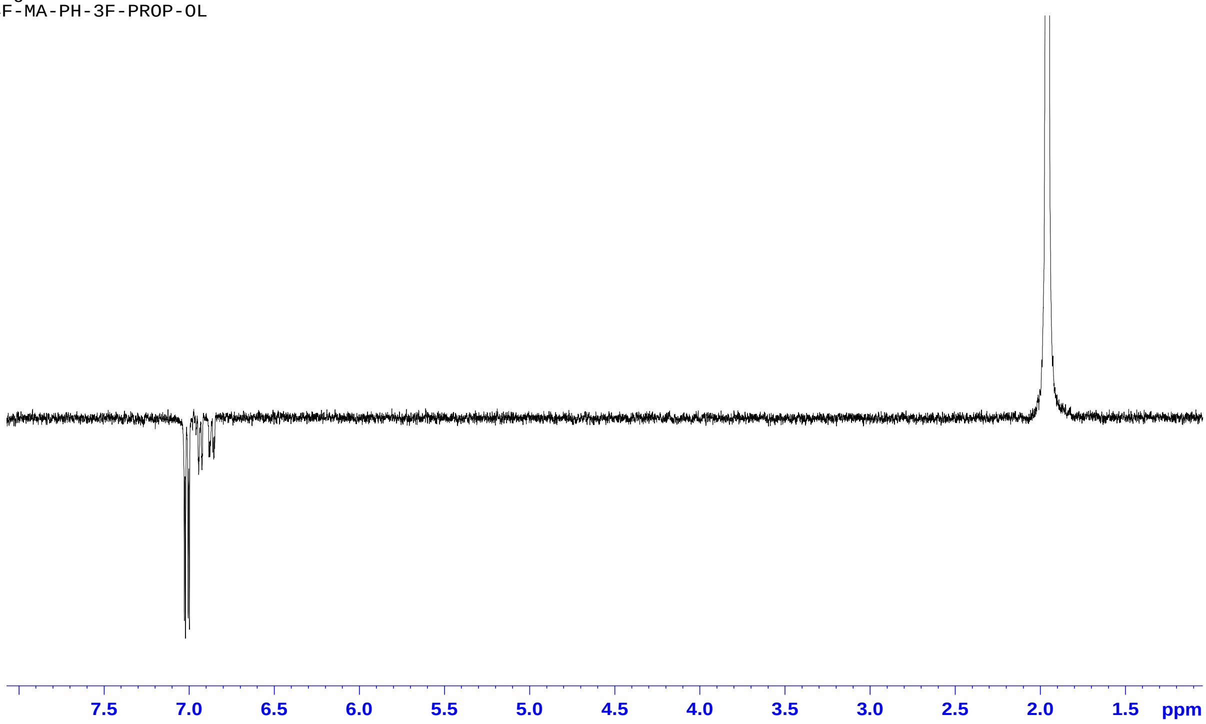


NOESY Spectrum of **3fa**

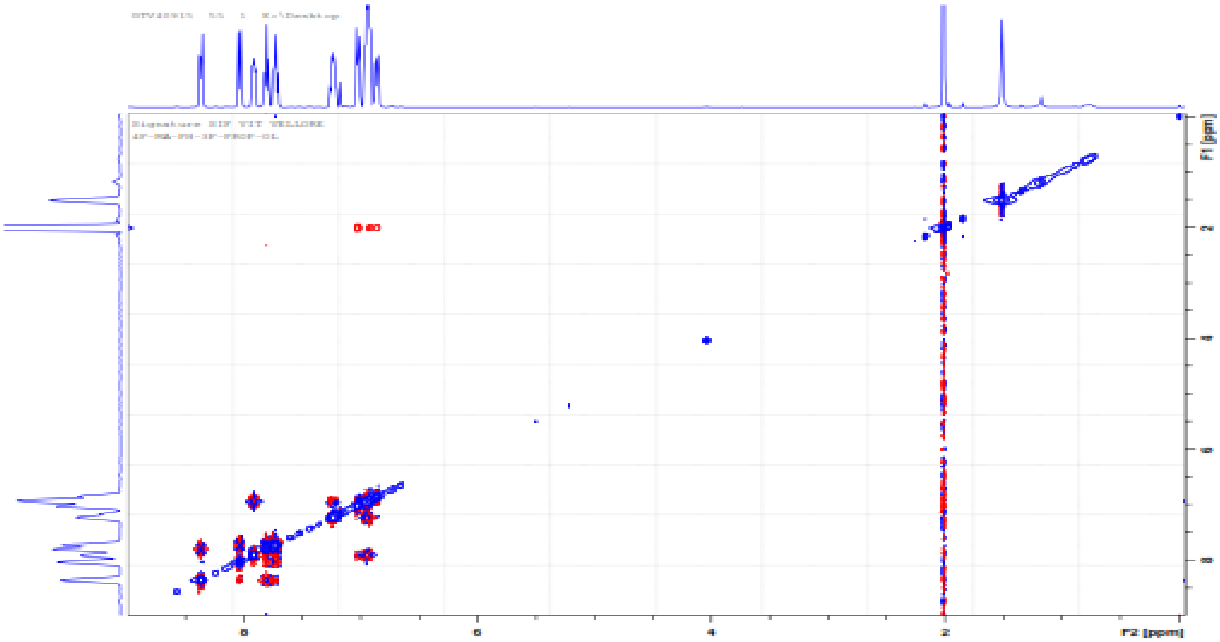


NOE Spectrum of **3cf**

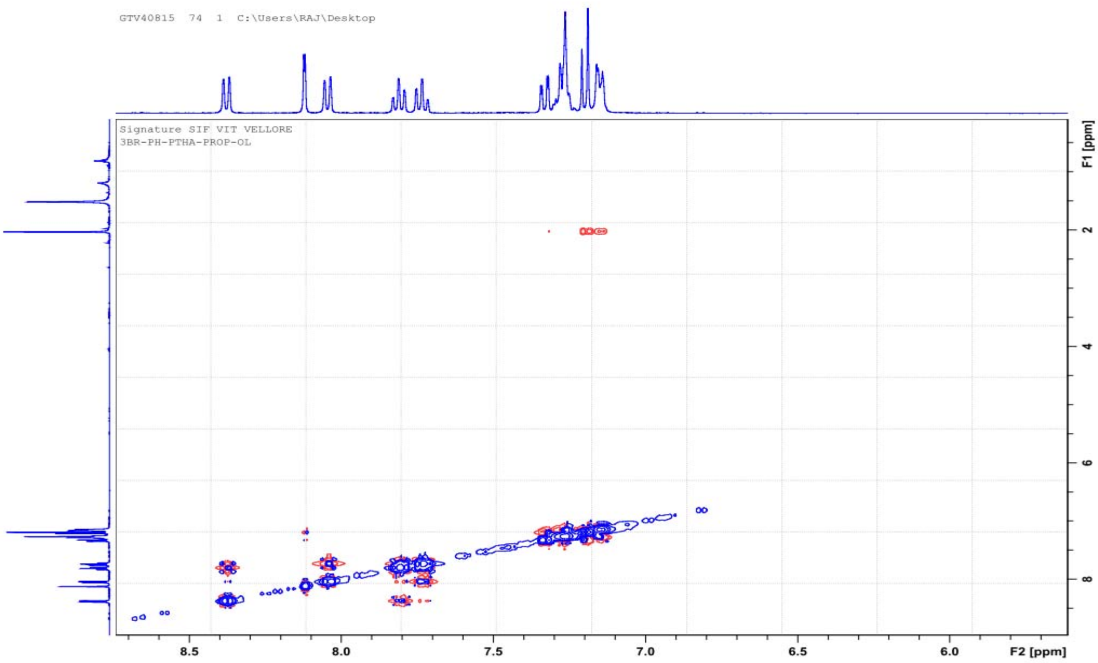
Signature SIF VIT VELLORE
4F-MA-PH-3F-PROP-OL



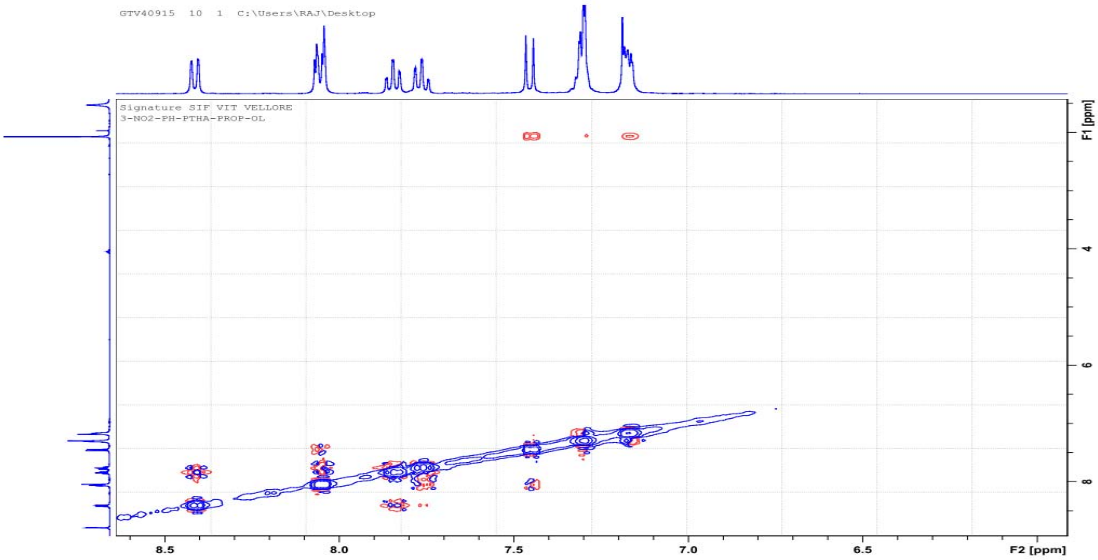
NOESY Spectrum of **3cf**



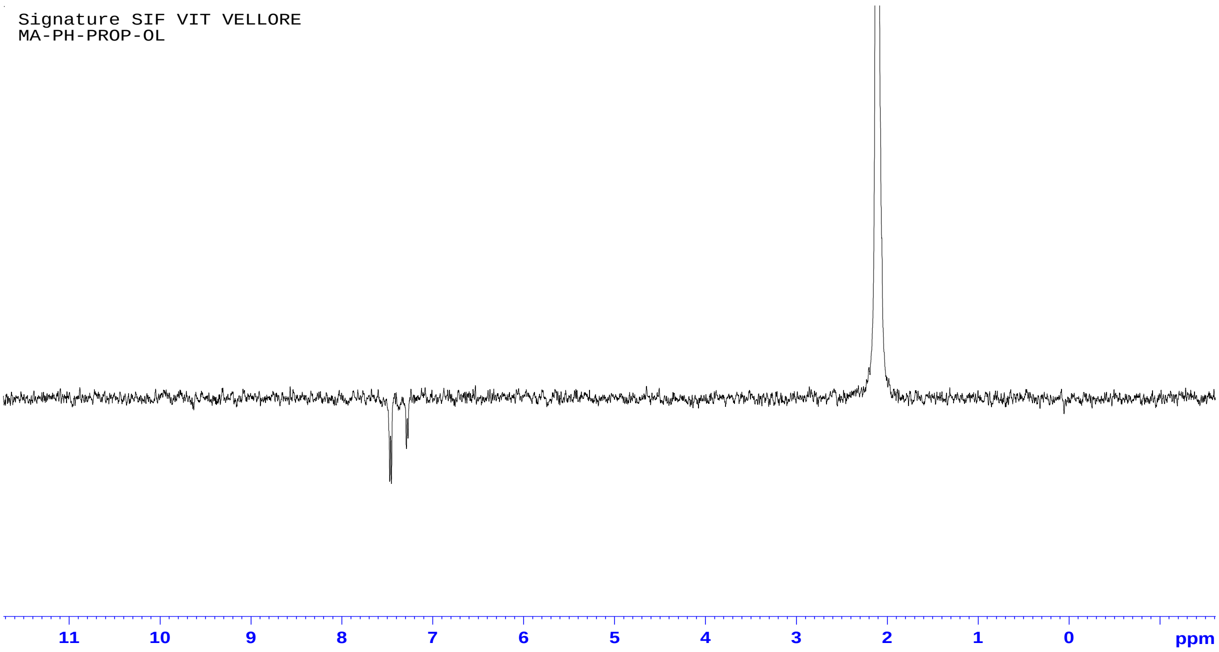
NOESY Spectrum of **3ha**



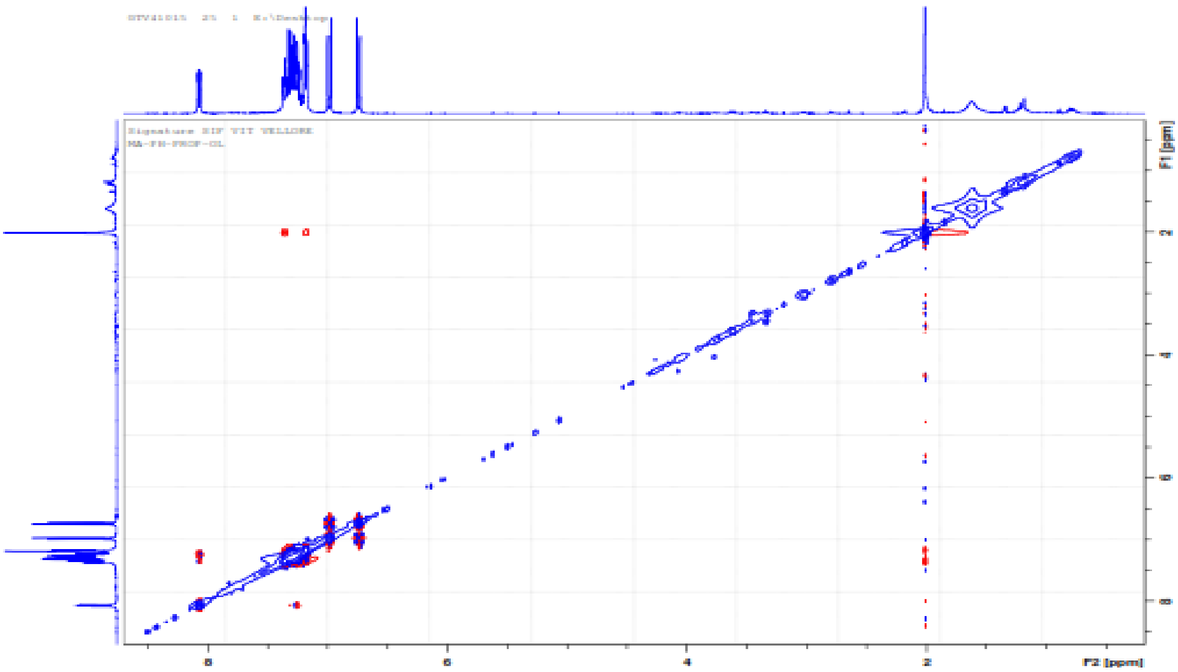
NOESY Spectrum of **3ia**



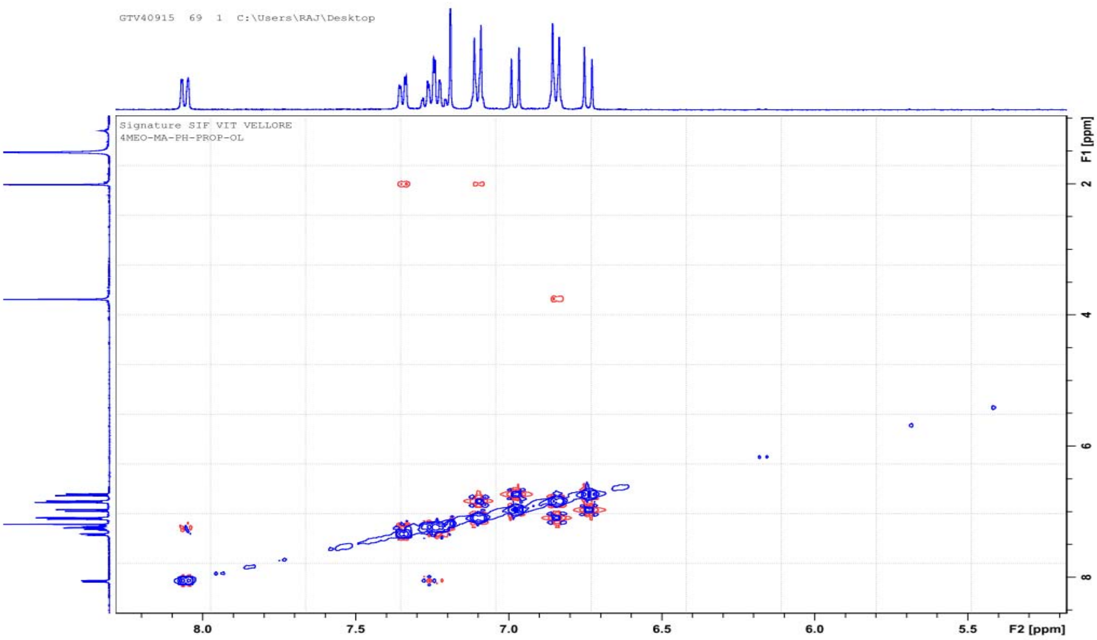
NOE Spectrum of **5aa**



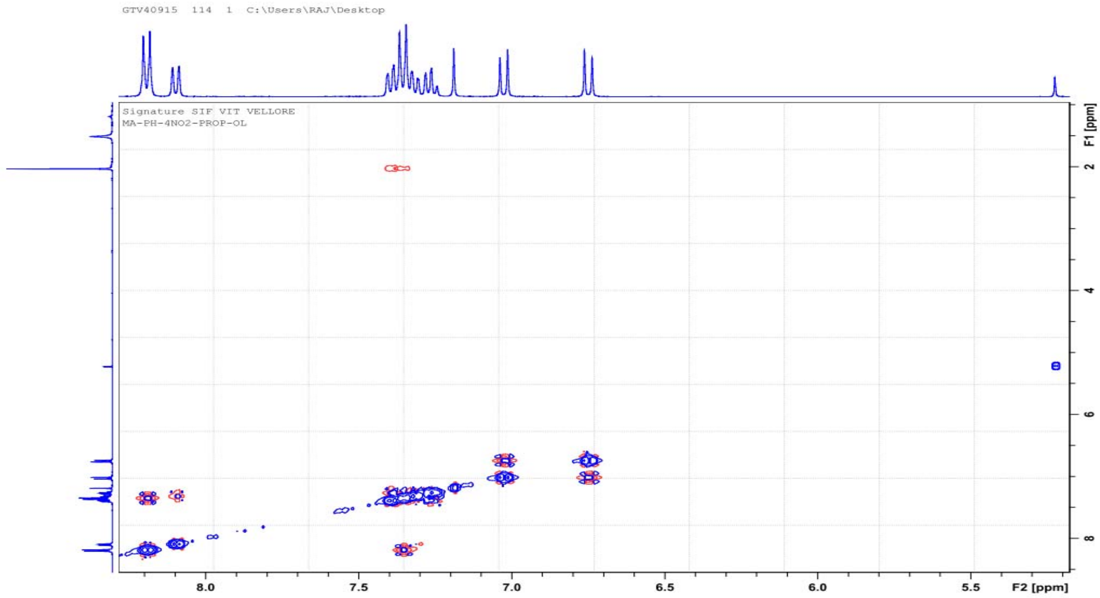
NOESY Spectrum of **5aa**



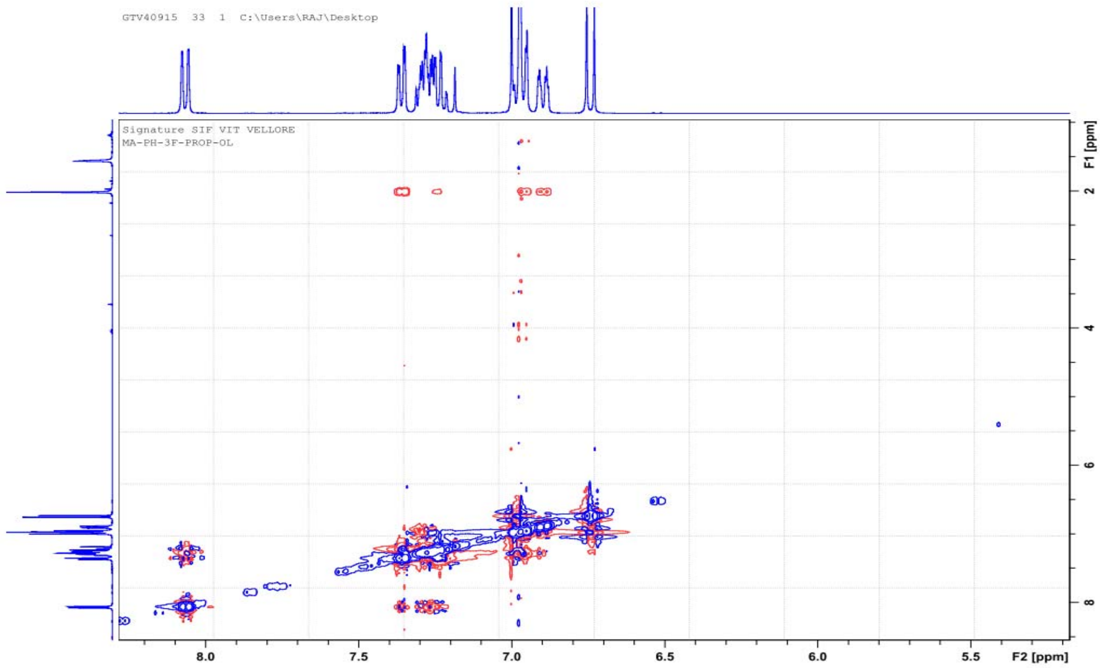
NOESY Spectrum of **5ac**



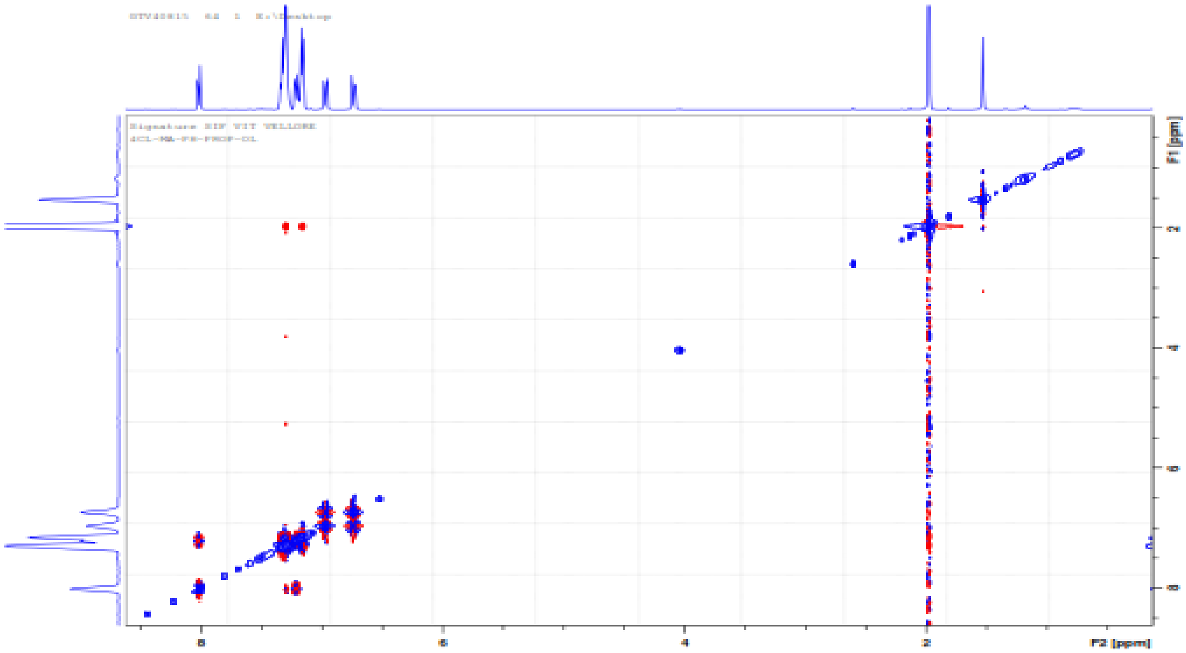
NOESY Spectrum of **5ae**



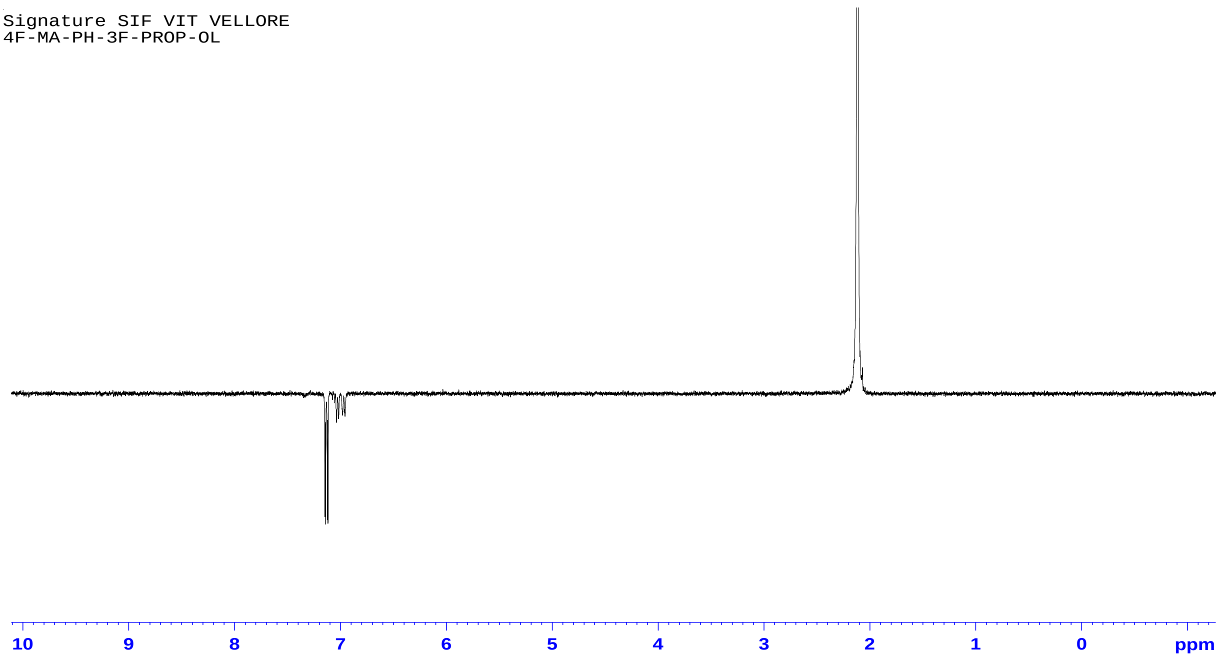
NOESY Spectrum of **5af**



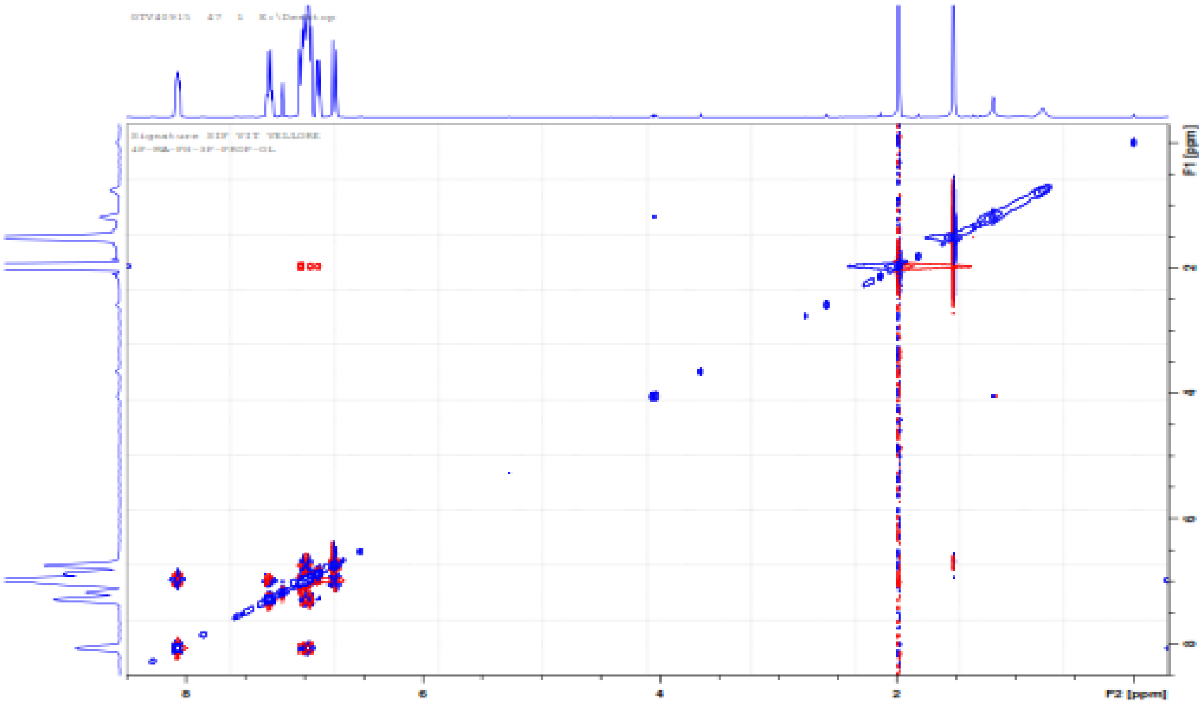
NOESY Spectrum of **5da**



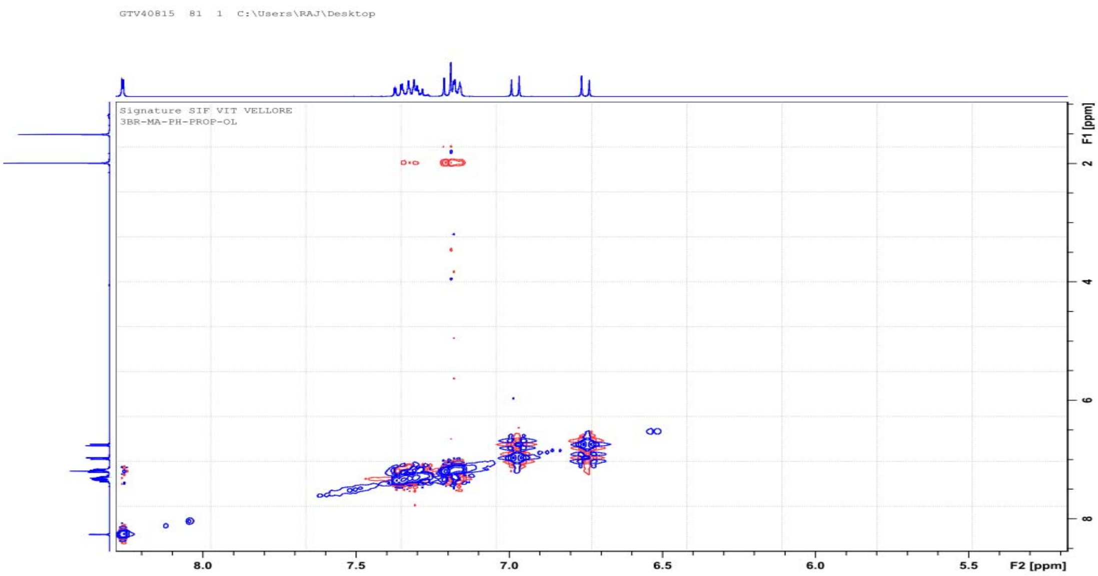
NOE Spectrum of **5cf**



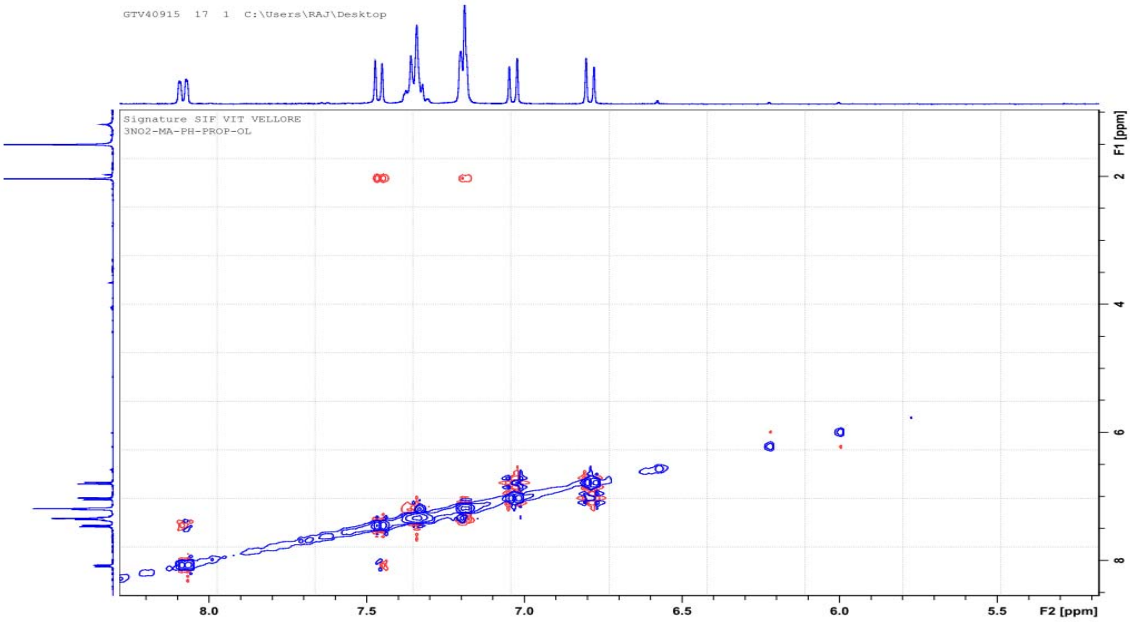
NOESY Spectrum of **5cf**



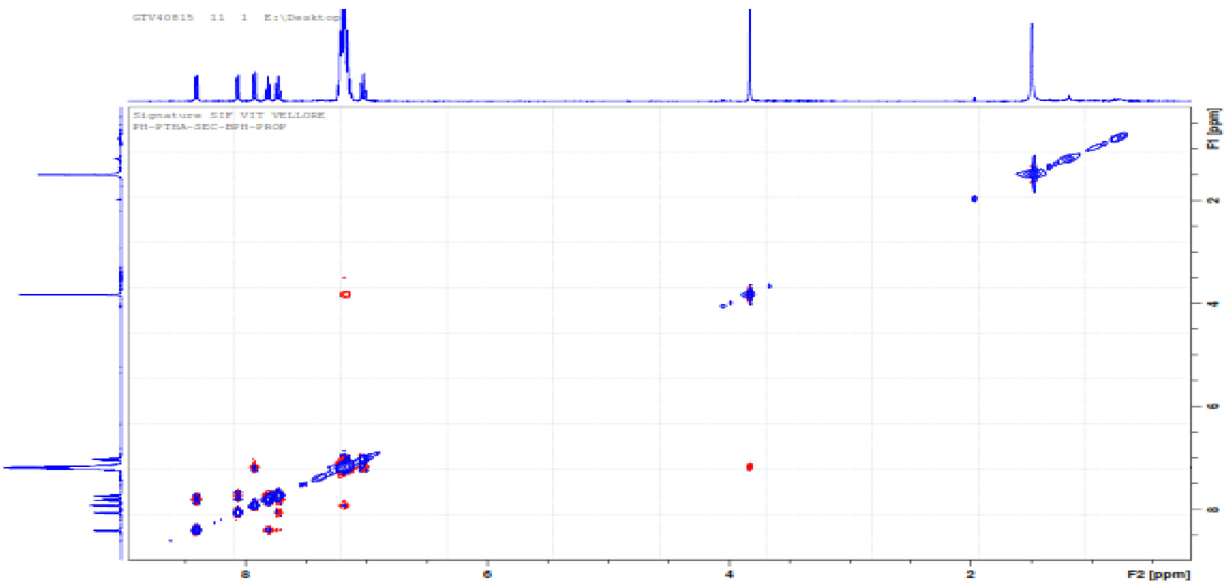
NOESY Spectrum of **5ha**



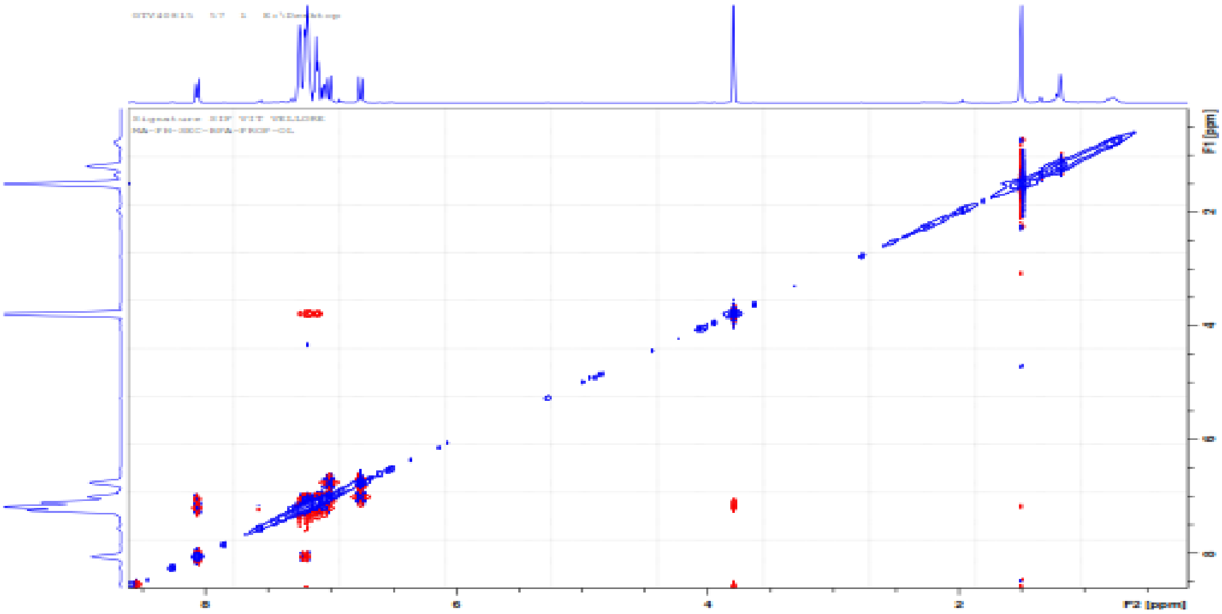
NOESY Spectrum of **5ia**



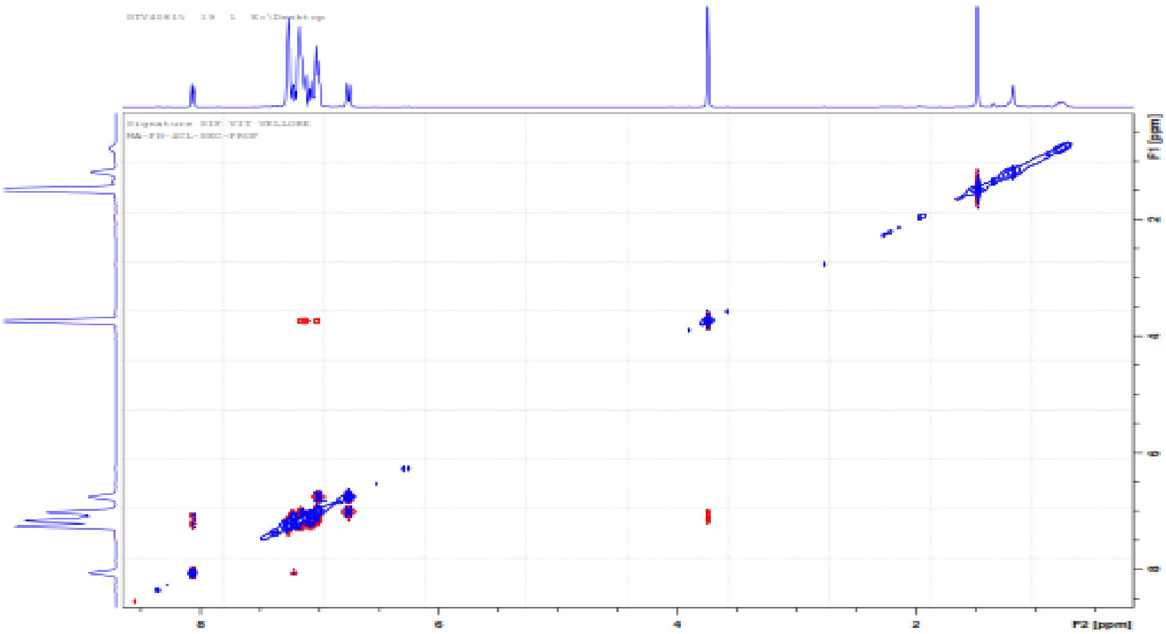
NOESY Spectrum of **7al**



NOESY Spectrum of **8al**



NOESY Spectrum of **8an**



NOESY Spectrum of **8ap**

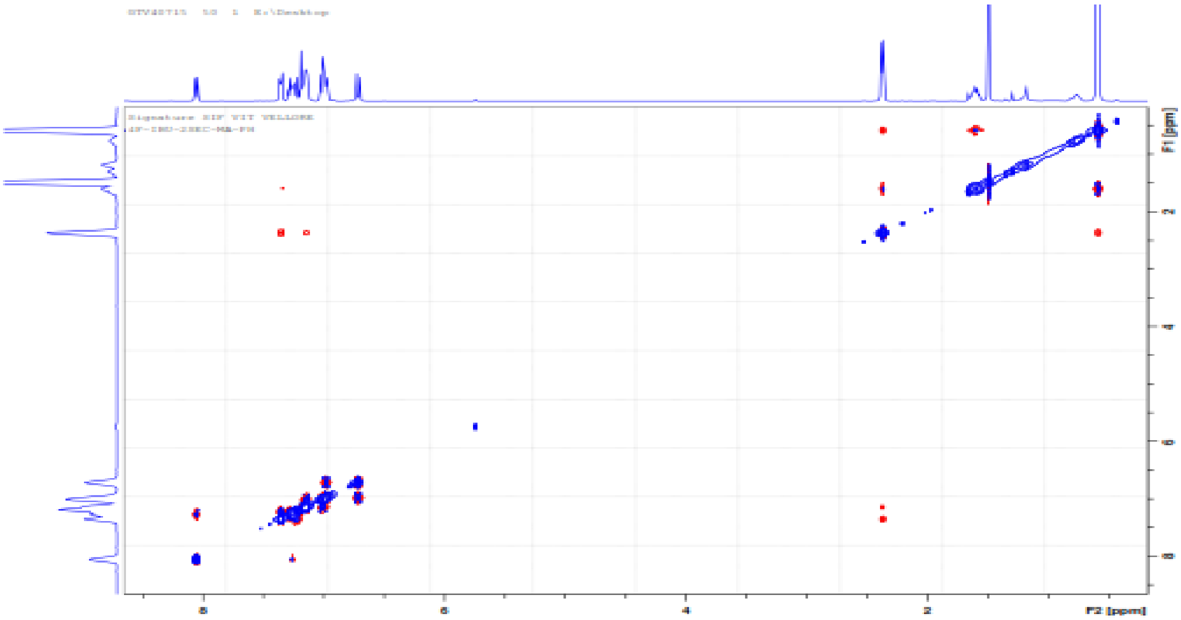
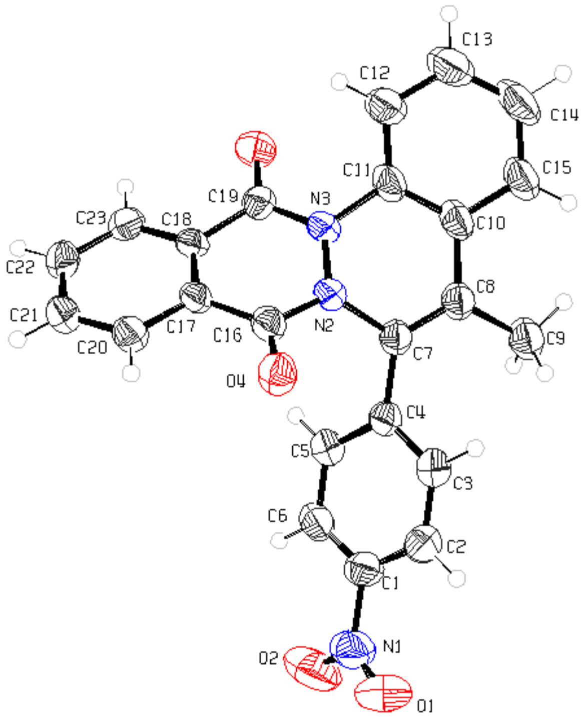
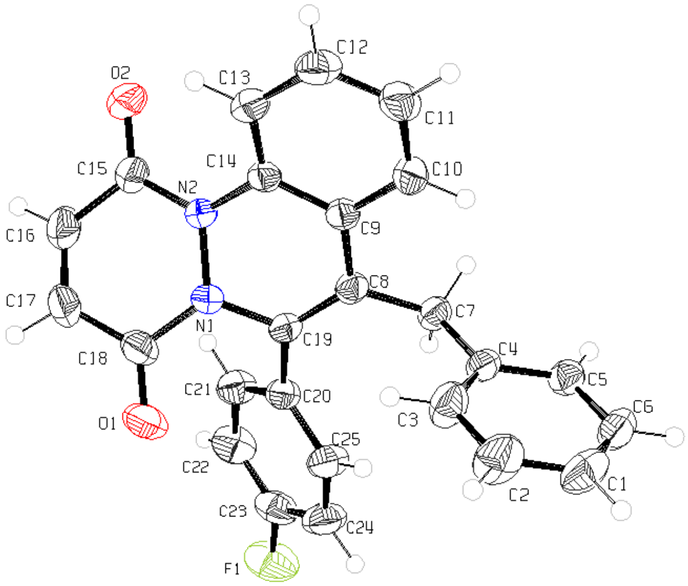


Figure S1: Crystal data and structure refinement for **3ae**



CCDC number	**CCDC1434966**
Formula	$C_{23}H_{15}N_3O_4$
Formula weight	397.38
Color	Yellow
Temperature/K	293(2)
Radiation	MoK\a
Wavelength/Å	0.71073
Crystal system	monoclinic
Space group	'P 21/c'
a (Å)	22.748(6)
b (Å)	10.773(3)
c (Å)	15.613(4)
α (°)	90
β (°)	102.346(8)
γ (°)	90
Volume (Å^3)	3737.7(17)
Z	8
Density (g/ml)	1.412
μ (1/mm)	0.099
F (000)	1648
θ (min, max)	2.101, 28.619
No. of unique reflns	9084
No. of parameters	541
*R*_obs, wR_2_obs	0.2069, 0.1076

Figure S2: Crystal data and structure refinement for **8am**



CCDC number	**CCDC1434961**
Formula	$C_{25}H_{17}FN_2O_2$
Formula weight	396.40
Color	Dark red
Temperature/K	293(2)
Radiation	MoK\a
Wavelength/Å	0.71073
Crystal system	monoclinic
Space group	'P 21/c'
a (Å)	10.9284(9)
b (Å)	18.6077(14)
c (Å)	10.9054(8)
α (°)	90
β (°)	118.516(2)
γ (°)	90
Volume ($Å^3$)	1948.6(3)
Z	4
Density (g/ml)	1.351
μ (1/mm)	0.093
F (000)	824
θ (min, max)	2.121, 28.310
No. of unique reflns	4838
No. of parameters	271
*R*_obs, *wR*2_obs	0.0493, 0.1333

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