Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Solvent H-bond Accepting Ability Induced Conformational Change and It's Influence Towards Fluorescence Enhancement and Dual Fluorescence of Hydroxy meta- GFP Chromophore Analogue

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S1: Materials and methods:

2-hydroxy-5-methoxybenzaldehyde, N-Acetyl glycine, Sodium acetate, Sodium carbonate were procured from Sigma-aldrich; glycine methyl ester hydrochloride, ethyl acetimidate hydrochloride, methylamine were procured from Acros organics; Methyl iodide was procured from Oligo Chemicals. Solvents used for spectroscopic measurements were of spectroscopic grade and were procured from Spectrochem. Thin layer chromatography (TLC) analyses were performed on Merck Kieselgel 60 F254 plate using 100-200 mesh size silica gel. ^{1}H NMR and ^{13}C NMR spectra were recorded in GEOL-400 (400 MHz) spectrometers. IR spectra were recorded on a Perkin Elmer (model – spectrum RX-1) FT-IR spectrometer with the KBr pellets for solid sample and in chloroform for liquid samples. Mass spectra (TOF MS ES+) were taken in a QTOF Micromass system.

S2: Details of single crystal X-ray measurement

mOMe-MBDI and mOMe-HBDI were dissolved in acetonitrile in a 10 mL conical flask. The suspension was heated until a clear solution is obtained. The resulting mixture was boiled for 10 min and then filtered. The filtrate was left to evaporate slowly at ambient condition. The single crystals suitable for X-ray diffraction were obtained within one week. The crystals were mounted on a glass pip. Intensity data of single crystals were collected on a SuperNova, Dual, Cu at zero, Eos diffractometer using graphite monochromated Mo Kα (λ = 0.71073 Å) radiation. The crystals of mOMe-HBDI and mOMe-MBDI were kept at 293(2)K during data collection. Crystal structures of mOMe-HBDI and mOMe-MBDI were solved by direct methods using SHELEXL-97 and refined by full matrix least squares on F2 with anisotropic displacement parameters for non-H atoms using SHELXL-97.[1] Hydrogen atoms associated with carbon atoms were fixed in geometrically constrained positions. Structure graphics shown in the figures were created using the X-Seed software package version 2.0.[2]

S3: Details of NMR measurement:

^{1}H NMR spectra were recorded in Toluene-d_8, $CDCl_3$, DMSO-d_6, CD_3CN and THF-d_8 in GEOL-400 (400 MHz) and Bruker AVANCE III 500 (500MHz) spectrometer. Chemical shift (δ in ppm) values are reported relative to tetramethylsilane (^{1}H NMR) as internal standard to residual signal of the solvents (for ^{1}H NMR: Toluene-d_8, 2.08 ppm, CDCl3, 7.26 ppm; DMSO-d_6, 2.50 ppm, CD_3CN, 1.94 ppm, and for THF-d_8, 3.58 ppm).

S4: Steady state and time resolved optical measurements:

(a) Steady state:

Steady state absorption and corrected emission spectra were taken in a U-4100 Hitachi spectrophotometer and Fluoromax-3 Horiba Jobin Yvon spectrofluorimeter respectively. Solutions of all the compounds, were prepared keeping in mind that the absorbance value is less than 0.1 at the absorption maxima. Quantum Yield (Q.Y.) determination was accomplished by comparison of the wavelength integrated intensity of the unknown to that of the standard. Fluorescence quantum yields were calculated with solutions having absorbance less than 0.05 to avoid inner filter effect. To measure the Q.Y. of mOMe-HBDI and mOMe-MBDI, coumarin153 was used as the reference compound. For mOMe-HBDI and mOMe-MBDI both the compounds and the reference were excited at 390 nm. Q.Y. of all the compounds was calculated using the following equation:

$$Q = Q(Ref)\frac{OD(Ref)}{OD}\frac{I}{I(Ref)}\frac{n^2}{n^2(Ref)} \qquad \text{---- eq—(1)}$$

where, 'Q', 'I' and 'n' stands for Quantum yield, Integrated intensity and refractive index of the solvents respectively.

(b) Time resolved:

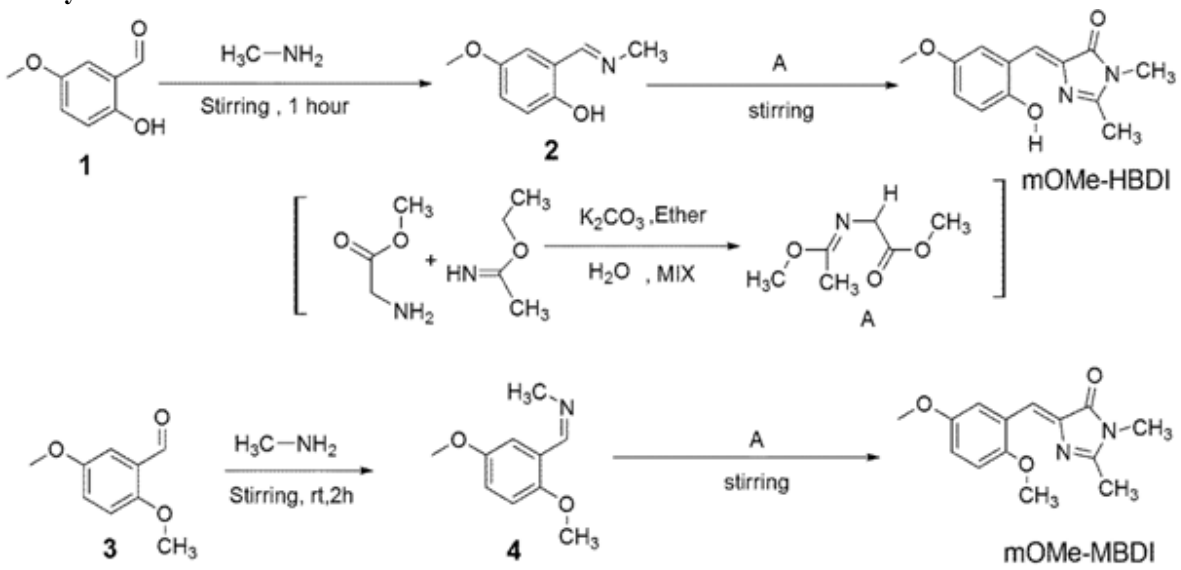
(i) Picosecond TCSPC measurement:

Fluorescence lifetime measurements at ps-ns time domain were carried out using a time correlated single photon counting (TCSPC) spectrometer (Horiba Jobin Yvon IBH). Diode laser with λ_{ex} = 377 nm and 402 nm were used as the excitation sources and an MCP photomultiplier tube (PMT) (Hamamatsu R3809U-50 series) as the detector. The width of the instrument response function (IRF), which was limited by the fwhm of the exciting pulse, was less than 100 ps for 377 nm and 402 nm excitation source. IRF was recorded using a scatterer (dilute solution of ludox in water). Nonlinear least squares iterative reconvolution procedure using IBH DAS6 (Version 2.2) was employed to fit the fluorescence decay curve using a single exponential decay equation. The quality of the fit was assessed from the $\chi 2$ values and the distribution of the residuals.

(ii) Femtosecond fluorescence up-conversion measurement:

Femtosecond fluorescence transients were collected using femtosecond up-conversion setup (FOG 100, CDP, Russia). The second harmonic (400 nm) of a mode locked Ti-sapphire laser (Tsunami, Spectra physics) was used as the excitation source for the samples. The fundamental beam (800 nm) was frequency doubled in nonlinear crystal (1 mm BBO, Θ =250 ,ϕ =900). The sample was placed inside one mm thick rotating quartz cell. The fluorescence emitted from the sample was up-converted in a nonlinear crystal (0.5 mm BBO, Θ= 380 , ϕ= 900) using the fundamental beam as the gate pulse. The up-converted light is dispersed in a monochromator and detected using photon counting electronics. The instrument response function of the apparatus is 280 fs. The decays were deconvoluted using a Gaussian shape of the exciting pulse using commercial software (IGOR-Pro, Wavemetrics). All the experiments were performed at 20^0C.

S5: Synthesis and characterisation:



Scheme-S1: Synthesis of mOMe-HBDI and mOMe-MBDI[3]

Synthesis of 4-methoxy-2-((methylamino)methyl)phenol (2) :
The Schiff base was prepared following a literature procedure[3] by mixing 2-hydroxy-5-methoxybenzaldehyde (**1**) (300 mg,1.97 mmol) with methyl amine (40 wt% in ethanol)(0.5mmol) in 5 mL ethanol and stirring
the reaction mixture at r.t for 2h. The yield of the reaction was almost quantitative. So after evaporing ethanol and methyl amine in a rotavapour, the compound (325 mg, 1.97 mmol) was used for the next step without purification.
^{1}H NMR (JEOL-400 MHz, CDCl3) δ 3.46 (s, 3H) δ 3.76 (s, 3H) δ 6.74 (broad (structureless), 1H) δ 6.89 (broad, 2H), δ 8.28 (s, 1H) δ 12.93 (s, 1H)
^{13}C NMR (JEOL-400 MHz, CDCl3) : 46.11, 55.85, 114.63, 117.57, 118.50, 118.79, 151.82, 155.11, 165.81.
MS calculated for [C9H11NO2 +H+] : 166.1 found : 166.1

Synthesis of 2-methyl-4-methylene-1H-imidazol-5(4H)-one (A): The compound was synthesized following literature procedure. K_2CO_3 (50 mmol,6.91 gm) and methyl glycinate hydrochloride (50 mmol, 6.26 gm) were suspended in Et_2O (125mL), followed by addition of H_2O (20mL), then addition of ethyl acetimidate hydrochloride (50 mmol). The mixture was shaken for 6 min then the ether was decanted off. An additional portion of Et_2O (75 mL) was added, the mixture was shaken for 6 min. Then the Et_2O was decanted off. The combined organic portions were dried over anhydrous $MgSO_4$ and filtered to separate $MgSO_4$. Et_2O was separated by a rotavapor. This compound is unstable at room temperature so further reaction was carried out without any characterisation of the compound.

Synthesis of: [(Z)-(4)-(2-hydroxy-5-dimethoxybenzylidine)-1,2-dimethyl-1H-imidazole-5(4H)-one [mOMe-HBDI] : The prepared aromatic Schiff base (**2**) (1.97 mmol, 325 mg) was

combined with the imidate (**A**) produced in scheme 1, in absolute ethanol (3 mL) and the reaction was allowed to stir in a capped round bottom flask overnight at r.t. The precipitate was filtered and washed sequentially with Et_2O (~2 mL) and EtOH (~1mL) to yield (65% , 315 mg) the pure product as yellow powder .

^{1}H NMR (JEOL-400 MHz, CDCl3) δ 2.38 (s, 3H) δ 3.23(s, 3H) δ 3.77(s, 3H) δ 6.77(d, J= 3.2 Hz, 1H) δ 6.89 (d, J=11.1 Hz, 1H) δ 6.97 (dd, J=3.5 Hz, 11.3 Hz, 1H) δ 7.11 (s, 1H) δ 13.28 (broad s, 1H)

^{13}C NMR (JEOL-100 MHz, CDCl3): 15.21, 26.81, 55.78, 118.31, 119.38, 120.05, 121.77, 129.91, 133.19, 152.26, 152.84, 157.67, 168.01

FT-IR data (neat): 2937-3008(alkane C-H stretch) , 1708(C=O stretch), 1638(alkene C=C stretch), 1581(aromatic C=C stretch), 1492 (C=N stretch), 1401, 1270, 1228, 1138, 1042, 812

MS calculated for [C13H14N2O3+Na+] : 269.1, Found : 269.1

Synthesis of N-(2,5-dimethoxybenzylidine) methanamine (4) : The Schiff base was prepared by mixing 2-methoxy-5-methoxybenzaldehyde (3) (300 mg,1.80 mmol) with methylamine (40wt% in ethanol) (0.5mmol) in 5 mL ethanol and stiring the reaction mixture at r.t for 2 hr. The yield of the reaction was almost quantitative. So after evaporation of ethanol and methyl amine in a rotavapour, the compound (323 mg) was used for the next step without purification.

^{1}H NMR (JEOL-400 MHz, CDCl3) δ 3.49 (d, J=1.43 Hz, 3H) δ 3.77 (s, 3H) δ 3.79 (s, 3H) δ 6.82(d, J= 11.2 Hz, 1H) δ 6.91 (dd, J=3.86 Hz, 11.3 Hz, 1H), δ 7.43 (d, J=3.85 Hz, 1H) δ 8.66 (d, J=1.5 Hz, 1H)

^{13}C NMR (JEOL-400 MHz, CDCl3) : 48.34, 55.68, 56.12, 109.98, 112.71, 118.66, 125.00, 153.07, 153.67, 158.33.

MS calculated for [C10H13NO2 +H+] : 180.1 found : 180.1

Synthesis of [(Z)-(4)-(2,5-dimethoxybenzylidine)-1,2-dimethyl-1H-imidazole-5(4H)-one) [mOMe-MBDI] : The prepared aromatic Schiff base (**4**) (l.80 mmol, 323 mg) was combined with the imidate (**A**) produced in scheme-1, in absolute ethanol (3 mL) and the reaction was allowed to stirred in a capped R.B flask overnight at r.t. The precipitated product was filtered and washed sequentially with Et_2O (~2 mL) and EtOH (~1mL) to yield (65%, 304 mg) the pure product as yellow solid.

^{1}H NMR (JEOL-400 MHz, CDCl3) δ 2.36 (s, 3H) δ 3.18 (s, 3H) δ 3.82 (s, 3H) δ 3.84(s, 3H) δ 6.83 (d, J=11.3 Hz, 1H) δ 6.91 (dd, J=11.1 Hz, 3.5 Hz, 1H) δ 7.63 (s, 1H) δ 8.42 (d, J=3.5 Hz, 1H)

^{13}C NMR (JEOL-100 MHz, CDCl3): 15.70, 26.54, 55.72, 56.13, 111.76, 116.92, 117.86, 121.16, 123.67, 138.30, 153.39, 153.82, 161.90, 170.65

FT-IR data (neat):2933 (alkane C-H stretch) , 1704 (C=O stretch), 1637 (alkene C=C stretch), 1615 (aromatic C=C stretch), 1490 (C=N stretch), 1295, 1231, 1141, 1051, 1020

MS calculated for [C14H16N2O3 +H+] : 261.1 found : 261.1

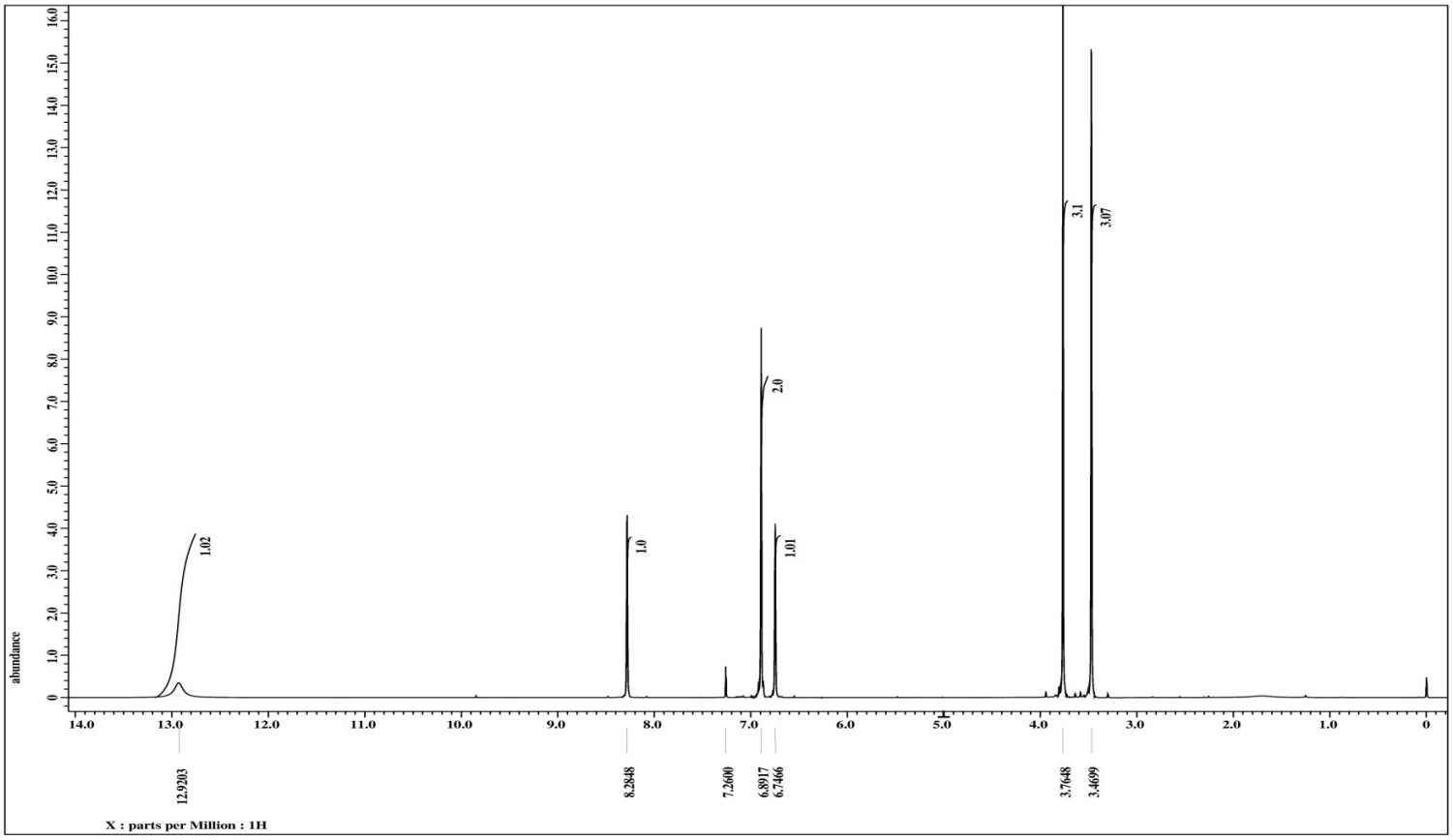


Figure-S1: ^{1}H NMR spectrum of compound-2

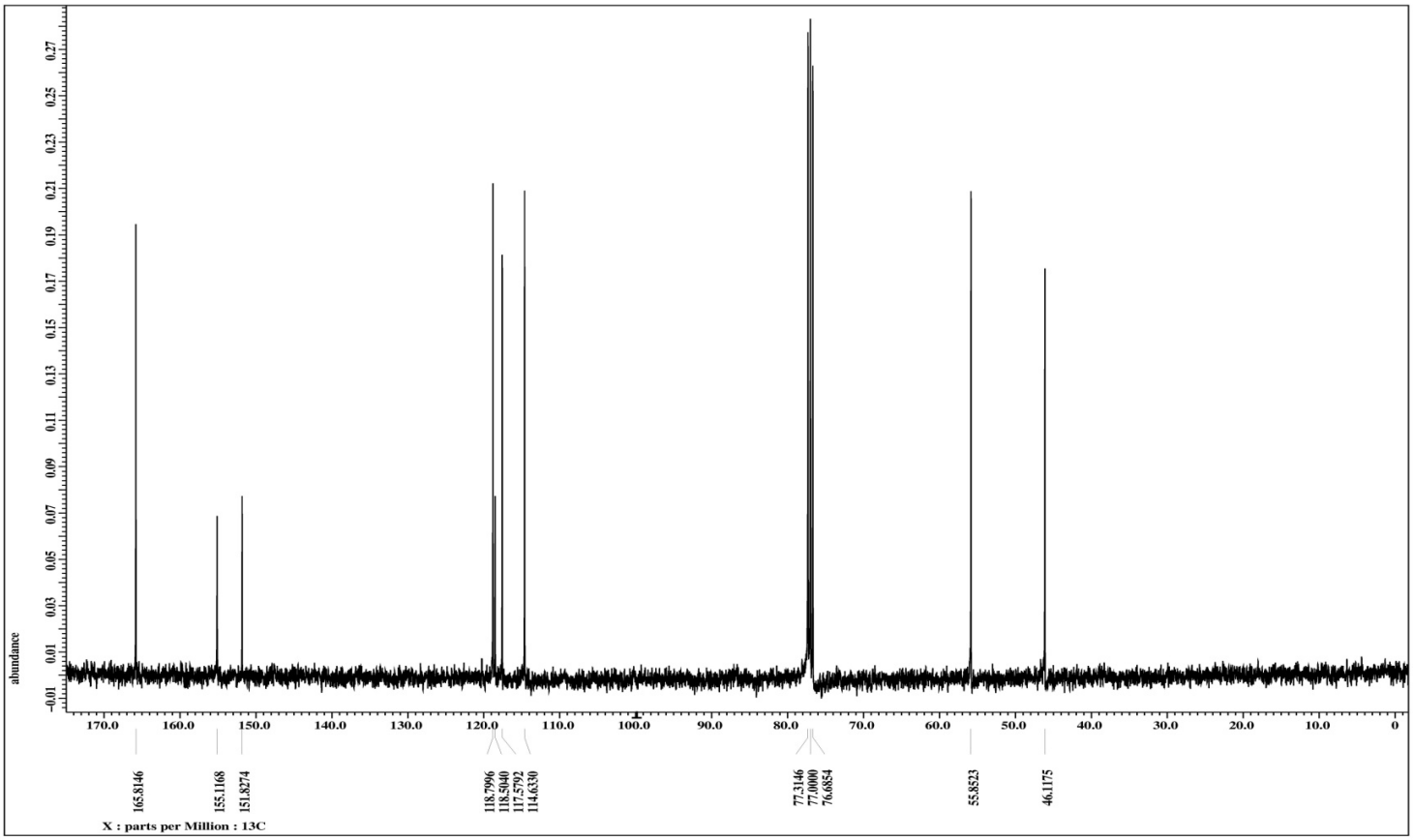


Figure-S2: ^{13}C NMR spectrum of compound-2

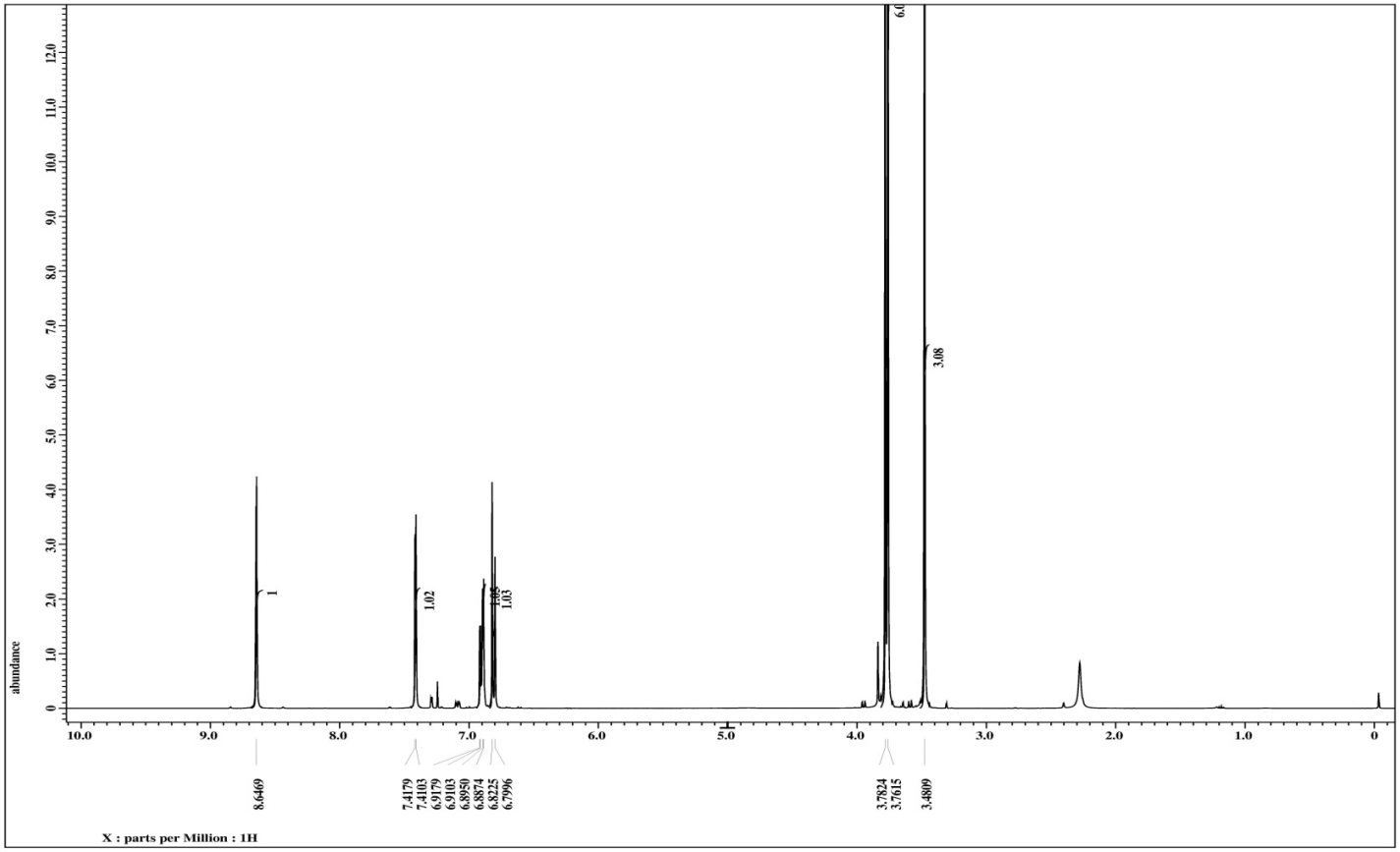


Figure-S3: ^{1}H NMR spectrum of compound-4

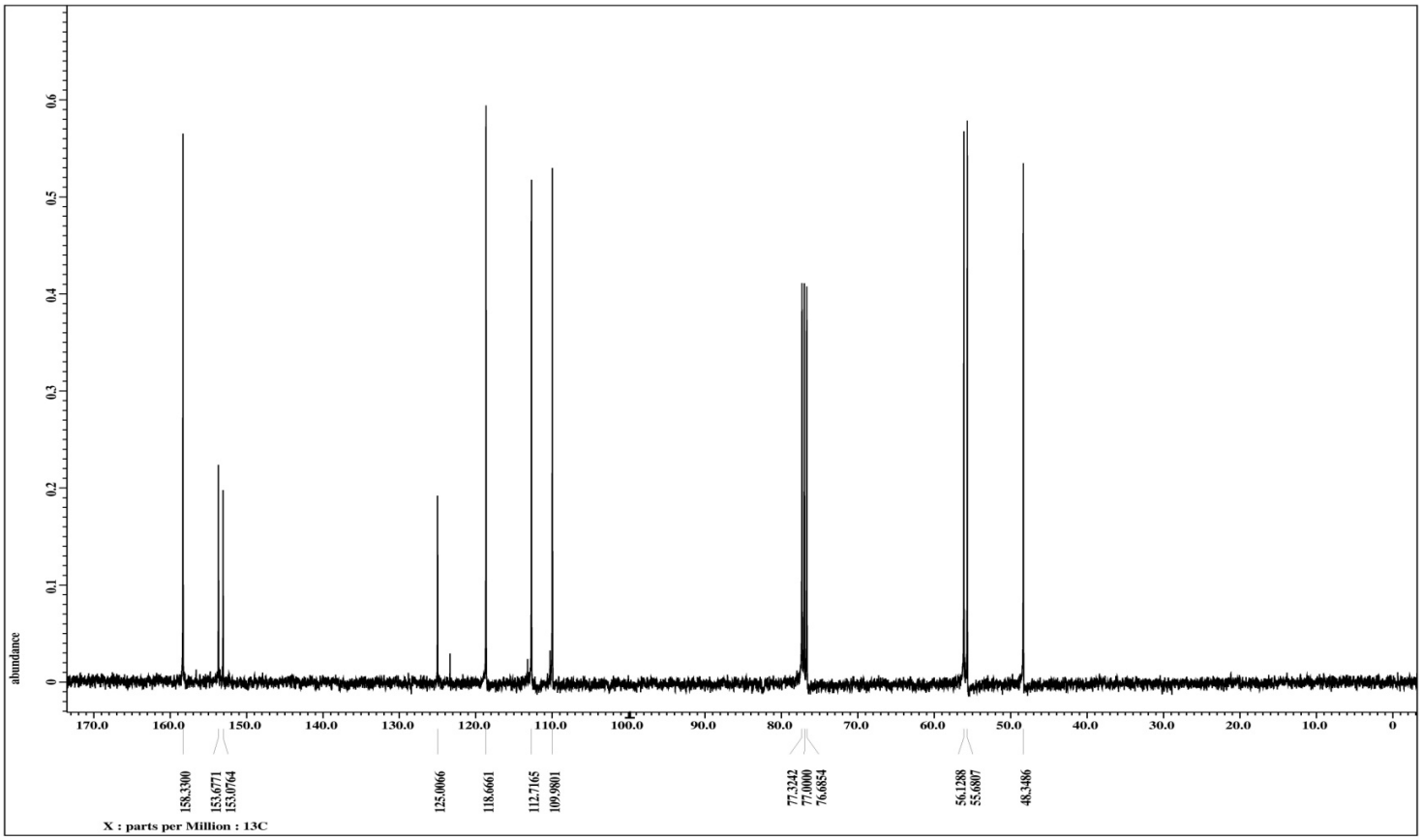


Figure-S4: ^{13}C NMR spectrum of compound-4

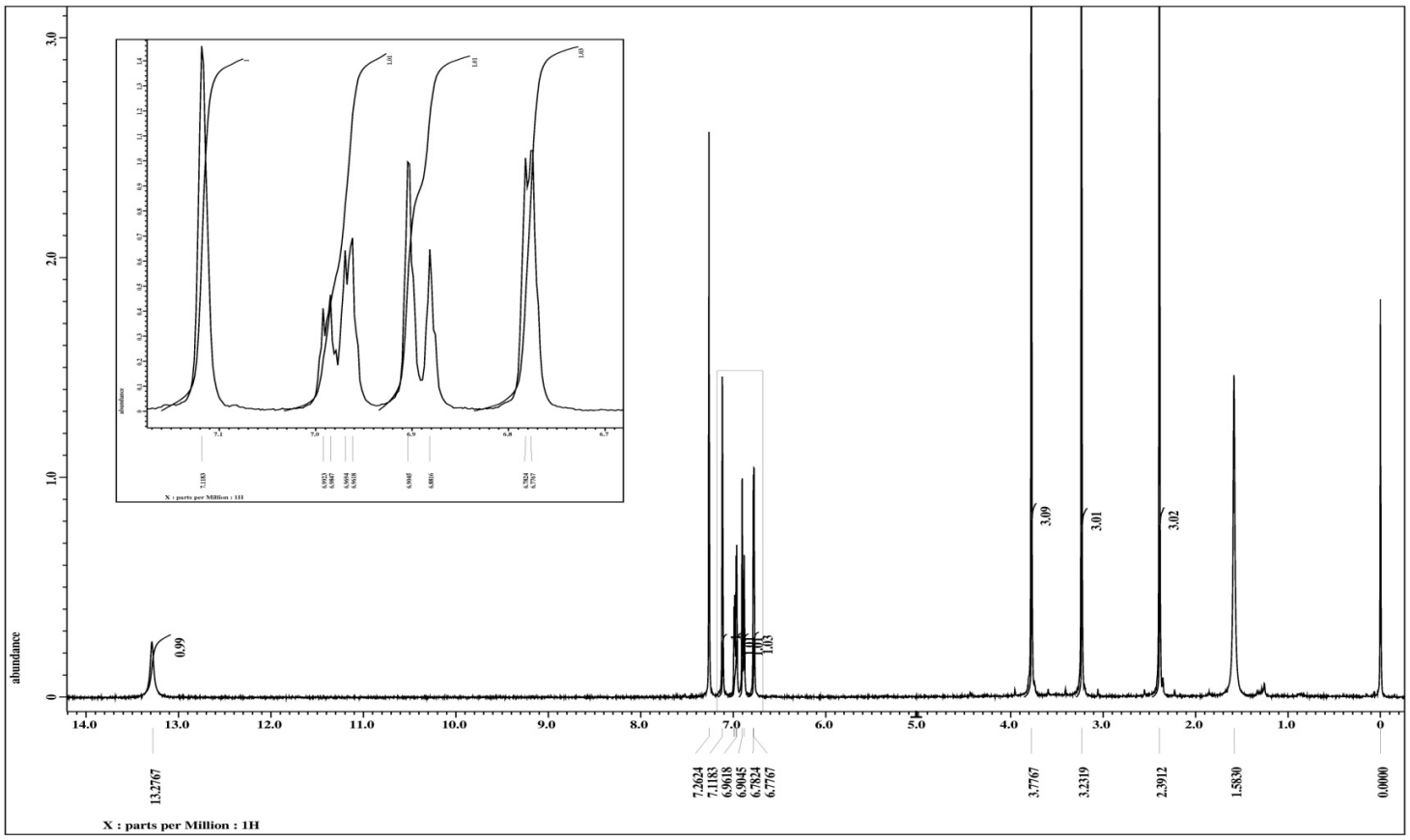


Figure-S5: ^{1}H NMR spectrum of mOMe-HBDI

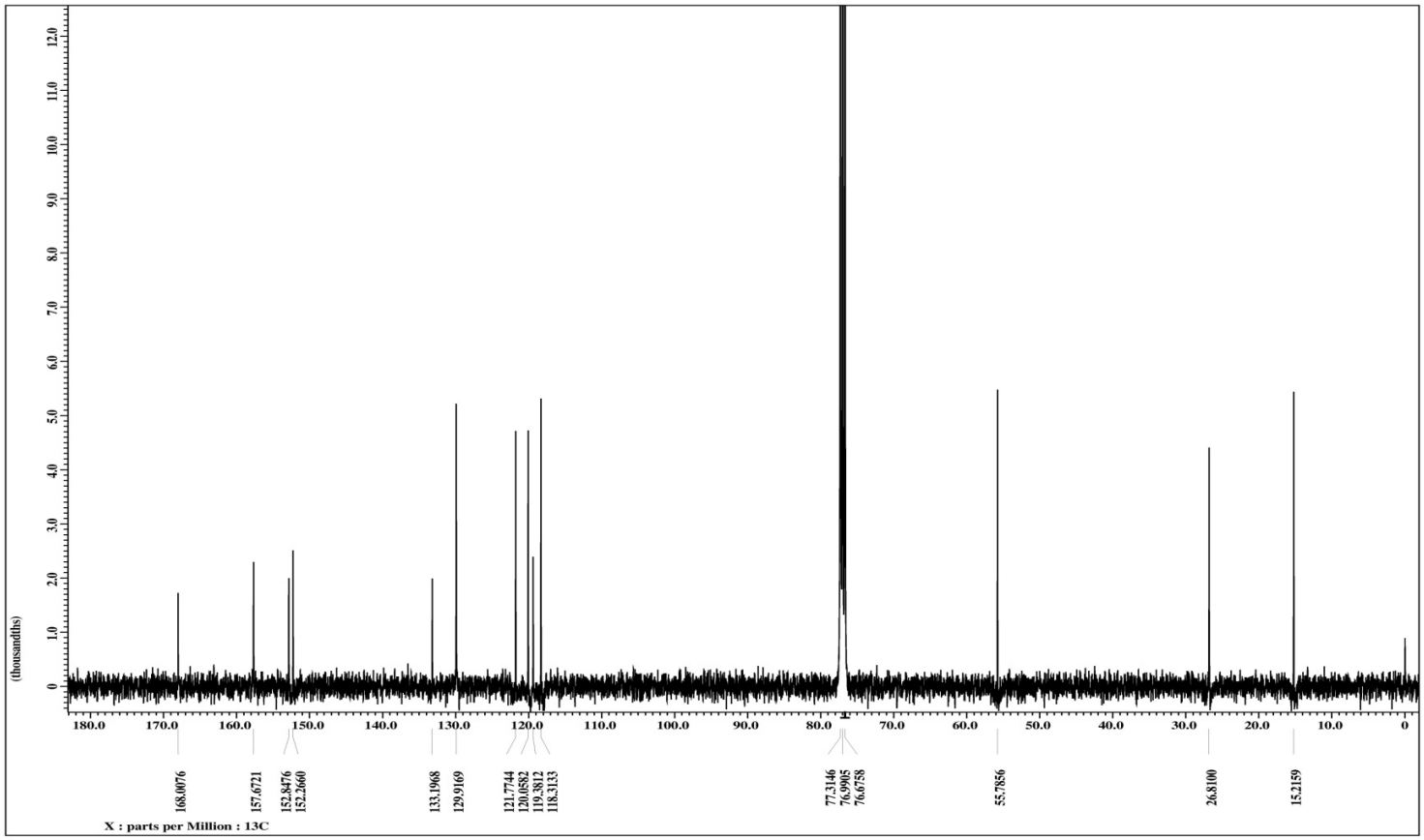


Figure-S6: ^{13}C NMR spectrum of mOMe-HBDI

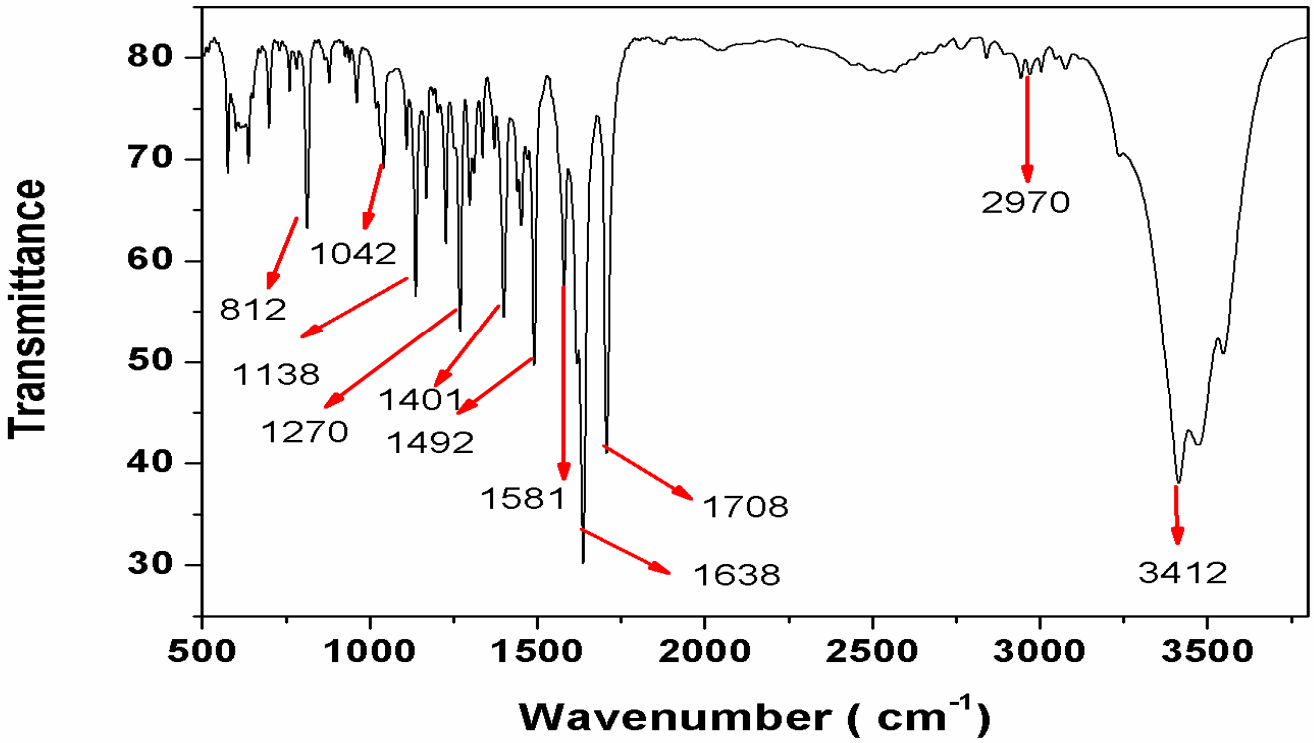


Figure-S7: IR spectrum of mOMe-HBDI

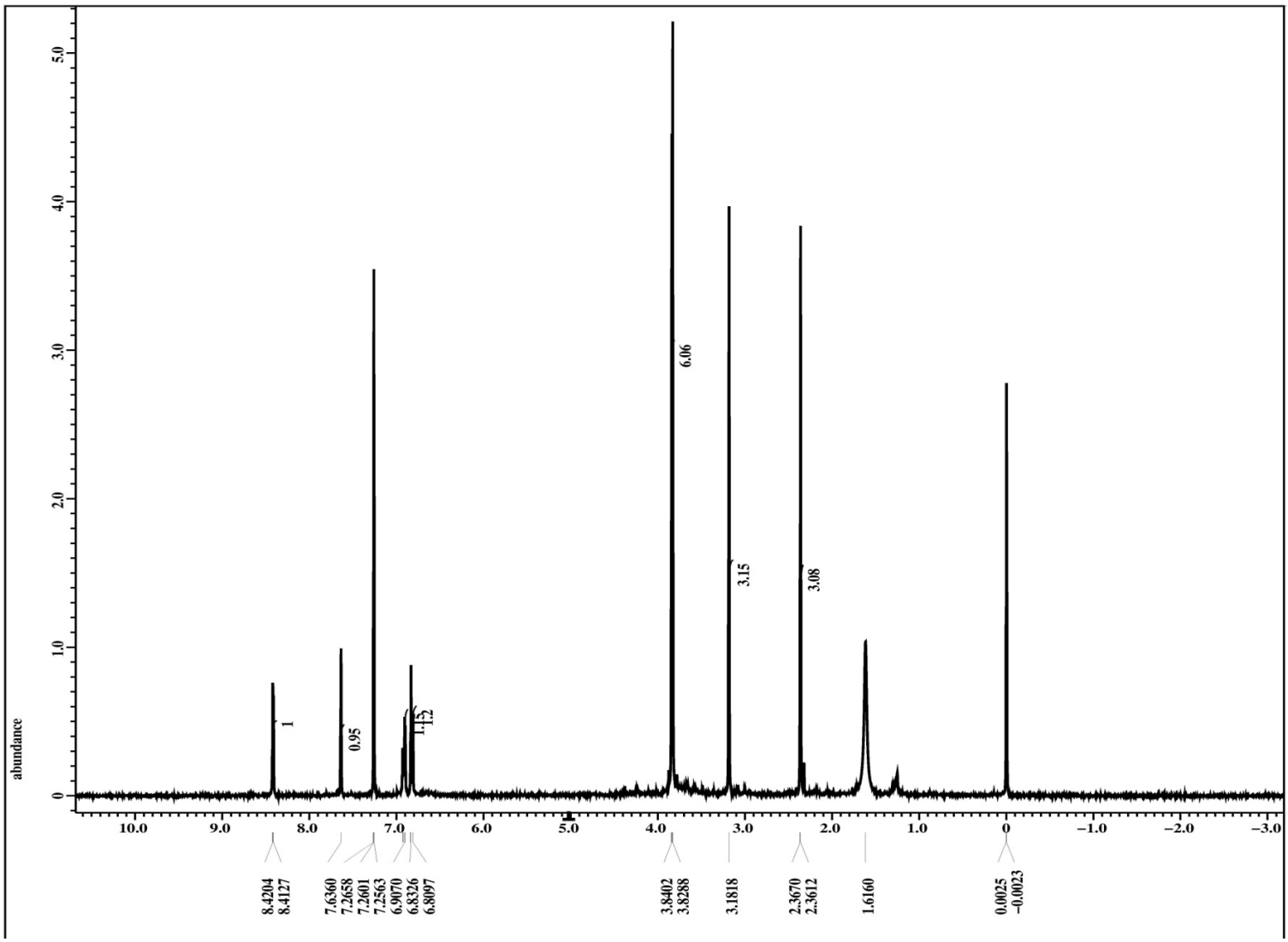


Figure-S8: ^{1}H NMR spectrum of mOMe-MBDI

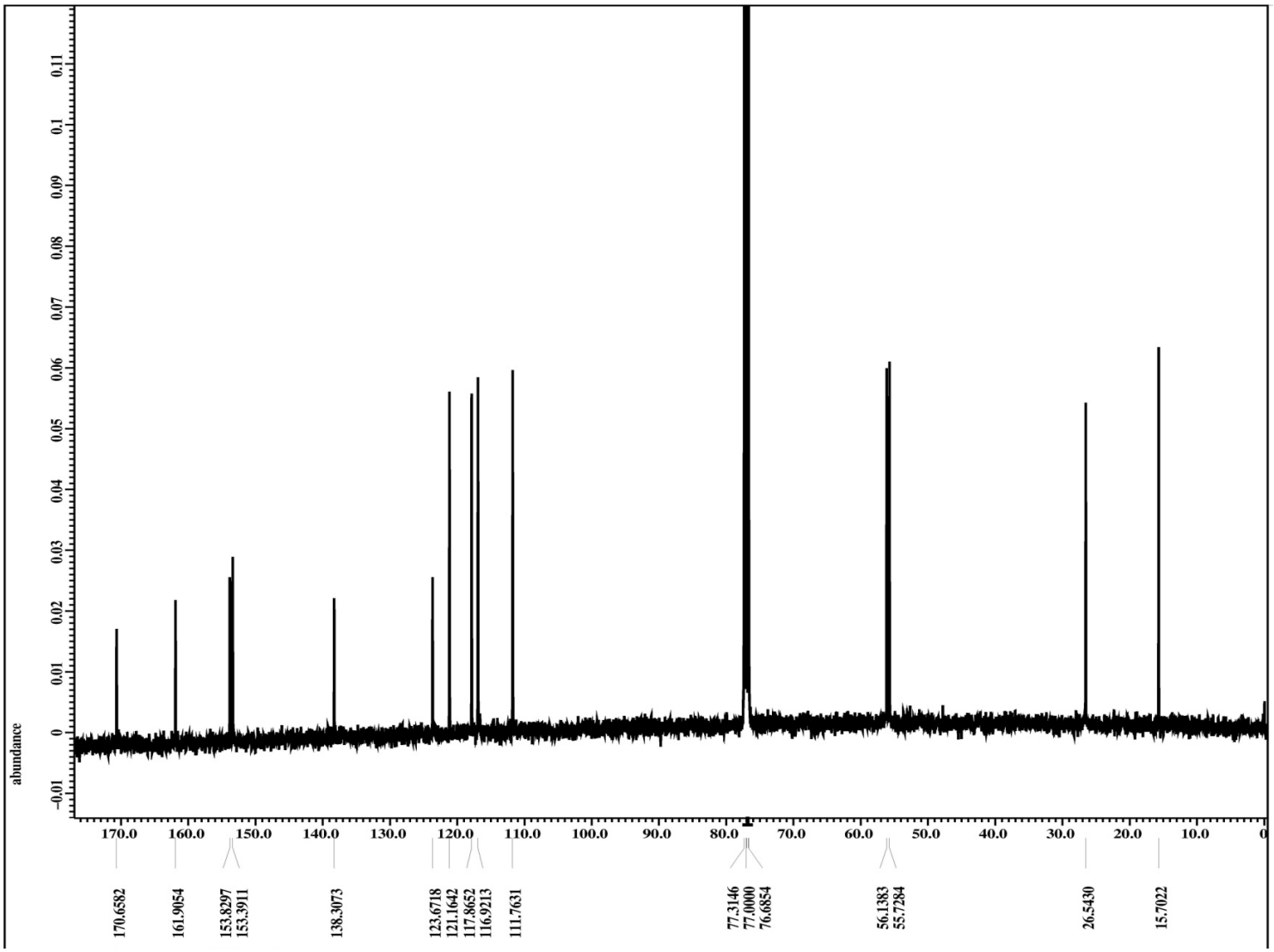


Figure-S9: ^{13}C NMR spectrum of mOMe-MBDI

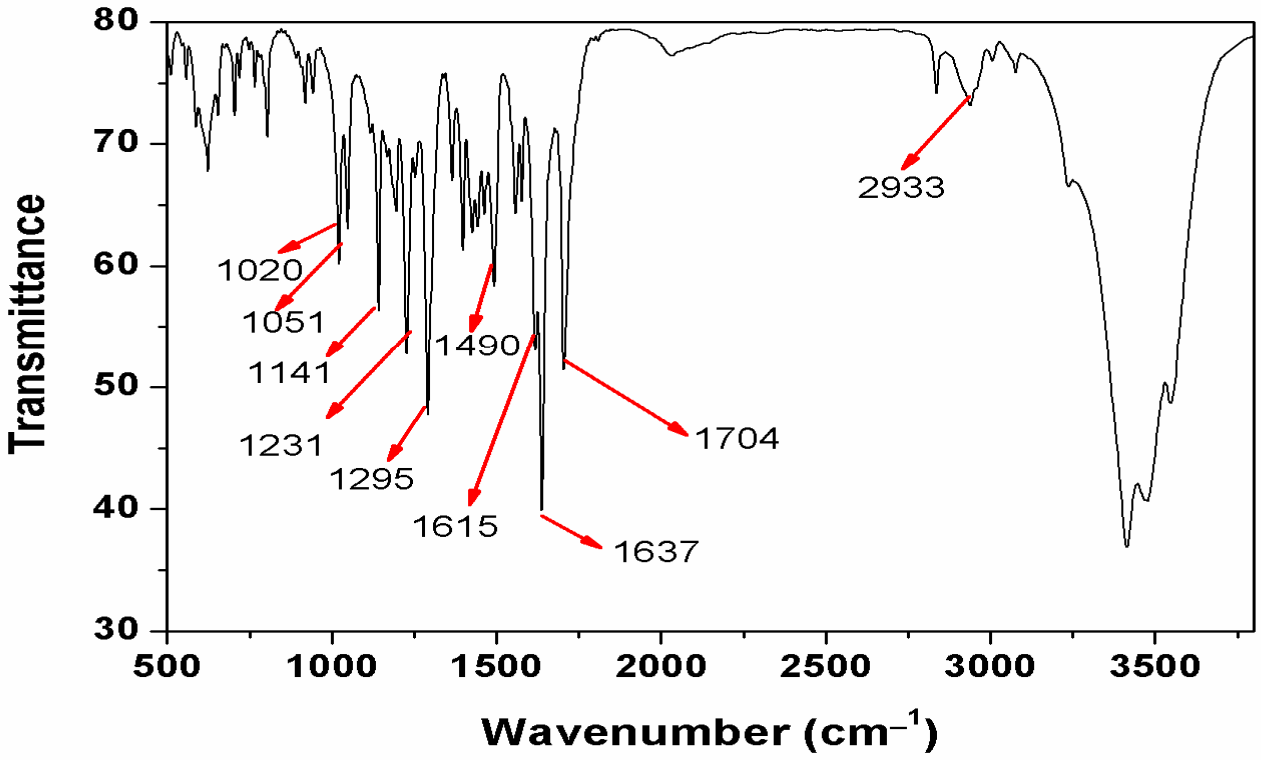


Figure-S10: IR spectrum of mOMe-MBDI

S6: **Absorption and emission spectra of mOMe-HBDI in alkaline solution**

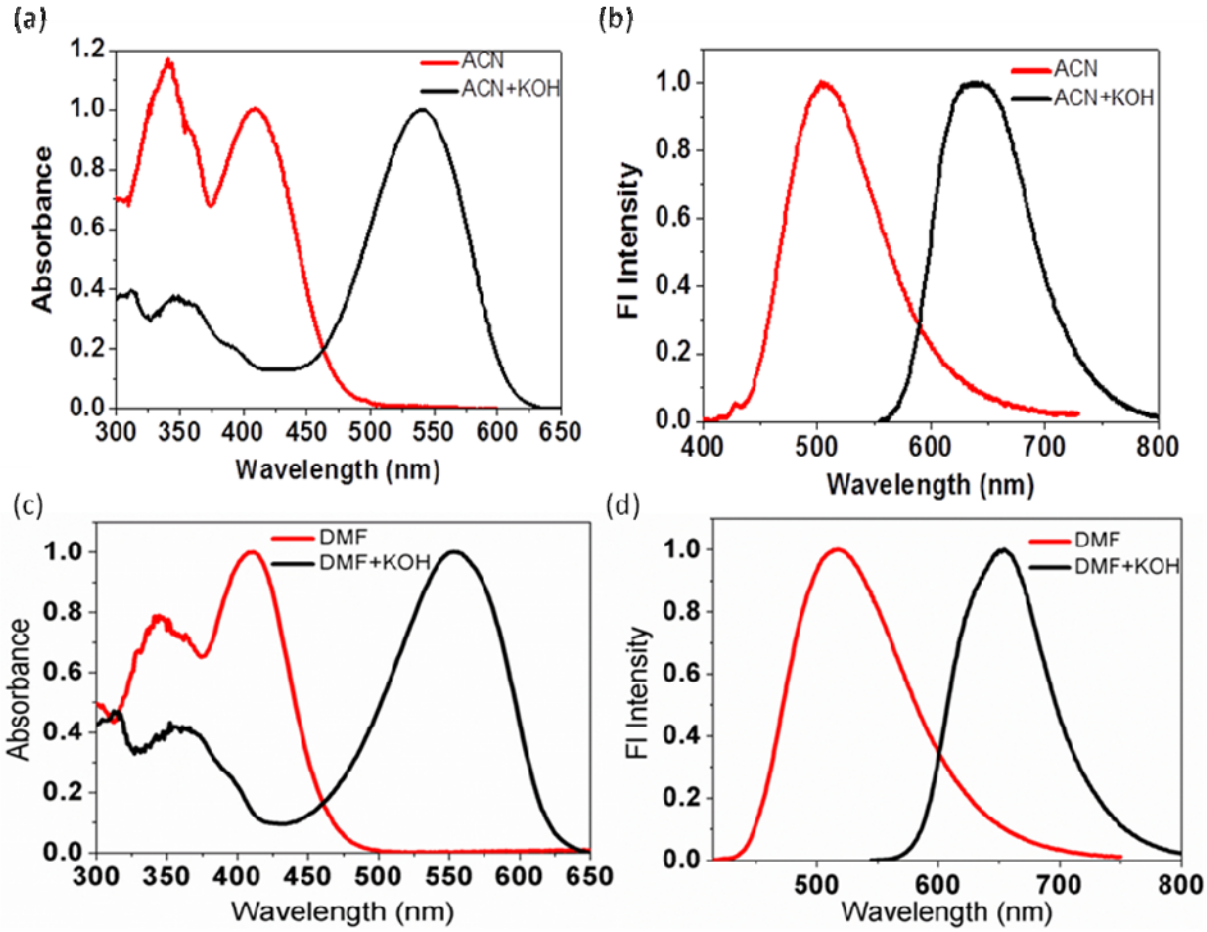


Figure-S11: Normalised (a) Absorption spectra of mOMe-HBDI in ACN and alkaline ACN with KOH (b) Emission spectra of mOMe-HBDI in ACN and in alkaline ACN (c) Absorption spectra of mOMe-HBDI in DMF and alkaline DMF with KOH (d) Emission spectra of mOMe-HBDI in DMF and alkaline DMF with KOH showing the absorption and emission spectra of normal and anionic (deprotonated) form.

S7: **Excitation spectra of mOMe-HBDI**

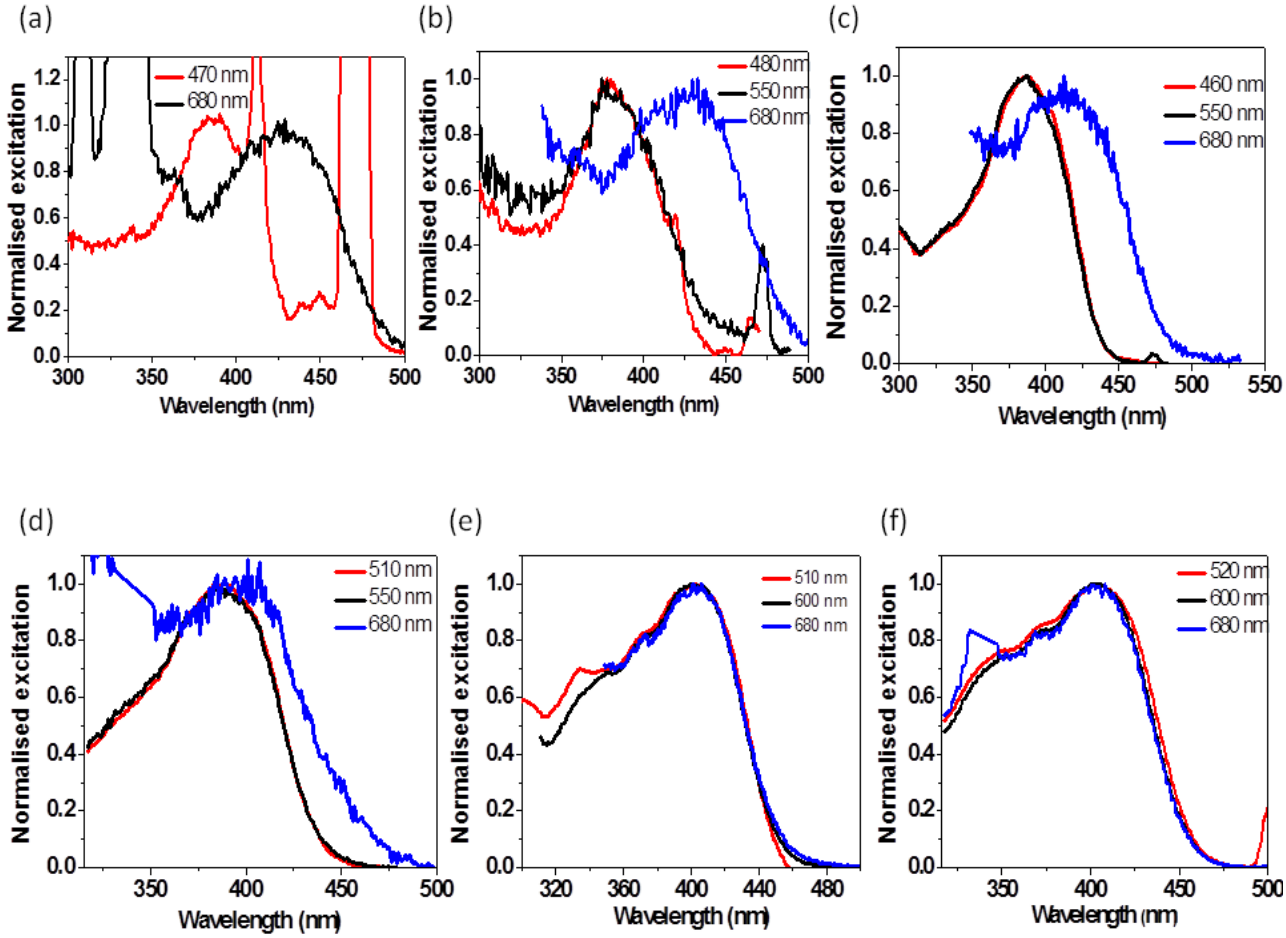


Figure-S12: Normalised excitation spectra of mOMe-HBDI in different solvents (a) Toluene (b) DCM (c) EtOAc (d) ACN (e) DMF (f) DMSO.

S8: **Time resolved fluorescence decay for all derivatives in different solvents**

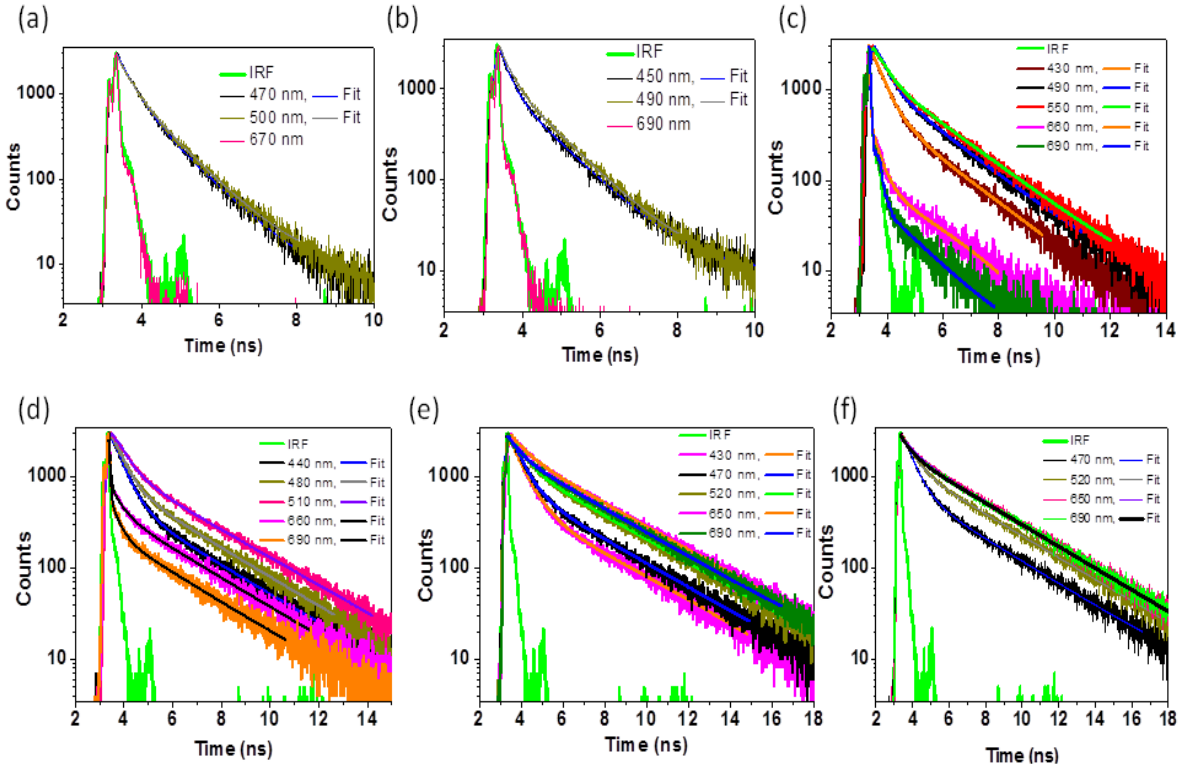


Figure-S13: Fluorescence decay (TCSPC) of mOMe-HBDI in different fluid organic solvents of different polarity (a) Toluene (b) DCM (c) EtOAc (d) ACN (e) DMF and (f) DMSO.

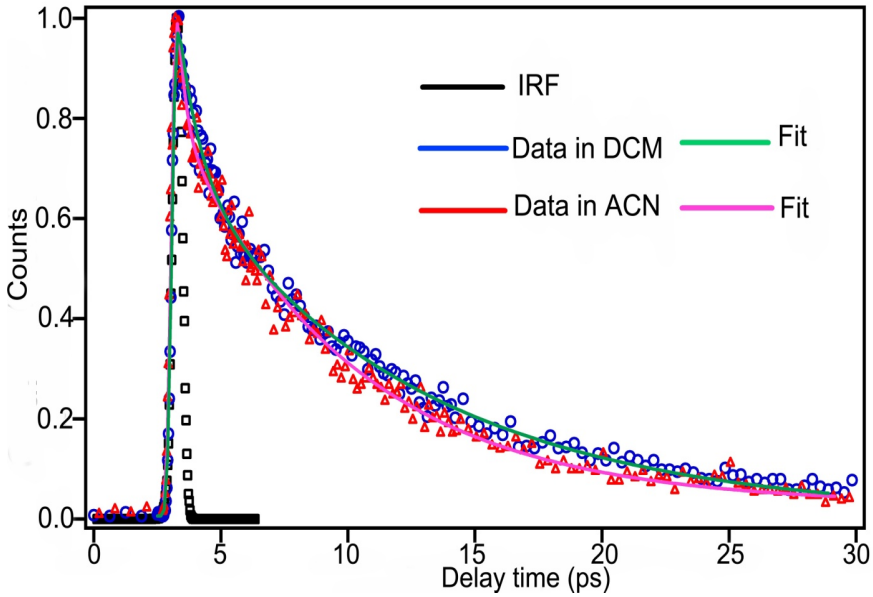


Figure-S14: Femtosecond fluorescence Up- conversion of mOMe-HBDI in DCM and ACN monitoring at the emission maxima of proton transfer band in respective solvents.

S9: **Crystallographic data of compounds.**

Table S1: Crystallographic table of compounds.

	mOMe-MBDI	mOMe-HBDI
Chemical Formula	C14H16N2O3	C13H14N2O3
Formula weight	260.29	246.26
Cryst. system	Monoclinic	Orthorhombic
Space group	*P2(1)/n*	*Pna21*
a (Å)	8.3642 (5)	13.6811 (11)
b (Å)	7.8279 (5)	11.8839 (12)
c (Å)	20.8234(14)	7.3549 (6)
α (°)	90.00	90.00
β (°)	90.819 (6)	90.00
γ (°)	90.00	90.00
Vol (Å^3)	1363.25 (15)	1195.80 (19)
D_{calcd} (g/cm^3)	1.258	1.368
μ (mm^{-1})	0.090	0.099
θ range (°)	1.96-27.00	2.2630-24.6640
Z	4	4
range *h*	–10 to+7	-17 to +9
range *k*	–4 to +10	-7 to +14
range *l*	-26 to +23	-7 to +9
Reflns collected	4942	2588

Independent reflns	2901	1520
Obsd reflns	2092	1818
T (K)	293(2)	293 (2)
*R*1	0.0694	0.0535
*wR*2	0.2220	0.1403
GOF	1.147	1.065
CCDC No.	1417290	1417289

S10: Details of computational analysis

All the calculations were carried out using Gaussian 09 software package.[4] The electronic ground state geometry optimization in the gas phase has been performed using Density Functional Theory (DFT). Becke's three-parameter hybrid exchange functional and Lee-Yang-Parr correlation functional (B3LYP) were utilized in the calculation of Frontier Molecular Orbitals with a 6-31++G basis set.

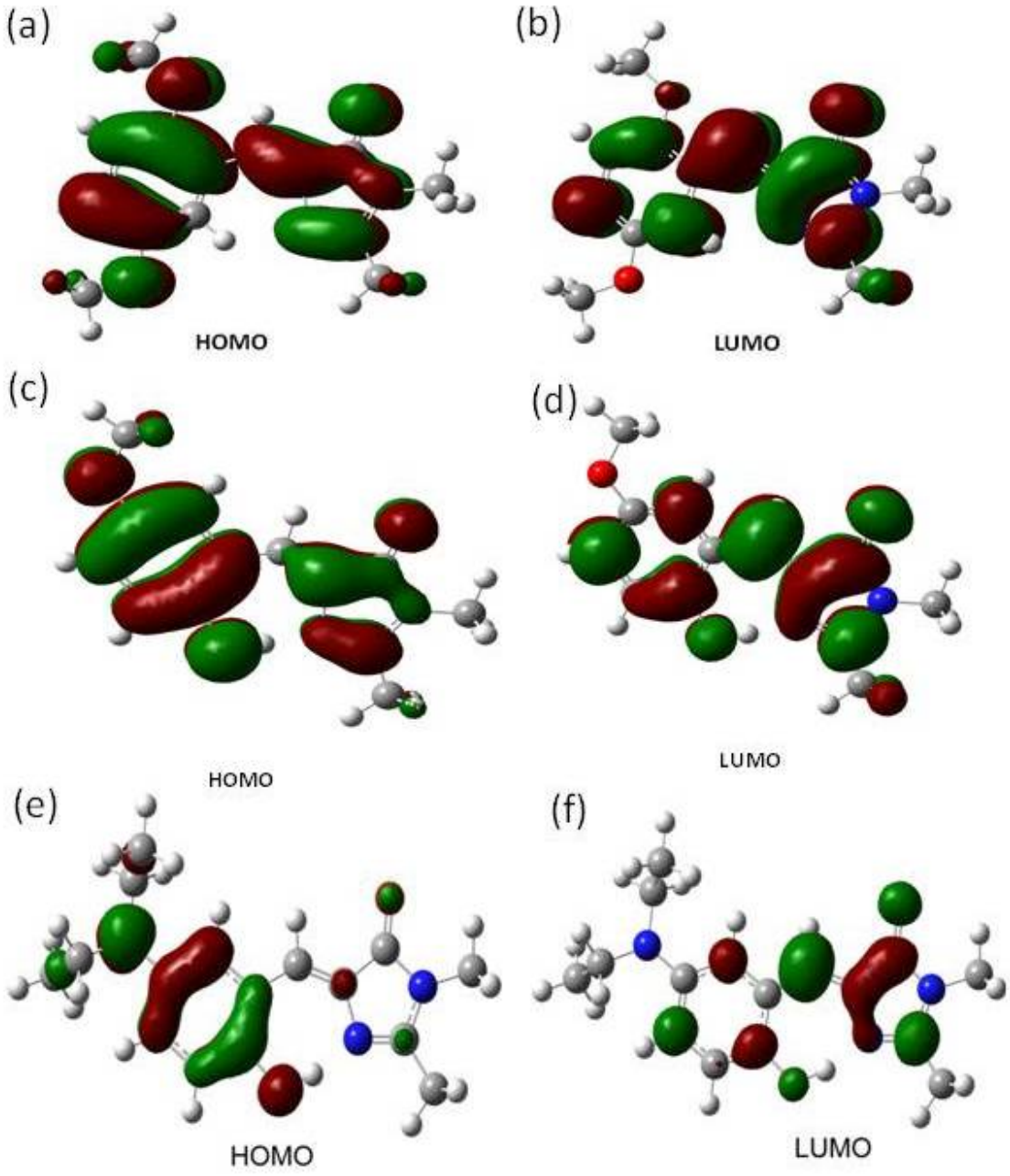


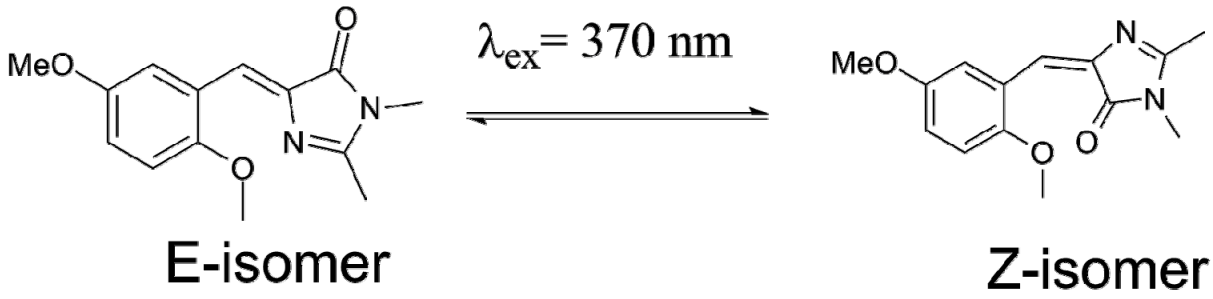
Figure S15: Frontier molecular orbitals of mOMe-MBDI (a, b), mOMe-HBDI (c, d) and MOHIM (e,f) calculated at B3LYP /6-31G^{++} level.

S11: Calculation of ZE Isomerisation efficiency:

To measure Z-E isomerisation quantum yield (ϕ_{ZE}), solutions of low (mM) concentration range were used and irradiated with 370 nm light (8W mercury lamp) without applying any special filter. The irradiation was followed by ^{1}H NMR at different time intervals. Since distinctive ^{1}H NMR signal was obtained for Z and E isomer, integration of the NMR peak corresponding to each isomer allowed us to know the isomer ratio at a certain time of irradiation. p-HBDI served as the reference standard (φ_{ZE}= 0.48 in ACN)[5]. The isomerisation quantum yield was calculated with the help of the following equation: [5,6]

$$\frac{C_r \times V_r \times P_r}{\Phi_{ZEr} \times t_r} = \frac{C_s \times V_s \times P_s}{\Phi_{ZE_s} \times t_s} \qquad \text{---------- eq-2}$$

where 'C' is the concentration of the substrate, 'P' is the amount (%) of the initial Z isomer that undergoes conversion to the E-isomer after irradiation, 'V' is the volume of solutions, 't' is the irradiation time and the subscripts 'r' and 's' stands for the reference standard (p-HBDI) and the substrate (mOMe-MBDI) respectively. 'P' was determined from the integrated intensity of the ^{1}H NMR peak for E-isomer. The sample of ~10^{-3} (M) concentration was prepared in NMR tube (Sigma Aldrich) and was kept in UV chamber for irradiation with 370 nm light source.



Scheme S2: Z-E isomerisation of mOMe-MBDI exposed at 370 nm

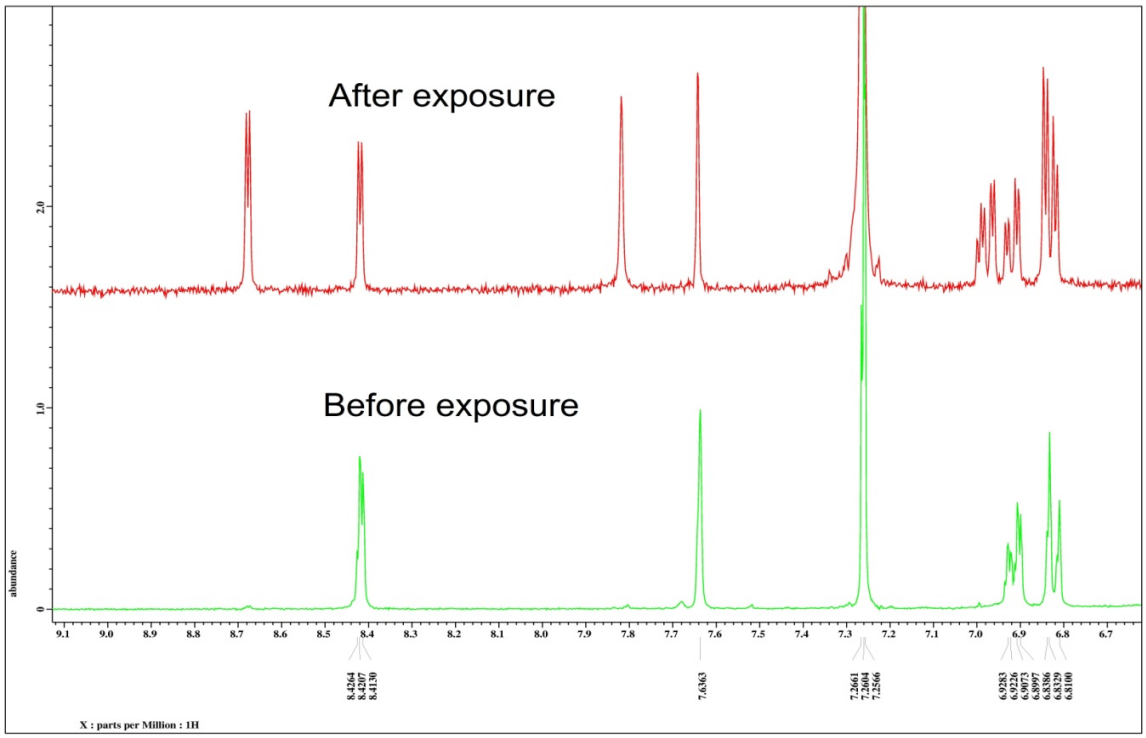


Figure-S16: ZE isomerisation of mOMe-MBDI in $CDCl_3$. Only aromatic region has been shown for clarity

Table S2: Table containing ZE isomerisation quantum yield in different solvent

Compound	Solvent	ϕ_{ZE}
mOMe-MBDI	CDCl3	0.54
	DMSO-d6	0.41

S12: Ground state conformational analysis from ^{1}H NMR of MOMIM and MOHIM.

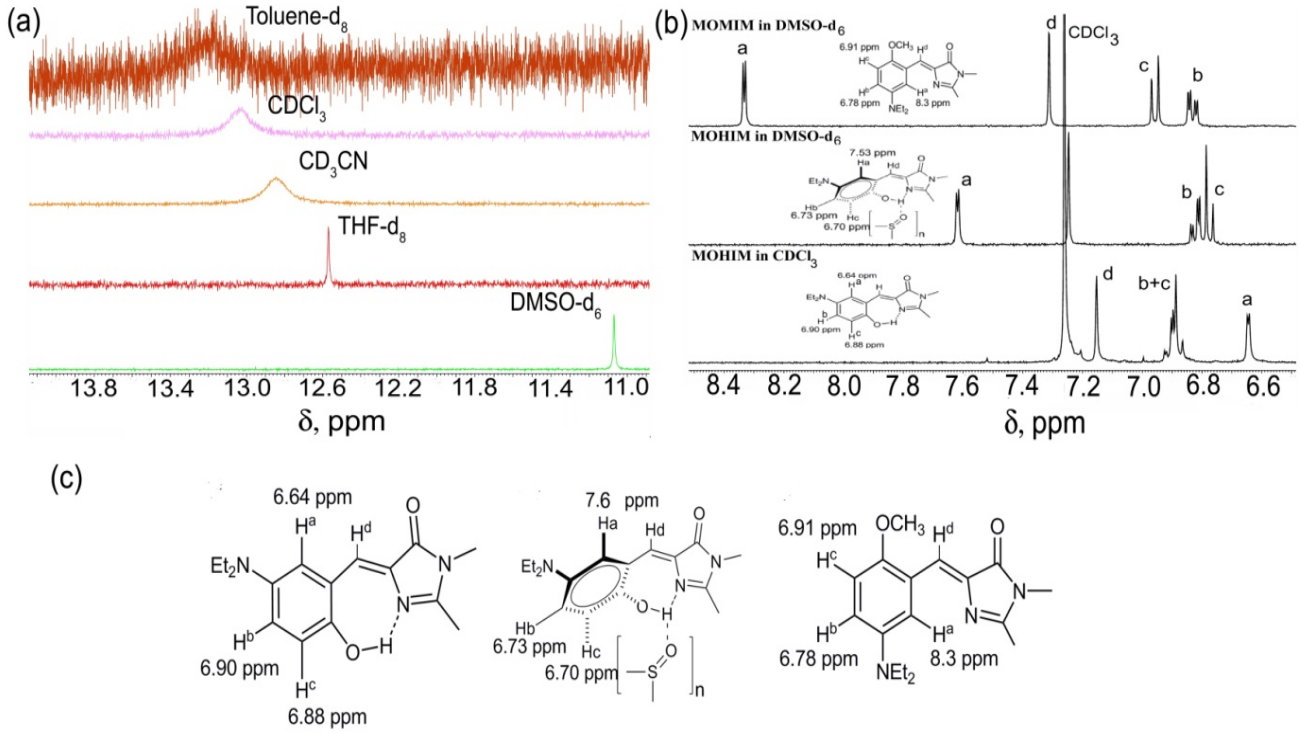


Figure S17: OH peak in ^{1}H NMR spectrum of MOHIM in different deuterated organic solvents (a). ^{1}H NMR spectrum showing the shift of 'a' proton indicating solution state variation in conformation of MOHIM and MOMIM (b). Molecular structure with conformation in solution; MOHIM in $CDCl_3$ (left), MOHIM in DMSO-d_6 (middle) MOMIM in $CDCl_3$ (right) (c).

S13: Steady state and time resolved spectroscopic studies of MOHIM and MOMIM.

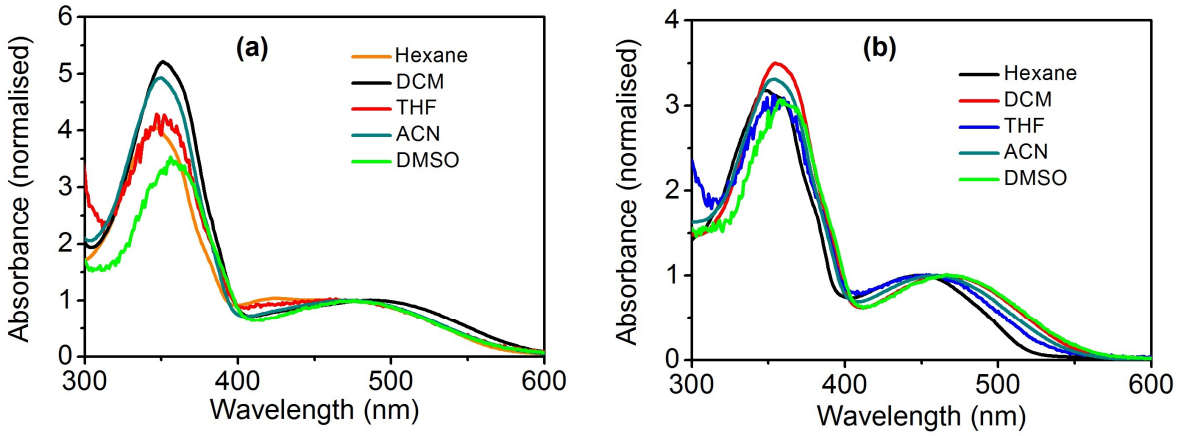


Figure S18: Absorption spectra of MOHIM (a) and MOMIM (b). Following literature reports[6-8] longer wavelength absorption band to $S_1 \leftarrow S_0$ transition and shorter wavelength absorption band to $S_2 \leftarrow S_0$ transition.

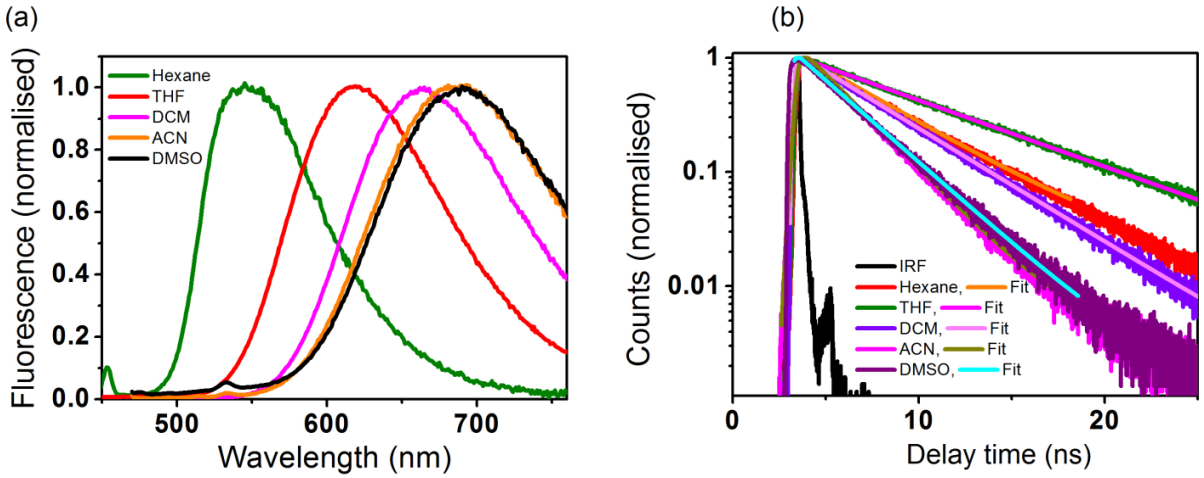


Figure S19: steady state (a) and time resolved (b) fluorescence behaviour of MOMIM.

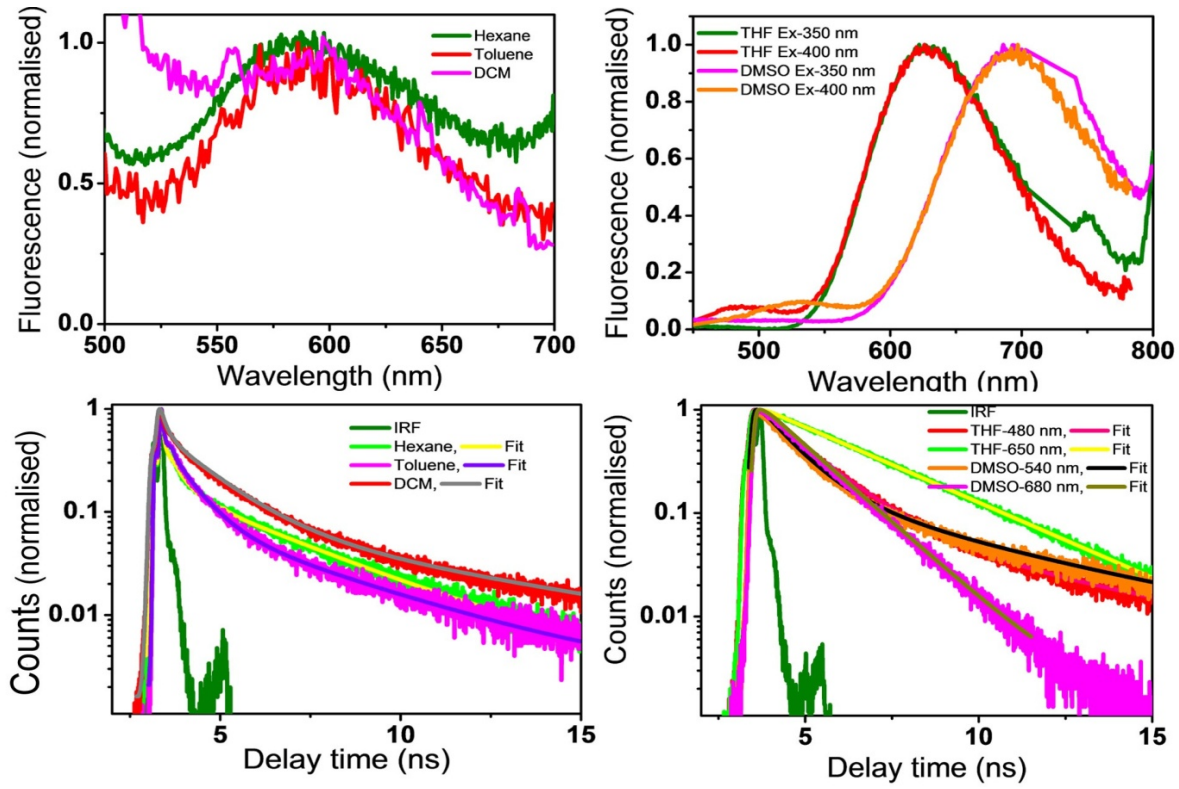


Figure S20: steady state (upper panel) and time resolved (lower panel) fluorescence behaviour of MOHIM.

Table S3: Table containing all the photophysical data of MOMIM and MOHIM

Compound	Solvent	Polarity index	λ_{abs} (nm)	λ_{em} (nm)	ϕ_{fl}^{*}	λ_{mon} (nm)	τ_1 ns	τ_2 ns	τ_3 ns
MOMIM	Hexane	0.0	350, 447	545	0.10	550	5.12		
	DCM	3.1	354, 466	661	0.02	660	4.12		
	THF	4.0	353, 460	620	0.03	620	7.44		
	ACN	5.8	353, 463	688	0.006	690	2.78		
	DMF	6.4	359, 461	671	0.010	670	4.16		
	DMSO	7.2	358, 473	695	0.006	690	3.02		
Compound	Solvent	Solvent basicity β value	λ_{abs} (nm)	λ_{em} (nm)	ϕ_{fl}^{*}	λ_{mon} (nm)	τ_1 ns (B1)	τ_2 ns (B2)	τ_3 ns (B3)
MOHIM	Hexane	0.0	346, 471	588	~10^{-4}	590	<0.07 (22.18)	0.40(17.32)	3.00(60.50)
	DCM	0.10	351, 487	591	~10^{-4}	590	0.12 (13.19)	1.35(49.96)	6.85(36.84)
	THF	0.55	349, 473	493, 630	0.003	500 650	1.40 (75.13) 3.00 (100)	5.85(24.87)	
	DMF	0.69	354,476	528,690	0.002	530 690	0.50 (8.42) 1.65 (100)	3.55(91.42)	
	DMSO	0.76	349, 476	535, 696	0.005	540 700	1.0 (55.47) 1.44 (100)	4.70 (44.53)	

S14: Solvent polarity index (P') and H-bond accepting ability (β) parameter:

The polarity index P' has been defined[9] as the measure of the ability of a solvent to interact with various polar test solutes.

$$P' = \log(K''_g)_{ethanol} + \log(K''_g)_{dioxane} + \log(K''_g)_{nitromethane} \quad \text{----------eq-3}$$

Where K''_g refers to the solute solubility constant corrected for the molecular weights of both solvent and solute.[9] Magnitudes of solvent polarity index (P') have been adopted from reference 9.

The term hydrogen-bond acceptor (HBA) refers to the acceptance of the proton of a hydrogen bond. The hydrogen bond accepting (HBA) ability has been defined as the parameter β. It is related by the Kamlet-Taft equation with the spectral shift ν of the solute in different solvent as[10]

$$\nu(1000/cm) = \nu_0 + p\pi^* + a\alpha + b\beta \quad \text{----------eq-4}$$

where, α and β are solvent hydrogen bond donating acidity and solvent hydrogen bond accepting basicity of solvents respectively. π* is the solvent dipolarity/ polarisability parameter. Solute parameters p can be related to the relative dipole moments of the molecules. Proton susceptibility parameters a and b reflect the relative proton basicity and acidity of the chromophore.[10] Magnitudes of H-bond accepting ability (β) parameter have been adopted from reference 10.

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