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ORIGINAL ARTICLE

An efficient protocol for the synthesis of highly sensitive indole imines utilizing green chemistry: optimization of reaction conditions

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Abstract
Novel and highly sensitive indole-based imines have been synthesized. Their synthesis has been compared employing a variety of protocols. Ultimately, a convenient, economical and high yielding set of conditions employing green chemistry have been designed for their synthesis.

Keywords Indole · Imines · Schiff bases · Green chemistry

Introduction

The Schiff bases, a subclass of imines [1–3] first discovered by Schiff in 1864 [1], are compounds with the general formula RHC = N-R^1, where R^1 may be aryl, cycloalkyl or heterocyclic groups [1,3,4]. Schiff bases have been found to exhibit a broad range of biological activities such as anticancer [5–7], antitumor [8], anti-inflammatory [9], insecticidal [10], antibacterial [11–15], antituberculosis [16,17], antimicrobial [18,19], anticonvulsant [20], antifungal [15, 21,22], antimalarial [23] and antiviral [15,24], (including antiHIV-1 [25]) activities. Imines, acting as ligands to furnish extensively used coordination complexes [26], have physiological and pharmacological importance [27], are being widely used for metal ion extraction [28] and heavy metal ion estimation in environmental samples [29]. Imines often play a major role in organic catalysis [30], e.g., cyclopropanation and epoxidation of alkenes [31,32], ring-opening polymerization of lactide [33], trimethylsilyl-cyanation of aldehyde [34], enantioselective oxidation of MeSPh [35] and enantioselective epoxidation of silyl enol ethers [28].

The nucleophilic attack of an amine at the C=O functionality is a reversible reaction and the likelihood of imine formation largely depends on the rate of H_2O removal [36]. Use of azeotropic distillation [37], dehydrating agents (Na_2SO_4 or molecular sieves etc.) [38] and dehydrating solvents [$Si(OMe)_4$ or $CH(OMe)_3$, etc.] [39,40] also facilitates H_2O removal. A lot of catalysts such as organic acids, mineral acids, Lewis acids, natural catalysts, polymers or even dehydrating agents are used for the synthesis of imine in appreciable yield (Table 1).

Green chemistry requires cleaner and eco-friendly methods of synthesis. Replacement of toxic, costly and volatile organic solvents is of prime importance. Enhancement in reaction efficiency, selectivity, ease of product separation and purification are being achieved by solvent-free approaches [41–47]. Acceptable yields of imines have also been reported in H_2O, as suspension, using no acid catalyst [48] and MW-assisted solvent-free conditions. Better selectivity and easy workup showed improvement in reaction rates [49] but this methodology is limited to small-scale reactions [50]. Table 1 presents a comparison of reported Schiff-base synthesis by protocols (entries 1–34) using organic solvents/H_2O with catalysts applying green strategies [51–80].

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Table 1 Comparison of Schiff-base synthesis by different reported methods

Entry	Eq[£]	*T*	*T* (°C)	Solvent	Catalyst	Technique	% Yields
1	1:1	24 h	Ambient	H_2O/EtOH	None	Stirring [51]	70–80
2	1:1	24 h	Ambient	EtOH	None	Reflux [52]	66
3	1:1	13–15 min	45	MeOH	None	Reflux [53]	56
4	1:1	2 h	40–50	EtOH	None	Heating [54]	77–96
5	1:5	18 h	Reflux	EtOH	None	Reflux [55]	60–87
6	1:1	3 h	Ambient	EtOH	Glacial AcOH	Stirring [56]	98
7	1:1	9–10 min	45	MeOH	Glacial AcOH	Reflux [53]	43
8	1:1	3 h	Reflux	–	Glacial AcOH	Reflux [57]	68
9	1:1	3 h	40	Dry $PhNH_2$	*p*-TsOH	Heating [58]	70
10	1:1	30–40 min	Ambient	H_2O	Conc. H_2SO_4	Stirring [59]	67
11	1:1	4 h	Reflux	EtOH	Conc.H_2SO_4	Reflux [58]	Low yield
12	1:1	5 h	0–5	H_2O	Conc. HCl	Stirring [60]	78
13	–	–	–	–	Bu_2SnCl_2	Stirring [61]	80–90
14	1:1	3 h	Ambient	EtOH	–	SAMS[¥] [62]	90
15	1:1	1–12 h	Ambient	MeOH	$[ReBr_3(CO)_3]/[TcCl_3(CO)_3]$	Metal chelation [63]	69–75
16	1:1	3 h	Reflux	–	P_2O_5/Al_2O_3	Stirring [64]	80
17	1:1	20 min	Reflux	EtOH	$CeCl_3 \cdot 7H_2O$	Reflux [65]	68
18	1:1	3 h	Reflux	DCM	$Mg(ClO_4)_2$	Reflux[58]	50–75
19	1:1	0.5 h	Ambient	3–5 mL H_2O	–	Stirring [66]	55–90
20	1:1	10–12 min	Ambient	–	–	Grinding [67]	91
21	1:1	12 h	Ambient	–	–	Grinding [68]	>99
22	1:1	5 min	Ambient	Oil*	None	Grinding [53]	98
23	1:1	30–35 min	Ambient	None	P_2O_5/SiO_2	Grinding [69]	92
24	1:1	30 min	Ambient	None	P_2O_5/SiO_2	Grinding [70]	80
24	2:1	1.5 min	MW	Silica gel	None	MW-irradiation [71]	84
25	2:1	10 min	MW	None	*p*-TsOH	MW-irradiation [72]	75
26	1:1	2 min	MW	None	None	MW-irradiation [73]	85
27	1:1	2–3 h	50	None	$Fe_2(SO_4)_3$	Heating [74]	94.5
28	1:1	20 min	Ambient	–	CES^+ HCl	Grinding [75]	40–98
29	1:1	1–120 min	Ambient/reflux	EtOH[¤]/PhH/CH_2Cl_2/Et_2O	MCM-41-SO_3H[#¤]	Stirring/Reflux [76]	60–96
30	1:1	30 min	Ambient	–	lemon juice	Stirring [77]	94
31	1:1	6 min	Ambient	–	–	Grinding [78]	85–99
32	1:1	1–24 h	60–90	–	PPG	Heating [78]	90–99
33	1:1	6–7 min	Ambient	–	–	Jet milling [79]	91–93
34	1:1	3–10 min	Ambient	EtOH	Chitosan	Stirring [80]	65–90

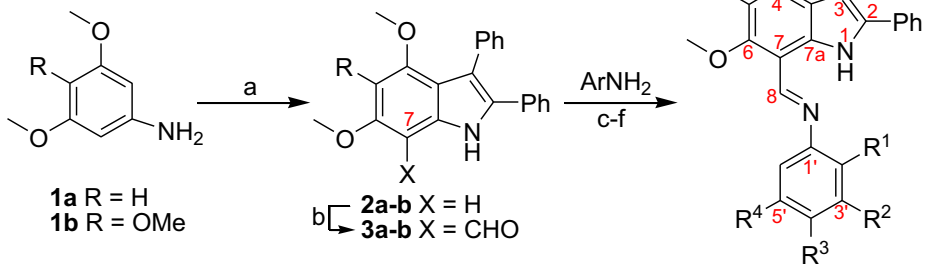
[£]Eq. of aldehyde to amine; *p*-TsOH = *p*-toluenesulphonic acid monohydrate; SAMS[¥] = Self-assembled monolayers on Au and Si substrates; ^CES = chicken egg shells; [#]MCM-41-SO_3H = Nano-ordered MCM-41 anchored SO_2OH (NaOH and Na_2CO_3 is also used to diazotize); [¤] best yield

MW microwave irradiation; *PPG* poly(propyleneglycol)

The use of aromatic solvents under high temperature conditions poses a severe health risk. Dehydrating agents are not usually efficient enough to trap all the H_2O produced during a reaction. Therefore, the exploration of a convenient, high yielding and environment friendly methodology for furnishing targeted indole-fused imines was pursued. The condensation of 7-formylindoles with various aromatic 1°-amines was carried out using different conditions which included:

1. Natural lemon juice catalyzed condensation.
2. Condensation by refluxing in dry solvent (EtOH/MeOH) without catalyst.
3. The H_2O-assisted condensation.
4. Catalyst- and solvent-free condensation (SFC).

The use of above protocols offered several advantages such as:



R					
H	OMe	R^1	R^2	R^3	R^4
4a	**4b**	H	H	H	H
5a	**5b**	H	H	Cl	H
6a	**6b**	H	Cl	H	H
7a	**-**	Cl	Cl	H	H
8a	**8b**	H	H	Me	H
9a	**9b**	H	Me	H	H
10a	**10b**	Me	Me	H	H
11a	**11b**	H	H	OMe	H
12a	**12b**	H	OMe	OMe	OMe
13a	**13b**	H	H	NO_2	H
14a	**14b**	H	NO_2	H	H
15a	**15b**	H	H	Br	H

Scheme 1 **a** benzoin, $PhNH_2$, AcOH, reflux; **b** $POCl_3$, DMF; **c** lemon juice (5 mL), ambient; **d** dry EtOH, reflux; **e** 180 ºC; **f** $H_2O/CHCl_3$ (15:1), reflux

1. Use of economically inexpensive and harmless reaction media (e.g., H_2O/lemon juice).
2. Avoidance of drying agents and catalysts.
3. Ease of product isolation (just simple filtration from reaction medium) in all above cited approaches (except 1).

The main indole nucleus of **2a** and **2b** has already been recognized for its anticancer, antimicrobial and many other biological activities. These indole imines can serve as a target for exploration of the aforementioned and many other biological activities. Furthermore, the position of donor (N) atoms in indole imines **4–15** makes these substrates potent ligands for complexation/chelation. If bound with metals to furnish six-member ring, these kinds of ligands can assume an excellent inhibitory character.

Results and discussion

We adopted a modified Bischler indole synthesis [81–83] to produce a series of 4,6-dimethoxy-2,3-diphenyl-(1*H*)-indoles **2a** and 4,5,6-trimethoxy-2,3-diphenyl-(1*H*)-indoles **2b** by employing commercially available substituted $PhNH_2$ **1a–b** and benzoin. The indole ring formation was verified by various spectroscopic techniques. Concrete evidence was provided by single-crystal XRD studies (Fig. 1, Table 4). Indoles **2a–b** were formylated via a Vilsmeier–Haack reaction in which the chlorinating agent is the chloroiminium ion intermediate, generated from the reaction between DMF and $POCl_3$ [84]. 7-Fomylindoles 3a–b were condensed with a variety of $PhNH_2$ derivatives to afford novel indole imines **4–15** (Scheme 1).

The disappearance of a signal corresponding to H^7 in the aromatic region and the emergence of a new singlet at 10.41 ppm (CHO) confirm formylation. Supportive proof came from the ^{13}C-NMR, which recorded C^5 as a doublet and C^7 as a quaternary carbon. Moreover, the aldehyde C=O singlet emerged at 188.2 ppm. The downfield shift of C^7 may be due to electron withdrawing (–I and –R) effects of the aldehyde functionality. The bathochromic shift in the λ_{max} of formylated indoles **3a** and **3b** (372, 358 nm) as compared to reactants **2a–b** (322, 318 nm) and the appearance of C=O at 1606 cm^{-1} indicate the successful introduction of a carbonyl functionality. The EIMS of formylated indoles exhibited $[M]^{+\cdot}$ as the base signal, no further fragmentation was observed. The XRD studies finally concluded the structure of **3a–b** (Fig. 1, Table 4).

In the beginning the conversion of reactants into products remained incomplete after changing a variety of protocols. This pointed out the reversibility of imines. We observed that the acidic nature of silica on TLC (for monitoring the progress of reaction) was misguiding the completion of reaction, converting the product (imine) back into the reactant (aldehyde) on the TLC plate. The TLC plate was neutralized by eluting with Et_3N and *n*-hexane (2:3), prior to TLC to monitor the progress of the reaction. Similarly, the use of neutralized $CHCl_3$ (obtained by eluting through a thin and short column packed with $NaHCO_3$) for TLC showed no decomposition. With this strategy no traces of reactant were observed, showing completion of reaction.

The reversibility in the formation of imine would be due to the poor electrophilicity of C=O (attributed to strong +R effect of OMe groups of indole ring) as well as the poor nucleophilicity of anilines. Since column chromatography could not be adopted under such circumstances, therefore, attempts were made to synthesize imines with complete consumption of reactants. Four strategies gave fruitful results briefly discussed in the introduction.

Employing NaOH [85], HCl [60] and AcOH [53,56,57] resulted in no product formation. To avoid harsh conditions

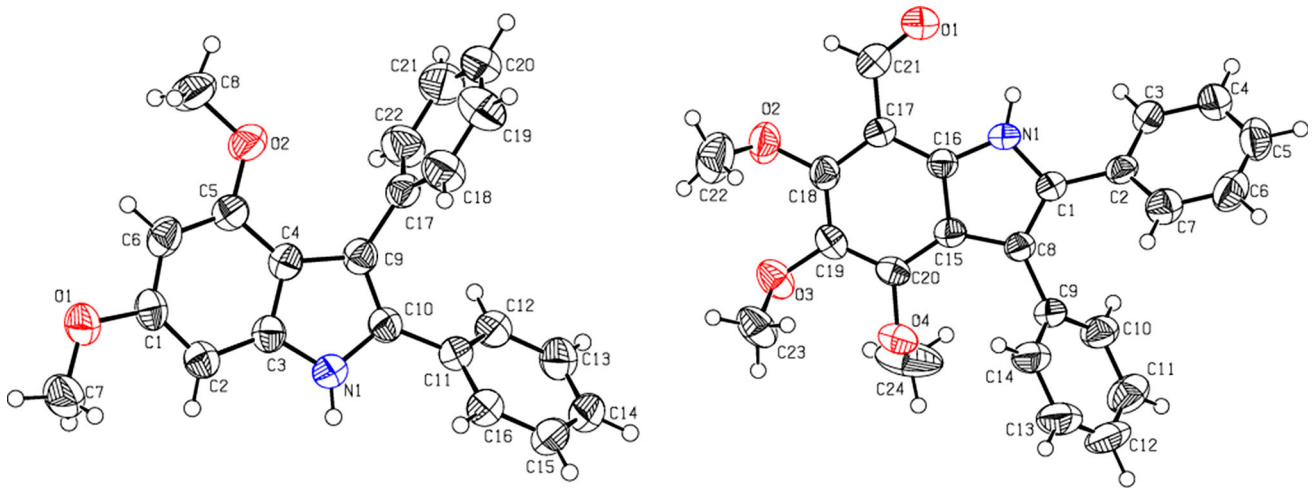


Fig. 1 ORTEP presentation of 2a (left) and 3b (right)

Table 2 Optimization of conditions for imine synthesis

Entry	Indole	Aniline^	Reagent	Temperature (time)	Solvent	Product (% Yield)
1*	**3a**	0.02	NaOH	Ambient (½ h)	EtOH	***
2	**3a**	1	AcOH (2–3 drops)	Ambient (48 h)	EtOH	**
3	**3a**	1.5	AcOH (2–3 drops)	Reflux (8 h)	EtOH	**
4	**3a**	1	HCl (2–3 drops)	Ambient (48 h)	EtOH	–
5	**3a**	1.5	HCl (2–3 drops)	Reflux (8 h)	EtOH	–
6	**3a**	1	Lemon juice (2–3 drops)	Ambient (24 h)	–	–
7	**3a**	3	Lemon juice (5 mL)	Ambient (48 h)	–	**4a** (74)
8	**3a**	1	–	Reflux (72 h)	Dry EtOH≠	**
9	**3a**	3	–	Reflux (72 h)	Dry EtOH≠	**4a** (81)
10	**3a**	1	–	120 °C (5 min)	–	–
11	**3a**	1	–	180 °C (5 min)	–	**
12	**3a**	3	–	180 °C (5 min)	–	**4a** (86)
13	**3a**	1	$H_2O/CHCl_3$(15:1)	Reflux (24 h)	–	**
14	**3a**	3	$H_2O/CHCl_3$(15:1)	Reflux (24 h)	–	**
15	**3b**	1	AcOH (2–3 drops)	Ambient (48 h)	EtOH	**
16	**3b**	1.5	AcOH (2–3 drops)	Reflux (8 h)	EtOH	**
17	**3b**	1	HCl (2–3 drops)	Ambient (48 h)	EtOH	–
18	**3b**	1.5	HCl (2–3 drops)	Reflux (8 h)	EtOH	–
19	**3b**	1	Lemon juice (2–3 drops)	Ambient (24 h)	–	—
20	**3b**	3	Lemon juice (5 mL)	Ambient (48 h)	–	**4b** (78)
21	**3b**	1	–	Reflux (72 h)	Dry EtOH≠	**
22	**3b**	3	–	Reflux (72 h)	Dry EtOH≠	**4b** (88)
23	**3b**	1	–	120 °C (5 min)	–	—
24	**3b**	1	–	180 °C (5 min)	–	**
25	**3b**	3	–	180 °C (5 min)	–	**4b** (90)
26	**3b**	1	$H_2O/CHCl_3$(15:1)	Reflux (24 h)	–	**
27	**3b**	3	$H_2O/CHCl_3$(15:1)	Reflux (24 h)	–	**4b** (86)

^Equivalents to 7-formylindole **3a/3b**; *the reactants were ground with 2.0 equivalents of NaOH in mortar and pastel; **mixture of product and reactant; ***a number of products formed; ≠molecular sieves

Table 3 Comparison of yields of imines 4–15 using different protocols

Compound	R	R^1	R^2	R^3	R^4	Lemon juice*	H_2O-mediated[£]	DryEtOH[#]	SFC[¥]
4a	H	H	H	H	H	74	**	81	86
5a	H	H	H	Cl	H	80	**	86	90
6a	H	H	Cl	H	H	64	**	71	78
7a	H	Cl	Cl	H	H	84	**	86	92
8a	H	H	H	Me	H	85	**	95	98
9a	H	H	Me	H	H	90	**	95	98
10a	H	Me	Me	H	H	72	**	83	88
11a	H	H	H	OMe	H	72	**	81	89
12a	H	H	OMe	OMe	OMe	70	**	79	87
13a	H	H	H	NO_2	H	92	**	95	98
14a	H	H	NO_2	H	H	68	**	76	82
15a	H	H	H	Br	H	76	**	80	88
4b	H	H	H	H	H	78	86	88	90
5b	OMe	H	H	Cl	H	77	81	82	84
6b	OMe	H	Cl	H	H	89	89	90	92
8b	OMe	H	H	Me	H	75	78	85	88
9b	OMe	H	Me	H	H	88	94	92	96
10b	OMe	Me	Me	H	H	72	82	84	88
11b	OMe	H	H	OMe	H	72	80	83	87
12b	OMe	H	OMe	OMe	OMe	70	82	85	89
13b	OMe	H	H	NO_2	H	78	85	91	82
14b	OMe	H	NO_2	H	H	72	77	80	95
15b	OMe	H	H	Br	H	82	88	91	94

**Product + reactant; *lemon juice as catalyst and solvent, 48 h stirring; [#]dry EtOH as solvent, 72 h reflux; [¥]heating at 180 °C for 5 min under neat conditions; [£]H_2O (15 mL)/$CHCl_3$(1 mL), 24 h reflux

and the need to use high temperature, a reported procedure, in which lemon juice was used as a catalyst, was tried [77,78]. The use of natural lemon juice as a catalyst has a few advantages over other catalysts, since it is an eco-friendly method, which in our case afforded better results (60–80% yield). Lemon juice may contain some organic acids and metals (which may coordinate to C=O to increase the electrophilicity of 7-formylindoles **3a–b**) that may contribute to its better catalytic profile. The imines thus formed were separated by partitioning between $CHCl_3$ and H_2O. A little decomposition of imines was observed upon workup, which may be due to acidic aqueous medium. Neutralizating the reaction mixture first with 0.5M *aq* $NaHCO_3$ followed by partitioning with $CHCl_3$ avoided the decomposition of imines; however, this did not improve the reaction yield.

To avoid acidic medium, 7-formylindoles **3a–b** and $PhNH_2$ derivatives were refluxed in dry EtOH, which afforded crystalline product in better yield (70–95%) by just washing thoroughly with dry EtOH/MeOH to remove unreactive aniline. The long reaction duration ($\geq$ 70 h) drove us to think about an alternate strategy.

The H_2O-assisted condensation proved to be detrimental for the formation of imines **4a–15a**; however, the same strategy furnished better yields (77–94%) for imines **4b–15b** (Table 2). The condensation of anilines with 7-formylindoles **3a–b** in molten state (solvent-free condition, SFC) provided excellent yields (78–98%, Table 2). The accumulation of H_2O-droplets above the reactants near the neck of flask indicated the progress of reaction.

In order to check the effect of substituents, on indole and phenyl rings, on the yield of product the aforementioned conditions were employed for the condensation of 7-formylindoles **3a/3b** with a variety of substituted aniline. The comparison of yields of the product is displayed in Table 3.

The successful condensation of 7-formylindoles **3a–b** with various substituted $PhNH_2$ to afford the desired imines was verified by various spectroscopic techniques. Primarily, the transformation was supported by the disappearance of IR absorptions of HC=O at 1608, 1647 cm^{-1} for **3a–b**, respectively, and emergence of new signals at 1560 $\pm$ 20 cm^{-1} indicating C=N absorptions. The λ_{max} indicated a

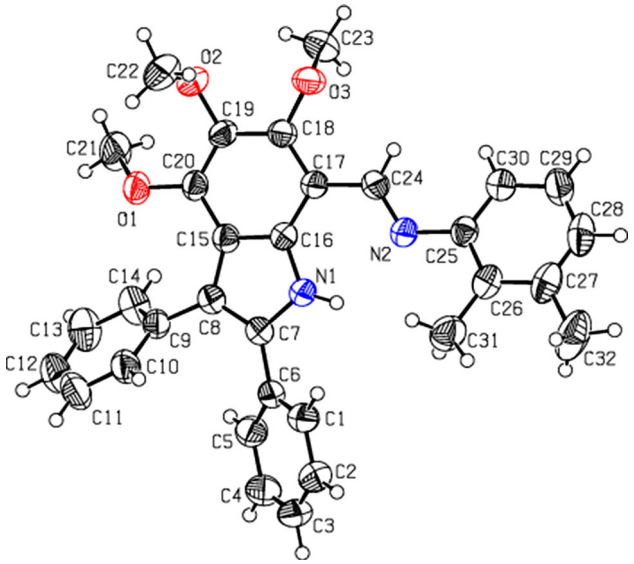


Fig. 2 ORTEP presentation of **10b**

bathochromic shift from 355 ± 20 (**3a–b**) to 370 ± 20 nm (**4–15**) due to an increase in conjugation. The expected increase in λ_{max} was about 450–500 nm due to increase in conjugation of an additional aromatic ring. It indicates that the resonance of additional phenyl ring to indole nucleus would be restricted due to the presence of two phenyl groups at indolic ring, which pushes the incoming phenyl ring out of plane; hence, its contribution to the resonance is not observed in UV/Vis studies.

The disappearance of a singlet of HC=O at 10.41/10.43 ppm of **3a** and **3b**, respectively, and the appearance of a singlet corresponding to HC=N at 9.00 ± 0.15 ppm in the ^{1} H-NMR confirmed the imine formation. Furthermore, additional signals of aromatic protons also authenticated the attachment of aniline fragment with indole nucleus. The downfield shift of NH signal from 10.43 ± 0.02 ppm (in reactants) to 11.5 ± 0.3 (in imines) is due to H-bonding between indolic NH and iminic nitrogen (HC=N). The presence of additional signals in the aromatic region corresponding to the aniline fragment confirmed the formation of imines. The disappearance of a methine carbon at 189 ± 1 ppm (corresponding to CHO) and the appearance of a methine carbon at 155 ± 4 ppm (corresponding to HC=N) in broad band ^{13} C-NMR supports our claim of successful imine formation. The XRD studies of a representative of imine (**10b**) ultimately confirmed the imine synthesis beyond any doubt (Fig. 2, Table 4).

Conclusion

The comparison of a variety of protocols for indole-based imine synthesis indicated high reversibility of the products to respective reactants (7-formylindole **3a–b** and amines) under acidic conditions. The lemon catalyzed, H_2O-assisted, EtOH-mediated and neat conditions furnished fruitful results. The lemon catalyzed protocol, although a green approach, furnished lower yields even after the use of neutralized $CHCl_3$. The EtOH-mediated strategy gave fair yields that required dry reaction conditions and reflux for a long duration, which increased the cost and decreased the efficiency of reaction. The H_2O-assisted protocol proved inadequate for the synthesis of indole imines **4a–15a** but produced good results for indole imines **4b–15b**. Stability and good yield may be favored by the presence of three methoxy groups in case of 4,5,6-trimethoxyindole imines **4b–15b**. Most efficient, economical and high yielding protocol was solvent-free synthesis, which yielded both kind of indole imines (**4a–15a** and **4b–15b**) rapidly in excellent yields.

Experimental section

Pre-coated silica gel (0.25 mm thick layer over Al sheet, Merck, Darmstadt, Germany) TLC was used to monitor reactions. Glass column-packed silica gel (0.6–0.2 mm, 60Å mesh size, Merck) was used for purification. IR spectra were recorded on a Prestige 21 (Shimadzu, Japan) as KBr disks. UV/Vis spectra were recorded on a Thermo Spectronic (UV-1700) spectrophotometer as solution in MeOH/$CHCl_3$. ^{1}H-NMR and ^{13}C-NMR were recorded in $CDCl_3$ on a Bruker AVANCE DPX (300, 400 or 500 MHz) spectrometer (Bruker, Billarica, MA) using TMS as internal standard (s, d, t, q, dd, ddd and m stands for singlet, doublet, triplet, quarterate, double doublet, doublet of double doublet and multiplet, respectively). HR ESI was recorded on a Q-TOF Ultima API (Micromass, Waters, Milford, MA) at the Biomedical Mass Spectrometry Facility (BMSF), UNSW, Sydney (Australia). Single-crystal X-Ray data were recorded on a Bruker Kappa APEX 11 CCD diffractometer. Crystallographic data in this article have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 1,562,669, 1,526,270 and 1,562,120 for **2a**, **3b** and **10b**, respectively. The X-ray structure was obtained by Prof Dr Muhammad Nawaz Tahir, Department of Physics, University of Sargodha, Sargodha (Pakistan).

Representative procedure for the synthesis of indoles 2a–b

A mixture of 3,5-$(OMe)_2$ **1a** or 3,4,5-$(OMe)_3C_6H_2NH_2$ **1b** (13.1 mmol, 3 eq) and 2-hydroxy-1,2-diphenylethanone (benzoin, 13.1 mmol, 3 eq) was stirred at 120 °C for 2 h. The mixture was cooled to ambient temperature and stirred upon the addition of $PhNH_2$ (4.4 mmol, 1 eq) and AcOH (8.1 mL,

Table 4 Crystal data of **2a**, **3b** and **10b**

Parameters	2a	3b	10b
Chemical formula	$C_{22}H_{19}NO_2$	$C_{24}H_{21}NO_4$	$C_{32}H_{30}N_2O_3$
M_r	329.38	387.42	490.58
Crystal system, space group	Monoclinic, $P2_1/n$	Monoclinic, $P2_1/c$	Triclinic, $\bar{P}1$
Temperature (K)	296	296	296
a, b, c (Å)	11.7435 (16), 9.4480 (12), 15.940 (2)	6.4296 (7), 19.445 (3), 15.858 (2)	10.4673 (10), 11.3389 (12), 11.9563 (11)
β(°)	106.682 (7)	96.230 (6)	111.371 (3), 98.510 (3), 90.301 (3)
V (Å^3)	1694.2 (4)	1970.9 (4)	1304.2 (2)
Z	4	4	2
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
μ(mm^{-1})	0.08	0.09	0.08
Crystal size (mm)	0.30 × 0.26 × 0.24	0.35 × 0.18 × 0.16	0.38 × 0.28 × 0.26
T_{min}, T_{max}	0.965, 0.985	0.960, 0.990	0.965, 0.988
Number of measured, independent and observed [$I > 2\sigma(I)$] reflections	14,818, 3912, 1657	14,638, 3829, 1668	21,177, 5701, 3479
R_{int}	0.072	0.086	0.033
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.651	0.617	0.639
R[$F^2 > 2\sigma(F^2)$],$wR(F^2)$, S	0.055, 0.138, 0.94	0.062,0.161, 0.97	0.046, 0.130, 1.02
No. of reflections	3912	3829	5701
No. of parameters	229	265	339
H-atom treatment		H-atom parameters constrained	
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (eÅ^{-3})	0.19, −0.15	0.18, −0.21	0.18, −0.21

8.5 g, 0.141 mol, 32 eq). The resulting mixture was further stirred for 5 h at 130 ºC. The resulting mixture was cooled to ambient temperature and filtered. The crude product was washed with MeOH to afford a white solid (50–60%).

4,6-Dimethoxy-2,3-diphenyl-(1H)-indole ***2a*** 3,5-$(OMe)_2$ $C_6H_3NH_2$ **1a** (2.01 g, 13.1 mmol, 3 eq), benzoin (2.8 g,13.1 mmol, 3 eq); **2a** as colorless solid (2.4 g, 56%); R_f: 0.3 (EtOAc/*n*-hexane, 2:3); mp: 240–242 °C; log ε (λ_{max} in nm): 5.56330 (274), 4.62403 (325); $\acute{\upsilon}_{max}$ (cm^{-1}): 3343 (N–H); δ_H in ppm (300 MHz): 3.73, 3.92 (3H each, s, OC$\underline{H}_3$), 6.26 (d, 1H, $J = 1.9$ Hz, H^5), 6.57 (1H, d, $J = 1.9$ Hz, H^7), 7.22–7.45 (10H, m, 2 × Ph), 8.16 (1H, bs, NH); δ_C in ppm (75 MHz): 55.2, 55.7 (q, O$\underline{C}H_3$), 86.5, 92.5 (d, C^5 and C^7), 113.0, 115.0 (s, C^3 and C^{3a}), 125.9, 126.9 (d, $C^{4'}$ and $C^{4''}$), 127.3, 127.8, 128.5, 131.5 (all 2× , d, $C^{2'}$,$C^{3'}$, $C^{2''}$ and $C^{3''}$), 131.9, 133.0 (s, $C^{1'}$ and $C^{1''}$), 135.9, 137.4 (s, C^2 and C^{7a}), 155.3, 157.8 (s, C^4 and C^6); LR EIMS (m/z, amu): 329 $[M]^{+\cdot}$ (100%), 314 $[M–Me^{\cdot}]^+$ (54%); CHNS analysis: found for $C_{22}H_{19}NO_2$: C (79.9%); H (5.7%), N (4.2%), requires: C (80.2%); H (5.8%); N (4.3%); Crystallographic data: Molecular Formula: $C_{22}H_{19}NO_2$, Molecular mass [amu]: 329.38, Crystal System: Monoclinic, a, b, c [Å]: 11.7435(16), 9.4480(12), 15.940(2), α, β, γ [°]: 90, 106.682(7), 90, Density of crystal (calc.) [g/cm^3]: 1.291.

4,5,6-Trimethoxy-2,3-diphenyl-(1H)-indole ***2b*** 3,4,5-$(OMe)_3$ $C_6H_2NH_2$ **1b** (2.40 g, 13.1 mmol, 3 eq), benzoin (2.8 g, 13.1 mmol, 3 eq); **3b** as off white crystalline solid (2.4 g, 50%); R_f: 0.25 (EtOAc/*n*-hexane, 1:7); mp: 218–220 °C; log ε (λ_{max} in nm): 2.89228 (318); $\acute{\upsilon}_{max}$ (cm^{-1}): 3363 (N–H); δ_H in ppm (300 MHz): 3.36, 3.72, 3.87 (3H each, s, OC$\underline{H}_3$), 6.78 (1H, s, H^7), 7.23–7.48 (10H , m, 2 × Ph), 8.12 (bs, 1H, N$\underline{H}$); δ_C in ppm (75 MHz): 56.3, 60.9, 61.2 (q, O$\underline{C}H_3$), 90.7 (d, C^7), 113.5, 115.8 (s, C^3 and C^{3a}), 126.4, 127.2 (d, $C^{4'}$ and $C^{4''}$), 127.9, 128.0, 128.7, 131.3 (all 2× , d, $C^{2'}$,$C^{3'}$, $C^{2''}$ and $C^{3''}$), 132.9, 133.0, (s, $C^{1'}$ and $C^{1''}$), 133.4, 136.6 (s, C^2 and C^{7a}), 136.8, 146.7, 151.0 (all s, C^4, C^5 and C^6); LR EIMS (m/z, amu): 359 $[M]^{+\cdot}$ (100%).

General procedure for formylation of indoles 3a–b

The indole **2a/2b** (3 mmol, 1 eq) was added to a stirred solution of $POCl_3$ (0.85 mL, 1.4 g, 9 mmol, 3 eq) in DMF (20 mL) at ambient temperature. The reaction was stirred at room temperature for 2.5 h before being quenched with chilled H_2O

(100 mL) and was basified with *aq.* NaOH solution (50 mL of 1 M). The resulting precipitate was filtered, washed with chilled H_2O and dried over *anhydrous* silica in desiccator under reduced pressure to afford aldehyde (90–92%) as a yellow solid.

4,6-Dimethoxy-2,3-diphenyl-(1H)-indole-7-carbaldehyde ***3a*** Indole **2a** (0.99 g), **3a** as yellow solid (0.99 g, 92%); R_f: 0.18 ($CHCl_3$/*n*-hexane, 1:4); mp: 180–182 °C; log ε (λ_{max} in nm): 3.770941 (326), 3.59740 (372); $\acute{\upsilon}_{max}$ (cm^{-1}): 1608 (C=O), 3298 (N–H); δ_H in ppm (300 MHz): 3.81, 4.00 (3H each, s, OC$\underline{H}_3$), 6.15 (1H, s, H^5), 7.23–7.36 (10H, m, 2 Ph), 10.41 (1H, s, D_2O non-exchangeable, C$\underline{H}$O), 10.59 (1H, bs, D_2O exchangeable, N$\underline{H}$); δ_C in ppm (75 MHz): 55.5, 56.4 (q, O$\underline{C}H_3$), 86.9 (d, C^5), 104.2 (s, C^7), 112.76, 114.7 (s, C^3 and C^{3a}), 126.2, 127.3 (d, $C^{4'}$ and $C^{4''}$), 127.5, 127.9, 128.5, 131.3 (all 2×, d, $C^{2'}$,$C^{3'}$, $C^{2''}$ and $C^{3''}$), 132.2, 133.3 (s, $C^{1'}$ and $C^{1''}$), 135.4, 136.8 (s, C^2 and C^{7a}), 161.7, 163.0 (s, C^4 and C^6), 188.2 (d, C^8); LR EIMS (m/z, amu): 357 $[M]^{+\cdot}$ (100%).

4,5,6-Trimethoxy-2,3-diphenyl-(1H)-indole-7-carbaldehyde ***3b*** Indole **2b** (1.08 g), **3b** as yellow solid (0.93 g, 80%); R_f: 0.65 ($CHCl_3$/*n*-hexane, 3:7); mp: 158 °C; log ε (λ_{max} in nm): 3.92456 (358); $\acute{\upsilon}_{max}$ (cm^{-1}): 1647 (C=O), 3347 (N–H); δ_H in ppm (500 MHz): 3.62, 3.89, 4.10 (3H each, s, OC$\underline{H}_3$), 7.26–7.40 (10H, m, 2Ph), 10.43 (1H, s, D_2O non-exchangeable, C$\underline{H}$O), 10.45 (1H, bs, D_2O exchangeable, N$\underline{H}$); δ_C in ppm (125 MHz): 61.5 (q, O$\underline{C}H_3$), 63.2 (2×, q, O$\underline{C}H_3$), 107.8 (s, C^7), 114.3, 118.8 (s, C^3 and C^{3a}), 126.6, 127.7 (d, $C^{4'}$ and $C^{4''}$), 128.0, 127.8, 128.6, 131.2 (all 2×, d, $C^{2'}$,$C^{3'}$, $C^{2''}$ and $C^{3''}$), 131.8, 132.0 (s, $C^{1'}$ and $C^{1''}$), 134.6, 135.2 (s, C^2 and C^{7a}), 153.1 (s, C^5), 154.0 (2×, s, C^4 and C^6), 190.0 (d, C^8); LR EIMS (m/z, amu): 388.3 $[M + 1]^{+\cdot}$ (26%); 387.3 $[M]^{+\cdot}$ (100%), 372.3 $[M–Me]^{+\cdot}$ (34%); crystallographic data; molecular formula: $C_{24}H_{21}NO_4$; molecular mass [amu]: 387.42; crystal system: monoclinic; a, b, c [Å]: 6.4296(7), 19.445(3), 15.858(2); α, β, γ [°]90: 96.230(6), 90; density of crystal (calc.) [g/cm^3] 1.306.

Procedures for the synthesis of imines 4a–15a, 4b–6b, 8b–15b

Procedure-A A mixture of 4,6-dimethoxy-2,3-diphenyl-1*H*-indole-7-carbaldehyde **3a**/4,5,6-trimethoxy-2,3-diphenyl-1*H*-indole-7-carbaldehyde **3b** (1.0/1.1 g, 2.8 mmol, 1 eq) and $PhNH_2$ derivatives (8.4 mmol, 3 eq) in dry EtOH (30 mL) with activated molecular sieves, was refluxed under stirring for 24 h. The resulting crystals (70–90%) were thoroughly washed with MeOH to remove excess of $PhNH_2$derivatives.
Procedure-B To a well stirred mixture of **3a/3b** (1.0/1.1 g, 2.8 mmol, 1 eq) and lemon juice extract (5 mL of 1.9 to 2.2 pH), the $PhNH_2$ derivatives (8.4 mmol, 3 eq) were added. The mixture was stirred at room temperature for 48 h. The reaction mixture was partitioned between H_2O (25 mL) and neutralized $CHCl_3$ (3 × 25 mL). The combined organic extract was dried over *anhydrous* Na_2SO_4, filtered and concentrated under reduced pressure to afford reddish yellow solid (70–90%). This impure product was thoroughly washed with MeOH, to remove excess $PhNH_2$derivatives, which afforded pure bright yellow imine.
Procedure-C A homogenous mixture of **3a/3b** (1.0/1.1 g, 2.8 mmol, 1 eq) and $PhNH_2$ derivatives (8.4 mmol, 3 eq) in $CHCl_3$ (1 mL) was refluxed in H_2O (15 mL) for 24 h. Upon the completion of reaction, the resulting solid (70–95%) was thoroughly washed with MeOH to remove excess of $PhNH_2$derivatives.
Procedure-D A mixture of solid **3a/3b** (1.0/1.1 g, 2.8 mmol, 1 eq) and $PhNH_2$ derivatives (8.4 mmol, 3 eq) was stirred at 200 °C for 24–48 h in a flask without stopper. The H_2O produced as a by-product was collected at the neck of the flask. Upon the completion of reaction, the resulting solid (70–95%) was thoroughly washed with MeOH to remove excess of $PhNH_2$derivatives.

N-Phenyl (4,6-dimethoxy-2,3-diphenyl-1H-indol-7-yl) methanimine ***4a*** $PhNH_2$ (0.77 mL, 1.0 g); **4a** as light yellow crystals (1.04 g, 86%); R_f: 0.33 ($CHCl_3$/*n*-hexane, 1:4); mp: 255 − −257 °C; log ε (λ_{max} in nm): 3.53965 (363); $\acute{\upsilon}_{max}$ (cm^{-1}): 1585 (C=N), 3329 (N–H); δ_H in ppm (300 MHz): 3.80, 3.98 (3H each, s, OC$\underline{H}_3$), 6.24 (1H, s, H^5), 7.21–7.44 (15H, m, 3 Ph), 9.11 (1H, s, $\underline{H}$C=N), 11.54 (1H, bs, N$\underline{H}$); LR EIMS (m/z, amu): 433 $[M + 1]^{+\cdot}$ (25%), 432 $[M]^{+\cdot}$ (100%).

N-(4-Chlorophenyl)(4,6-dimethoxy-2,3-diphenyl-1H-indol-7-yl)methanimine ***5a*** 4-$ClC_6H_4NH_2$ (1.1 g); **5a** as bright yellow crystals (1.18 g, 90%); R_f: 0.30 ($CHCl_3$/*n*-hexane, 1:4); mp: 235 °C; log ε (λ_{max} in nm): 4.24303 (379); $\acute{\upsilon}_{max}$ (cm^{-1}): 1566 (C=N), 3338 (N–H); δ_H in ppm (400 MHz): 3.78, 3.97 (3H each, s, OC$\underline{H}_3$), 6.20 (1H, s, H^5), 7.20–7.42 (14H, m, 3 Ph), 9.07 (1H, s, $\underline{H}$C=N), 11.41 (1H, bs, N$\underline{H}$); δ_C in ppm (100 MHz): 55.4, 55.7 (q, O$\underline{C}H_3$), 87.7 (d, C^5), 101.9 (s, C^7), 113.2, 114.6 (s, C^3 and C^{3a}), 122.5 (2×, d, $C^{3'''}$), 126.1, 127.0 (d, $C^{4'}$ and $C^{4''}$), 127.4, 127.8, 128.5, 131.5 (2×, d, $C^{2'}$,$C^{3'}$, $C^{2''}$ and $C^{3''}$), 129.2 (2×, d, $C^{2'''}$), 130.5 (s, $C^{4'''}$), 132.9 (2×, s, $C^{1''}$, $C^{1'}$), 135.9, 136.6 (s, C^2 and C^{7a}), 151.4 (s, $C^{1'''}$), 156.5 (d, C^8) 159.1, 159.6 (s, C^4 and C^6); CHNS analysis: found for $C_{29}H_{23}ClN_2O_2$: C (72.19%), H (4.56%), N (6.08%), requires: C (74.59%), H (4.96%), Cl (7.59%), N (6.00%), O (6.85%).

N-(3-Chlorophenyl)(4,6-dimethoxy-2,3-diphenyl-1H-indol-7-yl)methanimine ***6a*** 3-$ClC_6H_4NH_2$ (0.9 mL, 1.1 g); **6a** as light yellow crystals (1.02 g, 78%); R_f: 0.69 ($CHCl_3$/*n*-hexane, 1:1); mp: 185 °C; log ε (λ_{max} in nm): 4.02584 (379); $\acute{\upsilon}_{max}$ (cm^{-1}): 1566 (C=N), 3338 (N–H); δ_H in ppm (400 MHz): 3.79, 3.98 (3H each, s, OC$\underline{H}_3$), 6.22 (1H, s, H^5), 7.14–7.41 (m, 14H), 9.07 (1H, s, $\underline{H}$C=N), 11.36 (1H, bs,

NH); δ_C in ppm (100 MHz): 55.4, 56.6 (q, OCH$_3$), 87.6 (d, C^5), 101.7 (s, C^7), 113.0, 114.6 (s, C^3 and C^{3a}), 119.8, 121.3, 125.0 (d, C$^{2'''}$, C$^{4'''}$ and C$^{6'''}$), 126.1, 126.9 (d, C$^{4'}$ and C$^{4''}$), 127.4, 127.8, 128.5, 131.5 (2× , d, C$^{2'}$,C$^{3'}$, C$^{2''}$ and C$^{3''}$), 130.5 (d, C$^{5'''}$), 132.8, 132.9 (s, C$^{1'}$ and C$^{1''}$), 134.6 (s, C$^{3'''}$), 135.9, 136.6 (s, C^2 and C^{7a}), 151.3 (s, C$^{1'''}$), 157.0 (d, C^8), 159.3, 159.8 (s, C^4 and C^6). CHNS analysis: found for $C_{29}H_{23}ClN_2O_2$: C (72.93%), H (4.56%), N (5.69%), requires: C (74.59%), H (4.96%), Cl (7.59%), N (6.00%), O (6.85%).

N-(2,3-Dichlorophenyl)(4,6-dimethoxy-2,3-diphenyl-1H-indol-7-yl)methanimine ***7a*** 2,3-$Cl_2C_6H_3NH_2$ (1.4 g); **7a** as light yellow crystals (1.3 g, 92%); R_f: 0.33 ($CHCl_3$/*n*-hexane, 1:4); δ_H in ppm (400 MHz): 3.79, 3.97 (3H each, s, OCH$_3$), 6.21 (1H, s, H^5), 6.24 (1H, dd, J = 8.4.2.2 Hz, H^4), 7.21–7.44 (12H, m, 3 Ph), 9.05 (1H, s, HC=N), 11.28 (1H, bs, NH); δ_C in ppm (100 MHz): 55.4, 56.6 (q, OCH$_3$), 87.6 (d, C^5), 101.7 (s, C^7), 113.1, 114.7 (s, C^3 and C^{3a}), 121.1, 122.9 (d, C$^{4'''}$ and C$^{6'''}$), 126.2, 127.1 (d, C$^{4'}$ and C$^{4''}$) 127.5, 127.8 (2× , d, any two of C$^{2'}$,C$^{3'}$, C$^{2''}$ and C$^{3''}$), 128.4 (s, C$^{3'''}$), 130.7 (d, C$^{5'''}$), 128.5, 131.5 (2× , d, any two of C$^{2'}$,C$^{3'}$, C$^{2''}$ and C$^{3''}$), 132.7, 132.8 (s, C$^{1'}$ and C$^{1''}$), 133.0 (s, C$^{2'''}$), 135.8, 136.6 (s, C^2 and C^{7a}) 152.5 (s, C$^{1'''}$), 157.2 (d, C^8) 159.5, 159.9 (s, C^4 and C^6). CHNS analysis: found for $C_{29}H_{22}Cl_2N_2O_2$: C (66.86%), H (4.75%), N (5.25%), requires: C (69.47%), H (4.42%), Cl (14.14%), N (5.59%), O (6.38%).

N-(4-methylphenyl)(4,6-dimethoxy-2,3-diphenyl-1H-indol-7-yl)methanimine ***8a*** 4-$MeC_6H_4NH_2$ (0.9 g); **8a** as light yellow crystals (1.28 g, 98%); R_f: 0.3 ($CHCl_3$/*n*-hexane, 1:4); mp: 180 °C; log ε (λ_{max} in nm): 4.41288 (372); υ_{max} (cm^{-1}): 1581 (C=N), 3294 (N–H); δ_H in ppm (400 MHz): 2.38 (3H, s, ArCH$_3$), 3.79, 3.97 (3H each, s, OCH$_3$), 6.23 (1H, s, H^5), 7.20–7.42 (14H, m, 3 Ph), 9.11 (1H, s, HC=N), 11.56 (1H, bs, NH); δ_C in ppm (100 MHz): 20.9 (q, CH$_3$), 55.4, 56.8 (q, OCH$_3$), 87.9 (d, C^5), 102.2 (s, C^7), 113.2, 114.5 (s, C^3 and C^{3a}), 121.1 (2× , d, C^3), 126.0, 126.9 (d, C$^{4'}$ and C$^{4''}$), 127.4 (2× , d, C$^{2'''}$), 127.8, 128.5, 129.7, 131.5 (all 2× , d, C$^{2'}$,C$^{3'}$, C$^{2''}$ and C$^{3''}$), 132.5, 133.0 (s, C$^{1'}$ and C$^{1''}$), 134.8, 136.6 (s, C^2 and C^{7a}), 134.6 (s, C$^{4'''}$), 150.3 (s, C$^{1'''}$), 155.5 (d, C^8), 158.6, 159.2 (s, C^4 and C^6). CHNS analysis: found for $C_{30}H_{26}N_2O_2$: C (76.80%), H (6.10%), N (5.79%), requires: C (80.69%), H (5.87%), N (6.27%), O (7.17%).

N-(3-Methylphenyl)(4,6-dimethoxy-2,3-diphenyl-1H-indol-7-yl)methanimine ***9***a 3-$MeC_6H_4NH_2$ (0.9 mL, 0.9 g); **9a** as pale yellow crystals (1.28 g, 98%); R_f: 0.78 ($CHCl_3$/*n*-hexane, 1:1); mp: 193 °C; log ε (λ_{max} in nm): 4.16495 (363); υ_{max} (cm^{-1}): 1573 (C=N), 3318 (N–H); δ_H in ppm (400 MHz): 2.40 (3H, s, CH$_3$), 3.73, 3.91 (3H each, s, OCH$_3$), 6.17 (1H, s, H^5), 7.04–7.37 (14H, m, 3 Ph), 8.98 (1H, s, HC=N), 11.57(1H, bs, NH); δ_C in ppm (100 MHz): 18.5 (q, CH$_3$), 52.3, 56.5 (q, OCH$_3$), 87.8 (d, C^5), 102.3 (s, C^7), 113.2, 114.5 (s, C^3 and C^{3a}), 118.0 (d, C$^{4'''}$), 125.1 (d, C$^{2'''}$), 126.1 (d, C$^{4'}$/C$^{4''}$), 127.0 (2× , d, C$^{4'}$/C$^{4''}$ and C$^{6'''}$), 127.5, 127.7, 128.5, 131.5 (all 2× , d, C$^{2'}$,C$^{3'}$, C$^{2''}$ and C$^{3''}$), 130.2 (d, C$^{5'''}$), 131.7, 132.9 (s, C$^{1'}$ and C$^{1''}$), 136.0, 136.7 (s, C^2 and C^{7a}), 148.6 (s, C$^{3'''}$), 151.8 (s, C$^{1'''}$), 155.6 (d, C^8), 158.7, 159.3 (s, C^4 and C^6). CHNS analysis: found for $C_{30}H_{26}N_2O_2$: C (69.73%), H (5.21%), N (5.0%), requires: C (80.69%), H (5.87%), N (6.27%), O (7.17%).

N-(2,3-Dimethylphenyl)(4,6-dimethoxy-2,3-diphenyl-1H-indol-7-yl) methanimine ***10a*** 2,3-$Me_2C_6H_3NH_2$ (1 mL, 0.99 g); **10a** as yellow crystals (1.13 g, 88%); R_f: 0.35 ($CHCl_3$/*n*-hexane, 1:4); mp: 205 °C; log ε (λ_{max} in nm): 4.67862 (364); υ_{max} (cm^{-1}): 1585 (C=N), 3350 (N–H); δ_H in ppm (400 MHz): 2.35, 2.39 (3H each, s, ArCH$_3$), 3.78, 3.96 (3H each, s, OCH$_3$), 6.23 (1H, s, H^5), 6.93 (1H, d, J = 7.7 Hz, H$^{4'''}$), 7.03 (1H, d, J = 7.4 Hz, H$^{6'''}$), 7.12–7.44 (11H, m, 2 Ph and H$^{5'''}$), 9.01 (1H, s, HC=N), 11.62 (1H, bs, NH); δ_C in ppm (100 MHz): 14.3, 20.3 (q, CH$_3$), 55.4, 56.8 (q, OCH$_3$), 87.9 (d, C^5), 102.4 (s, C^7), 113.2, 114.5 (s, C^3 and C^{3a}), 121.1 (d, C$^{4'''}$), 126.1, 126.2, 126.7, 126.9 (all d, C$^{4'}$,C$^{4''}$, C$^{5'''}$ and C$^{6'''}$), 127.4, 127.8, 128.5, 131.5 (all 2× , d, C$^{2'}$,C$^{3'}$, C$^{2''}$ and C$^{3''}$), 129.9 (s, C$^{2'''}$/C$^{3'''}$), 132.8, 132.9 (s, C$^{1'}$ and C$^{1''}$), 136.1 (s, C$^{2'''}$/C$^{3'''}$), 136.7, 137.3 (s, C^2 and C^{7a}) 152.1 (s, C$^{1'''}$), 155.7 (d, C^8) 158.6, 159.2 (s, C^4 and C^6). CHNS analysis: found for $C_{31}H_{28}N_2O_2$: C (77.03%), H (5.12%), N (5.49%), requires: C (80.84%), H (6.13%), N (6.08%), O (6.95%).

N-(4-Methoxyphenyl)(4,6-dimethoxy-2,3-diphenyl-1H-indol-7-yl)methanimine ***11a*** 4-$MeOC_6H_4NH_2$ (1.0 g); **11a** as greenish yellow crystals (1.15 g, 89%); R_f: 0.61 ($CHCl_3$/*n*-hexane, 1:1); mp: 171 ° C; log ε (λ_{max} in nm): 3.65085 (379); υ_{max} (cm^{-1}): 1543 (C=N), 3345 (N–H); δ_H in ppm (400 MHz): 3.69 (3H, s, OCH$_3$ at 4"'), 3.76, 3.89 (3H each, s, OCH$_3$), 6.14 (1H, s, H^5), 6.87 (2H, d, J = 8.2, H$^{3'''}$), 7.12–7.34 (12H, m, 2 Ph and H$^{2'''}$), 9.03 (1H, s, HC=N), 11.50 (1H, bs, NH); δ_C in ppm (100 MHz): 55.3, 55.6, 56.8 (all q, OCH$_3$), 87.9 (d, C^5), 102.2 (s, C^7), 113.1, 114.5 (s, C^3 and C^{3a}), 114.4 (2× , d, C$^{3'''}$), 122.2 (2× , d, C$^{2'''}$), 126.1, 126.9 (d, C$^{4'}$ and C$^{4''}$), 127.4, 127.8, 128.5, 131.5 (all 2× , d, C$^{2'}$,C$^{3'}$, C$^{2''}$ and C$^{3''}$), 132.9, 133.1 (s, C$^{1'}$ and C$^{1''}$), 136.1, 136.6 (s, C^2 and C^{7a}), 146.0 (s, C$^{1'''}$), 154.6 (d, C^8), 154.6 (s, C^4), 158.5, 159.1 (s, C$^{4'''}$ and C^6). CHNS analysis: found for $C_{30}H_{26}N_2O_3$: C (74.04%), H (4.97%), N (4.88%), requires: C (77.90%), H (5.67%), N (6.06%), O (10.38%).

N-(3,4,5-Trimethoxyphenyl)(4,6-dimethoxy-2,3-diphenyl-1H-indol-7-yl) methanimine ***12a*** 3,4,5-$(OMe)_3C_6H_2NH_2$ (1.54 g); **12a** as shiny yellow crystals (1.27 g, 87%); R_f: 0.08 ($CHCl_3$/*n*-hexane, 1:4); mp: 215 °C; log ε (λ_{max} in nm): 4.07061 (379); υ_{max} (cm^{-1}): 1581 (C=N), 3337 (N–H); δ_H in ppm (400 MHz): 3.73, 3.80, 3.92 (3H each, s, OCH$_3$), 3.86 (6H, s, OCH$_3$), 6.17 (1H, s, H^5), 6.44 (2H, s, H$^{2'''}$ and H$^{6'''}$), 7.12–7.36 (10H, m, 2 Ph), 8.99 (1H, s, HC=N), 11.33 (1H,

bs, NH); δ_C in ppm (100 MHz): 55.4, 56.2, 56.3, 56.8, 61.1 (q, OCH$_3$), 87.7 (d, C^5), 98.5 (2× , d, C$^{2'''}$ and C$^{6'''}$), 101.9 (s, C^7), 113.1, 114.6 (s, C^3 and C^{3a}), 126.1, 127.0 (d, C$^{4'}$ and C$^{4''}$), 127.5, 127.9, 128.5, 131.5 (all 2× , d, C$^{2'}$,C$^{3'}$, C$^{2''}$ and C$^{3''}$), 133.0 (2× , s, C$^{1'}$ and C$^{1''}$), 136.0, 137.6 (s, C^2 and C^{7a}), 149.4 (s, C$^{1'''}$), 153.6 (d, C^8), 156.0 (3× , s, C$^{3'''}$, C$^{4'''}$, C$^{5'''}$), 158.9, 159.4 (s, C^4 and C^6). CHNS analysis: found for $C_{32}H_{30}N_2O_5$: C (72.57%), H (5.09%), N (4.69%), requires: C (73.55%), H (5.79%), N (5.36%), O (15.31%).

N-(4-Nitrophenyl)(4,6-dimethoxy-2,3-diphenyl-1H-indol-7-yl)methanimine ***13a*** 4-$NO_2C_6H_4NH_2$ (1.2 g); **13a** as rusty yellow crystals (1.31 g, 98%); R_f: 0.52 ($CHCl_3$/*n*-hexane, 1:3); mp: 266 °C; log ε (λ_{max} in nm) 3.98706 (351); $\acute{\upsilon}_{max}$ (cm^{-1}): 1583 (C=N), 3345 N–H); δ_H in ppm (400 MHz): 3.82, 3.98 (3H each, s, OCH$_3$), 7.08–7.29 (10H, m, 2 Ph), 7.36 (2H, d, J = 5.0Hz, H$^{2'''}$), 8.25 (2H, d, J = 5.0Hz, H$^{3'''}$), 9.14 (1H, s, HC=N), 11.25 (1H, bs, NH).

N-(3-Nitrophenyl)(4,6-dimethoxy-2,3-diphenyl-1H-indol-7-yl)methanimine ***14a*** 3-$NO_2C_6H_4NH_2$ (1.2 g); **14a** as orange crystals (1.1 g, 82%); R_f: 0.18 ($CHCl_3$/*n*-hexane, 1:1); mp: 268 °C; log ε (λ_{max} in nm): 4.15902 (347); $\acute{\upsilon}_{max}$ (cm^{-1}): 1578 (C=N), 3310 (N–H); δ_H in ppm (400 MHz): 3.80, 3.99 (3H each, s, OCH$_3$), 6.22 (1H, s, H^5), 7.22–7.58 (12H, m, 3 Ph), 8.03 (1H, d, J = 7.8 Hz, H$^{4'''}$), 8.10 (1H, t, J = 2.0 Hz, H$^{2'''}$), 9.13 (1H, s, HC=N), 11.26 (1H, bs, NH); δ_C in ppm (100 MHz): 55.4, 56.5 (q, OCH$_3$), 87.5 (d, C^5), 101.7 (s, C^7), 113.0, 114.8 (s, C^3 and C^{3a}), 115.6 (d, C$^{5'''}$), 119.5 (d, C$^{6'''}$), 126.2, 127.1 (d, C$^{4'}$ and C$^{4''}$), 127.5, 127.8, 128.6, 131.4 (all 2× , d, C$^{2'}$,C$^{3'}$, C$^{2''}$ and C$^{3''}$), 128.1 (d, C$^{4'''}$), 129.7 (d, C$^{2'''}$), 132.8, 133.0 (s, C$^{1'}$ and C$^{1''}$), 135.7, 136.6 (s, C^2 and C^{7a}), 149.1 (s, C^3), 154.2 (s, C^1), 157.2 (d, C^8), 159.8, 160.2 (s, C^4 and C^6). CHNS analysis: found for $C_{29}H_{23}N_3O_4$: C (69.59%), H (4.57%), N (7.84%), requires: C (72.94%), H (4.85%), N (8.80%), O (13.40%).

N-(4-Bromophenyl)(4,6-dimethoxy-2,3-diphenyl-1H-indol-7-yl)methanimine ***15a*** 4-$BrC_6H_4NH_2$ (1.5 g); **15a** as dark yellow crystals (1.26 g, 88%); R_f: 0.71 (EtOAc/$CHCl_3$/*n*-hexane, 1:3:6); mp: 246 °C; log ε (λ_{max} in nm): 4.46683 (382); $\acute{\upsilon}_{max}$, cm^{-1} (KBr): 1578 (C=N), 3336 (N–H); δ_H in ppm (400 MHz): 3.73, 3.91 (3H each, s, OCH$_3$), 6.15 (1H, s, H^5), 7.09 (1H, d, J = 8.7Hz, H$^{3'''}$), 7.13–7.35 (10H, m, 2 Ph), 7.43 (1H, d, J = 8.0Hz, H$^{2'''}$), 9.00 (1H, s, HC=N), 11.33 (1H, bs, NH); δ_C in ppm (100 MHz): 55.4, 56.6 (q, OCH$_3$), 87.6 (d, C^5), 101.9 (s, C^7), 113.0, 114.6 (s, C^3 and C^{3a}), 118.5 (s, C$^{4'''}$), 123.0 (2× , d, C$^{3'''}$), 126.1, 127.0 (d, C$^{4'}$ and C$^{4''}$), 127.5, 131.5, 128.6, 131.4 (all 2× , d, C$^{2'}$,C$^{3'}$, C$^{2''}$ and C$^{3''}$), 132.1 (2× , d, C$^{2'''}$), 132.9, 133.0 (s, C$^{1'}$ and C$^{1''}$), 135.9, 136.6 (s, C^2 and C^{7a}), 151.9 (s, C$^{1'''}$), 156.5 (d, C^8), 159.1, 159.6 (s, C^4 and C^6).

N-Phenyl(4,5,6-trimethoxy-2,3-diphenyl-1H-indol-7-yl)methanimine ***4b*** $PhNH_2$ (0.77 mL, 1.0 g); **4b** as yellow crystals (1.08 g, 90%); R_f: 0.44 ($CHCl_3$/*n*-hexane, 1:1); mp: 168 °C; log ε (λ_{max} in nm): 5.25953 (364); $\acute{\upsilon}_{max}$ (cm^{-1}): 1570 (C=N), 3390 (N–H); δ_H in ppm (500 MHz): 3.55, 3.90, 4.04 (3H each, s, OCH$_3$), 7.21–7.43 (15H, m, 3 Ph), 9.04 (1H, s, HC=N), 11.38 (1H, bs, NH); δ_C in ppm (125 MHz): 61.3 , 61.6, 62.9 (q, OCH$_3$), 108.7 (s, C^7), 114.3, 118.8 (s, C^3 and C^{3a}), 121.2 (4× , d, C$^{2'''}$ and C$^{3'''}$), 126.4, 127.4 (d, C$^{4'}$ and C$^{4''}$), 127.7, 129.3, 128.6, 131.3 (2× , d, C$^{2'}$, C$^{3'}$, C$^{2''}$ and C$^{3''}$), 128.0 (d, C$^{4'''}$), 131.7, 132.5 (s, C$^{1'}$ and C$^{1''}$), 134.9, 135.7 (s, C^2 and C^{7a}), 142.2 (s, C$^{1'''}$), 151.3, 152.5, 153.5 (s, C^4, C^5 and C^6), 156.7 (d, C^8). CHNS analysis: found for $C_{30}H_{26}N_2O_3$: C (77.53%), H (5.61%), N (5.81%), requires: C (77.90%), H (5.67%), N (6.06%), O (10.38%).

N-(4-Chlorophenyl)(4,5,6-trimethoxy-2,3-diphenyl-1H-indol-7-yl)methanimine ***5b*** -$ClC_6H_4NH_2$ (1.1 g); **5b** as light yellow crystals (1.08 g, 84%); R_f: 0.60 ($CHCl_3$/*n*-hexane, 1:4); mp: 150 ° C; log ε (λ_{max} in nm): 5.39486 (364); $\acute{\upsilon}_{max}$ (cm^{-1}): 1595 (C=N), 3350 (N–H); δ_H in ppm (400 MHz): 3.50, 3.80, 3.99 (3H each, s, OCH$_3$), 7.17–7.36 (14H, m, 3 Ph), 8.95 (1H, s, HC=N), 11.22 (1H, bs, NH); δ_C in ppm (100 MHz): 61.4 , 61.6, 63.0 (all q, OCH$_3$), 108.3 (s, C^7), 114.3, 118.6 (s, C^3 and C^{3a}), 122.5 (2× , d, C$^{3'''}$), 126.5, 127.4 (d, C$^{4'}$ and C$^{4''}$), 127.8, 128.0, 128.7 (all 2× , d, any three of C$^{2'}$, C$^{3'}$, C$^{2''}$ and C$^{3''}$), 129.4 (2× , d, C$^{2'''}$), 131.3 (higher than 2× , s of C$^{4'''}$ and d of C$^{2'}$/C$^{3'}$/C$^{2''}$/C$^{3''}$ merged), 131.7, 132.6 (s, C$^{1''}$, C$^{1'}$), 134.6, 135.6 (s, C^2 and C^{7a}), 140.0 (s, C$^{1'''}$), 150.9, 152.1, 153.4 (all s, C^4, C^5 and C^6), 157.0 (d, C^8). CHNS analysis: found for $C_{30}H_{25}ClN_2O_3$: C (69.99%), H (4.76%), N (5.04%), requires: C (72.50%), H (5.07%), Cl (7.13%), N (5.64%), O (9.66%).

N-(3-Chlorophenyl)(4,5,6-trimethoxy-2,3-diphenyl-1H-indol-7-yl)methanimine ***6b*** 3-$ClC_6H_4NH_2$ (0.9 mL, 1.1 g); **6b** as bright yellow crystals (1.18 g, 92%); R_f: 0.60 ($CHCl_3$/*n*-hexane, 1:1); mp: 149 °C; log ε (λ_{max} in nm): 4.70187 (370); $\acute{\upsilon}_{max}$ (cm^{-1}): 1558 (C=N), 3348 (N–H); δ_H in ppm (500 MHz): 3.59, 3.92, 4.08 (3H each, s, OCH$_3$), 7.24–7.45 (14H, m, 3 Ph), 9.02 (1H, s, HC=N), 11.28 (1H, bs, NH); δ_C in ppm (125 MHz): 61.3 , 61.6, 63.0 (all q, OCH$_3$), 108.0 (s, C^7), 114.5, 118.7 (s, C^3 and C^{3a}), 119.7, 121.3 (d, C$^{4'''}$ and C$^{6'''}$), 125.7 (d, C$^{2'''}$), 126.5, 127.5 (d, C$^{4'}$ and C$^{4''}$), 127.7, 128.0, 128.6, 131.3 (all 2× , d, C$^{2'}$, C$^{3'}$, C$^{2''}$ and C$^{3''}$), 130.3 (s, C$^{5'''}$), 131.7, 132.5 (s, C$^{1'}$ and C$^{1''}$), 134.4 (s, C$^{3'''}$), 134.9, 135.6 (s, C^2 and C^{7a}) 144.0 (s, C$^{1'''}$), 151.0, 152.0, 153.4 (all s, C^4, C^5 and C^6), 157.6 (d, C^8).

N-(4-methylphenyl)(4,5,6-trimethoxy-2,3-diphenyl-1H-indol-7-yl)methanimine **8b** 4-$MeC_6H_4NH_2$ (0.9 g); **8b** as greenish yellow crystals (1.08 g, 88%); R_f: 0.63 ($CHCl_3$/*n*-hexane, 1:1); mp: 154 °C; log ε (λ_{max} in nm): 4.18727 (369); $\acute{\upsilon}_{max}$ (cm^{-1}): 1589 (C=N), 3387 (N–H); δ_H in ppm (400 MHz): 2.45 (3H, s, ArCH$_3$), 3.60, 3.90, 4.09 (3H each, s, OCH$_3$), 7.30–7.50 (14H, m, 3 Ph), 9.11 (1H, s, HC=N), 11.45 (1H, bs,

NH); δ_C in ppm (100 MHz): 21.1 (q, $\underline{C}H_3$), 61.4 , 61.6, 63.0 (all q, $O\underline{C}H_3$), 108.6 (s, C^7), 114.1, 118.6 (s, C^3 and C^{3a}), 121.1 (2× , d, $C^{3'''}$), 126.4, 127.3 (d, $C^{4'}$ and $C^{4''}$), 127.7 127.9, 128.6, 131.3 (all 2× , d, $C^{2'}$, $C^{3'}$, $C^{2''}$ and $C^{3''}$), 129.9 (2× , d, $C^{2'''}$), 131.8, 132.7 (s, $C^{1'}$ and $C^{1''}$), 134.6 (s, C^2/C^{7a}), 135.7 (2× , s, C^2/C^{7a} and $C^{4'''}$), 140.1 (s, $C^{1'''}$), 149.8, 151.4, 153.0 (all s, C^4, C^5 and C^6), 156.0 (d, C^8). CHNS analysis: found for $C_{31}H_{28}N_2O_3$: C (77.23%), H (5.57%), N (4.84%), requires: C (78.13%), H (5.92%), N (5.88%), O (10.07%).

N-(3-Methylphenyl)(4,5,6-trimethoxy-2,3-diphenyl-1H-indol-7-yl)methanimine ***9b*** 3-$MeC_6H_4NH_2$ (0.9 mL, 0.9 g); **9b** as Light yellow crystals (1.18 g, 96%); R_f: 0.69 ($CHCl_3$/*n*-hexane, 1:1); mp: 165 °C; log ε (λ_{max} in nm): 4.58235 (364); $\acute{\upsilon}_{max}$ (cm^{-1}): 1580 (C=N), 3348 (N–H); δ_H in ppm (500 MHz): 2.45 (3H, s, $ArC\underline{H}_3$), 3.56, 3.93, 4.06 (3H each, s, $OC\underline{H}_3$), 7.12 (1H, d, J = 7.5Hz, $H^{4'''}$), 7.20 (1H, d, J = 7.5Hz, $H^{6'''}$), 7.22–7.47 (12H, m, 2 Ph, $H^{2'''}$ and $H^{5'''}$), 9.01 (1H, s, $\underline{H}C$=N), 11.47 (1H, bs, N$\underline{H}$).

N-(2,3-Dimethylphenyl)(4,5,6-trimethoxy-2,3-diphenyl-1H-indol-7-yl)methanimine ***10b*** 2,3-$Me_2C_6H_3NH_2$ (1 mL, 0.99 g); **10b** as dark yellow crystals (1.11 g, 88%); R_f: 0.63 ($CHCl_3$/*n*-hexane, 1:1); mp: 186 °C; log ε (λ_{max} in nm): 4.80254 (362); $\acute{\upsilon}_{max}$ (cm^{-1}): 1570 (C=N), 3336 (N–H); δ_H in ppm (500 MHz): 2.28, 2.31 (3H each, s, $ArC\underline{H}_3$), 3.46, 3.83, 3.95 (3H each, s, $OC\underline{H}_3$), 6.86 (1H, d, J = 7.5 Hz, $H^{4'''}$), 7.01 (1H, d, J = 7.5 Hz, $H^{6'''}$), 7.13–7.36 (11H, m, 2 Ph and $H^{5'''}$), 8.87 (1H, s, $\underline{H}C$=N), 11.37 (1H, bs, N$\underline{H}$); δ_C in ppm (125 MHz): 14.2, 20.2 (q, $\underline{C}H_3$), 61.4 , 61.6, 63.0 (q, $O\underline{C}H_3$), 108.8 (s, C^7), 114.4, 118.8 (s, C^3 and C^{3a}), 116.1 (d, $C^{4'''}$), 126.4, 127.4 (d, $C^{4'}$ and $C^{4''}$), 127.8 (4× , d, $C^{5'''}$,$C^{6'''}$ and any two of $C^{2'}$, $C^{3'}$, $C^{2''}$, $C^{3''}$), 128.6, 131.3 (2× , d, any two of $C^{2'}$, $C^{3'}$, $C^{2''}$, $C^{3''}$), 128.6 (s, $C^{2'''}$), 132.0, 131.7 (s, $C^{1'}$ and $C^{1''}$), 135.2, 135.7 (s, C^2 and C^{7a}), 138.5 (s, $C^{3'''}$), 141.1 (s, $C^{1'''}$), 150.5, 151.9, 153.1 (all s, C^4, C^5 and C^6), 156.2 (d, C^8). CHNS analysis: found for $C_{32}H_{30}N_2O_3$: C (77.84%), H (5.16%), N (4.81%), requires: C (78.34%), H (6.16%), N (5.71%), O (9.78%); Crystallographic data: molecular formula: $C_{32}H_{30}N_2O_3$; molecular mass [amu]: 490.58; crystal system: triclinic; a, b, c [Å]: 10.4673(10), 11.3389(12), 11.9563(11); α, β, γ[°]:111.371(3), 98.510(3), 90.301(3); density of crystal (calc.) [g/cm^3]: 1.249.

N-(4-Methoxyphenyl)(4,5,6-trimethoxy-2,3-diphenyl-1H-indol-7-yl)methanimine ***11b*** 4-$MeOC_6H_4NH_2$ (1.0 g); **11b** as greenish yellow crystals (1.11 g, 87%); R_f: 0.54 ($CHCl_3$/*n*-hexane, 1:1); mp: 157 °C; log ε (λ_{max} in nm): 4.37780 (375); $\acute{\upsilon}_{max}$ (cm^{-1}): 1591 (C=N), 3336 (N–H); δ_H in ppm (400 MHz): 3.47 (3H, s, $OC\underline{H}_3$ at $C^{4'''}$), 3.78, 3.84, 3.96 (3H each, s, $OC\underline{H}_3$), 6.91 (2H, d, J = 8.8, $H^{3'''}$), 7.18-7.37, (12H, m, 2 Ph, and $H^{2'''}$), 8.98 (1H, s, $\underline{H}C$=N), 11.33 (1H, bs, N$\underline{H}$); δ_C in ppm (100 MHz): 55.6, 61.4 , 61.7, 63.0 (q, $O\underline{C}H_3$), 108.6 (s, C^7), 114.2, 118.7 (s, C^3 and C^{3a}), 114.5 (2× , d, $C^{3'''}$), 122.3 (2× , d, $C^{2'''}$), 126.4, 127.3 (d, $C^{4'}$ and $C^{4''}$), 127.7, 127.9, 128.6, 131.3 (2× , d, $C^{2'}$, $C^{3'}$, $C^{2''}$, $C^{3''}$), 131.7, 132.7 (s, $C^{1'}$ and $C^{1''}$), 134.5, 135.7 (s, C^2 and C^{7a}), 140.0 (s, $C^{1'''}$), 145.4, 151.2, 152.8 (s, C^4, C^5 and C^6), 154.8 (d, C^8), 158.2 (s, $C^{4'''}$). CHNS analysis: found for $C_{31}H_{28}N_2O_3$: C (74.83%), H (5.07%), N (5.14%), O (10.99%). requires: C (75.59%), H (5.72%), N (5.69%), O (12.99%).

N-(3,4,5-Trimethoxyphenyl)(4,5,6-trimethoxy-2,3-diphenyl-1H-indol-7-yl)methanimine ***12b*** 2,3,4-$(MeO)_3C_6H_2NH_2$ (1.54 g); **12b** as dark yellow crystals (1.27 g, 89%); R_f: 0.21 ($CHCl_3$/*n*-hexane, 1:1); mp: 163 °C; log ε (λ_{max} in nm): 4.33289 (372); $\acute{\upsilon}_{max}$ (cm^{-1}): 1576 (C=N), 3379 (N–H); δ_H in ppm (400 MHz): 3.50, 3.81, 3.84, 3.98 (3H each, s, $OC\underline{H}_3$), 3.86 (6H, s, $OC\underline{H}_3$at $C^{3'''}$ and $C^{5'''}$), 6.45 (2H, s, $H^{2'''}$ and $H^{6'''}$), 7.17–7.36 (10H, m, 2 Ph), 8.94 (1H, s, $\underline{H}C$=N), 11.12 (1H, bs, N$\underline{H}$); δ_C in ppm (100 MHz): 56.3 (2× , q, $O\underline{C}H_3$at $C^{3'''}$ and $C^{5'''}$), 61.0, 61.4, 61.7, 63.0 (q, $O\underline{C}H_3$), 98.5 (2× , d, $C^{2'''}$ and $C^{6'''}$), 108.3 (s, C^7), 114.0, 118.7 (s, C^3 and C^{3a}), 126.4, 127.4 (d, $C^{4'}$ and $C^{4''}$), 127.7, 128.0, 128.6, 131.3 (2× , d, $C^{2'}$, $C^{3'}$, $C^{2''}$ and $C^{3''}$), 131.7, 132.6 (2× , s, $C^{1'}$ and $C^{1''}$), 134.6, 135.5 (s, C^2 and C^{7a}), 140.0 (s, $C^{1'''}$), 148.9, 151.7, 153.1 (s, C^4, C^5 and C^6), 153.7(d, C^8), 156.3 (3× , s, $C^{3'''}$, $C^{4'''}$, $C^{5'''}$). CHNS analysis: found for $C_{32}H_{30}N_2O_5$: C (72.25%), H (4.99%), N (5.02%), requires: C (73.55%), H (5.79%), N (5.36%), O (15.31%).

N-(4-Nitrophenyl)(4,5,6-dimethoxy-2,3-diphenyl-1H-indol-7-yl)methanimine ***13b*** 4-$NO_2C_6H_4NH_2$ (1.2 g); **13b** as dark yellow crystals (1.07 g, 82%); R_f: 0.62 ($CHCl_3$/*n*-hexane, 1:1); mp: 168 °C; log ε (λ_{max} in nm): 4.04059 (375); $\acute{\upsilon}_{max}$ (cm^{-1}): 1584 (C=N), 3356 (N–H); δ_H in ppm (400 MHz): 3.59, 3.88, 4.07 (3H each, s, $OC\underline{H}_3$), 7.22–7.38 (12H, m, 2 Ph, $H^{5'''}$ and $H^{6'''}$), 7.40 (1H, d, J = 7.8Hz, $H^{4'''}$), 8.34 (1H, t, J = 2.0 Hz, $H^{2'''}$), 9.10 (1H, s, $\underline{H}C$=N), 11.14 (1H, bs, N$\underline{H}$).

N-(3-Nitrophenyl)(4,5,6-trimethoxy-2,3-diphenyl-1H-indol-7-yl)methanimine ***14b*** 3-$NO_2C_6H_4NH_2$ (1.2 g); **14b** as golden yellow crystals (1.25 g, 95%); R_f: 0.51 ($CHCl_3$/*n*-hexane, 1:1); mp: 179 °C; log ε (λ_{max} in nm): 5.16388 (388); $\acute{\upsilon}_{max}$ (cm^{-1}): 1576 (C=N), 3350 (N–H); δ_H in ppm (500 MHz): 3.53, 3.84, 4.00 (3H each, s, $OC\underline{H}_3$), 7.19–7.29 (10H, m, 2 Ph), 7.36 (2H, d, J = 5.0Hz, $H^{2'''}$), 8.25 (2H, d, J = 5.0 Hz, $H^{3'''}$), 8.96 (1H, s, $\underline{H}C$=N), 10.98 (1H, bs, N$\underline{H}$); δ_C in ppm (125 MHz): 61.3, 61.5, 62.9 (q, $O\underline{C}H_3$), 107.8 (s, C^7), 114.6, 118.7 (s, C^3 and C^{3a}), 121.8 (2× , d, $C^{2'''}$), 125.2 (2× , d, $C^{3'''}$), 127.6, 127.7 (d, $C^{4'}$ and $C^{4''}$), 127.8, 127.9, 128.7, 131.2 (2× , d, $C^{2'}$, $C^{3'}$, $C^{2''}$ and $C^{3''}$), 131.2, 131.8 (s, $C^{1'}$ and $C^{1''}$), 134.7, 135.4 (s, C^2 and C^{7a}), 145.4 (s, C^4/C^5/C^6), 153.2 (2× , s, any two of C^4, C^5 and C^6), 154.1 (s, $C^{4'''}$), 159.1 (d of C^8 and s of C^1 merged).

N-(4-Bromophenyl)(4,5,6-trimethoxy-2,3-diphenyl-1H-indol-7-yl)methanimine ***15b*** 4-$BrC_6H_4NH_2$ (1.5 g); **15b** as orange

yellow crystals (1.31 g, 94%); R_f: 0.66 ($CHCl_3$/*n*-hexane, 1:1); mp: 152 °C; log ε (λ_{max} in nm): 4.78249 (373); υ_{max} (cm^{-1}): 1583 (C=N), 3356 (N–H); δ_H in ppm (500 MHz): 3.59, 3.92, 4.07 (3H each, s, $OC\underline{H}_3$), 7.23–7.48 (14H, m, 3 Ph), 9.09 (1H, s, $\underline{H}C{=}N$), 11.49 (1H, bs, $N\underline{H}$). CHNS analysis: found for $C_{30}H_{25}BrN_2O_3$: C (64.25%), H (4.09%), N (5.12%), requires: C (66.55%), H (4.65%), Br (14.76%), N (5.17%), O (8.86%).

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