Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information

Synthesis, Spectral, XRD and Theoretical studies on 3-ethyl-5-methyl-2,6-diarylpiperidin-4-on-1-ium picrates

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Contents

1. **Fig S1.** FT-IR spectrum of compound **1**
2. **Fig S2.** FT-IR spectrum of compound **2**
3. **Fig S3.** FT-IR spectrum of compound **3**
4. **Fig S4.** ^{1}H NMR spectrum of compound **1**
5. **Fig S5.** ^{1}H NMR spectrum of compound **2**
6. **Fig S6.** ^{1}H NMR spectrum of compound **3**
7. **Fig S7.** ^{13}C NMR spectrum of compound **1**
8. **Fig S8.** ^{13}C NMR spectrum of compound **2**
9. **Fig S9.** ^{13}C NMR spectrum of compound **3**
10. **Table S1.** Crystal data and structure refinement details.
11. **Table S2.** Bond lengths (Å) and bond angles (º) for non-H atoms with esd's in parenthesis
12. **Table S3.** Contributions of interacting atoms in crystal **1**.
13. **Table S4.** Optimized parameter of compounds **1-3**.
14. **Table S5.** Observed and computed wavenumber of compounds **1-3.**
15. **Table S6.** Second order perturbation theory analysis of Fock matrix in NBO basis.

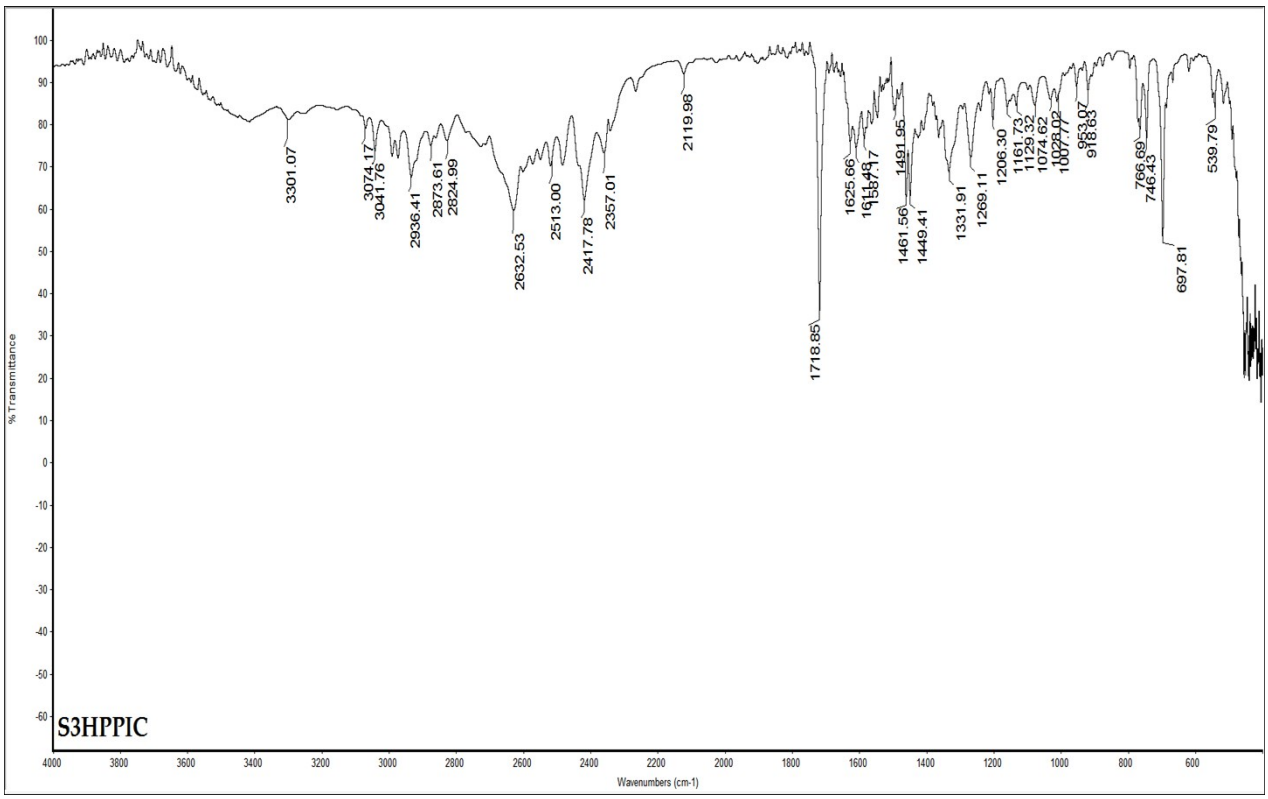

Fig S1. FT-IR spectrum of compound **1**

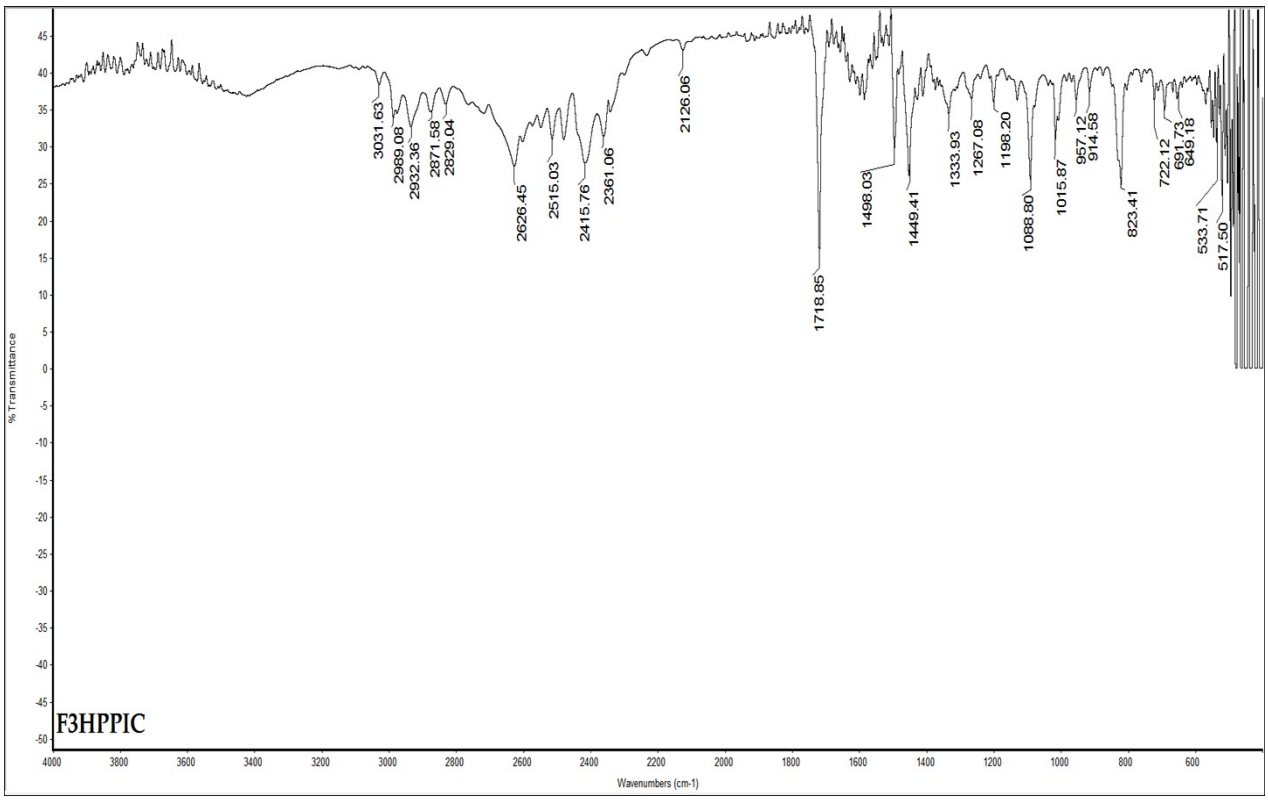

Fig S2. FT-IR spectrum of compound **2**

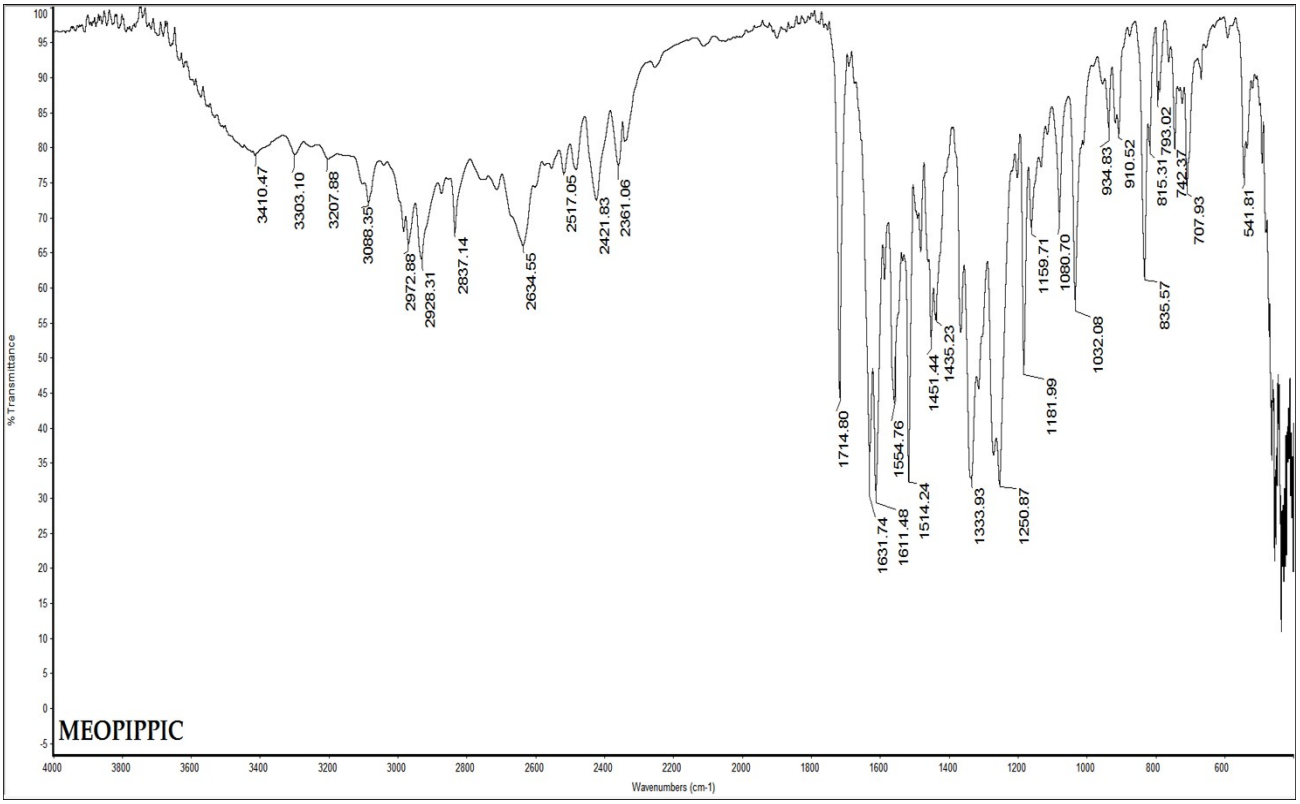

Fig S3. FT-IR spectrum of compound **3**

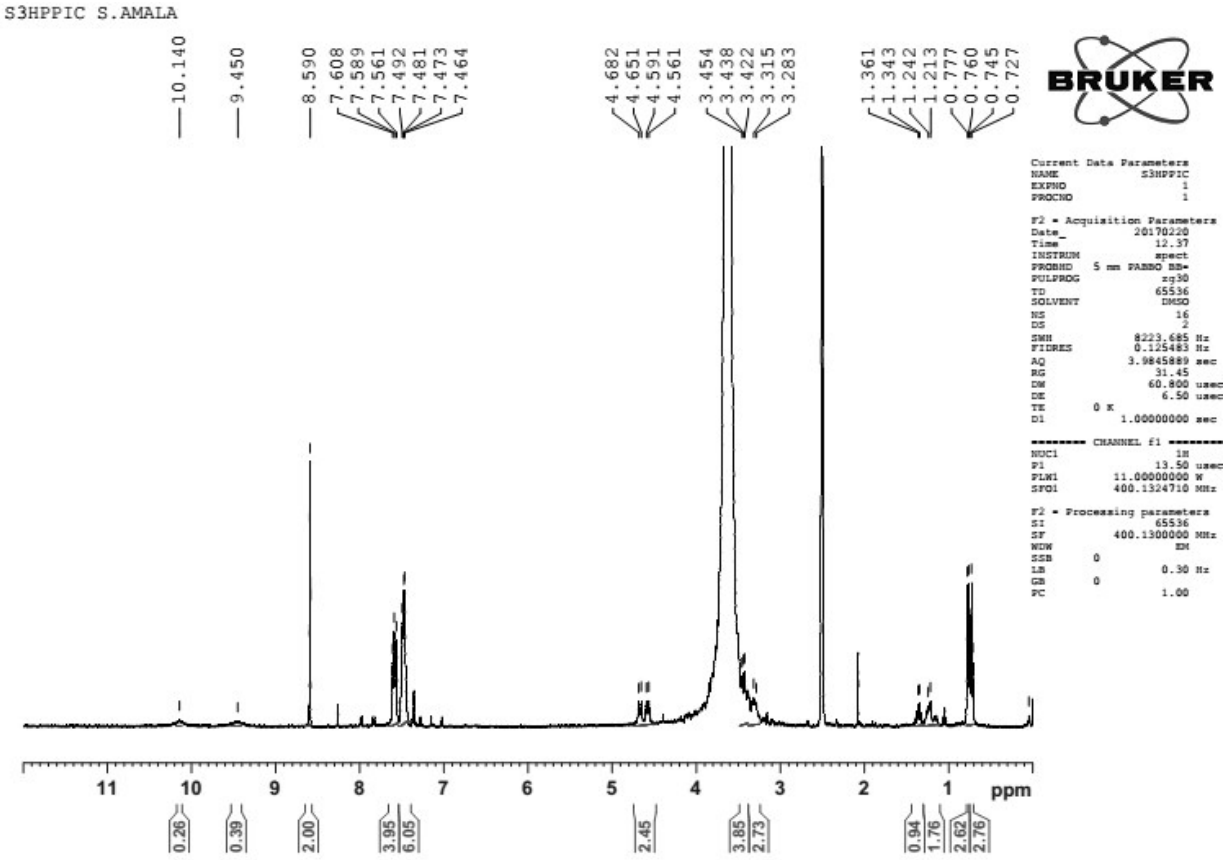

Fig S4. ^{1}H NMR spectrum of compound **1**

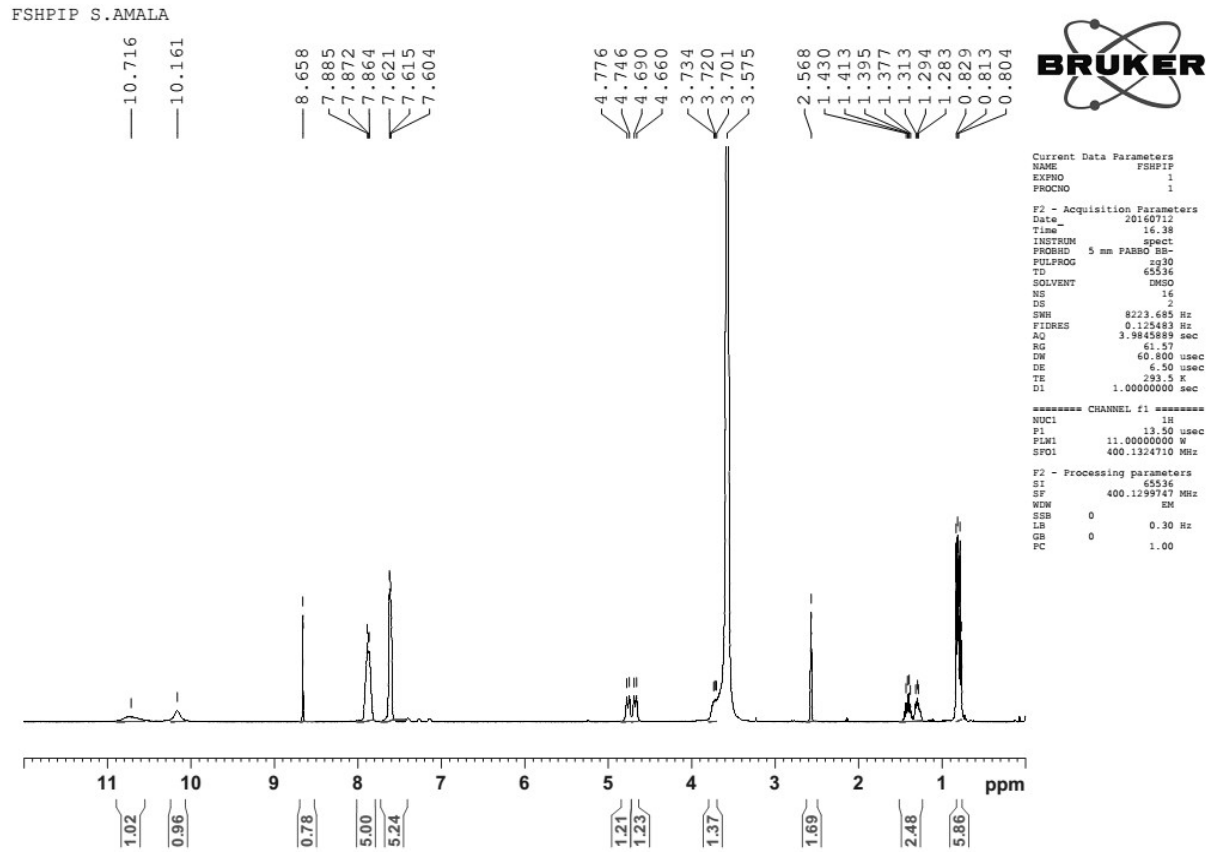

Fig S5. [1]H NMR spectrum of compound **2**

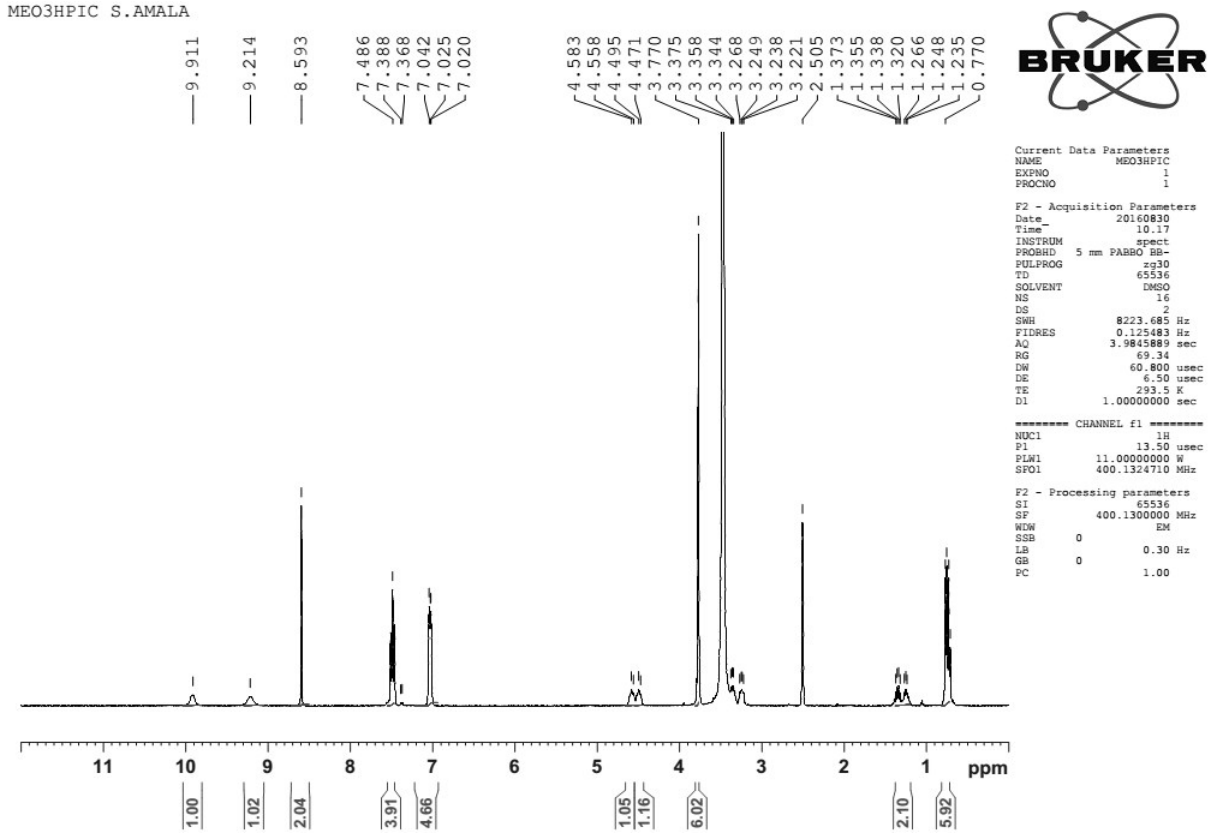

Fig S6. [1]H NMR spectrum of compound **3**

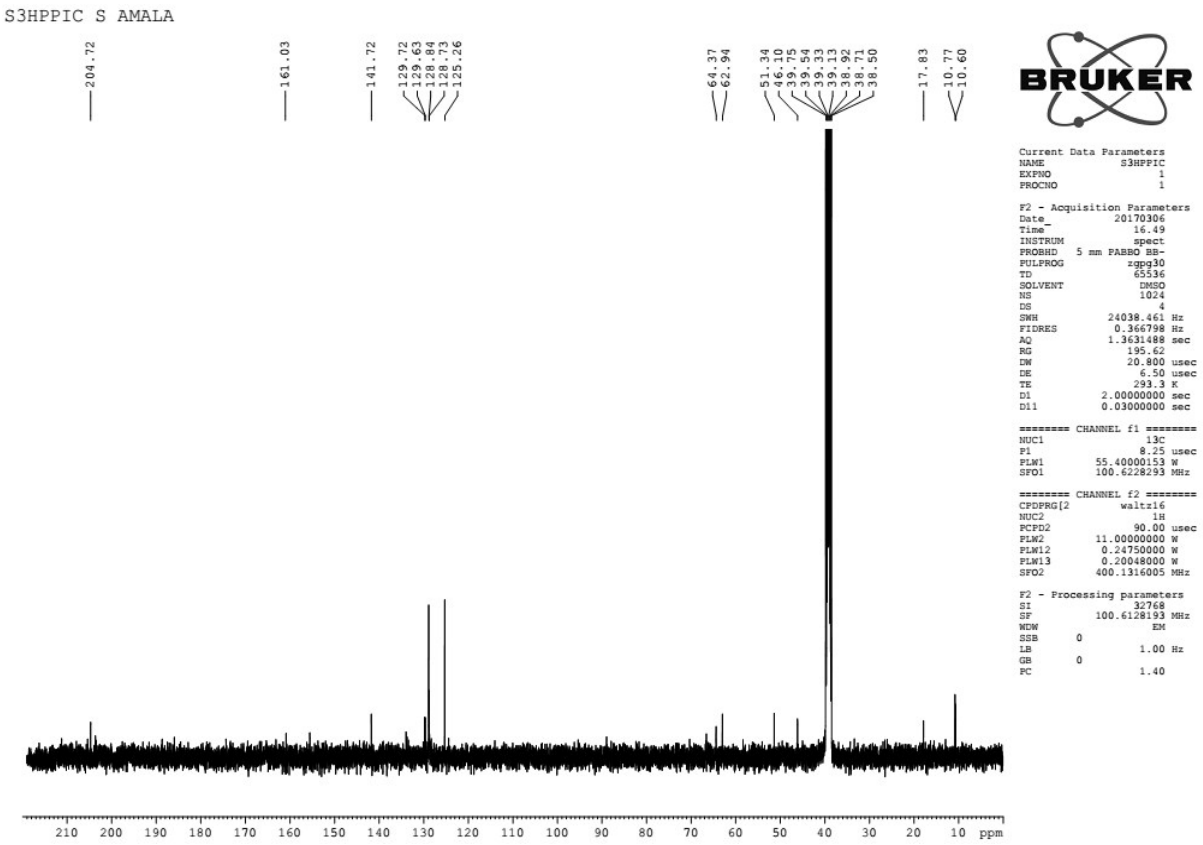

Fig S7. ^{13}C NMR spectrum of compound **1**

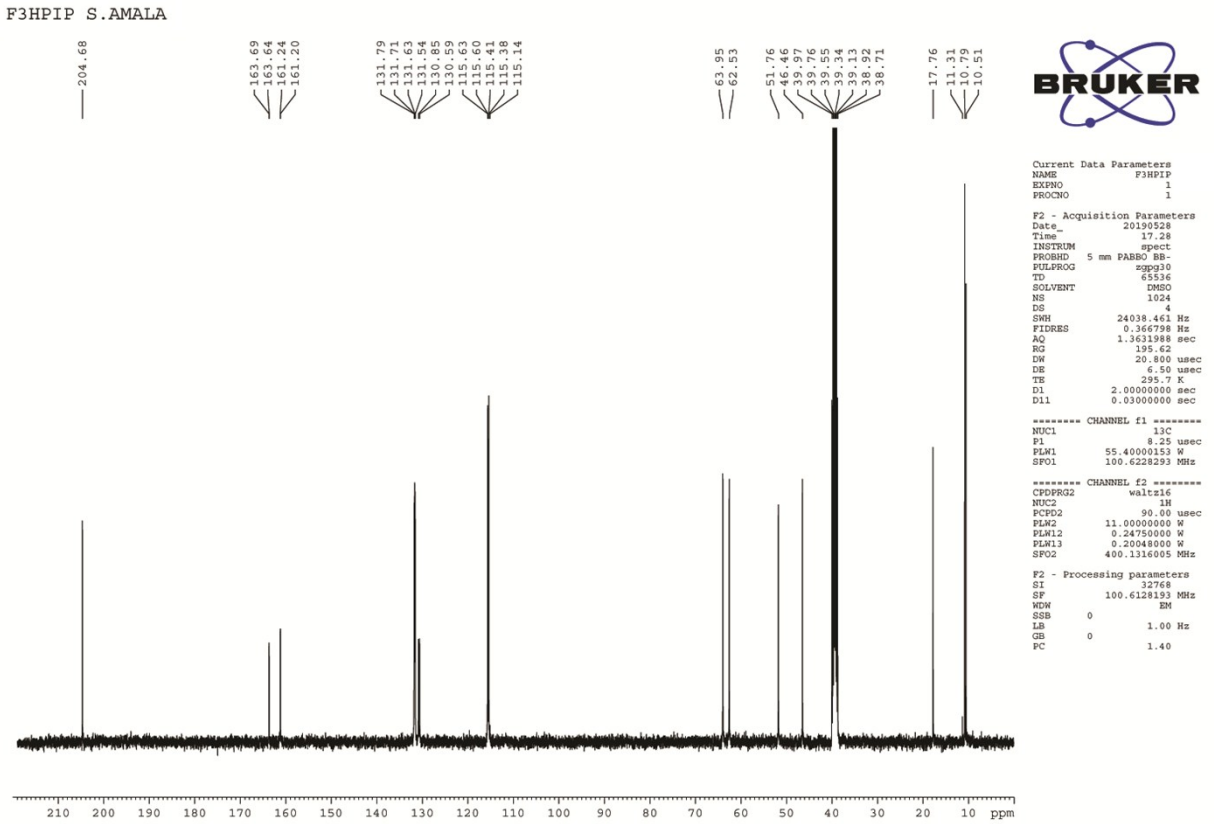

Fig S8. ^{13}C NMR spectrum of compound **2**

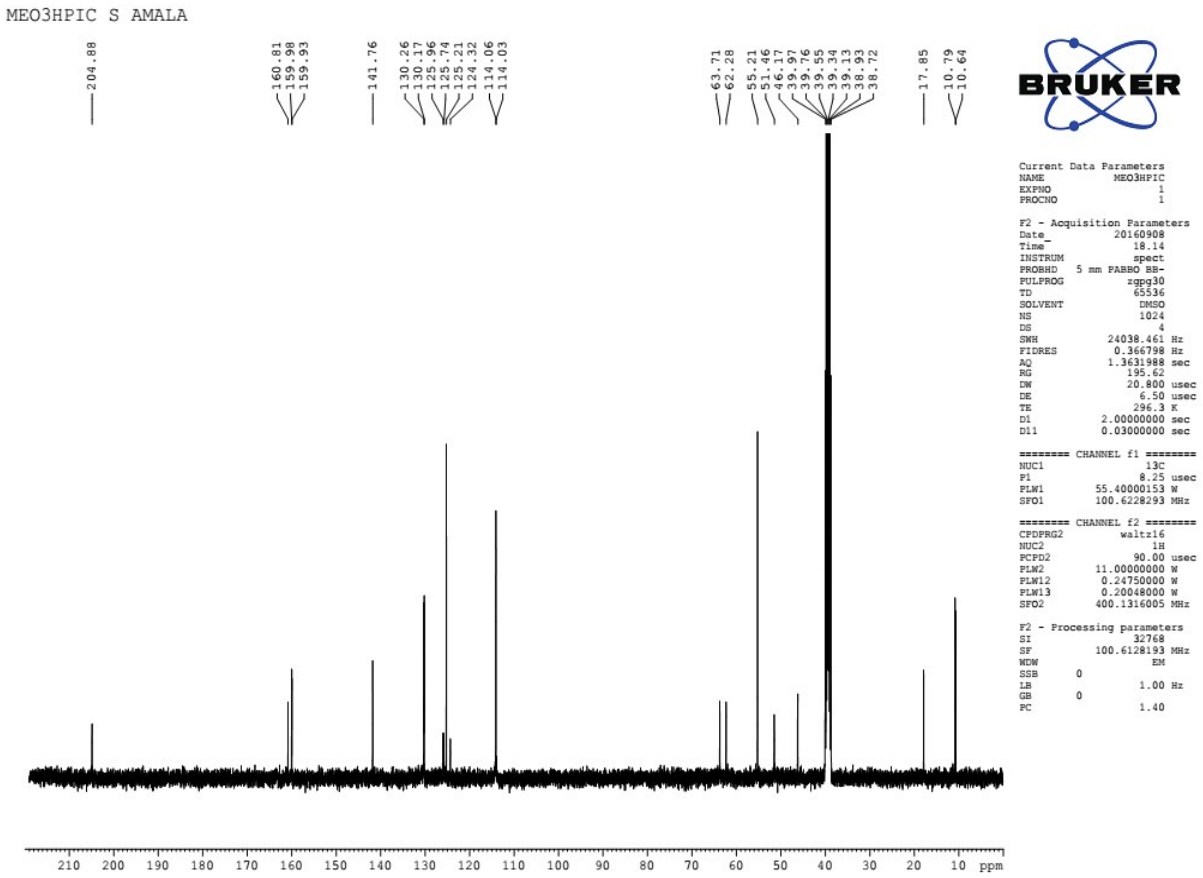

Fig S9. ^{13}C NMR spectrum of compound **3**

Table S1. Crystal data and structure refinement details.

CCDC Number	CCDC 1529858
Empirical formula	C_{28} H_{30} N_4 O_{10}
Formula weight	582.56
Temperature	292(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	C2/c
Unit cell dimensions	a = 22.0277(12) Å
	b = 13.4965(7) Å; β = 118.2720(10)°.
	c = 21.8512(12) Å
Volume	5721.3(5) $Å^3$
Z	8
Density (calculated)	1.353 Mg/m^3
Absorption coefficient	0.104 mm^{-1}
F(000)	2448
Theta range for data collection	2.100 to 24.999°.
Index ranges	-26<=h<=26, -16<=k<=16, -25<=l<=25
Reflections collected	33089
Independent reflections	5044 [R(int) = 0.0212]
Completeness to theta = 24.999°	100.0 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5044 / 2 / 387
Goodness-of-fit on F^2	1.043
Final R indices [I>2sigma(I)]	R1 = 6.6%, wR2 = 19.5%
R indices (all data)	R1 = 7.4%, wR2 = 20.6%
Largest diff. peak and hole	1.099 and -0.380 $e.Å^{-3}$

Table S2. Bond lengths (Å) and bond angles (º) for non-H atoms with esd's in parenthesis.

Atom	Bond length	Atoms	Bond angle
O(1)-C(3)	1.217(3)	C(9)-O(9)-C(27)	118.3(3)
O(2)-C(21)	1.246(3)	C(18)-O(10)-C(28)	119.1(3)
O(3)-N(2)	1.212(3)	C(5)-N(1)-C(1)	112.3(2)
O(4)-N(2)	1.206(3)	O(4)-N(2)-O(3)	122.5(2)
O(5)-N(3)	1.220(3)	O(4)-N(2)-C(22)	117.8(2)
O(6)-N(3)	1.223(3)	O(3)-N(2)-C(22)	119.7(2)
O(7)-N(4)	1.224(4)	O(5)-N(3)-O(6)	122.6(2)
O(8)-N(4)	1.222(3)	O(5)-N(3)-C(24)	119.6(2)
O(9)-C(9)	1.356(4)	O(6)-N(3)-C(24)	117.8(2)
O(9)-C(27)	1.413(6)	C(6)-C(1)-N(1)	111.2(2)
O(10)-C(18)	1.367(3)	C(6)-C(1)-C(2)	114.3(2)
O(10)-C(28)	1.390(5)	N(1)-C(1)-C(2)	108.1(2)
N(1)-C(5)	1.508(3)	O(1)-C(3)-C(4)	123.0(2)
N(1)-C(1)	1.514(3)	O(1)-C(3)-C(2)	121.8(2)
N(2)-C(22)	1.454(3)	C(4)-C(3)-C(2)	115.2(2)
N(3)-C(24)	1.439(3)	C(3)-C(4)-C(13)	112.9(2)
N(4)-C(26)	1.451(3)	C(3)-C(4)-C(5)	107.9(2)
C(1)-C(6)	1.502(3)	C(13)-C(4)-C(5)	111.9(2)
C(1)-C(2)	1.545(3)	C(15)-C(5)-N(1)	110.8(2)
C(2)-C(12)	1.511(4)	C(15)-C(5)-C(4)	114.3(2)
C(2)-C(3)	1.514(3)	N(1)-C(5)-C(4)	108.5(2)
C(3)-C(4)	1.512(4)	C(7)-C(6)-C(11)	118.2(2)
C(4)-C(13)	1.522(4)	C(7)-C(6)-C(1)	121.8(2)
C(4)-C(5)	1.550(3)	C(11)-C(6)-C(1)	120.0(2)
C(5)-C(15)	1.507(3)	C(6)-C(7)-C(8)	121.4(3)
C(6)-C(7)	1.378(4)	C(10)-C(9)-C(8)	119.6(3)
C(6)-C(11)	1.387(4)	C(11)-C(10)-C(9)	120.2(3)
C(7)-C(8)	1.391(4)	C(16)-C(17)-C(18)	120.5(3)
C(8)-C(9)	1.384(5)	C(19)-C(18)-C(17)	119.5(3)
C(9)-C(10)	1.384(5)	C(19)-C(18)-O(10)	124.0(3)
C(10)-C(11)	1.371(4)	C(17)-C(18)-O(10)	116.4(3)
C(13)-C(14)	1.479(6)	C(18)-C(19)-C(20)	119.9(3)
C(15)-C(20)	1.371(4)	C(15)-C(20)-C(19)	121.0(3)
C(15)-C(16)	1.387(4)	O(2)-C(21)-C(22)	124.8(2)
C(16)-C(17)	1.365(4)	O(2)-C(21)-C(26)	123.6(2)
C(17)-C(18)	1.368(5)	C(22)-C(21)-C(26)	111.5(2)
C(18)-C(19)	1.366(5)	C(23)-C(22)-C(21)	124.4(2)
C(19)-C(20)	1.392(4)	C(23)-C(22)-N(2)	116.7(2)
C(21)-C(22)	1.441(3)	C(21)-C(22)-N(2)	118.8(2)
C(21)-C(26)	1.442(3)	C(22)-C(23)-C(24)	118.9(2)
C(22)-C(23)	1.367(3)	C(25)-C(24)-C(23)	121.3(2)
C(23)-C(24)	1.382(3)	C(25)-C(24)-N(3)	119.4(2)
C(24)-C(25)	1.372(3)	C(23)-C(24)-N(3)	119.3(2)
C(25)-C(26)	1.369(3)	C(26)-C(25)-C(24)	119.0(2)
		C(25)-C(26)-C(21)	124.5(2)

Table S3. Contributions of interacting atoms in crystal 1.

Interacting atoms	Contribution (%)
O···O	3.1
C···H	8.2
H···O	18.1
H···H	36.1
N···O	1
O···C	1.9
N···C	2.4

Table S4. Optimized parameter of compounds 1-3.

Bond length	**1**	**2**	**3**	XRD
C4-C3	1.531	1.531	1.530	1.512(4)
C3-O1	1.217	1.217	1.217	1.217(3)
C4-C5	1.549	1.549	1.549	1.550(3)
C5-N1	1.527	1.527	1.529	1.508(3)
C18-R18	1.013	1.345	1.360	1.367(3)
C9-R9	1.023	1.345	1.402	1.390(5)
C21-O2	1.262	1.263	1.261	1.246(3)
N4-O7	1.245	1.245	1.244	1.224(4)
N2-O4	1.233	1.233	1.233	1.206(3)
C21-C26	1.454	1.453	1.454	1.441(3)
C21-C22	1.377	1.377	1.377	1.367(3)
C25-C24	1.377	1.387	1.387	1.372(3)
N3-O6	1.233	1.233	1.233	1.223(3)
N3-O5	1.233	1.233	1.233	1.220(3)
Bond angle			DFT	
C3-C4-C5	111.4	111.3	111.2	107.9(2)
C4-C5-N1	108.1	108.1	107.9	110.8(2)
O3-C3-C4	122.9	122.9	122.9	121.8(2)
C2-C1-N1	110.5	110.5	110.4	108.1(2)
C10-C9-C8	119.7	122.0	119.5	116.2(3)
C19-C18-C17	120.3	122.0	119.5	119.5(3)
C16-C15-C20	118.9	118.7	118.1	122.9(2)
C26-C21-O2	125.6	125.6	125.6	123.6(2)
O7-N4-O8	122.6	122.6	122.6	124.0(3)
O3-N2-O4	124.2	124.2	124.2	122.5(2)
C26-N4-O8	118.8	118.8	118.7	118.2(3)
C24-C25-C26	119.8	119.8	119.8	119.0(2)
O5-N3-O6	124.7	124.7	124.6	122.6(2)
C21-C22-C23	123.1	123.6	123.9	124.5(2)
C21-C26-C25	124.1	124.5	125.1	124.2(2)
C22-C21-C26	112.6	112.8	113.1	111.5(2)
Dihedral angle				
C3-C4-C5-N1	-52.4	-52.5	-53.0	-50.21
O3-C3-C4-C5	-129.2	-128.4	-128.2	-
N1-C6-C5-C4	50.8	50.5	50.5	170.43
C15-C20-C19-C18	-	0.1		-

R=H, F and O for **1,2** and **3**, respectively

Table S5. Observed and computed wavenumber of compounds **1-3.**

Assignments	1			2			3		
	FT-IR	DFT		FT-IR	DFT		FT-IR	DFT	
		Scaled	IR Intensity		Scaled	IR Intensity		Scaled	IR Intensity
ν_{N-H}	3301	3346	25.57	3339	3350	24.88	3303	3347	23.48
$\nu_{ar\cdot C-H}$	3042	3088	21.29	3031	3081	32.45	3088	3088	120.91
$\nu_{ali\cdot C-H}$	2936	2998	36.40	2932	2298	35.75	2928	2963	36.37
$\nu_{C=O}$	1719	1732	149.98	1719	1728	149.55	1714	1730	151.07
$\nu_{C=C}$	1625	1620	329.20	1629	1635	239.11	1631	1619	398.12
ν_{asyNO2}	1587	1584	305.69	1579	1580	11.46	1555	1562	15.99
	1492	1595	18.01	1498	1499	52.83	1514	1540	263.16
	1462	1475	30.84				1451	14.62	16.08
ν_{syNO2}	1449	1445	301.46	1449	1450	302.86	1435	1441	340.71
	1332	1336	396.24	1344	1351	327.23	1334	1335	206.75
β_{C-H}	1269	1268	176.31	1267	1292	114.55	1251	1254	10.86
	1206	1234	13.84	1198	1182	12.22	1181	1192	15.42
	1162	1177	21.0				1159	1160	46.29
ν_{C-O}	1074	1084	11.12	1088	1089	32.44	1032	1030	70.05
Γ_{C-H}	953	958	16.72	957	958	18.58	935	998	16.55
	918	920	10.66	823	859	37.69	910	941	15.32
	766	767	21.73	722	733	20.21	707	720	24.37

ν- Stretching, β- in-plane bending, Γ-out-of-plane bending

Table S6. Second order perturbation theory analysis of Fock matrix in NBO basis.

Type	Donor(i)	Occupancy	Acceptor(j)	Occupancy	$E^{(2)}$ (kJ/mol)		
					1	**2**	**3**
σ-σ*	C4-C3	1.964	C4-C5	0.0254	2.93	2.89	2.93
σ-σ*			C4-C13	0.019	3.77	3.77	3.77
σ-σ*	C3-C2	1.964	C4-C13	0.019	7.66	7.66	7.70
σ-π*	C4-C5	1.963	C3-O1	0.080	10.71	10.96	11.09
σ-σ*			C3-O1	0.013	6.07	5.98	6.02
σ-π*	C5-N1	1.985	C15-C20	0.373	6.65	6.02	6.40
σ-σ*	C5-C15	1.976	C15-C20	0.024	9.67	10.04	10.63
σ-σ*			C19-C20	0.014	8.24	8.37	8.49
π-π*	C15-C20	1.692	C16-C17	0.298	81.80	89.66	87.45
π-π*			C18-C19	0.384	79.12	74.81	67.32
π-π*	C16-C17	1.703	C15-C20	0.079	86.32	76.78	72.30
π-π*			C18-C19	0.384	84.10	97.11	90.67
π-π*	C18-C19	1.647	C15-C20	0.079	90.75	93.43	98.83
π-π*			C16-C17	0.297	83.26	76.40	67.20
π-π*	C7-C8	1.698	C6-C11	0.376	74.42	78.16	73.72
π-π*			C9-C10	0.295	90.50	98.91	92.38
π-π*	C9-C10	1.698	C6-C11	0.376	97.40	94.22	99.45
π-π*			C7-C8	0.387	59.33	75.81	66.65
π-σ*	LP(1)O1	1.979	C4-C3	0.073	92.74	91.00	90.63
π-σ*			C2-C3	0.065	88.20	86.61	86.15
n- σ*	LP(2)O2	1.872	C21-C22	0.056	40.72	46.99	42.51
n- σ*			C21-C26	0.058	61.84	67.53	63.47
n- σ*	LP(2)O7	1.912	C26-N4	0.088	44.31	46.69	50.50
n- σ*			N4-O8	0.055	73.22	76.27	80.37
n- σ*	LP(2)O8	1.895	C26-N4	0.088	50.79	56.07	51.88
n- σ*			N4-O7	0.055	84.10	82.80	79.45
n- σ*	LP(2)O6	1.897	C24-N3	0.100	51.97	44.43	51.34
n- σ*			N3-O5	0.057	80.17	77.86	82.09
n- σ*	LP(2)O4	1.899	C22-N2	0.061	52.01	73.85	44.39
n- σ*			N2-O3	0.057	80.00	77.19	73.64
n- σ*	LP(2)O3	1.897	C22-N2	0.067	47.91	56.15	50.75
			N2-O4	0.057	82.76	80.00	83.76