Maleimide fused Boron-Fluorine complexes: Synthesis, Photophysical and electrochemical properties.

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1. Exprimental procedure for X-ray crystallogrphic analysis:

The crystal was obtained by slow evaporation of the samples in chloroform and acetone. A suitable single crystal was mounted in a glass fibre, and diffraction measurements were taken with a diffractometer with Cu Kα graphite monochromated radiation. The structure was solved by direct methods using the programme SHELXL-2013. The refinement and all further calculations were carried out using SHELXL-2013.

Table S1: selected bond length for crystal BF3(I).

Interaction	Distance (°A)
(a)C(29)-H(29)…..F(1)	2.4587
(b)C(9)-H(9)…..F(1)	2.4620
(c)(14)-H(14) …..F(2)	2.6923
(d)(9)-H(9)…..O(4)	2.4833

Table S2: Crystallographic data for crystal BF3(I).

Compound	BF3(I)
Empirical formula	C_{26} H_{17} BF_2 N_2 O

Formula weight	422.23
Temperature (K)	296 (2)
Wavelength (Å)	1.54178
Crystal habit	yellow needle
Crystal system	monoclinic
Space group	P 21/n
Unit cell dimensions	
a (Å)	11.0852(4)
b (Å)	12.5966(4)
c (Å)	14.3350(5)
α (°)	90
B (°)	98.6440(10)
γ (°)	90
V (Å^3)	1978.94(12)
Z, Calculated density (mg/m^3)	4, 1.417
Absorption coefficient (mm^{-1})	0.816
F(000)	872
Theta range for data collection (°)	4.7-66.6
Limiting indices	-13<= h<=12, -14<=k<=14,-14<=l<=16
Reflection collected	13660
Independent reflections	3482 [R_{int} = 0.0206]
Completeness to theta	99.8%
Absorption correction	Multi scan
Refinement method	Full-matrix least-squares on F^2
Refinement program	SHELXL-2013
Data / restraints / parameters	3482/0/289
Goodness-of-fit on F^2	1.044
Final R indices [I>2sigma(I)]	R1 = 0.0302, wR2= 0.0754
R indices (all data)	R1 = 0.0329, wR2=0.0774
Weighting scheme	w =1/[σ^2 (F_0^2)+(0.0346P)^2 + 0.734P] where P=(F_0^2+2F_c^2)/3
Largest diff. peak and hole (eÅ^{-3})	0.157 and -0.201

2. General experimental procedure:

The Stokes shift is calculated by following equation 1[1].

$$\nu_A - \nu_F = \left(\frac{1}{\lambda_A} - \frac{1}{\lambda_F}\right) \times 10^7 \quad \text{…….. (1)}$$

Where $\nu_A - \nu_F$, λ_A, λ_F are the Stokes shift, absorption and fluorescence maxima respectively.

The ability of the molecule to emit the absorbed light is quantify by fluorescence quantum yield (Φ_F). The quantum yield of the complexes were calculated by comparative method using quinine sulphate (λ_{ex} =345, Φ_F = 0.54 in 0.1 M H_2SO_4) as a standard according to equation 2.

$$\Phi_F = \Phi_{ref}\left(\frac{m}{m_R}\right)\left(\frac{n^2}{n_R^2}\right) \quad \ldots\ldots\ldots (2)$$

Where m is the slope of the line obtained from the plot of the integrated fluorescence intensity vs. absorbance. n is the refractive index of the solvent and subscript $_R$ refers to the reference fluorophore of the known quantum yield.

The oscillator strength demonstrates the effectiveness of the number of electrons which their transition from ground to excited state gives absorption area in the electron spectrum. Oscillator strength[2] of all compounds in different solvents is calculated by following equation 3 and are shown in Table 1.

$$f = 4.32 \times 10^{-9}\, \Delta\nu_{1/2}\varepsilon_{max} \quad \ldots\ldots (3)$$

The energy yield[3] of the fluorescence is calculated by following equation 4.

$$E_F = \emptyset_F \frac{\lambda_A}{\lambda_F} \quad \ldots\ldots\ldots (4)$$

3. Calculation of orientation polarisabilty :

The Lippert-Mataga polarity parameter is a measure of polarity of different solvents and calculated by following equation 5.

$$(\Delta f) = \frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{n^2 - 1}{2n^2 + 1} \quad \ldots\ldots\ldots (5)$$

In this (Δf) is the measure of orientation polarisation only, electronic polarisation part $\{(n^2-1)\,|\,(2n^2+1)\}$ has been subtracted from the total polarisation of the solvent $\{(\varepsilon-1)\,|\,(2\varepsilon+1)\}$. The electronic polarisation is an instantaneous process and occurs simultaneously with the electronic transition (absorption and emission of photon) hence, the effect of electronic polarisation will not be considered in measurement of photophysical parameter of the compound. The orientation polarizability of the different solvents is shown in Table S3.

Table S3: Orientation polarizability of different solvents.

Solvent	Dielectric constant Ɛ	Refractive index η	(Ɛ-1)/(2Ɛ+1)	(η^2-1)/(2η^2+1)	Orientation polarizability Δf
Toluene	2.38	1.496	0.2395	0.2263	0.0132
Dioxane	2.25	1.422	0.2272	0.2027	0.0245
THF	7.58	1.407	0.4071	0.1976	0.2095
DCM	8.93	1.424	0.4204	0.2033	0.2171
Acetone	20.7	1.358	0.4646	0.1802	0.2843
ACN	37.5	1.344	0.4802	0.1748	0.3054
Methanol	32.2	1.328	0.4770	0.1688	0.3082

4. Electrochemical studies: Electrochemical studies were carried out on electrochemical work station. The potential were reported vs Ferrocene as internal standard, glassy carbon as working electrode, platinum as counter electrode and $Ag/AgNO_3$ as reference electrode using scan rate of 100 mVs^{-1}. 1mmol sample was prepared in 0.1 M tetrabutyl ammonium hexaflourophosphate as a supporting electrolyte.

E_{HOMO} and E_{LUMO} were calculated by following equations.

$E_{HOMO} = [(E_{Ox}^{onset} - E_{1/2(ferrocene)} + 4.8)$ eV…… (6)

$E_{LUMO} = [(E_{red}^{onset} - E_{1/2(ferrocene)} + 4.8)$ eV…… (7)

5. Absorption edge:

The absorption coefficient (α) is calculated from absorbance (O.D.) by using the equation $\alpha = [2.303 \times (O.D.)]/L$ where, L is the thickness of the quartz cuvette (1mm).

The graph is plotted between hv vs $(\alpha hv)^2$ and then by extrapolating the linear portion of the curve will give a band gap of the compound.

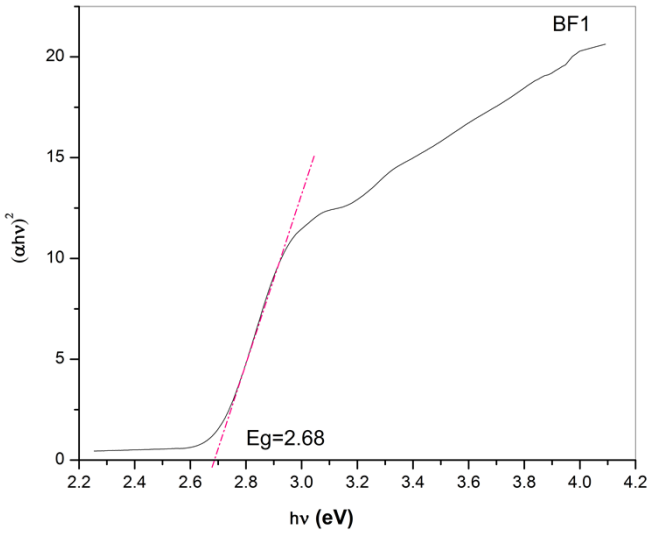


Fig S1: The absorption edge of BF1

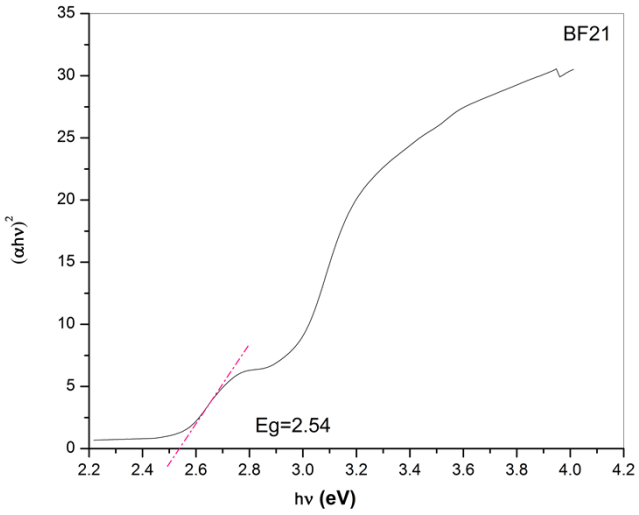


Fig S2: The absorption edge of BF21

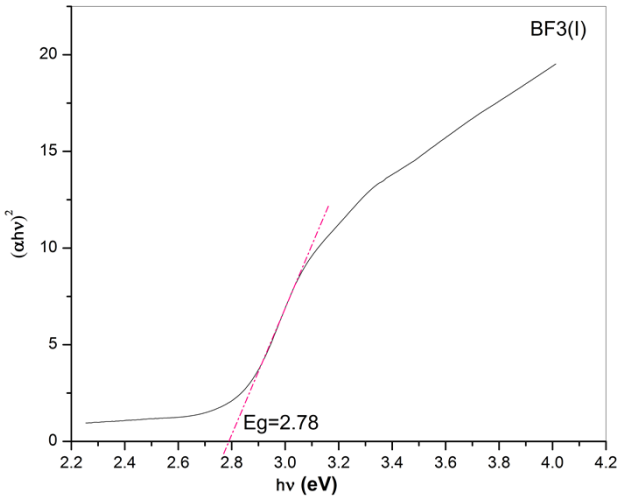


Fig S3: The absorption edge of BF3(I)

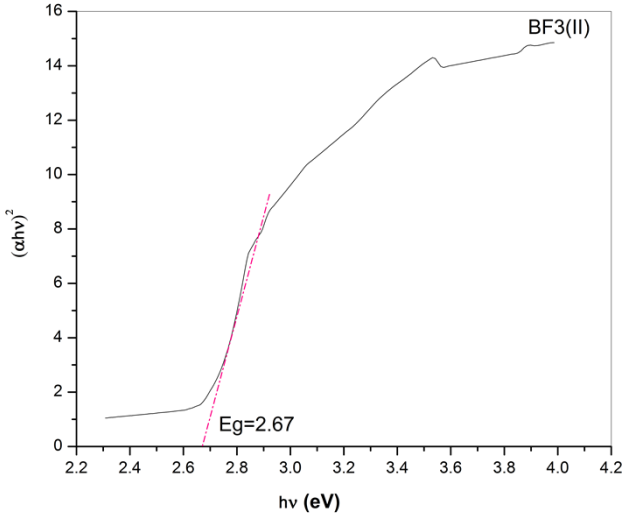


Fig S4: The absorption edge of BF3(II)

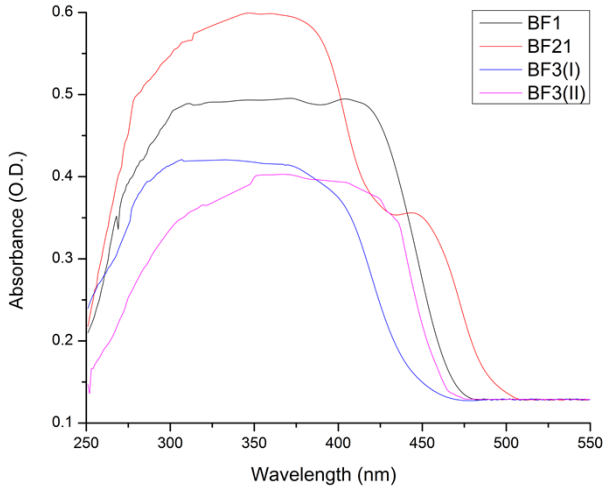


Fig S5: Solid state absorbance of BF compounds.

6. Synthesis and characterisation of compounds:

Compound 2a: 5g (0.033 mol) Benzoyl formic acid, 4.53g (0.033 mol) phenyl acetic acid and 50 ml acetic anhydride was heated to reflux at 150˚C for 5h. The reaction mass was cooled and quenched into ice cold water from which the solid precipitate out which was filtered and dried. The product was purified by crystallization using ethanol as a solvent. Yield: 5.67g (68.12%) Melting point: 148˚C (literature report: 153.5-155˚C)[4].

Compound 2b: Starting from benzoyl formic acid 5.0 g (0.033 mol), 6.20g (0.033 mol) naphthyl acetic acid and 50ml acetic anhydride compound 2b was synthesized and purified by a procedure similar to that of compound 2a. Yield: 6.32 g (63.20%) Melting point: 155˚C.

^{1}H NMR (δ in ppm) (500 MHz, $CDCl_3$): 8.01 (d, 1H), 7.94-7.91 (m, 1H), 7.57 (m, 1H), 7.54-7.46 (m, 5H), 7.40-7.31(m, 2H), 7.24-7.20 (m, 2H); HRMS (ESI-TOF) m/z $[M + H]^+$ Calcd for $C_{20}H_{12}O_3$: 301.0866. Found: 301.0825.

Compound 3a: In a sealed tube 2.0g (0.008 mol) of compound 2a, 0.94 g (0.016 mol) of acetamide and 10ml acetic anhydride were taken and heated at 180˚C for 24 h. The reaction mass was cooled and poured into ice cold water from which yellow colored solid precipitates out which was filtered, dried and purified by recrystallisation using ethanol as a solvent Yield: 1.57g (79.12%) Melting point: 213˚C (literature report: 218 ˚C)[5].

Compound 3b: Starting from compound 2b 2.0 g(0.006 mol), 0.78 g (0.013 mol) of acetamide and 10 ml of glacial acetic acid compound 3b was synthesized and purified by a similar procedure reported for compound 3a Yield:1.49g (75.34%) Melting point: 218˚C

^{1}H NMR (δ in ppm) (500 MHz, $CDCl_3$): 7.95 (m, 1H), 7.89 (m, 1H), 7.62 (s, 1H, -NH), 7.59-7.34(m, 7H), 7.28-7.24 (m, 2H), 7.19-7.16 (m, 1H), 2.04 (s, 1H, -OH).

Compound 4: In a sealed tube 2.0 g of compound 3a (0.008 mol), 3.97 ml of 2-methylpyridine (0.04 mol), and 3.28 g of $ZnCl_2$ (0.024 mol) were taken and heated at 200˚C for 24h. The brown reaction mass was extracted using water/dichloromethane. The organic layer was dried by anhydrous Na_2SO_4, and concentrated to dryness on a rotary evaporator. The crude product was

purified by column chromatography using hexane and ethyl acetate as eluent to afford compound 4. Yield: 1.22 g (47%).

^{1}H NMR (δ in ppm) (500 MHz, $CDCl_3$): 10.99 (s, 1H), 8.61(m, 1H), 7.64-7.60 (m, 1H), 7.45-7.40(m, 5H), 7.34-7.09(m, 7H), 5.86(s, 1H); HRMS (ESI-TOF) m/z $[M + H]^+$ Calcd for $C_{22}H_{16}N_2O$: 325.1343. Found: 325.1320.

Compound 5: Starting from compound 3a 2.0 g (0.008 mol), 5.47 ml of quinaldine (0.04 mol) and 3.28 g (0.024 mol) of $ZnCl_2$ compound 5 was synthesized and purified by a procedure similar to that of compound 4. Yield: 1.56 g (52%).

^{1}H NMR (δ in ppm) (500 MHz, $CDCl_3$): 11.25(s, 1H), 8.16(d, 1H), 8.08 (d, 1H), 7.75 (t, 2H), 7.55-7.50(m,1H), 7.48-7.42(m, 5H), 7.36(m, 2H), 7.30-7.24(m,4H), 5.99(s,1H); HRMS (ESI-TOF) m/z $[M + H]^+$ Calcd for $C_{26}H_{18}N_2O$: 375.1499. Found: 375.1478.

Compound (BF1): To the solution of 0.5 g (0.0015 mol) of compound 4 in 25ml of DCM, 1.5 ml of N-ethyl-N,N-diisopropylamine and 3 ml of $BF_3.Et_2O$ was added. The mixture was stirred under nitrogen for 24 h at room temperature. The residue was purified by column chromatography using hexane and ethyl acetate as eluent to afford compound BF1. Yield: 0.24 g (42%); mp: >300˚C

^{1}HNMR (δ in ppm) (300 MHz, $CDCl_3$):8.75 (d, 1H), 7.99(m, 1H), 7.46(m,6H), 7.38(d, 1H), 7.34-7.29(m, 2H), 7.27(s, 2H), 7.24(d, 1H),5.85(s, 1H); ^{13}CNMR: (75 MHz, $CDCl_3$) δ 172.82, 150.09, 149.79, 142.87, 142.44, 142.16, 134.06, 131.19, 130.06, 130.06, 129.33, 129.33, 129.13, 129.13,129.08, 129.08, 128.86, 128.21, 128.21, 125.00, 122.03, 97.99; ^{11}B NMR: (160 MHz, $CDCl_3$) δ 1.62 (t, J = 27.6 Hz); HRMS (ESI-TOF) m/z $[M + H]^+$ Calcd for $C_{22}H_{15}BF_2N_2O$: 373.1326. Found: 373.1303. Anal. Calculated for $C_{22}H_{15}BF_2N_2O$: C, 71.00; H, 4.06; N, 7.53%. Found: C, 70.90; H, 3.59; N, 7.70%.

Compound BF21: Compound BF21 was synthesized according to the procedure described for compound BF1. The product was purified by column chromatography using hexane and ethyl acetate as eluent to afford compound BF21. Yield : 0.24 g (44%); mp: >300˚C

^{1}HNMR (δ in ppm) (300 MHz, $CDCl_3$): 9.03 (d, 1H), 8.29 (d, 1H), 7.92-7.81(m, 2H), 7.63(m, 1H), 7.54-7.20(m,10H), 5.92(s,1H); ^{13}CNMR: (75 MHz, $CDCl_3$) δ 172.81, 152.42, 151.36,142.42, 141.77, 141.04, 134.46, 133.19, 130.16, 130.16, 131.05, 129.96, 129.31, 129.31, 129.20, 129.12,129.12, 129.02, 128.73, 128.26, 128.26, 127.68, 127.54, 124.34, 122.81, 98.96; ^{11}B NMR: (160 MHz, $CDCl_3$) δ 2.78 (t, J = 27.4 Hz); HRMS (ESI-TOF) m/z $[M + H]^+$ Calcd for $C_{26}H_{17}BF_2N_2O$: 423.1482. Found: 423.1459. Found: 423.1459. Anal. Calculated for $C_{26}H_{17}BF_2N_2O$: C, 73.96; H, 4.06; N, 6.63%. Found: C, 73.62; H, 3.79; N, 6.64%.

Compound 6: It was synthesized from 2g (0.006 mol) of compound 3b, 3.31ml (0.033 mol) 2-methylpyridine and 2.73g (0.02mol) $ZnCl_2$ according to procedure described for the synthesis of compound 4. The product was purified by column chromatography using hexane and ethyl acetate as eluent to afford compound 6. Two isomers formed were directly used for further reaction. Yield: 1.42g (57%).

HRMS (ESI-TOF) m/z $[M + H]^+$ Calcd for $C_{26}H_{18}N_2O$: 375.1492. Found: 375.1485.

Compound BF3 (I) & (II): To the solution of 1.0 g (0.02 mol) of compound 6 in 50 ml of DCM, 3 ml of N-ethyl-N,N-diisopropylamine and 6 ml of $BF_3.Et_2O$ was added. The mixture was stirred under nitrogen for 24 h at room temperature. The residue was purified by column chromatography using hexane and ethyl acetate as eluent to afford two isomer BF3(I) and BF3(II).

Compound BF3(I) Yield: 0.39g (35%); mp: >300˚C.

^{1}HNMR (δ in ppm) (300 MHz, $CDCl_3$): 8.75 (d, 1H), 8.00-7.87 (m, 3H), 7.73 (d, 1H), 7.59-7.38 (m, 7H), 7.21-7.08 (m, 4H), 5.50 (s, 1H); ^{13}CNMR: (75 MHz, $CDCl_3$) δ 172.89, 150.36, 150.11, 142.91, 142.06, 141.03, 135.46, 133.73, 131.38, 130.23, 129.56, 129.50, 129.50, 129.12, 128.98, 128.59, 128.17, 128.17, 127.68, 127.01, 126.61, 125.56, 125.56, 124.90, 121.95, 97.91; ^{11}B NMR: (160 MHz, $CDCl_3$) δ 1.66 (t, J = 24.6 Hz); HRMS (ESI-TOF) m/z $[M + H]^+$ Calcd for $C_{26}H_{17}BF_2N_2O$: 423.1482. Found: 423.1459. Anal. Calculated for $C_{26}H_{17}BF_2N_2O$: C, 73.96; H, 4.06; N, 6.63%. Found: C, 73.77; H, 3.85; N, 6.52%.

Compound BF3(II) Yield: 0.31 g (28%); mp: >300˚C.

^{1}HNMR (δ in ppm) (300 MHz, $CDCl_3$): 8.80 (d, 1H), 8.06-8.00(m, 1H), 7.86-7.65(m, 4H), 7.51-7.28(m, 7H), 7.22-7.14(m, 3H), 6.08 (s, 1H); HRMS (ESI-TOF) m/z $[M + H]^+$ Calcd for $C_{26}H_{17}BF_2N_2O$: 423.1482. Found: 423.1466. Anal. Calculated for $C_{26}H_{17}BF_2N_2O$: C, 73.96; H, 4.06; N, 6.63%. Found: C, 73.56; H, 3.74; N, 6.47%.

7. Fluorescence lifetime decay curves.

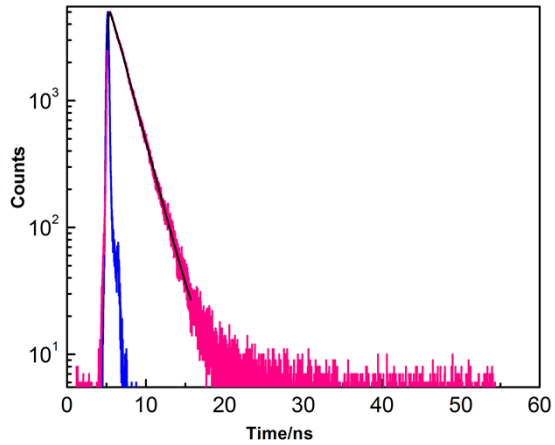


Fig S6: The fluorescence decay of Compound BF1 in DCM excited at 406 nm and measured by Single photon counting method whose emission at 478 nm.

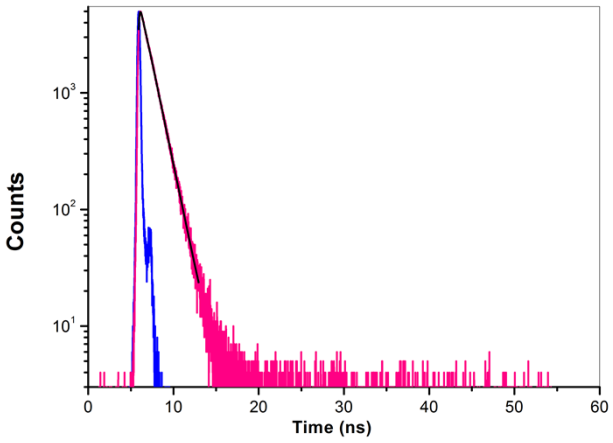


Fig S7: The fluorescence decay of Compound BF21 in DCM excited at 440 nm and measured by Single photon counting method whose emission at 479 nm.

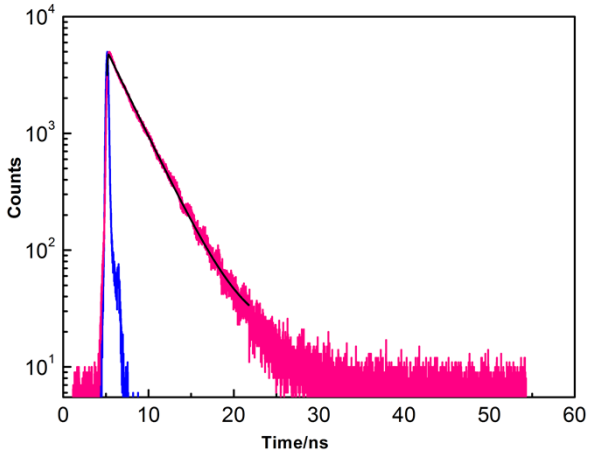


Fig S8: The fluorescence decay of Compound BF3(I) in DCM excited at 406 nm and measured by Single photon counting method whose emission at 533 nm.

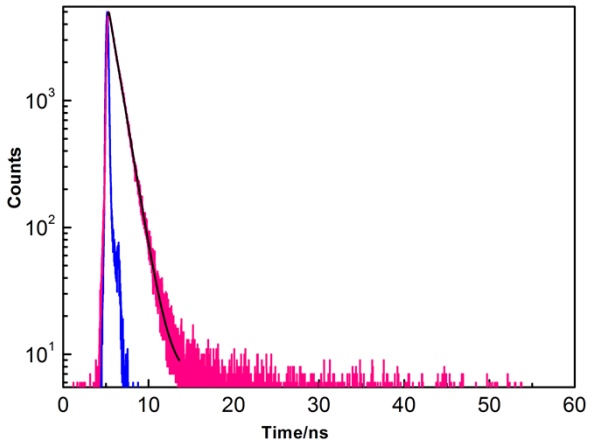


Fig S9: The fluorescence decay of Compound BF3(II) in DCM excited at 406 nm and measured by Single photon counting method whose emission at 535 nm.

8. The UV-vis and flourescence spectra of BF compounds.

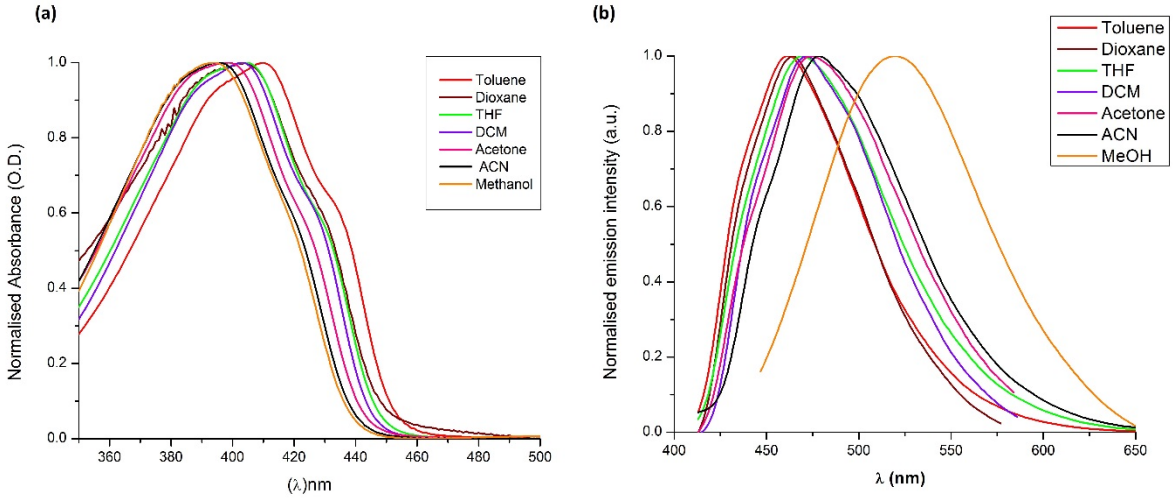


Fig S10 Normalised absorbance (a) and emission (b) graph of BF1

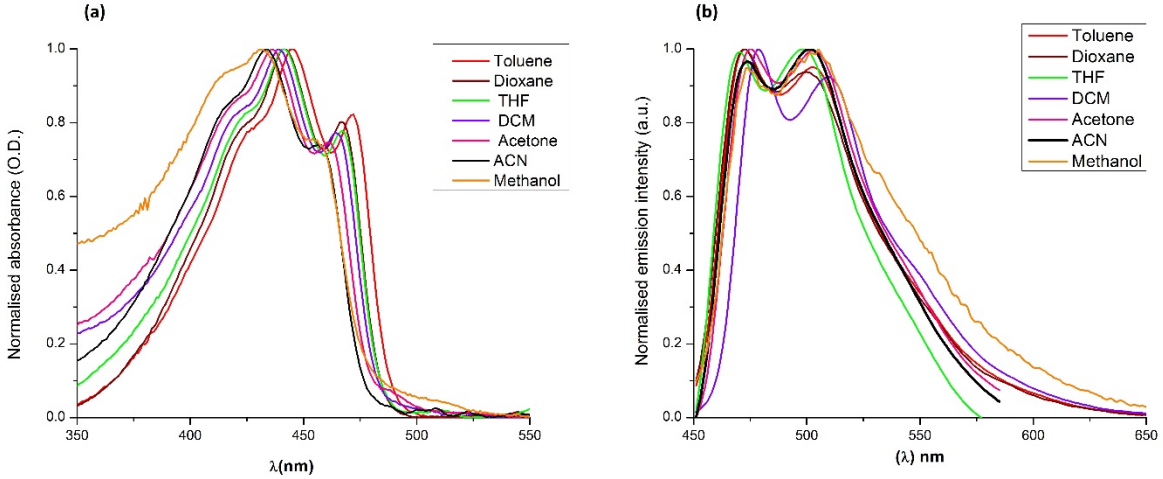


Fig S11: Normalised absorbance (a) and emission (b) graph of BF21

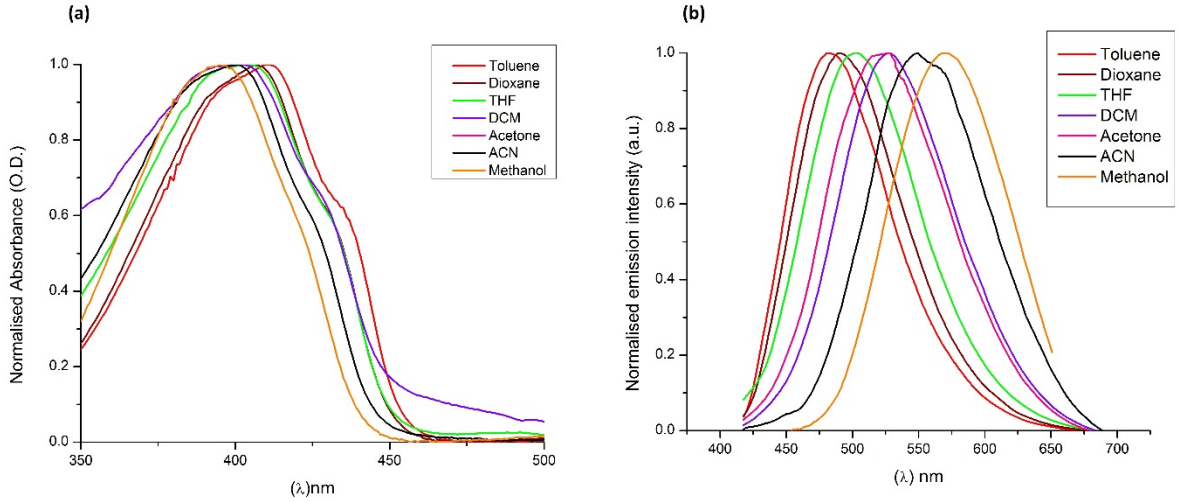


Fig S12: Normalised absorbance (a) and emission (b) graph of BF3(I)

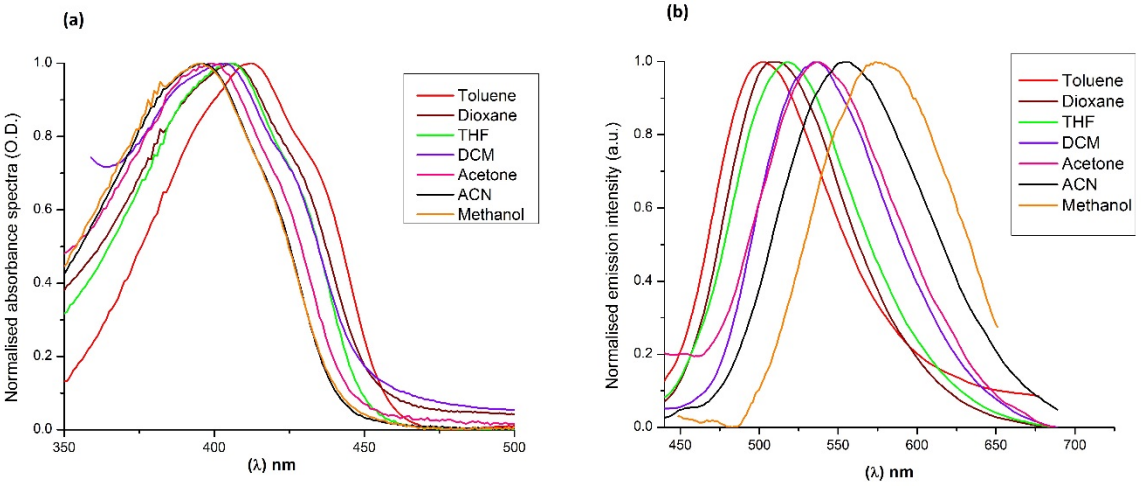


Fig S13: Normalised absorbance (a) and emission (b) graph of BF3(II)

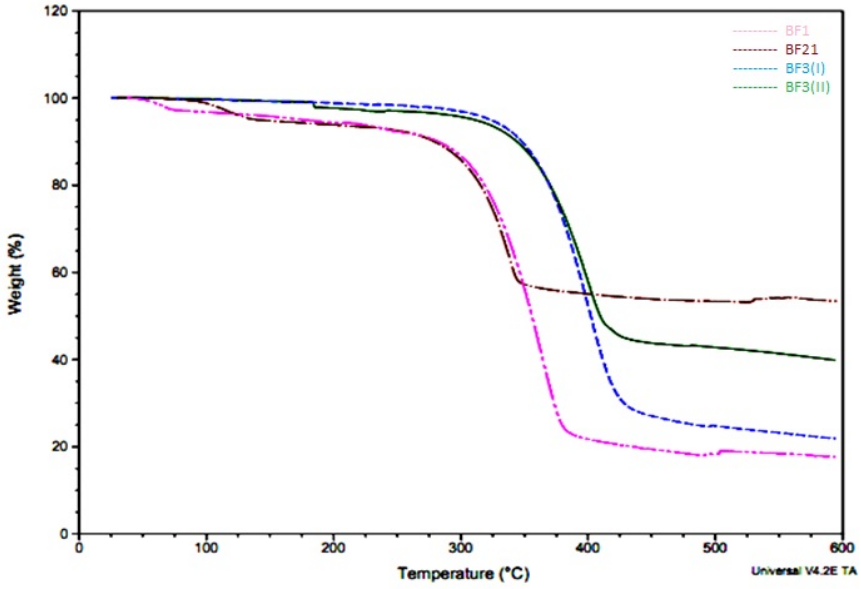
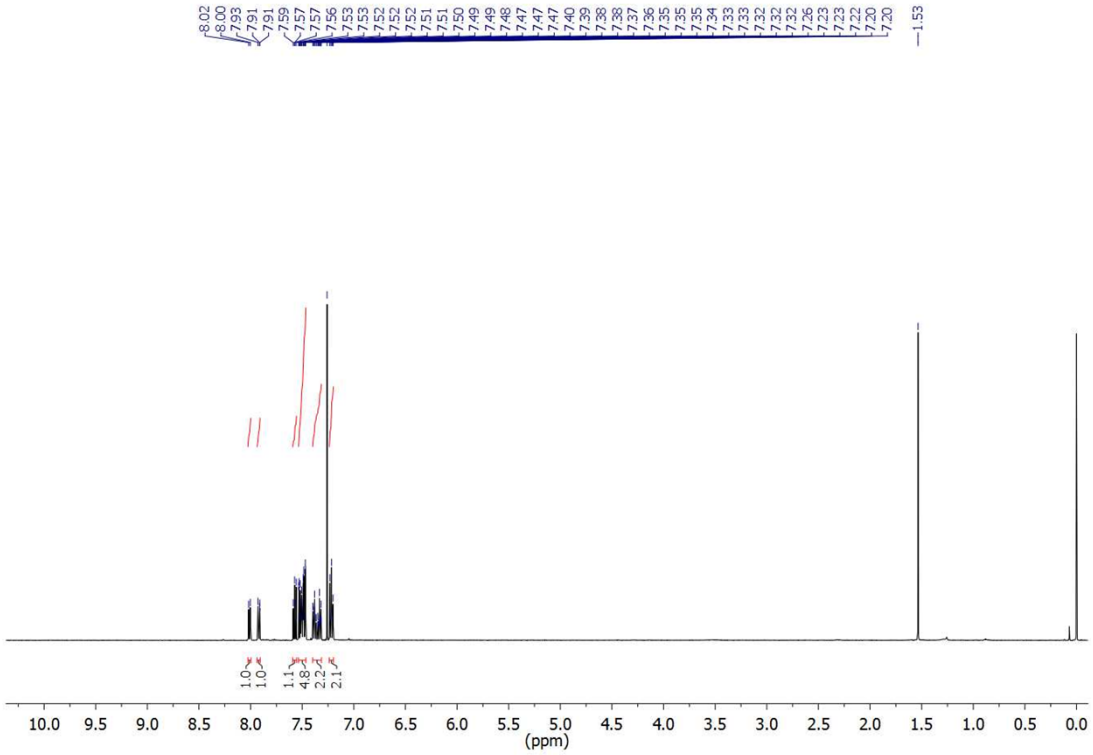


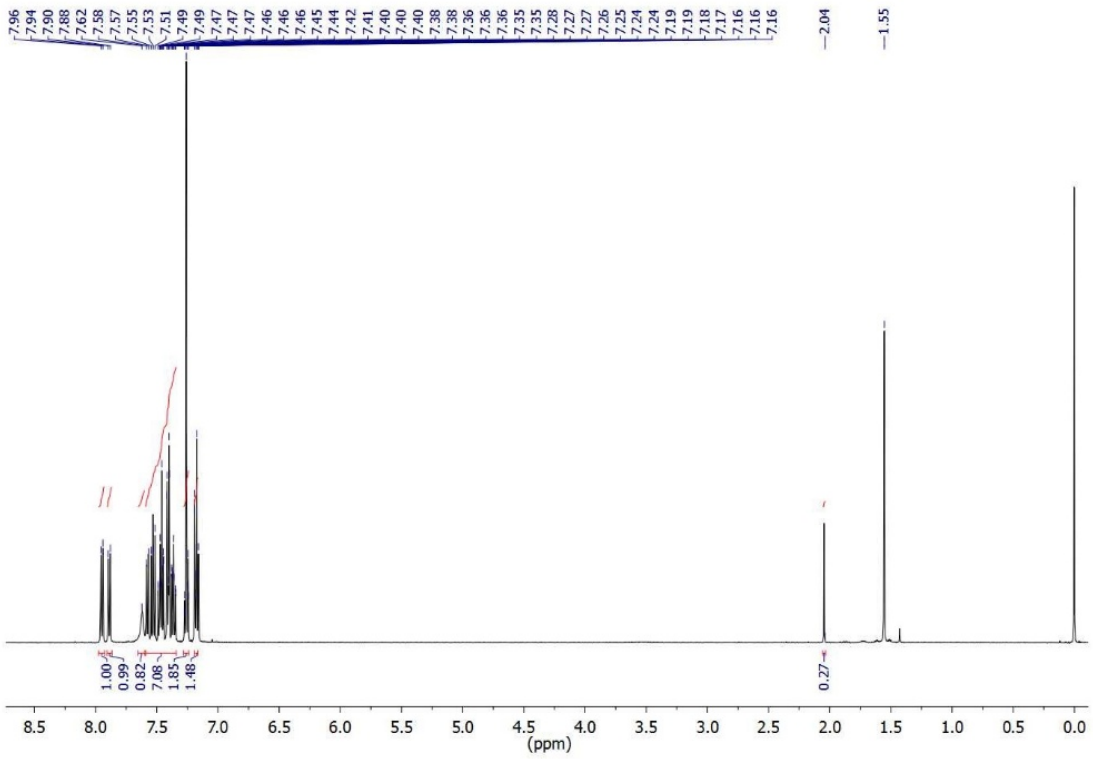
Fig S14: TGA graph of BF Compounds.

9. ^{1}H NMR of BF compounds.

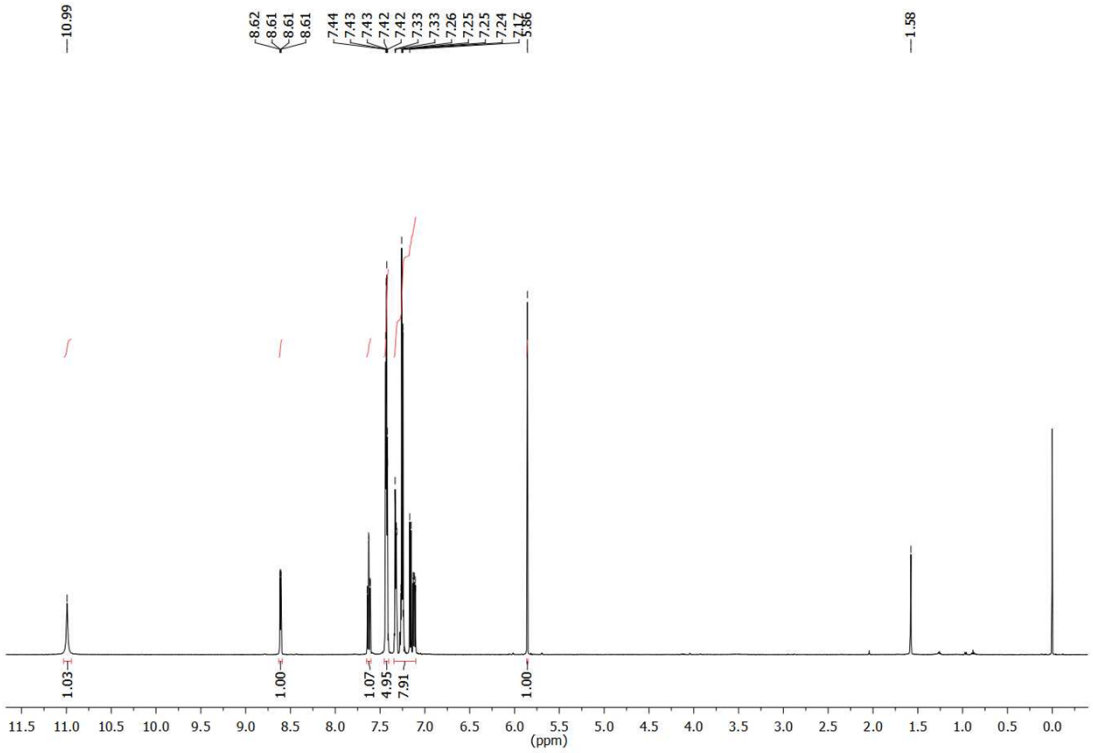
^{1}H NMR of compound 2b: 3-(napthalen-1-yl)-4-phenylfuran-2,5-dione



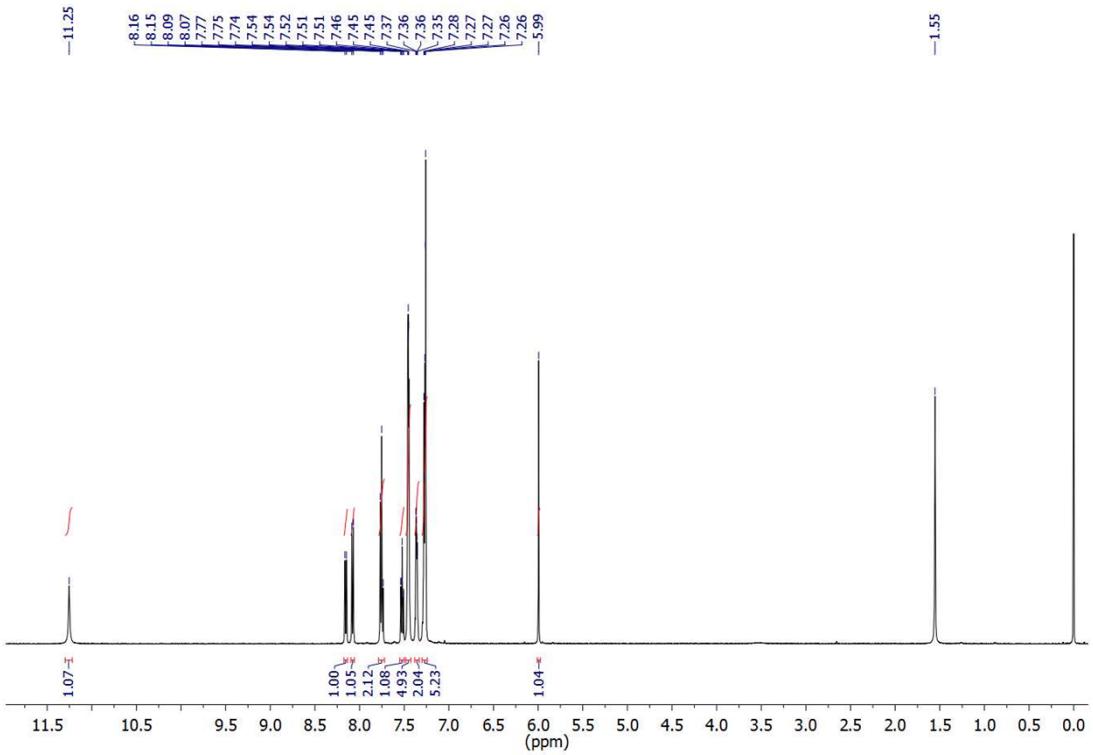
^{1}H NMR of compound 3b: 3-(napthalen-1-yl)-4-phenyl-1H-pyrrole-2,5-dione



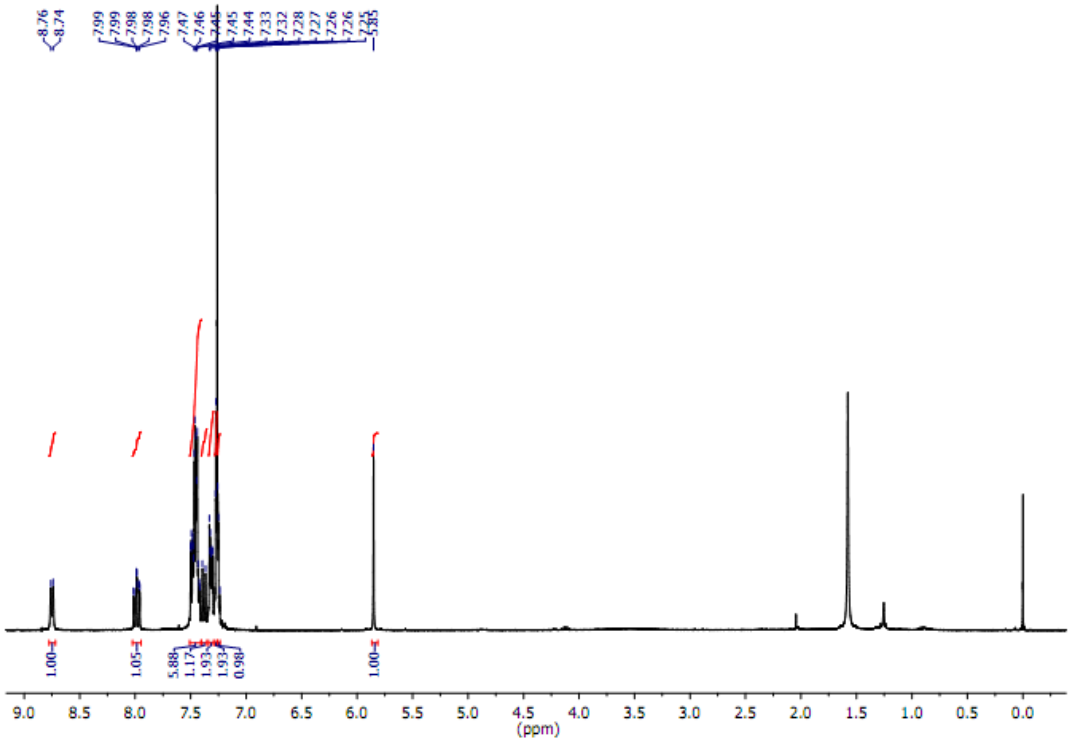
^{1}H NMR of compound 4 : (Z)-3,4-diphenyl-5-(pyridin-2-ylmethylene)-1H-pyrrol-2(5H)-one



^{1}H NMR of compound 5 : (Z)-3,4-diphenyl-5-(quinolin-2-ylmethylene)-1H-pyrrol-2(5H)-one

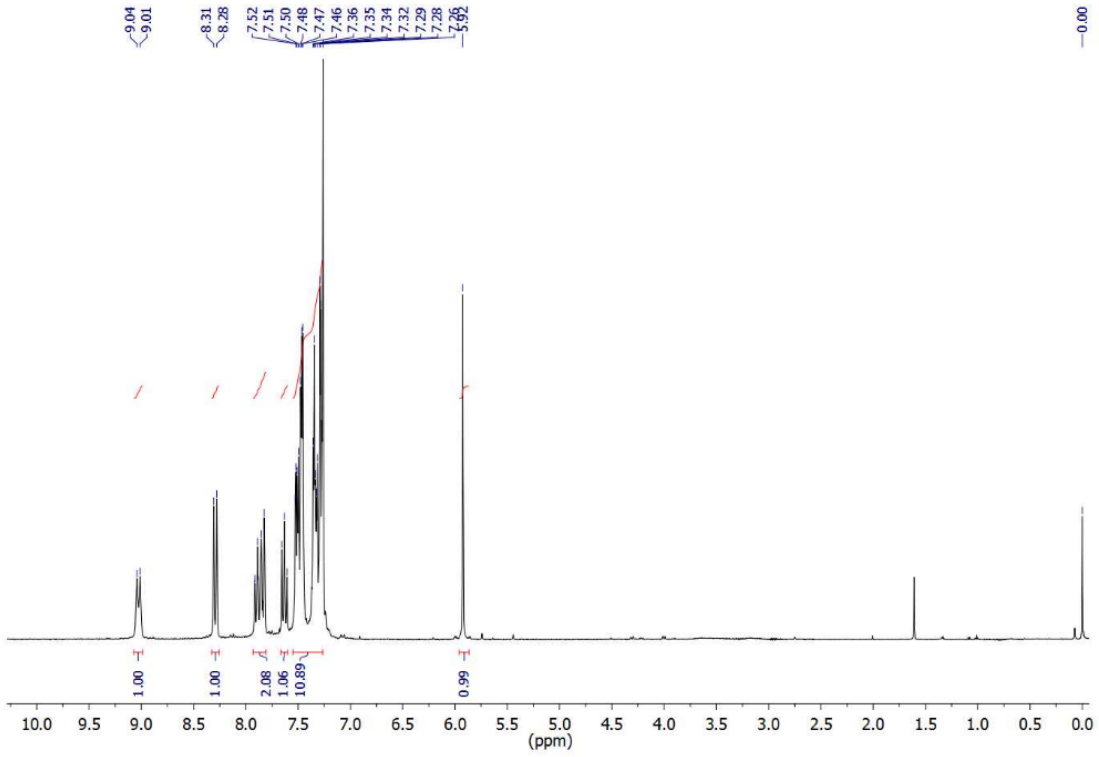


^{1}H NMR of compound BF1 : 5,5-diflouro-3-oxo-1,2-diphenyl-3,5-dihydropyrido[1,2-c]pyrrolo[2,1-f][1,3,2]diazaborinin-6-ium-5-uide

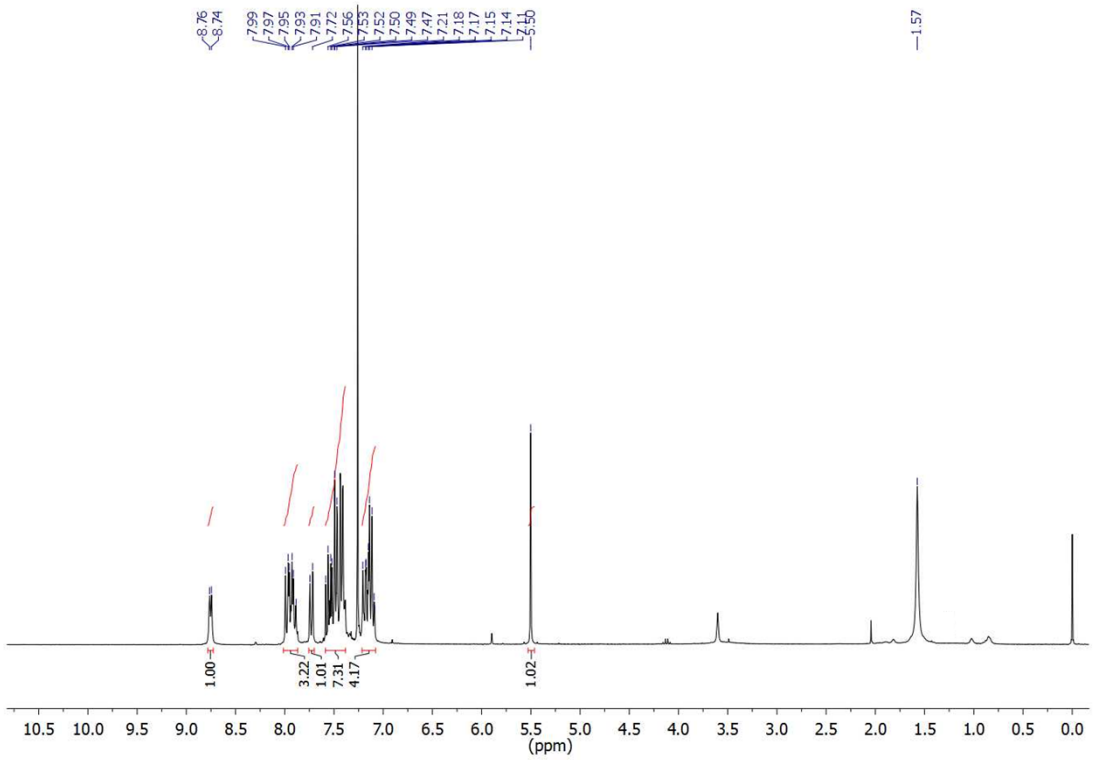


^{1}H NMR of compound BF21:

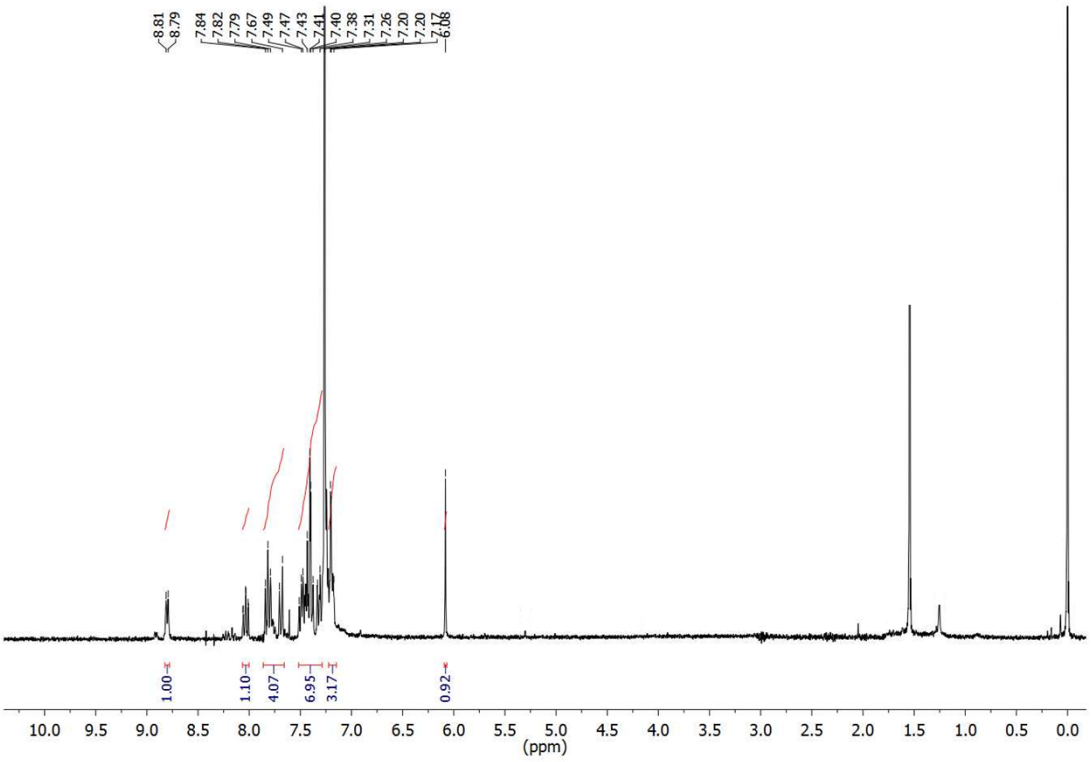
12,12-difluoro-10-oxo-8,9-diphenyl-10,12-dihydropyrrolo[1',2':3,4][1,3,2]diazaborinino[1,6-a]quinolin-13-ium-12-uide



^{1}H NMR of compound BF3(I): 5,5-diflouro-1-(napthalen-1-yl)-3-oxo-2-phenyl-3,5-dihydropyrido[1,2-c]pyrrolo[2,1-f][1,3,2]diazaborinin-6-ium-5-uide

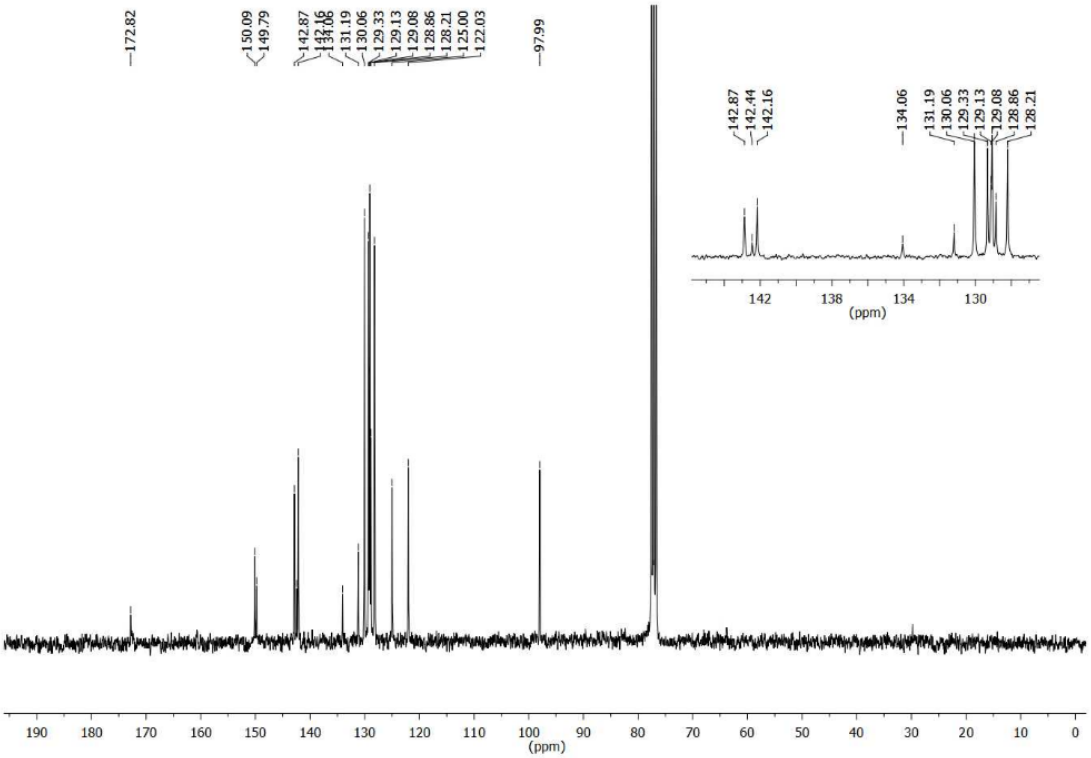


^{1}H NMR of compound BF3(II): 12,12-diflouro-9-(napthalen-1-yl)-10-oxo-phenyl-10,12-dihydropyrrolo[1',2':3,4][1,3,2]diazaborinino[1,6-a]quinolin-13-ium-12-uide

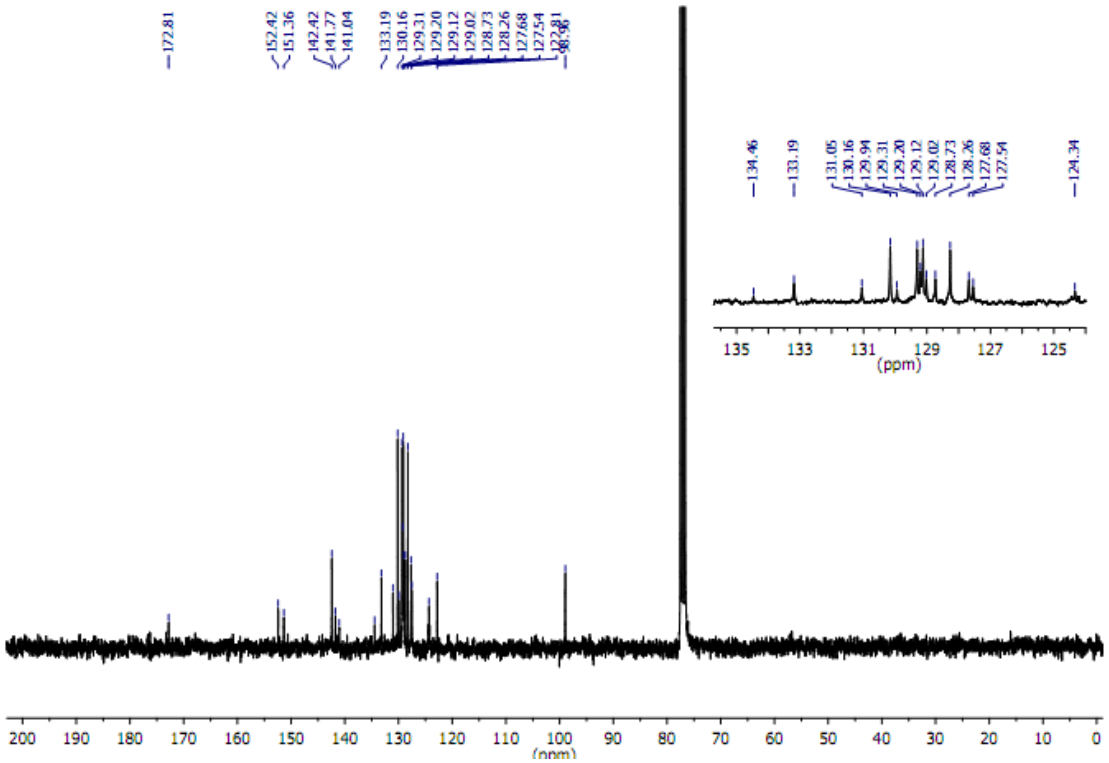


10. ^{13}C NMR of BF compounds.

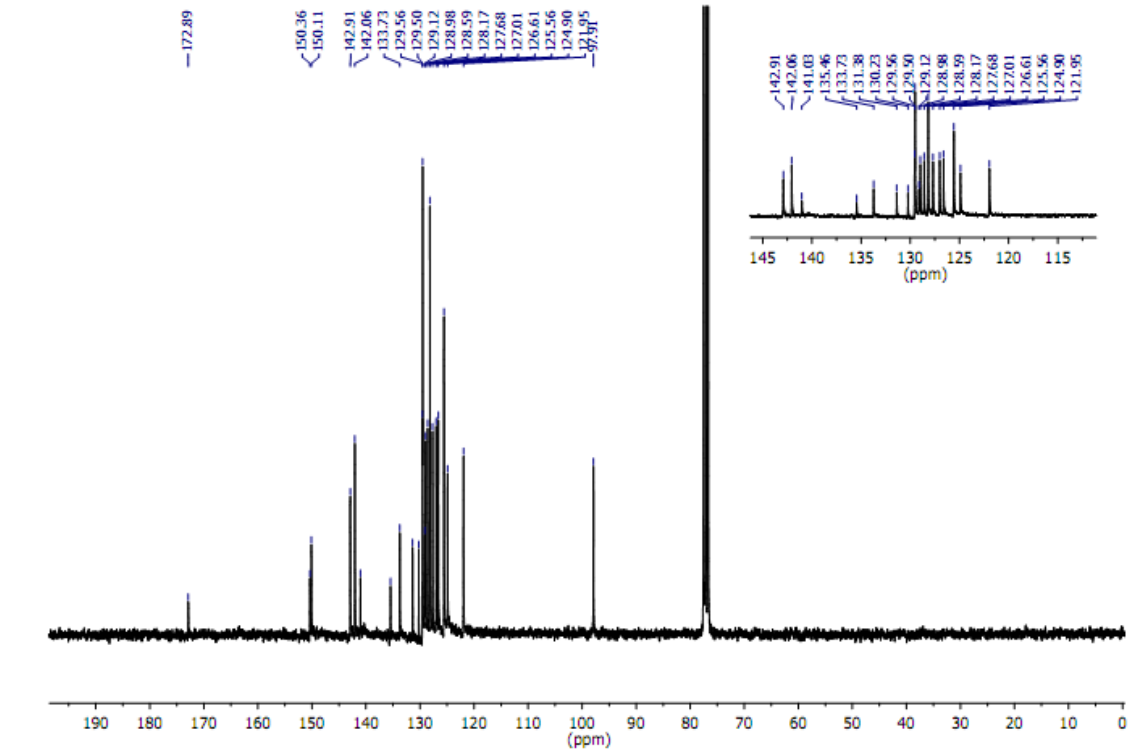
^{13}C of Compound BF1:



^{13}C of Compound BF21:

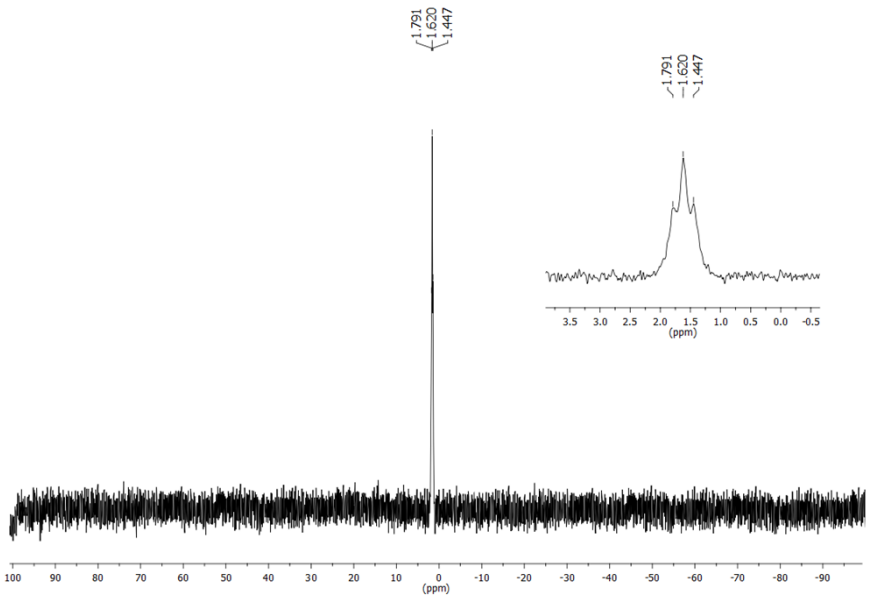


^{13}C Compound BF3(I):

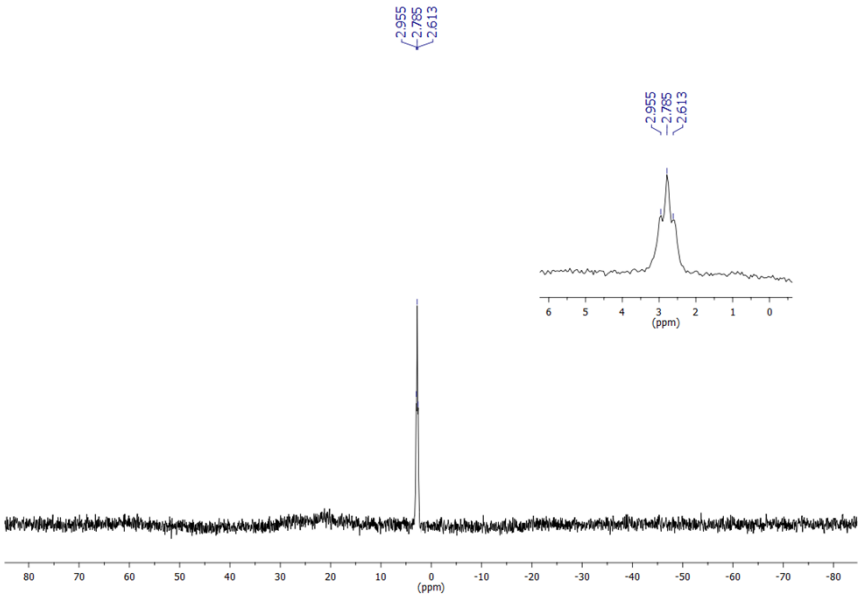


11. ^{11}B of spectra BF compounds.

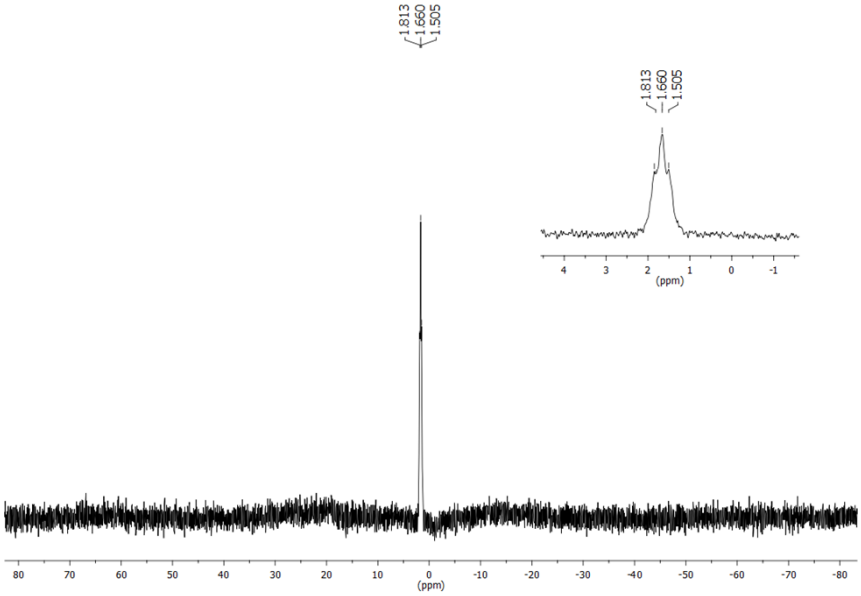
^{11}B compound BF1:



^{11}B compound BF21:

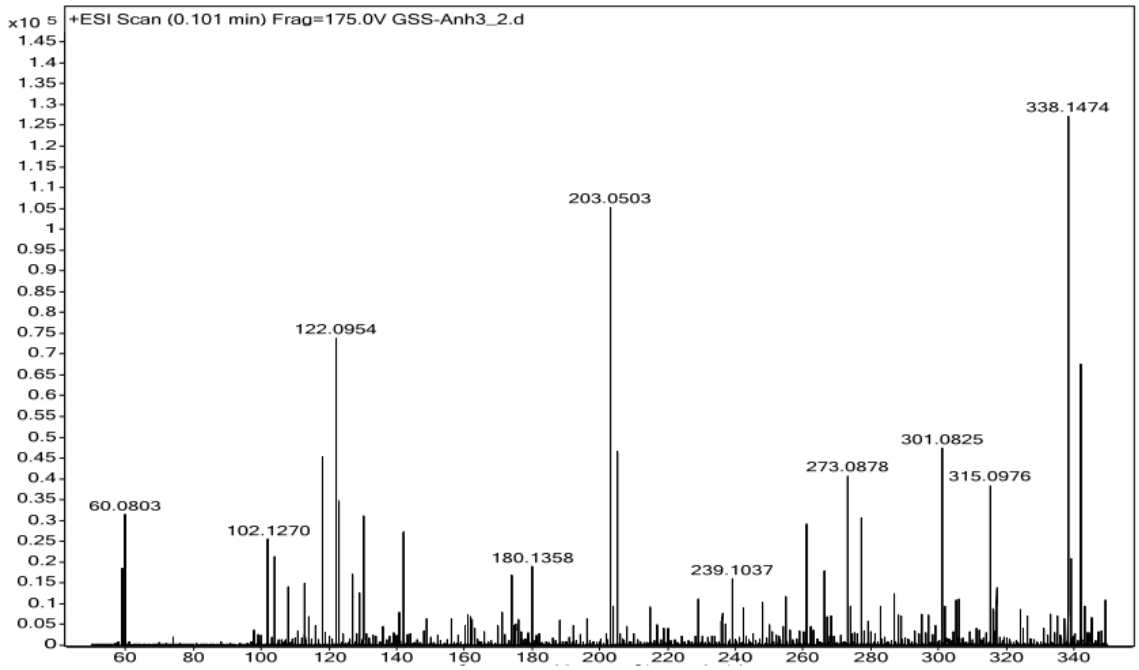


^{11}B compound BF3(I):

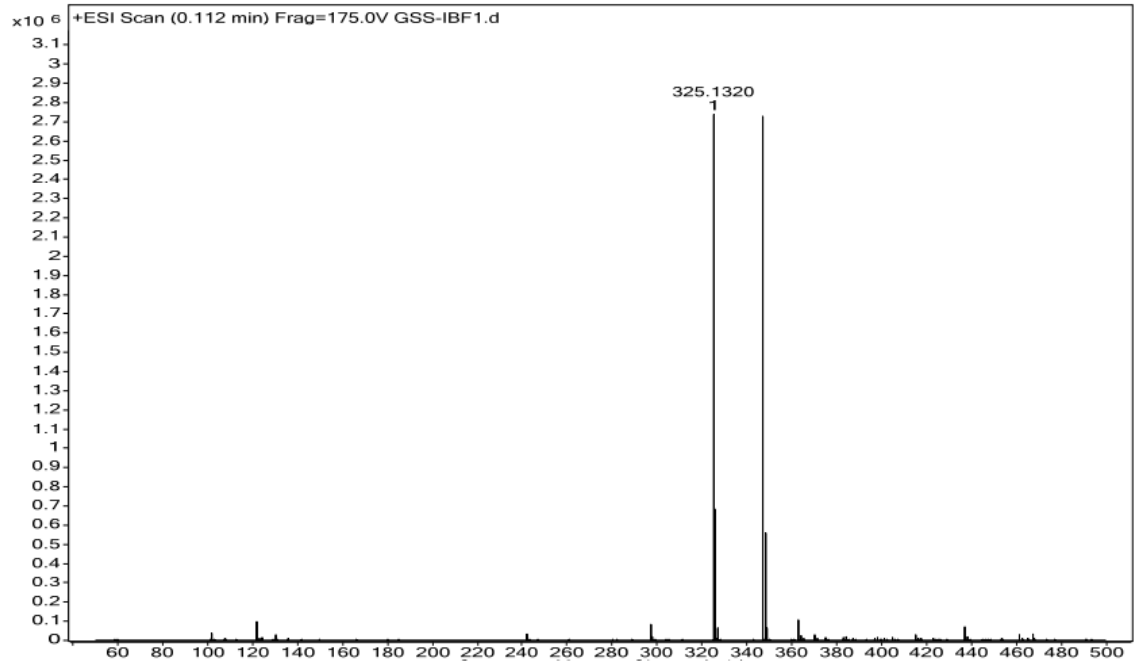


12. HR-MS of BF compounds.

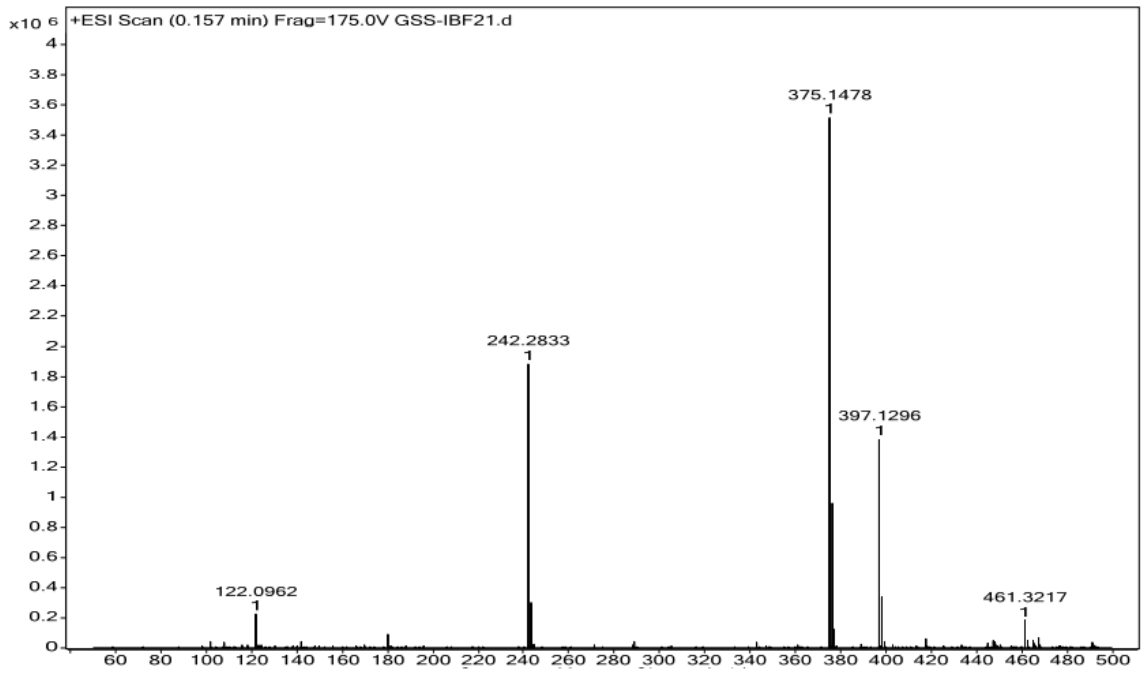
HR-MS of Compound 2b:



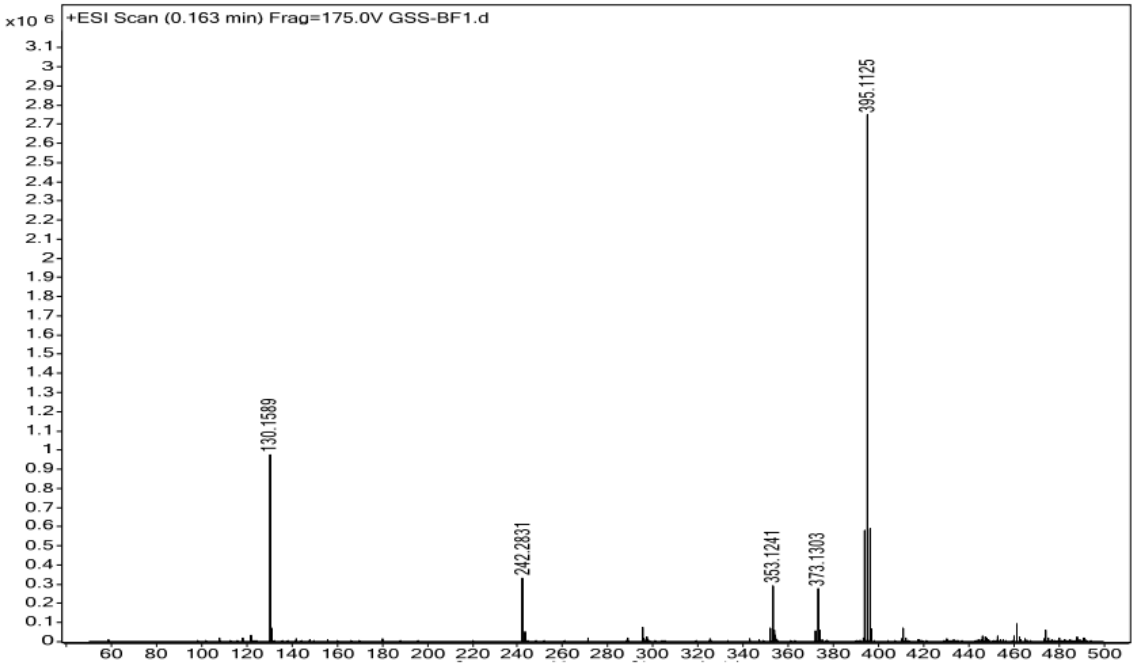
HR-MS of compound 4:



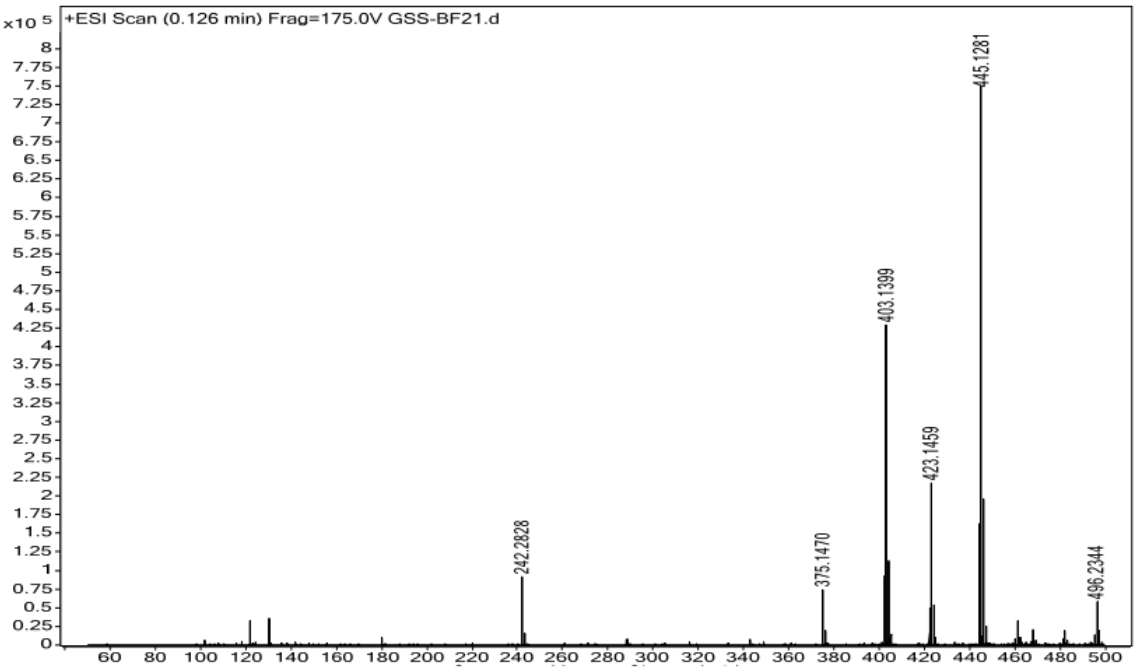
HR-MS of compound 5:



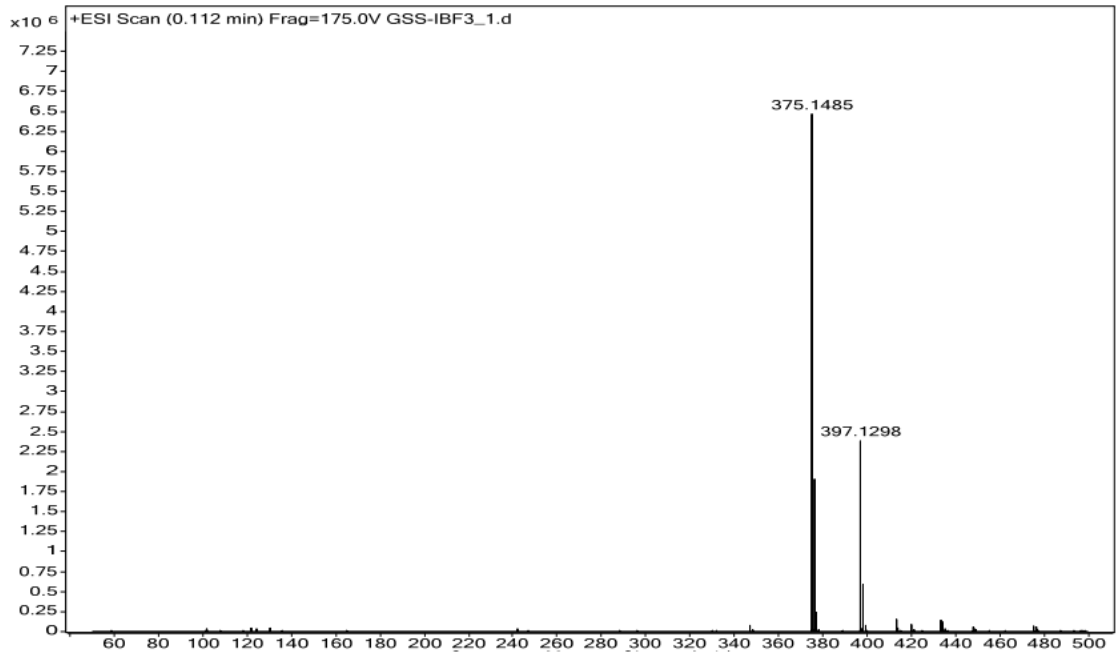
HR-MS of compound BF1:



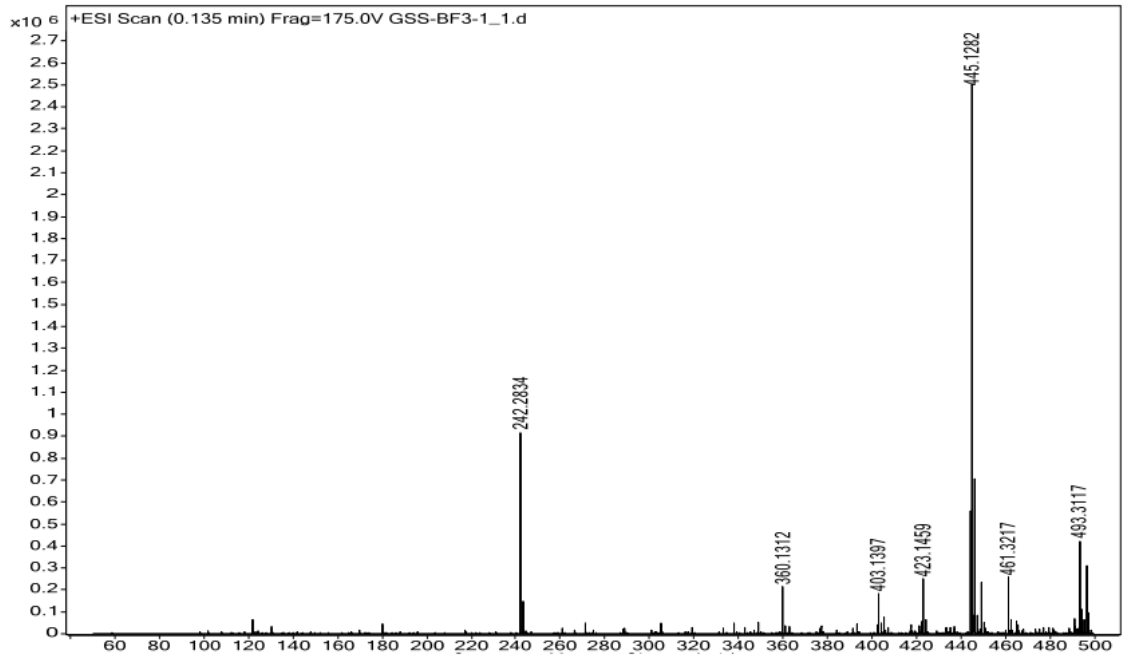
HR-MS of compound BF21:



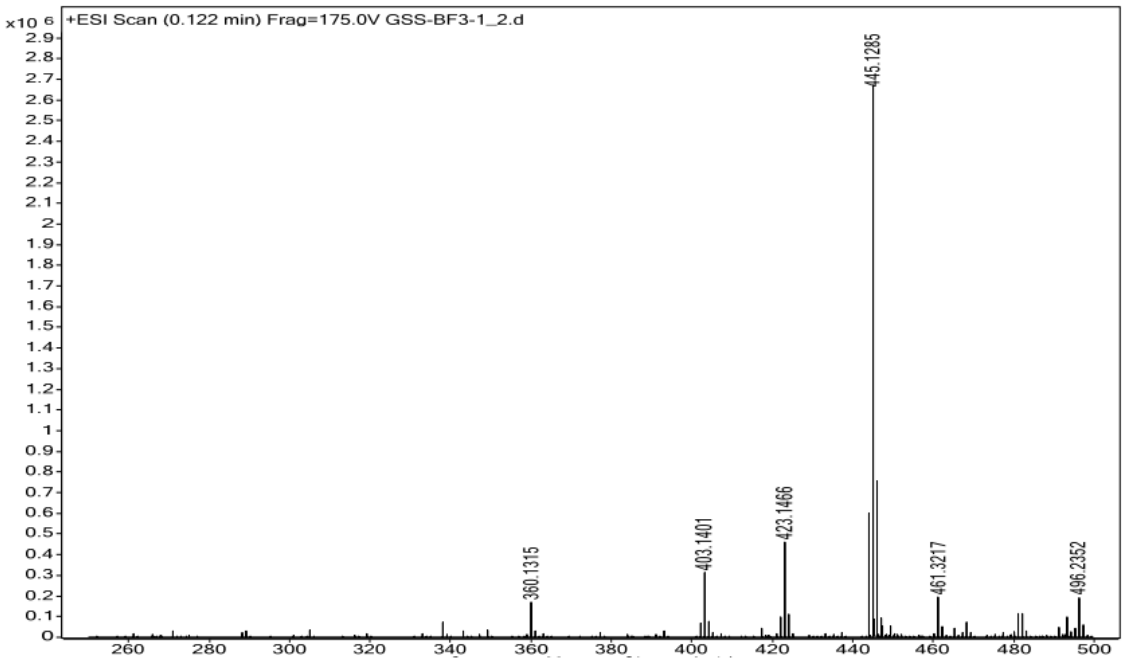
HR-MS of compound 6:



HR-MS of compound BF3(I):

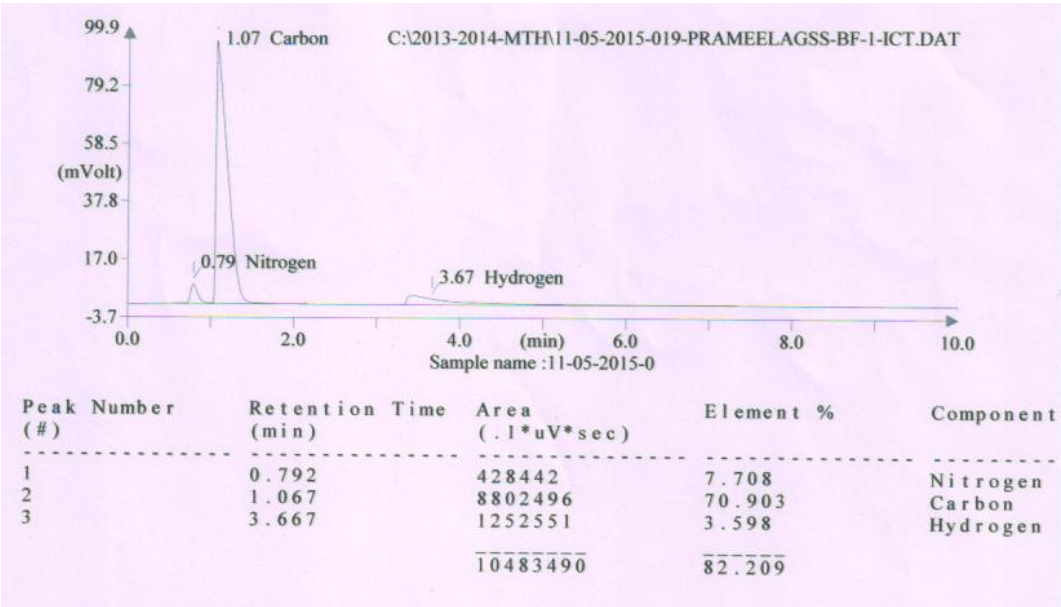


HR-MS of compound BF3(II):



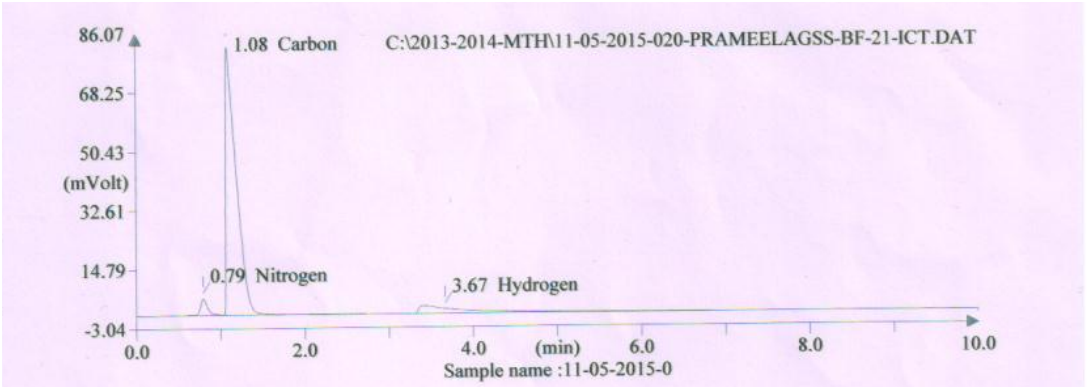
13. CHN analysis data of BF compounds.

BF1



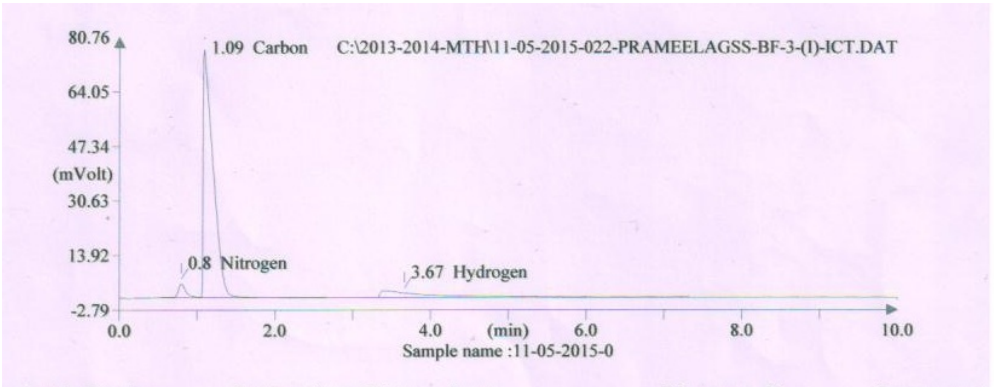
Peak Number (#)	Retention Time (min)	Area (.1*uV*sec)	Element %	Component
1	0.792	428442	7.708	Nitrogen
2	1.067	8802496	70.903	Carbon
3	3.667	1252551	3.598	Hydrogen
		10483490	82.209	

BF21



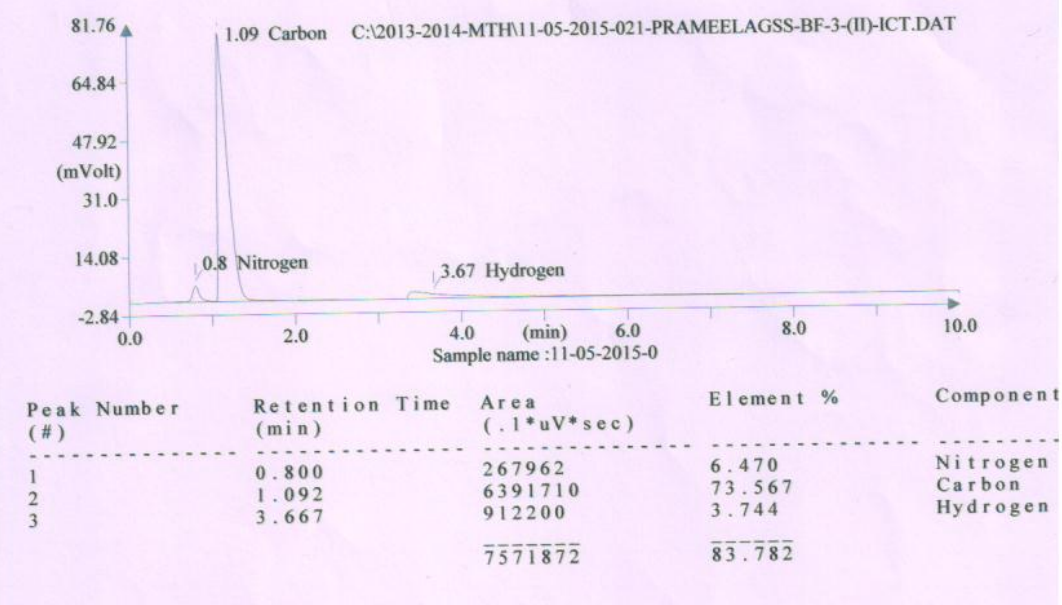
Peak Number (#)	Retention Time (min)	Area (.1*uV*sec)	Element %	Component
1	0.792	289783	6.647	Nitrogen
2	1.083	6821375	73.628	Carbon
3	3.667	986304	3.797	Hydrogen
		8097462	84.072	

BF3(I)



Peak Number (#)	Retention Time (min)	Area (.1*uV*sec)	Element %	Component
1	0.800	275179	6.528	Nitrogen
2	1.092	6553249	73.771	Carbon
3	3.667	960881	3.857	Hydrogen
		7789308	84.156	

BF3(II)



Peak Number (#)	Retention Time (min)	Area (.1*uV*sec)	Element %	Component
1	0.800	267962	6.470	Nitrogen
2	1.092	6391710	73.567	Carbon
3	3.667	912200	3.744	Hydrogen
		7571872	83.782	

References:

(1) N. V.Marinova, N. I. Georgiev, V. B. Bojinov, *J. Photochem. Photobiol. A Chem.*, 2011, **222**, 132-140.

(2) H. Shaki, K. Gharanjig, S. Rouhani, a. Khosravi, *J. Photochem. Photobiol. A Chem.*, 2010, **216**, 44– 50.

(3) V. B. Bojinov, N. I. Georgiev, and P. S. Nikolov, *J. Photochem. Photobiol. A Chem.*, 2008, **197**, 281–289.

(4) Hassner, A.; Isbister, R. J. *J. Am. Chem. Soc.* 1969, **52**, 6126-6128.

(5) Smith, P. A. S.; Krbechek, L. O.; Resemann, W. *J. Am. Chem. Soc.* 1964, **86**, 2025-2033.