Utilization of methanol and ethanol for 3,3'-Bis(indolyl)methane synthesis through activation of peroxymonosulfate over copper catalyst

Arpita Devi^a, Mrinmoy Manash Bharali^{b,c}, Subir Biswas^a, Tonmoy J. Bora^a, Jayanta K. Nath^d, Seonghwan Lee^e, Young-Bin Park^e, Lakshi Saikia^f, Manash J. Baruah^a, Kusum K. Bania^a*

^aDepartment of Chemical Sciences, Tezpur University, Assam, 784028, India. ^bDepartment of Organic synthesis and process Chemistry, CSIR-Indian Institute of Chemical Technology, Uppal Road, Hyderabad-500007, India. ^cAcademy of Scientific and Innovative Research (AcSIR), Ghaziabad-201002, India. ^dDepartment of Chemistry, S.B. Deorah College, Ulubari, Guwahati, Assam,781039, India. ^eDepartment of Mechanical Engineering, Ulsan National Institute of Science and Technology, UNST-gil 50, Ulju-gun, Ulsan, 44919, South Korea. ^fMaterial Science and Technology Division (MSTD),CSIR-North East Institute of Science and Technology, Jorhat, Assam,785006, India.

Corresponding Author's *E-mail: kusum@tezu.ernet.in

ORCID: 0000-0001-6535-3913

Table	of	contents
-------	----	----------

Table of Contents		
SL. No	Title	Page No
1	Physical Measurements	\$3-\$5
2	Characterisation of CuO catalyst	S6-S11
	2.1 XRD analysis, Fig. S1	S6
	2.2 XPS analysis, Fig. S2	S7
	2.3 SEM images, Fig. S3	S8
	2.4 TEM image and PSD of CuO catalyst, Fig. S4	S9
	2.5 EDX analysis, Fig. S5	S10
	2.6 IR and Raman analysis, Fig. S6	S11
3	Catalyst amount optimization, Fig. S7	S12
4	X-ray crystallographic analysis	S13-S14
	The C-H π and N-H π distances of the Compounds 3a , 3c and 3d , Table S1	S13
	Crystallographic data and refinement parameters for the compounds 3a , 3c and 3d , Table S2	S14
5	Characterisation of the deuterated compound di(1H-indol-3- yl)methane-d ₂ by ¹ H, ¹³ C and IR analysis, Fig. S8, S9 and S10	S15-S16

6	Catalyst recyclability study	
	(a) Activity of CuO catalyst in consecutive catalytic runs, Fig. S11	S17
	(b) Test to check the dissolution of CuO in different conditions, Fig. S12	S18
7	Preparation of Fe ₂ O ₃ catalyst and its characterization using XRD analysis, Fig. S13	S19
8	Comparative study with different catalytic systems, Table S3	S20
9	ESR spectra recorded for radical scavenging test, Fig. S14	S21
10	EPR and Cyclic Voltammetry study of CuO before and after reaction	S22
	(a) EPR analysis, Fig. S15	S22
	(b) Cyclic Voltammetry, Fig. S16	S22
11	Characterization of the Compounds	S23-S37
	NMR Analysis (3a-3k)	S23-S26
	NMR Spectra of compounds (3a-3k)	S27-37
12	References	S38

1. Physical measurements

All the characterizations and analysis were done by using the following analytical approaches to complete physical measurements. X-ray diffraction (XRD) of the sample was carried out in a Philips PANalytical Empyrean instrument, enabling low-angle measurement from 0-60° with a minimum step size (2 θ) of 0.0001, and BRUKER AXS, D8 FOCUS instrument in the 2θ value range of 5-80°. The X-ray photoelectron spectroscopy (XPS) analyses were measured with KRATOS (ESCA AXIS 165) spectrometer using Mg Ka (1253.6 eV) radiation as a source. The oven-dried samples (finely ground) were dusted on a graphite sheet (double stick) and mounted over the regular sample holder, before being transferred to an analysis chamber. The material was degassed overnight in a vacuum oven before recording the XPS. The binding energy values were corrected with reference to C 1s peak at 284.8 eV. The peaks were deconvoluted using Origin software (OriginPro 8.5). Scanning electron microscopic (SEM) images were recorded with JEOL, JAPAN (Model: JSM 6390LV) with resolution: 3nm, magnification: 3,00,000X, applied voltage: 30 kV (max.). The transmission electron microscopic (TEM) images were recorded on a JEOL (JEM-2010) instrument equipped with a CCD camera (slow-scan) with a 200 kV accelerating voltage. Energy dispersive X-ray (EDX) analysis were performed with JEOL, model No: 7582 (Oxford make), resolution: 137 eV at 5.9 KeV; Minimum weight % = .01%, sample size: 10mm dia, 1mm thick(max), dry and moisture free. The Infra-red (FTIR) spectra in the mid-IR range were recorded in a Frontier MIR-FIR from Perkin-Elmer having mid-IR range 400-4000 cm⁻¹. The IR spectra were recorded as KBr pellets. The Raman analyses were performed in an EZ Raman-N (Enwave Optronics) Raman spectrophotometer, having laser light of 150 mW, 785 nm incident wavelength through 100× (0.3 N.A.) objective lens. X-ray diffraction data were collected on a Bruker SMART Apex II CCD diffractometer using Mo K α (λ =0.71073 Å) radiation¹ and X-ray diffraction data for all crystals were collected using

Bruker SMART software. This software is also used for indexing and determination of the unit cell parameters. Cell structures were solved by direct method and refined by full-matrix least squares against F² of all data, using SHELXTL software. All the non-H-atoms were refined by full-matrix least squares in anisotropic, all H-atoms in isotropic approximation, against F^2 of all reflections. Some hydrogen atoms attached to these atoms were treated as 'riding' in calculated positions. The molecular structures were drawn at MERCURY². Thin Layer Chromatographic (TLC) plate (TLC Silica gel 60 F₂₅₄) was used for monitoring the progress of the reaction. The reactions were monitored through TLC by comparing the retention factor (R_f) of the reactant molecule with the reaction mixture. The isolated % yields are calculated after isolation of desired product using the following equation: % yield = [mole of isolated product/mole of limiting reactant] \times 100. ¹H NMR spectra are recorded on 400 spectrometers. ¹³C NMR spectra were recorded on 101MHz.¹H and ¹³C nuclear magnetic resonance (NMR) analyses were done byDRX-400 Varian, Bruker AVANCE III HD 400 MHz spectrometers. Mass spectrum (MS) was recorded in a Q-T of Electron Spray Ionization Mass spectroscopy (ESI-MS) instrument (model HAB 273) in DMSO (HPLC-grade). The EPR spectra were recorded by placing the samples in a cylindrical quartz cell and measured the ESR signals in an ESR spectrometer (JEOL instrument, Model- JES - FA200 ESR Spectrometer with X band). For this, DMPO was used as a spin scavenger. For identifying the presence of free radical, the DMPO mixed reaction mixture separated from CuO was quickly subjected to ESR measurement to record the spectrum. Similarly, the reverse was performed to get the sprectra of CuO during the course of the reaction by quickly separating the CuO from DMPO treated reaction mixture. It is to be mentioned herein that the ESR spectra were recorded thrice to get a well resolved spectra. The ESR measurements were taken according to the reported procedure.³ The cyclic voltammetry (CV) studies were performed in a CHI-600E meter from CH instruments using 3-electrode system: the glassy

carbon electrode (GCE) as a working electrode, Ag/AgCl as reference electrode and Pt wire as a counter electrode. The cyclic voltammogram of the CuO catalyst was recorded by dropcasting an ink preparedby mixing 1 mL of ethanol/H₂O, 1 mg of synthesized materials and 1 mL of Nafion (0.2% w/w) solution. The CV of the neat catalyst was recorded in acetonitrile using TBAP as the electrolyte and the same was recorded in ethanol with PMS.

2. Characterization of CuO catalyst:

2.1 XRD Analysis:



Fig. S1 X-ray diffraction (XRD) pattern of CuO catalyst (black line).

2.2 XPS Analysis:

XPS spectra of Cu 2p, O1s, and C 1s are shown in Fig.2. In the spectra of Cu 2p (Fig. S2a), the peaks at 953.7 eV and 933.6 eV were characteristic ofCu $2p_{1/2}$ and Cu $2p_{3/2}$ in CuO, respectively.⁴ The peak of Cu $2p_{1/2}$ was accompanied by a satellite peak at 961.9 eV and the peak ofCu $2p_{3/2}$ was accompanied by two satellite peaks at 943.6 and 941.2 eV.The XPS spectra of O1s(Fig. S2b) represented two peaks at 529.6 and 531.5 eV. The intense peak at 529.6 eV was assigned to lattice oxygen in CuO lattice. The second peak at 531.5 eV originated from the oxygen defects/vacancies within the CuO matrix.⁵ All of the above XPS peaks were fitted with respect to the C 1s peak having binding energy of 284.7 eV (C-C), 286.0 eV (C-O) and 288.8 eV (C=O) (Fig. S2c).



Fig.S2 XPS spectra of (a) Cu 2p and (b) O 1s in CuO catalyst and (c) C 1s.

2.3 SEM images of CuO catalyst



Fig. S3 SEM images of CuO in different magnifications.

2.4 TEM image and Particle-size distribution (PSD) of CuO catalyst



Fig. S4 (a) TEM image of CuO (b) Particle size distribution of CuO from TEM images.





Fig. S5 (a) SEM image of CuO catalyst considered for EDX elemental mapping of (b) Cu and (c) O and (d) EDX spectra showing the presence of all the elements in CuO material (e) The elemental amounts are given in weight% (Au is from Au grid).

2.6 IR and Raman analysis of CuO catalyst



Fig. S6 (a) IR and (b) Raman spectra of CuO catalyst. In the IR spectra, peaks at 3430cm⁻¹ and 1630 cm⁻¹ are characteristic of O-H vibration from the adsorbed water molecules on KBr pellets.

3. Catalyst amount optimization:



Fig. S7 Graphical representation showing optimized catalyst amount.

4. X-ray Crystallographic analysis:

The CIF files containing complete information of the studied structures of compounds 3a, 3c and 3d were deposited with CCDC, deposition number 2233103, 2233142 and 2235034 respectively which are freely available upon request from the Director, CCDC,12 Union Road, Cambridge CB21EZ, UK (Fax: +44-1223-336033;email:deposit@ccdc.cam.ac.uk) or from the following website: www.ccdc.cam.ac.uk/data_request/cif

The compound 3a crystallizes in orthorhombic $P2_12_12_1$ space group whereas compounds 3c and 3d crystallize in monoclinic *I 1 c 1* space group and Cc space group respectively. The asymmetric unit contain the whole molecule in each of the compound as shown in Fig. 2(a), (b) and (c) in manuscript.

The molecules in compound **3a** were connected through N-H... π (N...C_{centroid} distance ranging from 3.47 Å to 3.44 Å) interactions in solid state. On the other hand, in compound **3c**, the molecules were connected through C-H... π (C...C_{centroid} distance ranging from 3.24Å to 4.08 Å) interactions. Besides this, C-Cl... π (Cl...C_{centroid} distance of 3.88Ű) interaction also existed in the solid-state structure of **3c**. Both C-H... π and N-H... π (N...C_{centroid} distance of 3.22 Å) existed in compound 3d. The C-H... π (C...C_{centroid} distance of 4.11 Å) interaction in **3d** was weaker than that of **3c** which might be due to the presence of larger bromine atom in **3d**.

M	olecule	C-H π distance (<u>A°</u>)	N-H π distance (<u>A°</u>)
Ce	ompound 3a	-	3.47 A° to 3.44 A°

3.24 A° to 4.08 A°

4.11 A°

Compound 3c

Compound 3d

Table S1: The C-H... π and N-H... π distances of the Compounds **3a**, **3c** and **3d**

3.22 A°

Table S2: Crystallograph	ic data and	l refinement	parameters	for the co	mpounds 3a ,	3c and
<u>3d:</u>						

Compound name	Compound 3a	Compound 3c	Compound 3d
chemical formula	$C_{18}H_{16}N_2$	$C_{18}H_{14}Cl_2N_2$	$C_{18}H_{14}Br_2N_2$
CCDC deposition number	2233103	2233142	2235034
formula mass	260.33	329.21	418.11
crystal system	Orthorhombic	Monoclinic	Monoclinic
space group	P 21 21 21	11C1	Сс
a/Å	6.607(2)	7.817(15)	12.960(5)
b/Å	10.064(2)	18.49(3)	18.557(10)
c/Å	21.600(4)	11.24(2)	7.814(3)
α/°	90.00	90.00	90.00
β/°	90.00	96.61(4)	120.687(9)
γ/°	90.00	90.00	90.00
V/Å3	1436.1(6)	1614(5)	1616.2(13)
T/K	296(2)	296(2)	296(2)
Density (g cm ⁻³)	1.204	1.355	1.718
Z	4	4	4
radiation type	Μο Κα	Μο Κα	Μο Κα
absorption coefficient, μ/mm-1	0.071	0.399	5.013
Total no. of reflections measured	3681	4036	3876
Reflections, $I > 2\sigma(I)$	2145	3327	2185
Complete to 2θ (%)	98.3	99.6	97.7
Ranges (h, k, l)	$-8 \le h \le 8$ $-13 \le k \le 13$ $-28 \le 1 \le 28$	$-10 \le h \le 10$ $-24 \le k \le 24$ $-14 \le 1 \le 14$	$\begin{array}{c} -17 \leq h \leq 17 \\ -24 \leq k \leq 24 \\ -10 \leq l \leq 10 \end{array}$
Data/ Restraints/Parameters	3681/0/245	4036/5/209	3876/3/208
R indices $[I > 2\sigma(I)]$	0.0627	0.0480	0.0529
R indices (all data)	0.1120	0.0610	0.1275
wR(F2) (all data)	0.1528	0.1238	0.1278
Goodness-of-fit	1.015	1.089	0.920

5. Characterisation of the deuterated compound *di*(*1H-indol-3-yl*)*methane-d*₂by ¹H, ¹³C and IR analysis:

Compound (d-3i): di(1H-indol-3-yl)methane-d₂



¹**H NMR (400 MHz, CDCl₃)**: δ 7.95 (s, 2H), 7.62 (d, *J* = 7.9 Hz, 2H), 7.35 (d, *J* = 8.1 Hz, 2H), 7.18 (t, *J* = 7.6 Hz, 2H), 7.08 (t, *J* = 7.5 Hz, 2H), 6.93 (d, *J* = 2.2 Hz, 2H).

¹³C NMR (101 MHz, CDCl₃): δ 136.6, 127.7, 122.3, 121.9, 119.3, 119.3, 115.7, 111.2, 29.8.



Fig. S8 ¹H NMR of di(1H-indol-3-yl)methane-d₂.



Fig. S9 ¹³C spectra of di(1H-indol-3-yl)methane-d₂.



Fig.S10 Comparison of IR spectra of di(1H-indol-3-yl)methane and its deuterated form $di(1H-indol-3-yl)methane-d_2$.

6. Catalyst Recyclability study:

(a) Activity of CuO catalyst in consecutive catalytic runs:

The recyclability test for the catalyst was done by abstracting the CuO catalyst after the first run of the reaction of indole with ethanol by a simple filtration process. Prior to its application for the next cycle, the catalyst was washed several times with hot water, ethanol and DCM to remove any bound organic components. Fortunately, the catalyst was recyclable upto 6th consecutive runs without any significant loss in catalytic activity. The reused catalyst was characterised by PXRD analysis which indicated the loss of originality of the material during its recyclability test.



Fig. S11 (a) Showing % yield of 3,3'-BIM of indole in each consecutive run of CuO catalyst (b) PXRD spectra of the recycled catalyst after six consecutive runs.



(b) Test to check the dissolution of CuO in different conditions:

Fig S12: (a) CuO catalyst in ethanol; (b) CuO in ethanol and PMS (aqueous); (c) photograph taken after shaking (b) for 2-3 min showing no dissolution of CuO; (d) photograph of (b) under UV light irradiation showing no Tyndall effect; (e), (f), (g), (h) photographs recorded similarly in methanol.

7. Preparation of Fe₂O₃ catalyst and its characterization using XRD analysis:

 Fe_2O_3 nanoparticles were synthesized by direct precipitation method using $Fe(NO_3)_3.9H_2O$ and KOH as precursors. Aqueous solutions of $Fe(NO_3)_3.9H_2O$ (0.2M) and KOH (0.4M) were prepared. The KOH solution was slowly added into the $Fe(NO_3)_3.9H_2O$ solution at room temperature under vigorous stirring. The obtained precipitate was washed several times with distilled water and ethanol. This resultant $Fe(OH)_3$ precipitate was calcined at 400 °C for 4h to obtain Fe_2O_3 .

The synthesized material was characterized by XRD. The XRD pattern of the sample composed of several diffraction peaks at (012), (104), (110), (113), (024), (116), (018), (214) and (300) assigned to the diffraction planes of α -Fe₂O₃ phase (JCPDS 79–0007).⁶



Figure S13: X-ray diffraction (XRD) pattern of Fe₂O₃ catalyst.

8. Comparative study with different catalytic systems:



 Table S3: Comparative table with different catalysts

Entry	Catalytic system	% Yield
1.	CuO	Nil
2.	PMS	Trace
3.	$Fe_2O_3 + PMS$	30%
4.	CuO + PMS	85%

9. ESR spectra recorded for radical scavenging test:



Fig. S14: EPR spectra of the reaction medium recorded after treating with DMPO separated from CuO.

10. EPR and Cyclic Voltammetry study of CuO before and after reaction





Fig. S15: EPR spectra of the CuO catalyst (red line) and EPR signal of the same recorded by extracting very quickly from the reaction mixture after 15 minutes of reaction.

(b) Cyclic Voltammetry:



Fig. S16 a) CV of CuO catalyst recorded in acetonitrile using TBAP as the electrolyte,b) CV of CuO recorded in Ethanol+PMS+H₂O. Water was used to dissolve the PMS.

11. Characterization of Compounds (3a-3k)

NMR Analysis: ¹H and ¹³C NMR

Compound 3a): 3,3'-(ethane-1,1-diyl)bis(1H-indole)^{7,8}



¹**H** NMR (400 MHz, CDCl₃): δ 7.85 (s, 2H), 7.57 (d, J = 7.9 Hz, 2H), 7.33 (d, J = 8.1 Hz, 2H), 7.16 (t, J = 7.6 Hz, 2H), 7.04 (t, J = 7.5 Hz, 2H), 6.90 (s, 2H), 4.67 (q, J = 7.0 Hz, 1H), 1.80 (d, J = 7.1 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃): δ 136.8, 127.1, 121.9, 121.8, 121.3, 119.9, 119.1, 111.2, 28.3, 21.9.

Compound 3b): 3,3'-(ethane-1,1-diyl)bis(5-methoxy-1H-indole)⁸



¹**H NMR (400 MHz, CDCl₃)**: δ 7.81 (s, 2H), 7.23 (d, *J* = 8.8 Hz, 2H), 7.01 (s, 2H), 6.93 – 6.80 (m, 4H), 4.57 (q, *J* = 7.0 Hz, 1H), 3.77 (s, 6H), 1.79 (d, *J* = 7.1 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃): δ 153.8, 131.9, 127.4, 122.2, 121.4, 111.8, 111.7, 102.0, 56.2, 28.3, 21.5.

Compound 3c): 3,3'-(ethane-1,1-diyl)bis(5-chloro-1H-indole)⁸



¹**H NMR (400 MHz, CDCl₃)**: δ 7.95 (s, 2H), 7.46 (s, 2H), 7.24 (d, *J* = 1.8 Hz, 2H), 7.09 (d, *J* = 8.6 Hz, 2H), 6.94 (s, 2H), 4.52 (q, *J* = 7.0 Hz, 1H), 1.75 (d, *J* = 7.1 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃): δ 135.2, 127.9, 124.9, 122.7, 122.3, 121.0, 119.2, 112.3, 28.3, 21.6.

Compound 3d): 3,3'-(ethane-1,1-diyl)bis(5-bromo-1H-indole)⁸



¹**H NMR (400 MHz, CDCl**₃) δ 7.97 (s, 2H), 7.64 (s, 2H), 7.28 – 7.23 (m, 2H), 7.22 (d, *J* = 8.5 Hz, 2H), 6.94 (s, 2H), 4.53 (q, *J* = 7.1 Hz, 1H), 1.76 (d, *J* = 7.1 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃): δ 135.5, 128.6, 124.9, 122.5, 122.3, 120.9, 112.7, 112.6, 28.3, 21.7.

Compound 3e): 3,3'-(ethane-1,1-diyl)bis(1H-indole-5-carbonitrile)⁸



¹**H NMR (400 MHz, CDCl₃)**: δ 8.47 (s, 2H), 7.76 (s, 2H), 7.42 (d, *J* = 8.4 Hz, 2H), 7.37 (d, *J* = 7.0 Hz, 2H), 7.18 (d, *J* = 1.7 Hz, 2H), 4.61 (q, *J* = 7.1 Hz, 1H), 1.81 (d, *J* = 7.1 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃): δ 138.6, 126.5, 125.5, 125.1, 123.3, 121.7, 120.9, 112.3, 102.2, 29.8, 21.6.

Compound 3f): 3,3'-(ethane-1,1-diyl)bis(7-methyl-1H-indole)⁷



¹**H NMR (400 MHz, CDCl₃)**: δ 7.80 (s, 2H), 7.43 (dd, J = 4.8, 4.3 Hz, 2H), 6.99 – 6.94 (m, 4H), 6.92 (dd, J = 2.3, 0.7 Hz, 2H), 4.66 (q, J = 7.1 Hz, 1H), 2.47 (s, 6H), 1.80 (d, J = 7.1 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃): δ 136.3, 126.6, 122.5, 121.0, 120.3, 119.4, 117.6, 28.5, 21.9, 16.8.

Compound 3g): 3,3'-(ethane-1,1-diyl)bis(7-methoxy-1H-indole)



¹**H** NMR (400 MHz, CDCl₃): δ 8.12 (s, 2H), 7.18 (d, J = 8.0 Hz, 2H), 6.95 (t, J = 7.8 Hz, 2H), 6.89 (d, J = 3.0 Hz, 2H), 6.62 (d, J = 7.7 Hz, 2H), 4.63 (q, J = 7.1 Hz, 1H), 3.94 (s, 6H), 1.79 (d, J = 7.1 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃): δ 146.2, 128.4, 127.2, 122.3, 120.9, 119.5, 112.7, 101.8, 55.4, 28.6, 21.9.

Anal. Calcd. for C₂₀H₂₀N₂O₂: C, 74.98; H, 6.29; N, 8.74 found C, 75.11; H, 6.36; N, 8.88.

IR (KBr): 3415, 2928, 1446, 1077 cm⁻¹

Compound 3h): 3,3'-(ethane-1,1-diyl)bis(4-(benzyloxy)-1H-indole)



¹**H** NMR (400 MHz, CDCl₃): δ 7.70 (s, 2H), 7.14 (dd, *J* = 9.5, 3.6 Hz, 2H), 7.09 (d, *J* = 3.4 Hz, 6H), 7.05 (s, 2H), 7.02 (d, *J* = 7.9 Hz, 2H), 6.91 (d, *J* = 7.9 Hz, 2H), 6.57 (d, *J* = 1.5 Hz, 2H), 6.47 (d, *J* = 7.7 Hz, 2H), 5.32 (q, *J* = 6.9 Hz, 1H), 4.91 (dd, *J* = 36.2, 11.8 Hz, 4H), 1.63 (d, *J* = 7.0 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃): δ 154.1, 138.5, 137.5, 128.2, 127.2, 127.2, 124.1, 122.4, 120.1, 117.4, 104.5, 100.8, 77.4, 77.1, 76.8, 69.8, 29.9, 23.6.

HRMS (ESI)*m*/*z* [M+H]⁺calcd for C₃₂H₂₉N₂O₂: 473.2224, found 473.2219.

IR(KBr): 3410, 2922, 1450, 1070 cm⁻¹

Compound 3i): di(1H-indol-3-yl)methane^{9,10}



¹**H NMR (400 MHz, CDCl₃)**: δ 7.93 (s, 2H), 7.63 (d, *J* = 7.4 Hz, 2H), 7.36 (d, *J* = 8.1 Hz, 2H), 7.19 (t, *J* = 7.0 Hz, 2H), 7.09 (t, *J* = 8.0 Hz, 2H), 6.95 (s, 2H), 4.25 (s, 2H).

Compound 3j): bis(5-chloro-1H-indol-3-yl)methane¹⁰



¹**H NMR (400 MHz, CDCl₃)**: δ 7.99 (s, 2H), 7.53 (s, 2H), 7.26 (d, *J* = 6.9 Hz, 2H), 7.13 (d, *J* = 10.6 Hz, 2H), 6.96 (s, 2H), 4.13 (s, 2H).

¹³C NMR (101 MHz, CDCl₃): δ 135.0, 128.8, 125.1, 123.7, 122.4, 118.8, 115.1, 112.3, 21.3.

Compound 3k): bis(1-methyl-1H-indol-3-yl)methane⁹



¹**H NMR (400 MHz, CDCl₃):** δ 7.61 (d, *J* = 7.9 Hz, 2H), 7.27 (d, *J* = 9.1 Hz, 2H), 7.20 (t, *J* = 7.8 Hz, 2H), 7.07 (t, *J* = 7.4 Hz, 2H), 6.76 (s, 2H), 4.21 (s, 2H), 3.66 (s, 6H).

¹³C NMR (101 MHz, CDCl₃): δ 137.3, 128.0, 127.1, 121.5, 119.4, 118.7, 114.4, 109.2, 32.6, 21.1.

NMR Spectra of Isolated Compounds: : ¹H &¹³C Spectra

Compound 3a: 3,3'-(ethane-1,1-diyl)bis(1H-indole)









145





135 125 115 105 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 f1 (ppm)

Compound 3d:3,3'-(ethane-1,1-diyl)bis(5-bromo-1H-indole)









80 70 f1 (ppm) Ó

145

135

125

115

105

95 90 85





80 75 f1 (ppm) 70 65 60 55 50 45

40 35 30 25 20 15 10

Compound 3g: 3,3'-(ethane-1,1-diyl)bis(7-methoxy-1H-indole)



Compound 3h: 3,3'-(ethane-1,1-diyl)bis(4-(benzyloxy)-1H-indole)



Compound 3i:di(1H-indol-3-yl)methane















12. References:

1 SAINT Plus (v 6.14); Bruker AXS Inc.: Madison, WI, 2008.

2 Macrae et al., J. Appl. Cryst., 53, 226-235, 2020.

3 K. Wang, D. Huang, W. Wang, Y. Ji and J. Niu, Environ. Int., 2020, 137, 105562.

4 K. Gupta, M. Bersani and J. A. Darr, J. Mater. Chem. A., 2016, 4, 13786-1379.

5 M. A. Khan, N. Nayan, M. K. Ahmad and C. F. Soon, *Nanomater.*, 2020, 10, 1298.

6 M. Hjiri, J. Mater. Sci.: Mater. Electron., 2020, 31, 5025-5031.

7 T. Abe, S. Nakamura, R. Yanada, T. Choshi, S. Hibino and M. Ishikura, *Org. Lett.*, 2013, **15**, 3622-3625.

8 K. Ramachandiran, D. Muralidharan and P. T. Perumal, *Tetrahedron Lett.*, 2011, **52**, 3579-3583.

9 C. Qiao, X. F. Liu, H. C. Fu, H. P. Yang, Z. B. Zhang and L. N. He, *Chem. Asian J.*, 2018, **13**, 2664-2670.

10 C. Sun, X. Zou and F. Li, Chem. Eur. J., 2013, 19, 14030-14033.