Electronic Supporting Information for:

Green synthesis of fluorescent Schiff bases: Chemo-photophysical characterization, X-ray structures, and their bioimaging

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1. Experimental section

1.1 General remarks

The reagents were procured from Aldrich Chemical Company. Solvents were used without further purification. The syntheses were performed in ultrasonic bath Branson 2510R-DTH with 40 kHz of frequency. Retsch MM200 mixer mill at 25 Hz was used for the ball-milling experiments with a 20 mL stainless-steel vessel and 10 mm stainless balls. UV spectra were obtained with a Shimadzu 2401 PC UV/VIS spectrophotometer and emission spectra were performed on a Fluorolog-3 fluorescence spectrometer. Melting points were confirmed by Electrothermal Mel-Temp apparatus. ^{1}H NMR (400.00 MHz) and ^{13}C (100.00 MHz)) spectra were recorded using equipment Bruker advance DPX 400. All NMR spectra were performed in dimethyl sulfoxide deuterated (DMSO-d_6) as solvent. The ^{1}H and ^{13}C NMR shifts are referenced concerning $(CH_3)_4Si$. Chemical shifts are given parts per million (ppm) downfield from the reference, and all coupling constants (*J*) are reported in Hertz (Hz). High-resolution mass spectra were acquired by LC/MSD TOF on an Agilent Technologies instrument with APCI as chemical ionization in positive mode. Mass spectra were recorded on an AB Sciex API 2000™ LC/MS/MS System.

*1.2 Synthesis of Schiff bases **1-2***

Conventional heating

A mixture of de 4-aminobenzoic acid (2.0 mmol) and *p*-substituted aldehyde (2.0 mmol) in methanol was heating for 4 hours. After the solvent was evaporated in vacuum obtaining a colored solid as a product, solids were filtered and washed with cold methanol and hexane. Compounds **1** and **2** crystallized from MeOH-$CHCl_3$ (3:7) by slow evaporation.

Ultrasound

A mixture of de 4-aminobenzoic acid (2.0 mmol) and *p*-substituted aldehyde (2.0 mmol) in methanol was irradiated in an ultrasonic bath at 40 kHz for 30 min afforded a precipitated, which was washer and filtered with cool ethanol. For the solvent-free reaction, the reagents are mixed in a flask and subsequently irradiated with an ultrasound bath.

Mechanochemical

A mixture of de 4-aminobenzoic acid (2.0 mmol) and *p*-substituted aldehyde (2.0 mmol) was placed in a 20 ml stainless-steel vessel and 10 mm stainless balls. The vial

was placed in a vibrational ball mill and subjected to milling for 30 min with a 25 Hz frequency. The resulting powder was precipitated in MeOH/$CHCl_3$. For the synthesis of compound **2**, a Teflon seal was placed between the vessel and the top closure of the stainless-steel vessel. Solids are recrystallized in AcOEt and washed with cold methanol and hexane.

1.3 Crystal structure analysis

A suitable crystal covered with a layer of hydrocarbon/Paratone-N oil was selected and mounted on a Cryo-loop, and immediately placed in the low temperature nitrogen stream. The X-ray intensity data of **2** were measured at 100(2) K, on a Bruker SMART APEX II CCD area detector system whereas **1** were measured at 100(2) K, on a Bruker D8 Quest with a Photon 100 CMOS detector. These instruments are equipped with an Oxford Cryosystems 700 series cooler, a graphite monochromator, and a Mo Kα fine-focus sealed tube (λ = 0.71073 Å). Intensity data were processed using the Bruker Apex program suite. Absorption corrections were applied using SADABS. Initial atomic positions were located by direct methods using XS or XT, and the structures of the compounds were refined by the least-squares method using SHELXL[1-2] within Olex2[3] GUI. All the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included at calculated positions and refined riding on corresponding carbons. There are two molecules of **1** in the asymmetric unit. The core atoms of one of these molecules shows positional disorder over two sites, which was resolved satisfactorily. CCDC 2084947-2084948 files contain the supplementary crystallographic data. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge, CB2 1EZ, UK).

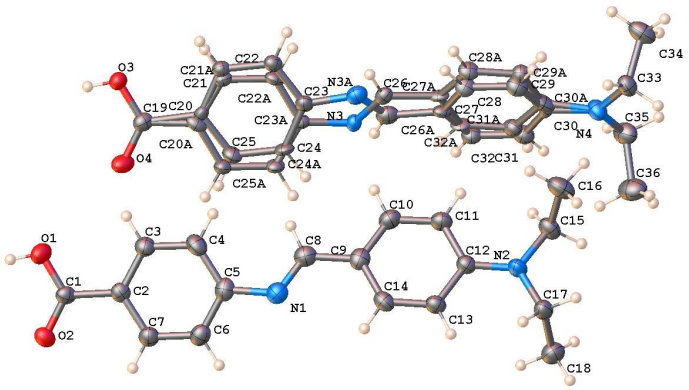


Figure S1. Structure of compound **2**.

Table S1. Crystal data and structure refinement for **1**.

Empirical formula	$C_{18}H_{20}N_2O_2$
Formula weight	296.36
Temperature/K	99.99
Crystal system	triclinic
Space group	P-1
a/Å	8.0487(7)
b/Å	14.0919(12)
c/Å	15.0169(13)
α/°	111.429(2)
β/°	101.274(3)
γ/°	94.147(3)
Volume/Å^3	1535.5(2)
Z	4
ρ_{calc}g/cm^3	1.282
μ/mm^{-1}	0.084
F(000)	632.0
Crystal size/mm^3	0.31 × 0.3 × 0.15
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.002 to 52.742
Index ranges	-10 ≤ h ≤ 10, -17 ≤ k ≤ 17, -18 ≤ l ≤ 18
Reflections collected	15564
Independent reflections	6253 [R_{int} = 0.0206, R_{sigma} = 0.0255]
Data/restraints/parameters	6253/11/481
Goodness-of-fit on F^2	1.042
Final R indexes [I>=2σ (I)]	R_1 = 0.0526, wR_2 = 0.1365
Final R indexes [all data]	R_1 = 0.0596, wR_2 = 0.1434
Largest diff. peak/hole / e Å^{-3}	0.67/-0.34

Table S2. Bond Lengths for 1.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O1	C1	1.2864(19)	N4	C35	1.458(2)
O2	C1	1.2641(18)	C19	C20	1.551(3)
N1	C5	1.419(2)	C19	C20A	1.425(3)
N1	C8	1.268(2)	C20	C25	1.3900
N2	C12	1.369(2)	C20	C21	1.3900
N2	C15	1.460(2)	C25	C24	1.3900
N2	C17	1.461(2)	C24	C23	1.3900
C1	C2	1.471(2)	C23	C22	1.3900
C2	C3	1.393(2)	C22	C21	1.3900
C2	C7	1.395(2)	C20A	C25A	1.3900
C3	C4	1.388(2)	C20A	C21A	1.3900
C4	C5	1.399(2)	C25A	C24A	1.3900
C5	C6	1.387(2)	C24A	C23A	1.3900
C6	C7	1.380(2)	C23A	C22A	1.3900
C8	C9	1.460(2)	C22A	C21A	1.3900
C9	C10	1.388(2)	C26	C27A	1.465(3)
C9	C14	1.402(2)	C26A	C27	1.467(3)
C10	C11	1.373(2)	C27	C28	1.3900
C11	C12	1.414(2)	C27	C32	1.3900
C12	C13	1.415(2)	C28	C29	1.3900
C13	C14	1.376(2)	C29	C30	1.3900

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C15	C16	1.513(3)	C30	C31	1.3900
C17	C18	1.513(2)	C31	C32	1.3900
O3	C19	1.2852(18)	C27A	C28A	1.3900
O4	C19	1.2609(19)	C27A	C32A	1.3900
N3	C23A	1.417(2)	C28A	C29A	1.3900
N3	C26	1.283(3)	C29A	C30A	1.3900
N3A	C23	1.424(3)	C30A	C31A	1.3900
N3A	C26A	1.272(3)	C31A	C32A	1.3900
N4	C30	1.350(3)	C33	C34	1.514(2)
N4	C30A	1.461(3)	C35	C36	1.519(3)
N4	C33	1.456(2)			

Table S3. Bond Lengths for 1.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C8	N1	C5	119.52(15)	C25	C20	C21	120.0
C12	N2	C15	121.96(13)	C21	C20	C19	121.4(3)
C12	N2	C17	121.92(13)	C20	C25	C24	120.0
C15	N2	C17	116.00(13)	C23	C24	C25	120.0
O1	C1	C2	117.68(13)	C24	C23	N3A	123.9(3)
O2	C1	O1	122.63(14)	C24	C23	C22	120.0
O2	C1	C2	119.69(13)	C22	C23	N3A	116.1(3)
C3	C2	C1	120.97(14)	C21	C22	C23	120.0

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C3	C2	C7	119.30(14)	C22	C21	C20	120.0
C7	C2	C1	119.72(13)	C25A	C20A	C19	120.5(3)
C4	C3	C2	119.98(15)	C25A	C20A	C21A	120.0
C3	C4	C5	120.62(15)	C21A	C20A	C19	119.0(3)
C4	C5	N1	125.96(15)	C20A	C25A	C24A	120.0
C6	C5	N1	115.19(15)	C25A	C24A	C23A	120.0
C6	C5	C4	118.85(15)	C24A	C23A	N3	116.7(2)
C7	C6	C5	120.79(15)	C22A	C23A	N3	123.1(2)
C6	C7	C2	120.42(15)	C22A	C23A	C24A	120.0
N1	C8	C9	121.47(15)	C21A	C22A	C23A	120.0
C10	C9	C8	119.77(15)	C22A	C21A	C20A	120.0
C10	C9	C14	117.50(15)	N3	C26	C27A	124.2(3)
C14	C9	C8	122.65(15)	N3A	C26A	C27	122.9(3)
C11	C10	C9	121.99(15)	C28	C27	C26A	123.0(3)
C10	C11	C12	120.93(14)	C28	C27	C32	120.0
N2	C12	C11	121.71(13)	C32	C27	C26A	117.0(3)
N2	C12	C13	121.20(13)	C27	C28	C29	120.0
C11	C12	C13	117.08(14)	C30	C29	C28	120.0
C14	C13	C12	120.80(14)	N4	C30	C29	121.9(3)
C13	C14	C9	121.66(14)	N4	C30	C31	118.1(3)
N2	C15	C16	112.47(14)	C29	C30	C31	120.0
N2	C17	C18	112.42(14)	C32	C31	C30	120.0

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C26	N3	C23A	122.3(3)	C31	C32	C27	120.0
C26A	N3A	C23	118.8(3)	C28A	C27A	C26	120.1(3)
C30	N4	C33	125.7(2)	C28A	C27A	C32A	120.0
C30	N4	C35	118.7(2)	C32A	C27A	C26	119.7(3)
C33	N4	C30A	119.1(2)	C29A	C28A	C27A	120.0
C33	N4	C35	115.55(13)	C30A	C29A	C28A	120.0
C35	N4	C30A	124.6(2)	C29A	C30A	N4	119.3(3)
O3	C19	C20	113.2(2)	C29A	C30A	C31A	120.0
O3	C19	C20A	122.2(2)	C31A	C30A	N4	120.4(3)
O4	C19	O3	123.04(14)	C32A	C31A	C30A	120.0
O4	C19	C20	123.7(2)	C31A	C32A	C27A	120.0
O4	C19	C20A	114.8(2)	N4	C33	C34	112.59(13)
C25	C20	C19	118.6(3)	N4	C35	C36	112.66(15)

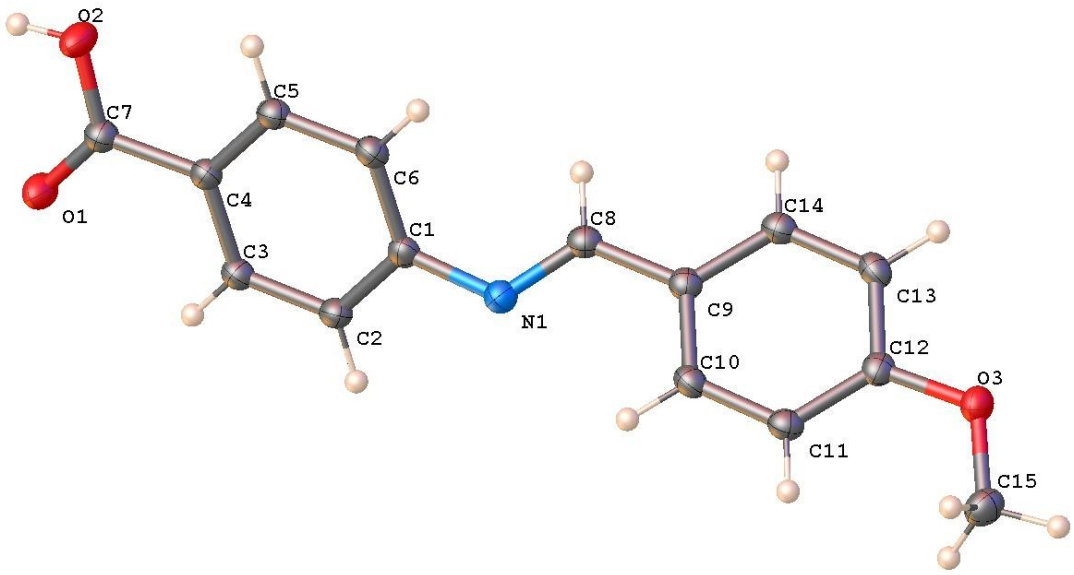


Figure S2. Structure of compound **2**.

Table S4. Crystal data and structure refinement for **1**.

Empirical formula	$C_{15}H_{13}NO_3$
Formula weight	255.26
Temperature/K	100.15
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	3.8262(6)
b/Å	15.078(2)
c/Å	21.190(3)
α/°	90
β/°	92.423(2)
γ/°	90
Volume/Å^3	1221.4(3)
Z	4

ρ_{calc}g/cm^3	1.388
μ/mm^{-1}	0.097
F(000)	536.0
Crystal size/mm^3	0.25 × 0.2 × 0.1
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.316 to 56.622
Index ranges	$-5 \leq h \leq 5$, $-19 \leq k \leq 20$, $-27 \leq l \leq 28$
Reflections collected	11643
Independent reflections	3025 [R_{int} = 0.0228, R_{sigma} = 0.0174]
Data/restraints/parameters	3025/0/174
Goodness-of-fit on F^2	1.050
Final R indexes [I>=2σ (I)]	R_1 = 0.0438, wR_2 = 0.1197
Final R indexes [all data]	R_1 = 0.0478, wR_2 = 0.1250
Largest diff. peak/hole / e Å^{-3}	0.42/-0.21

Table S5. Crystal data and structure refinement for **1**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O1	C7	1.2399(14)	C4	C5	1.3969(15)
O2	C7	1.3098(14)	C4	C7	1.4762(15)
O3	C12	1.3708(13)	C5	C6	1.3872(15)
O3	C15	1.4306(14)	C8	C9	1.4665(15)
N1	C1	1.4085(14)	C9	C10	1.3979(15)
N1	C8	1.2765(15)	C9	C14	1.4006(15)

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C1	C2	1.4004(15)	C10	C11	1.3858(15)
C1	C6	1.4009(15)	C11	C12	1.3961(15)
C2	C3	1.3841(15)	C12	C13	1.3956(15)
C3	C4	1.3973(15)	C13	C14	1.3831(15)

Table S6. Crystal data and structure refinement for **1**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C12	O3	C15	117.20(9)	O1	C7	C4	121.52(10)
C8	N1	C1	119.80(9)	O2	C7	C4	115.71(9)
C2	C1	N1	117.95(9)	N1	C8	C9	121.28(10)
C2	C1	C6	119.75(10)	C10	C9	C8	120.61(10)
C6	C1	N1	122.17(10)	C10	C9	C14	118.50(10)
C3	C2	C1	119.85(10)	C14	C9	C8	120.87(10)
C2	C3	C4	120.49(10)	C11	C10	C9	121.38(10)
C3	C4	C7	118.61(9)	C10	C11	C12	119.18(10)
C5	C4	C3	119.71(10)	O3	C12	C11	124.14(10)
C5	C4	C7	121.68(10)	O3	C12	C13	115.57(10)
C6	C5	C4	120.08(10)	C13	C12	C11	120.28(10)
C5	C6	C1	120.11(10)	C14	C13	C12	119.86(10)
O1	C7	O2	122.77(10)	C13	C14	C9	120.78(10)

1.4 NMR spectra of ^{1}H and ^{13}C.

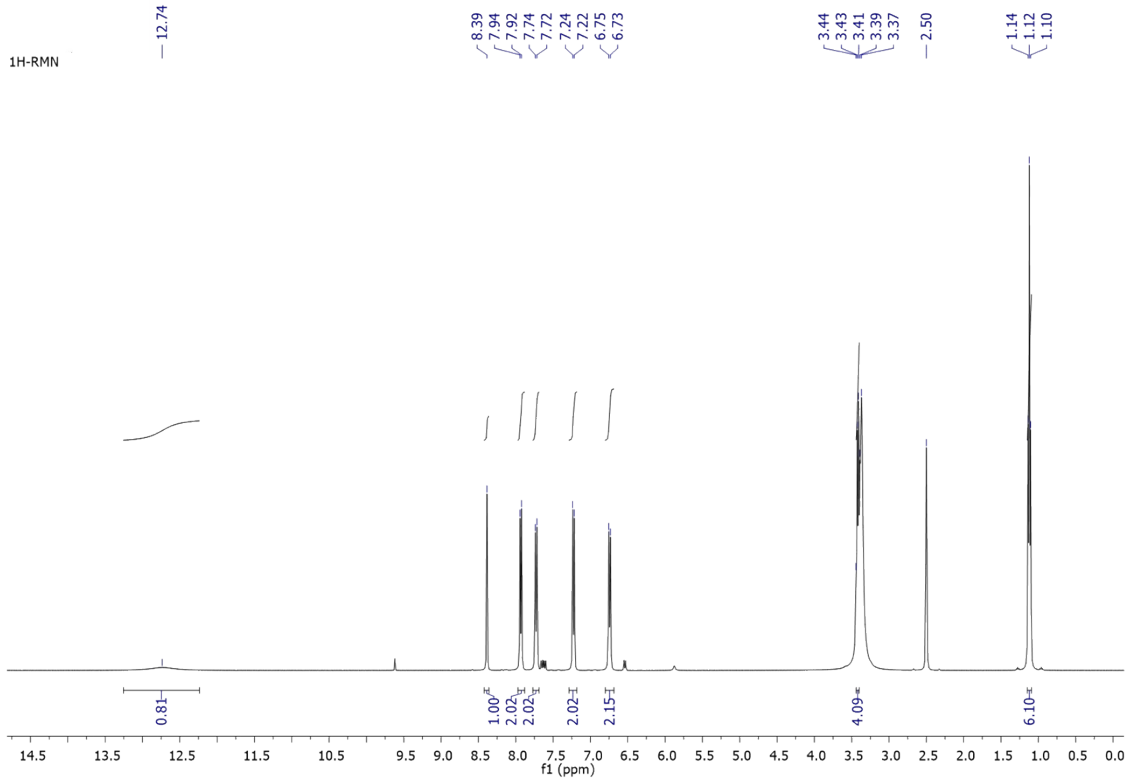


Figure S3. ^{1}H NMR spectrum for compound **1** in DMSO-d_6.

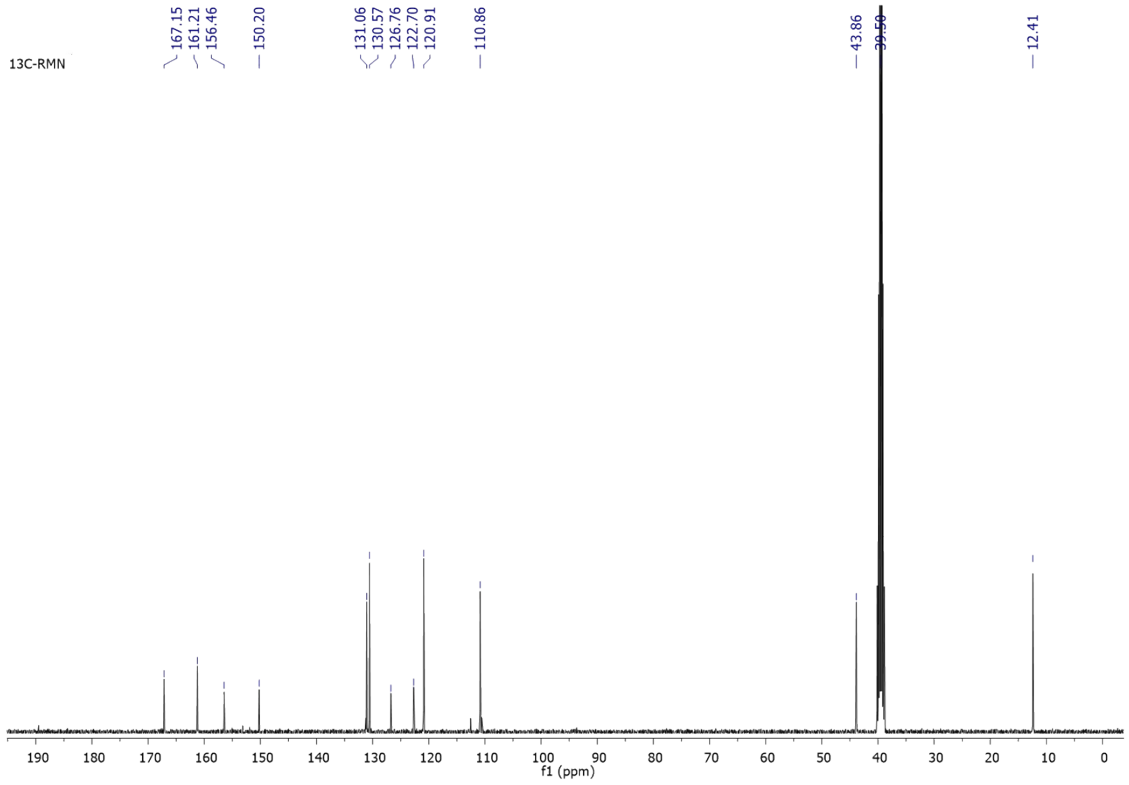


Figure S4. ^{13}C NMR spectrum for compound **1** in DMSO-d_6.

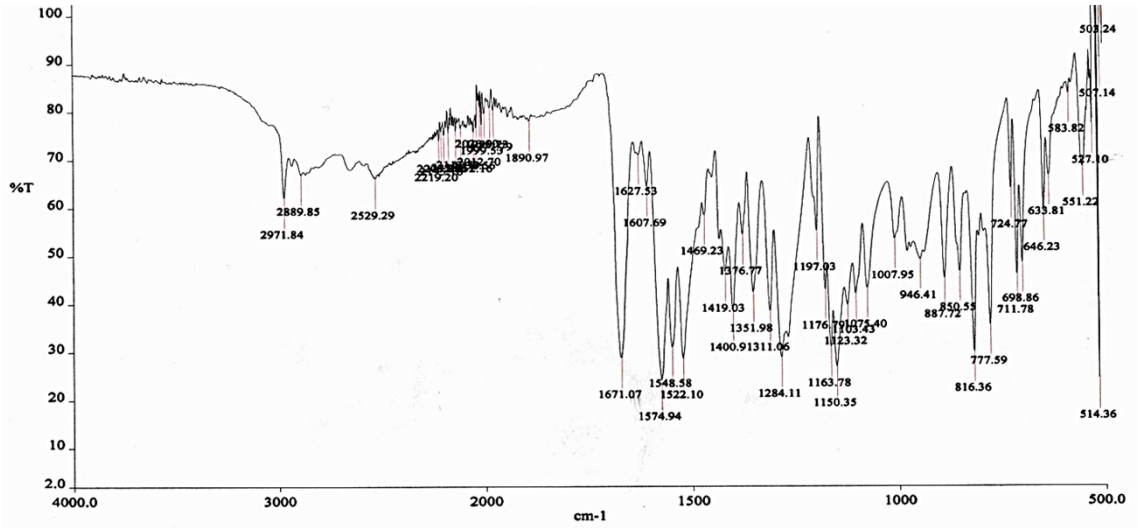


Figure S5. IR spectrum for compound **1**.

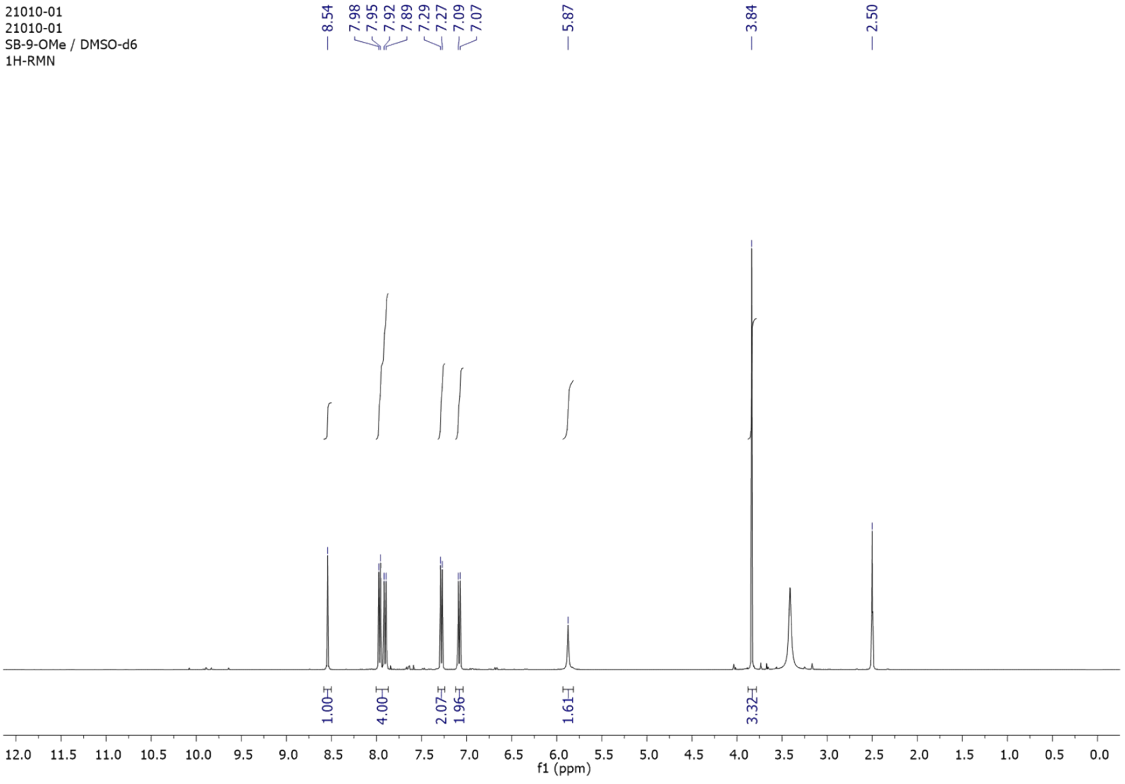


Figure S6. ^{1}H NMR spectrum for compound **2** in DMSO-d_6.

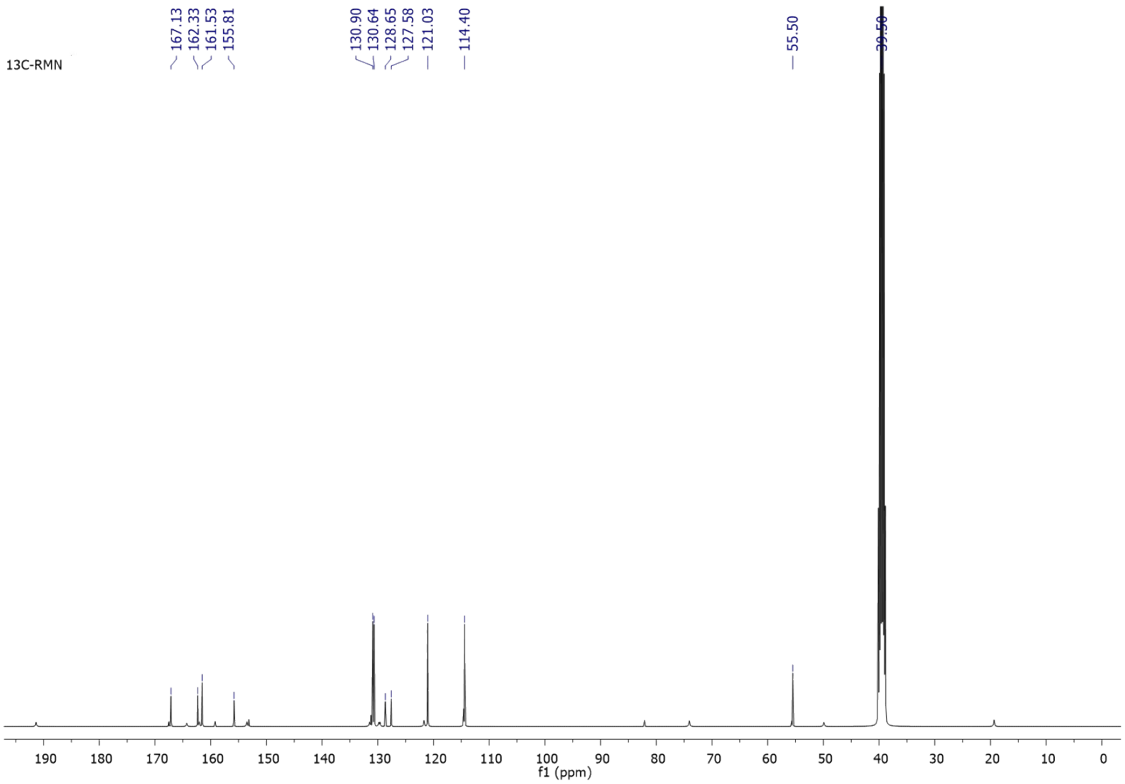


Figure S7. ^{1}H NMR spectrum for compound **2** in DMSO-d_6.

*1.5 UV absorption and emission spectra of **1** and **2**.*

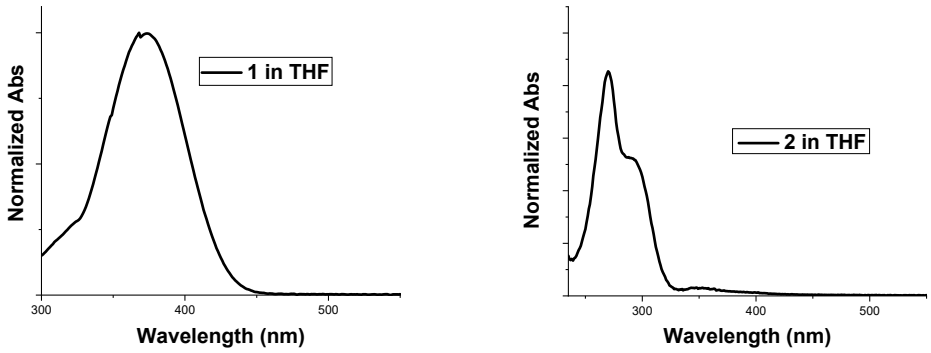


Figure S8. Absorption spectra of **1** (left) and **2** (right) in THF.

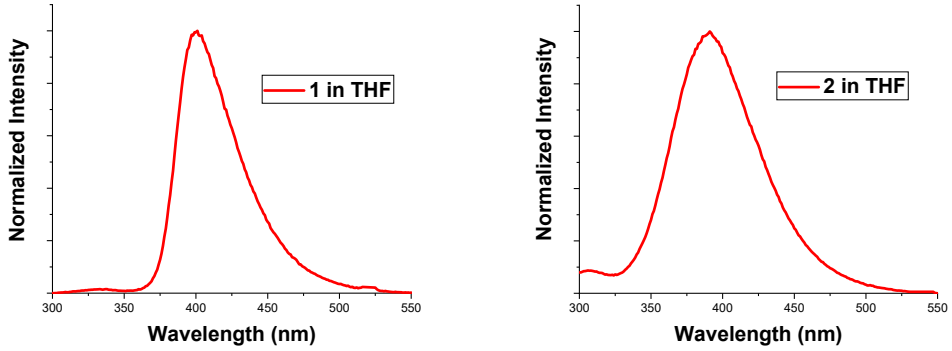
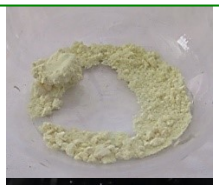
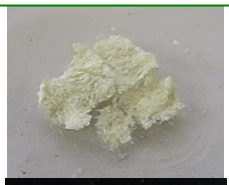


Figure S9. Emission spectra of **1** (left) and **2** (right) in THF.

Table S7. Pictures in solid state of compound **2** under day and UV (365 nm) light.

light	**Conventional Heating**	**US-dry**	**US-Methanol**	**MC**
Day light				
UV light 365 nm