

Cite this: *RSC Adv.*, 2019, 9, 24050

Received 24th June 2019

Accepted 23rd July 2019

DOI: 10.1039/c9ra04741g

rsc.li/rsc-advances

Synthesis of C2-tetrasubstituted indolin-3-ones via Cu-catalyzed oxidative dimerization of 2-aryl indoles and cross-addition with indoles†

Anoop Singh,^{‡a} Satheeshvarma Vanaparathi,^{‡a} Sachin Choudhary,^{‡a} Rangan Krishnan^b and Indresh Kumar^{‡*a}

An efficient protocol for the synthesis of 2,2-disubstituted indolin-3-ones under mild conditions has been developed. This reaction involves the copper-catalyzed *in situ* oxidative de-aromatization of 2-arylindoles to indol-3-one, followed by self-dimerization as well as cross-addition with indoles under mild conditions. The result generates a wide variety of C2-tetrasubstituted indolin-3-ones with good to high yields (62–82%).

Introduction

Indolin-3-ones are privileged scaffolds that function as intermediates for the synthesis of medicinally important compounds.¹ In particular, 2,2-disubstituted 1,2-dihydro-3*H*-indol-3-one, also known as pseudoindoxyls bearing C2 stereocenters have continually appeared in natural products such as austamide (I), strobilanthoside A (II), isatisine A (III), and halichrome A (IV), as well as in many other bioactive synthetic compounds (Fig. 1).² Moreover, compounds with this skeleton have also exhibited exciting applications in the areas of fluorescence labeling and optoelectronic materials in recent years.³

Owing to the wide utility of 2,2-disubstituted indolin-3-ones, several methods had been developed in the past few years which include; transition-metal catalyzed annulation reactions,⁴ the cascade Fischer indolization/Claisen rearrangement,⁵ and photooxidative rearrangements,⁶ along with other methods.⁷ Besides these methods, chemoselective addition of various nucleophiles to 2-aryl-indol-3-one, an activated cyclic C-acylimine, is another exciting way to access 2,2-disubstituted indolin-3-one derivatives.⁸ However, the synthesis of 2-aryl-3*H*-indol-3-ones requires troublesome multistep syntheses and are not easily accessible.⁹ To overcome this problem, some attention has recently been given to the chemistry of dearomative cascade reactions of 2-substituted indoles for the direct construction of C2-quaternary indolin-3-ones (Scheme 1a). In

this context, self-dimerization of 2-substituted indoles have been explored either through Cu-catalysis (Scheme 1a(i))¹⁰ or other metal-catalysis (Scheme 1a(ii)).¹¹ However, these methods required high temperature and sometimes hazardous components. Likewise, oxidative cross-addition of indole to 2-substituted indole could be another way to achieve C2-quaternary indolin-3-ones; however, that is a difficult task to accomplish in terms of selectivity. Guchhait and coworkers developed an exciting and the very first protocol for the cross-addition of indoles to 2-substituted indoles to access 2,2-disubstituted indolin-3-ones with a chiral center under Pd-catalysis in a chemoselective fashion (Scheme 1a(iii)).¹² Very recently, Yu and coworkers developed a metal-free approach for the cross-addition of indoles with a series of 2-substituted

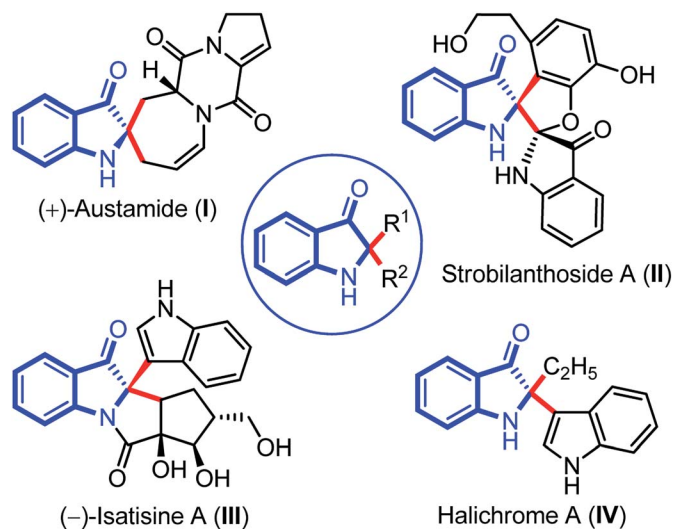


Fig. 1 2,2-disubstituted indolin-3-one as basic core in important natural products.

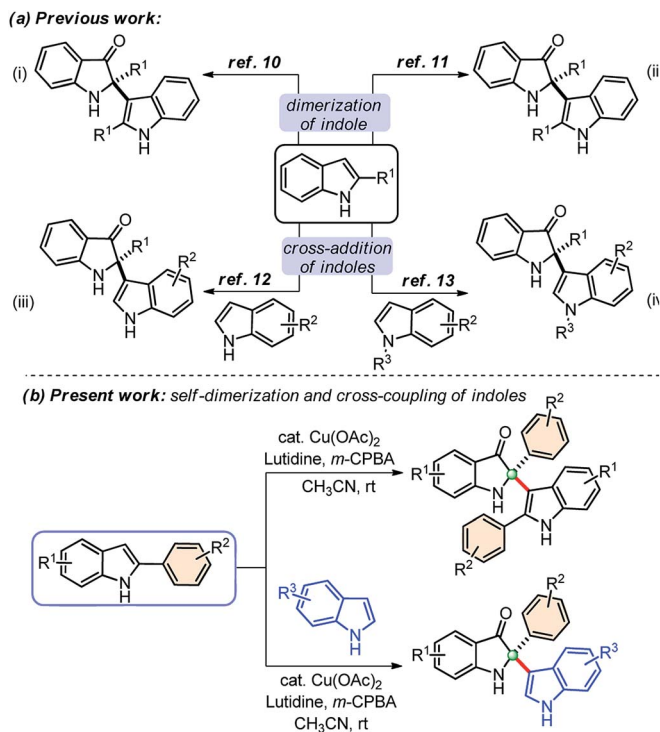
^aDepartment of Chemistry, Birla Institute of Technology and Science, Pilani 333 031, Rajasthan, India. E-mail: indresh.chemistry@gmail.com; indresh.kumar@pilani.bits-pilani.ac.in

^bDepartment of Chemistry, BITS Pilani, Hyderabad Campus, Secunderabad, India

† Electronic supplementary information (ESI) available. CCDC 1832862. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c9ra04741g

‡ Authors have contributed equally.





Scheme 1 Synthetic approaches from 2-aryl indoles to access 2,2-disubstituted indolin-3-ones.

indoles to rapidly access 2,2-disubstituted indolin-3-ones (Scheme 1a(iv)).¹³

Due to the high significance of C2-quaternary indolin-3-ones, and limitations of the existing methods, finding direct access to these compounds through the self-dimerization of 2-substituted indoles or the cross-addition of indoles with 2-substituted indoles under mild conditions, is still highly desirable. Here, we present such a general and straightforward finding for the synthesis of 2,2-disubstituted indolin-3-ones from 2-aryl indoles through copper-catalyzed self-dimerization and cross-addition with indoles at room temperature (Scheme 1(b)).

Results and discussion

Copper-catalyzed transformations are one of the most studied methods in synthetic chemistry due to their efficiency, good functional group tolerance.¹⁴ In this context, Cu-catalyzed tandem oxidative reactions of 2-aryl indol-3-ones, *in situ* generated from 2-arylindoles, have been explored to synthesize 2-arylbenzoxazinone,¹⁵ and polyhydropyrido[1,2-*a*]indoles/tetracyclic quinazolinones.¹⁶ Encouraged by these relevant precedents, we envisaged that a general copper-catalyzed method could be developed for the self-dimerization of 2-substituted indoles and cross-addition with indoles through the *in situ* generations of indol-3-ones under mild conditions. Herein, we describe the successful implementation of our protocol.

We begin this study for the oxidative cross-dimerization of 2-phenyl indole **1a** as model substrate to prepare 2-phenyl-2-(2-

phenyl-1*H*-indol-3-yl)indolin-3-one **2a**. In this context, optimization of the reaction conditions was carried out by employing several bases, oxidizing agents, catalysts and solvents, and the results are shown in Table 1. Initially, reaction failed to work, when **1a** was treated with catalysts CuCl (30 mol%), pyridine with; K₂S₂O₈ (entry 1, Table 1), oxone (entry 2, Table 1). Trace amount (<10%) of the product was obtained with air as oxidants in toluene (entry 3, Table 1) and DMSO (entry 4, Table 1) as solvents, respectively. However, product **2a** was obtained with low yield (34%), when the reaction was carried out with CuCl (cat.), pyridine, and TBHP (*tert*-butyl hydroperoxide) in CH₃CN (entry 5, Table 1) at room temperature. Additional efforts were made to improve the reaction yields either by changing the oxidants, base, and catalysts (entries 6–11, Table 1). An improvement in the reaction yields was observed by employing lutidine, in place of pyridine, with TBHP (45%) (entry 8, Table 1), and with *m*-CPBA (*meta*-chloro perbenzoic acid) (52%) (entry 10, Table 1). The dimerized product **2a** was obtained with moderate yield (63%) when Cu(OAc)₂ (entry 11, Table 1) was employed in place of CuCl as a catalyst with TBHP as oxidant, which was again improved to 75% yield by using *m*-CPBA as oxidant (entry 12, Table 1). Any additional change in the reaction conditions either; by changing oxidant (entry 12, Table 1) or lowering the catalyst loading (entry 14, Table 1) failed to improve the reaction yield. The reaction failed to produce any dimerization product in the absence of catalyst (entry 15, Table 1), and base (entry 16, Table 1). Thus, we preferred to perform this reaction to yield cross-dimerized product **2a** under the standardized conditions (entry 12, Table 1). Moreover, reaction

Table 1 Optimization of reaction conditions^a

Entry	Solvent	Catalyst	Base	Oxidant	Time (h)	Yield ^b (%)
1	Toluene	CuCl	Py	K ₂ S ₂ O ₈	24	n.r.
2	Toluene	CuCl	Py	Oxone	24	n.r.
3	Toluene	CuCl	Py	Air	24	<10
4	DMSO	CuCl	Py	Air	24	<10
5	CH ₃ CN	CuCl	Py	TBHP	24	34
6	CH ₃ CN	CuCl	Py	Oxone	24	25
7	CH ₃ CN	CuCl	Py	Air	24	30
8	CH ₃ CN	CuCl	Lutidine	TBHP	22	45
9	CH ₃ CN	CuCl	K ₂ CO ₃	TBHP	24	20
10	CH ₃ CN	CuCl	Lutidine	<i>m</i> -CPBA	20	52
11	CH ₃ CN	Cu(OAc) ₂	Lutidine	TBHP	20	63
12	CH ₃ CN	Cu(OAc) ₂	Lutidine	<i>m</i> -CPBA	18	75
13	CH ₃ CN	Cu(OAc) ₂	Lutidine	H ₂ O ₂	18	43
14 ^c	CH ₃ CN	Cu(OAc) ₂	Lutidine	<i>m</i> -CPBA	24	65
15	CH ₃ CN	—	Lutidine	<i>m</i> -CPBA	24	n.r.
16	CH ₃ CN	Cu(OAc) ₂	—	<i>m</i> -CPBA	24	n.r.

^a Unless otherwise indicated, the reaction was carried out with 2-phenylindole **1a** (0.5 mmol), solvent (3.0 mL), catalyst (30 mol%), base (1.0 mmol), oxidant (0.3 mmol), reaction time (h) at rt. ^b Isolated yield of **2a** refer to **1a**. ^c Cu(OAc)₂ (15 mmol%) was used.



only furnished 2-indoles substituted 3-oxindole **2a** through the addition of indole as a nucleophile at the C2-position of *in situ* generated indol-3-one in a chemoselective fashion.

Next, we explored the generality of our developed cross-dimerization protocol with variously substituted 2-aryl indoles **1a–k** under standardized conditions, and results are shown in Table 2. The reaction was found to be quite general concerning the substituents on both the aryl-rings of 2-aryl-indole **1** and accomplished within 14–22 h at room temperature to furnish corresponding cross-dimerized product, *i.e.*, 2-indoles substituted 3-oxindoles **2** in good to high yields (68–82%).

Table 2 Substrate scope for the self-dimerized synthesis of C2-quaternary indolin-3-ones^a

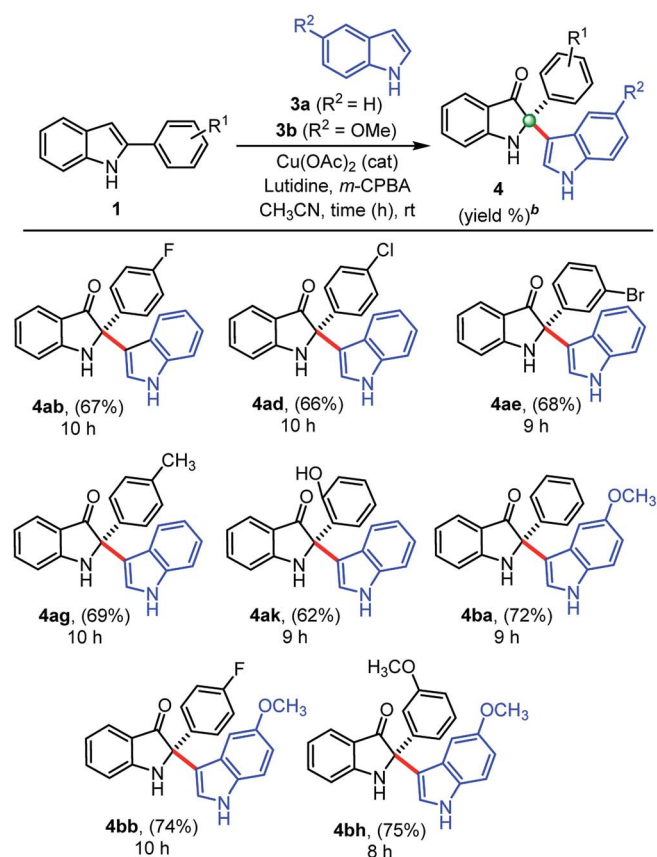


^a Unless otherwise indicated, the reaction was carried out with 2-phenylindole **1** (0.5 mmol), CH₃CN (3.0 mL), Cu(OAc)₂ (30 mol%), lutidine (1.0 mmol), *m*-CPBA (0.3 mmol), reaction time at rt. ^b Isolated yield of **2** refers to **1**.

Initially, electron-withdrawing substituents like 4-F, 3-Cl, 4-Cl, 3-Br substitutions on the phenyl ring of 2-aryl indole **1b**, **1c**, **1d**, and **1e** gave corresponding products **2b** (71%), **2c** (67%), **2d** (69%), and **2e** (68%), respectively. The electron-donating substituents like –CH₃ and –OCH₃ on the phenyl ring of 2-aryl indoles furnished similar products **2g**, **2h**, and **2i** with relatively higher yields (75–82%) than the substrates with electron-withdrawing groups. The product **2f** obtained in high yields (81%) when 5-bromo-2-phenyl-1*H*-indole **1f** was employed under standardized conditions. Moreover, densely substituted 2-aryl indole **1j** could furnish corresponding cross-dimerized product **2j** with moderate (64%) yields, due to the presence of internal steric hindrance. In case of 2-methyl indole as substrate, corresponding dimerized product **2k** was also obtained with good yield (71%). The developed protocol was found to be a general w.r.t. the alkyl/aryl substituents at the C2-position of indoles.

We also extended this developed protocol for the cross addition of indoles **3** at the C2-position of 2-arylindole **1**, and the results are shown in Table 3. Pleasingly, cross-addition of indoles furnished similar products in good to high yields, in all the cases, under similar reaction conditions. Initially, indole **3a**

Table 3 Substrate scope for the synthesis of indolin-3-ones through indole-addition^a



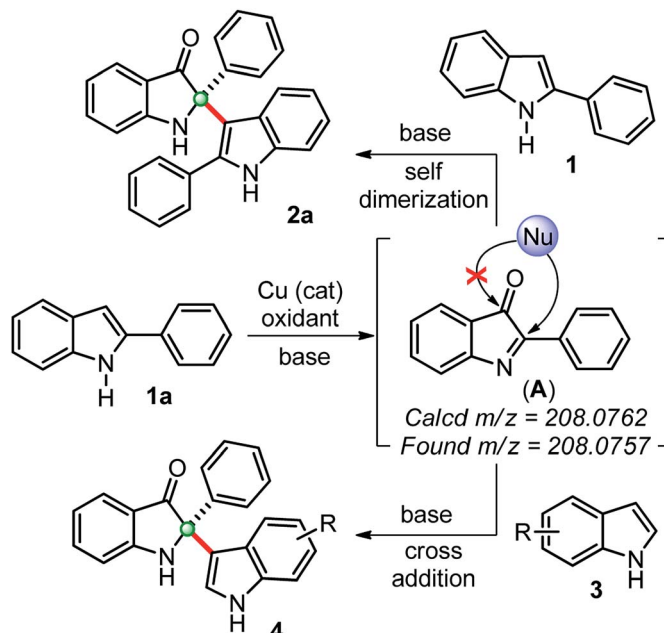
^a Unless otherwise indicated, the reaction was carried out with 2-phenylindole **1** (0.5 mmol), indole **3** (0.55 mmol), CH₃CN (3.0 mL), Cu(OAc)₂ (30 mol%), lutidine (1.0 mmol), *m*-CPBA (0.5 mmol), reaction time (h) at rt. ^b Isolated yield of **4** refers to **1**.



reacted with 2-aryl indoles (**1b**, **1d**, **1e**) substituted with electron-withdrawing groups (-F, -Cl, -Br) and furnished corresponding cross-addition products **4ab** (67%), **4ad** (66%), and **4ae** (68%), respectively. Similarly, products **4ag** (69%) and **4ak** (62%) were obtained, when simple indole **3a** reacted with 2-aryl indoles, **1g** and **1k** substituted with electron donating groups (-CH₃, -OH), respectively. Moreover, 5-methoxy indole **3b** furnished corresponding cross-addition products **4ba** (72%), **4bb** (74%), and **4bh** (75%) with improved yields, when treated with 2-phenylindole **1a** and other substituted 2-aryl indoles (**1b** and **1h**), respectively, in the presence of Cu(OAc)₂ (cat.), *m*-CPBA (1.0 equiv.), and lutidine (2.0 equiv.) as base at room temperature. Interestingly, the cross-addition reaction of indoles is relatively faster as compared to the cross-dimerization. In general, the self-dimerization products yields were found slightly more than that of the cross-addition reactions, because in case of cross-addition of indoles we also observed a trace amount (<10%) of self-dimerized products in almost all the cases.

The practical use of this method was also demonstrated to access both cross-dimerization of 2-arylindole and cross-addition of indole with 2-arylindole products on a gram-scale without much variation in yield, as shown in Scheme 2. Pleasingly, the gram-scale reaction successfully afforded **2g** with a higher yield (81%) (Scheme 2a) as compared to the small-scale response (Table 2). The single-crystal X-ray diffraction analysis confirmed the structure of cross-dimerized product **2g**.¹⁷ Moreover, 2,2-disubstituted indole-3-one **4bb** was isolated with 78% yield, when cross-addition of 2-substituted indole **1b** was performed with 4-methoxy indole **3b**, under standardized conditions (Scheme 2b).

Based on previous reports and our findings, a tentative mechanism for the synthesis of self-dimerized 2-phenyl-2-(2-phenyl-1*H*-indol-3-yl)indolin-3-ones **2** and cross-addition 2-(1*H*-indol-3-yl)-2-phenylindole-3-ones **4** is drawn, as shown in Scheme 3. Initially, the copper-catalyzed oxidation of 2-phenylindole **1a** to intermediate 2-phenylindole-3-one (**A**), which was confirmed by *in situ* HRMS data. This intermediate (**A**) undergoes a chemoselective C2-addition with another 2-phenylindole **1a** to furnish self-dimerization product **2a**.



Scheme 3 Plausible way of reaction for the synthesis of 2,2-disubstituted indole-2-ones through *in situ* generations of indole-3-one confirmed by HRMS.

Whereas, for the cross-addition product **4**, intermediate (**A**) was trapped with another indole moiety.

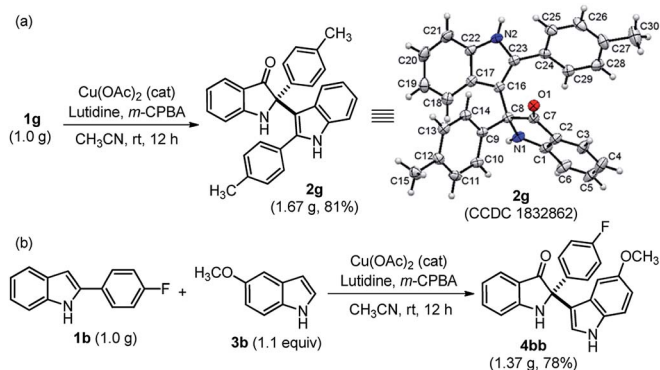
Conclusions

In summary, we have developed an efficient and general protocol for the synthesis of 2,2-disubstituted indolin-3-ones through the self-dimerization of 2-aryl indoles and cross-addition of 2-aryl indoles with indoles. This reaction proceeds with *in situ* generation of indol-3-one, followed by chemoselective nucleophilic addition under mild copper-catalyzed conditions. This simple strategy provides convenient and either way to access indolin-3-ones bearing C2-quaternary center in good to high yields. The developed protocol utilized nontoxic, readily available materials, and practically viable at the gram-scale synthesis.

Experimental

General remarks

All reactions were observed using thin-layer chromatography (on SiO₂ gel F254 plates) under standard condition. The desired compounds were purified through flash column chromatography packed with silica gel (100–200 meshes size) as the stationary phase and eluting solvent, hexane–ethyl acetate solvent mixture was used as mobile phase. Melting points were determined in open capillary tubes on an EZ-Melt Automated melting point apparatus and are uncorrected. NMR spectra were recorded on a Bruker AV 400 spectrometer. Chemical shifts were reported in parts per million (ppm) using deuterated solvent or tetramethylsilane (TMS) as an internal standard. High-resolution mass spectra (HRMS-ESI) were recorded using



Scheme 2 Practical utility at the gram-scale synthesis of **2g** and **4bb**. Single crystal X-ray structure of **2g** (the thermal ellipsoids are drawn at the 50% probability level).



quadrupole time-of-flight (Q-TOF) mass spectrometer (Applied Biosystem). All the chemicals were obtained from the commercial supplier and were used without purification.

Typical procedure for the synthesis of oxidative dimerized product 2

To a stirred solution of 2-phenylindole **1** (0.5 mmol) in CH₃CN (3.0 mL) was added lutidine (1.0 mmol), Cu(OAc)₂ (30 mol%) and *m*-CPBA (*meta*-chloroperoxybenzoic acid, 0.3 mmol) successively at room temperature. The combined reaction mixture was stirred at the same temperature until TLC confirmed the complete consumption of starting material. Subsequently, the reaction was quenched with H₂O (3.0 mL) and stirred with EtOAc (10 mL). The organic layer was separated, and the aqueous layer was again extracted with EtOAc (5.0 mL). The combined organic extracts were washed with brine, dried over Na₂SO₄ anhydrous, and concentrated under reduced pressure. Column chromatography purification through silica gel by eluting the mixture of hexane/EtOAc gave corresponding dimerized product **2** as mainly yellow solid with 64–82% yields.

2-Phenyl-2-(2-phenyl-1*H*-indol-3-yl)indolin-3-one (2a). Yellow solid (165 mg, 75% yield, mp = 207–212 °C). ¹H NMR (400 MHz, CDCl₃) δ 5.17 (s, 1H), 6.71 (d, *J* = 8.2 Hz, 1H), 6.80 (t, *J* = 7.7 Hz, 1H), 6.91–6.93 (m, 1H), 7.00 (d, *J* = 8.0 Hz, 1H), 7.10–7.20 (m, 8H), 7.23–7.27 (m, 1H), 7.32 (d, *J* = 8.1 Hz, 1H), 7.40 (d, *J* = 7.7 Hz, 1H), 7.42–7.46 (m, 1H), 7.48–7.51 (m, 2H), 8.11 (s, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 72.0, 110.7, 112.0, 112.2, 119.1, 120.0, 120.4, 121.5, 122.3, 125.4 (2C), 127.2 (2C), 127.3, 127.5, 127.6 (2C), 128.2 (2C), 129.7 (2C), 133.2, 135.5, 137.0, 137.1, 140.3, 159.4, 200.3. HRMS (ESI-TOF) *m/z*: calcd for C₂₈H₂₁N₂O [M + H]⁺ 401.1654, found 401.1637.

2-(4-Fluorophenyl)-2-(2-(4-fluorophenyl)-1*H*-indol-3-yl)indolin-3-one (2b). Yellow solid (175 mg, 71% yield, mp = 175–180 °C). ¹H NMR (400 MHz, CDCl₃) δ 5.20 (s, 1H), 6.77–6.95 (m, 8H), 7.05 (dd, *J* = 8.8, 5.3 Hz, 2H), 7.14–7.18 (m, 1H), 7.29–7.37 (m, 2H), 7.45–7.51 (m, 3H), 8.16 (s, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 71.3, 110.8, 112.4, 112.6, 114.5, 114.7, 114.9, 115.1, 119.6, 120.2, 120.4, 121.0, 122.6, 125.4, 127.1, 128.9, 128.9, 131.5, 131.6, 135.4, 135.8 (2C), 136.0, 137.4, 159.2, 162.4 (d, *J* = 246 Hz), 162.6 (d, *J* = 246 Hz), 200.1. HRMS (ESI-TOF) *m/z*: calcd for C₂₈H₁₉F₂N₂O [M + H]⁺ 437.1465, found 437.1445.

2-(3-Chlorophenyl)-2-(2-(3-chlorophenyl)-1*H*-indol-3-yl)indolin-3-one (2c). Yellow solid (156 mg, 67% yield, mp = 160–164 °C). ¹H NMR (400 MHz, CDCl₃) δ 5.21 (s, 1H), 6.86–6.91 (m, 2H), 6.94 (d, *J* = 4.0 Hz, 2H), 7.02 (m, 5H), 7.15–7.21 (m, 2H), 7.33 (d, *J* = 8.1 Hz, 1H), 7.38 (dt, *J* = 8.0 Hz, 4.0 Hz, 1H), 7.46 (d, *J* = 7.3 Hz, 1H), 7.50–7.55 (m, 2H), 8.20 (s, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 71.3, 111.0, 112.3, 112.6, 120.0, 120.4, 120.4, 120.9, 122.8, 125.4, 125.8, 126.9, 127.1, 127.7, 127.8, 128.4, 128.8, 129.4, 129.9, 133.6, 134.0, 134.5, 135.5, 135.9, 137.7, 141.93, 159.3, 199.9. HRMS (ESI-TOF) calcd for C₂₈H₁₉Cl₂N₂O *m/z*: [M + H]⁺ 469.0874, found 469.0848.

2-(4-Chlorophenyl)-2-(2-(4-chlorophenyl)-1*H*-indol-3-yl)indolin-3-one (2d). Yellow solid (161 mg, 69% yield, mp = 197–201 °C). ¹H NMR (400 MHz, CDCl₃) δ 5.20 (s, 1H), 6.85–6.89 (m, 2H), 6.91–6.99 (m, 2H), 7.03 (d, *J* = 8.5 Hz, 2H), 7.13 (d, *J* = 8.5 Hz, 2H), 7.17–7.22 (m, 3H), 7.35–7.41 (m, 2H), 7.47 (d, *J* = 8.7 Hz, 2H), 7.50–7.54 (m,

1H), 8.14 (s, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 71.40, 110.9, 120.3, 119.7, 120.3, 120.4, 121.0, 122.7, 125.4, 127.1, 127.8 (2C), 128.3 (2C), 128.6 (2C), 131.0 (2C), 131.2, 132.0, 133.6, 134.5, 135.5, 135.8, 137.5, 138.6, 159.2, 199.7. HRMS (ESI-TOF) *m/z*: calcd for C₂₈H₁₉Cl₂N₂O [M + H]⁺ 469.0874, found 469.0853.

2-(3-Bromophenyl)-2-(2-(3-bromophenyl)-1*H*-indol-3-yl)indolin-3-one (2e). Yellow solid (188 mg, 68% yield, mp = 122–126 °C). ¹H NMR (400 MHz, CDCl₃) δ 5.25 (s, 1H), 6.90–6.93 (m, 2H), 6.97 (d, *J* = 3.9 Hz, 2H), 7.00–7.06 (m, 2H), 7.11 (d, *J* = 7.7 Hz, 1H), 7.17–7.21 (m, 2H), 7.26–7.27 (m, 1H), 7.33–7.38 (m, 2H), 7.44 (d, *J* = 7.9 Hz, 1H), 7.48 (d, *J* = 7.7 Hz, 1H), 7.53–7.57 (m, 1H), 7.71 (t, *J* = 1.8 Hz, 1H), 8.27 (s, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 71.3, 111.0, 112.3, 112.7, 120.1, 120.3, 120.4, 120.9, 121.8, 122.3, 122.8, 125.5, 126.2, 126.9, 128.1, 129.0, 129.7, 129.9, 130.7, 131.3, 132.7, 134.7, 135.5, 135.9, 137.7, 142.1, 159.3, 199.9. HRMS (ESI-TOF) *m/z*: calcd for C₂₈H₁₉Br₂N₂O [M + H]⁺ 556.9864, found 556.9836.

5-Bromo-2-(5-bromo-2-phenyl-1*H*-indol-3-yl)-2-phenylindolin-3-one (2f). Yellow solid (225 mg, 81% yield, mp = 148–153 °C). ¹H NMR (400 MHz, CDCl₃) δ 5.13 (s, 1H), 6.58 (d, *J* = 8.5 Hz, 1H), 7.04 (d, *J* = 1.4 Hz, 1H), 7.11–7.15 (m, 2H), 7.19–7.25 (m, 7H), 7.29–7.33 (m, 1H), 7.41–7.43 (m, 2H), 7.48–7.51 (m, 2H), 8.15 (s, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 72.5, 111.2, 111.4, 112.1, 113.3, 113.7, 121.7, 124.0, 125.4, 127.0 (2C), 127.7, 127.9 (2C), 128.1, 128.5 (2C), 128.7, 128.9, 129.6 (2C), 132.6, 134.1, 138.1, 139.5, 139.7, 157.5, 198.6. HRMS (ESI-TOF) *m/z*: calcd for C₂₈H₁₉Br₂N₂O [M + H]⁺ 556.9864, found 556.9836.

2-(*p*-Tolyl)-2-(2-(*p*-tolyl)-1*H*-indol-3-yl)indolin-3-one (2g). Yellow solid (215 mg, 75% yield, mp = 159–161 °C). ¹H NMR (400 MHz, CDCl₃) δ 2.27 (s, 3H), 2.33 (s, 3H), 5.17 (s, 1H), 6.68 (d, *J* = 8.2 Hz, 1H), 6.78 (t, *J* = 7.4 Hz, 1H), 6.89–7.05 (m, 8H), 7.13 (t, *J* = 8.0 Hz, 1H), 7.28 (d, *J* = 8.1 Hz, 1H), 7.34–7.40 (m, 3H), 7.41–7.45 (m, 1H), 8.10 (s, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 21.0, 21.2, 71.9, 110.6, 111.8, 112.1, 118.8, 119.7, 120.3, 121.6 (2C), 122.1, 125.3, 127.1 (2C), 127.4, 128.3 (2C), 128.9 (2C), 129.5, 130.3, 135.4, 136.9, 137.0, 137.1, 137.4, 137.9, 159.1, 200.4. HRMS (ESI-TOF) *m/z*: calcd for C₃₀H₂₅N₂O [M + Na]⁺ 451.1787, found 451.1760.

2-(3-Methoxyphenyl)-2-(2-(3-methoxyphenyl)-1*H*-indol-3-yl)indolin-3-one (2h). Yellow solid (188 mg, 82% yield, mp = 206–210 °C). ¹H NMR (400 MHz, CDCl₃) δ 3.56 (s, 3H), 3.67 (s, 3H), 5.20 (s, 1H), 6.64 (m, 1H), 6.69–6.74 (m, 2H), 6.78–6.83 (m, 3H), 6.94 (t, *J* = 7.3 Hz, 1H), 7.05–7.17 (m, 6H), 7.32 (d, *J* = 8.2 Hz, 1H), 7.42–7.47 (m, 2H), 8.10 (s, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 54.9, 55.1, 71.9, 110.6, 111.7, 112.2, 112.8, 113.1, 114.7 (2C), 119.2, 119.7, 120.0, 120.4, 121.50, 121.7, 122.3, 125.3, 127.3, 128.8, 129.1, 134.5, 135.4, 136.9, 137.1, 141.9, 158.6, 159.2, 159.3, 200.1. HRMS (ESI-TOF) *m/z*: calcd for C₃₀H₂₅N₂O₃ [M + H]⁺ 461.1865, found 461.1843.

2-(4-Methoxyphenyl)-2-(2-(4-methoxyphenyl)-1*H*-indol-3-yl)indolin-3-one (2i). Yellow solid (181 mg, 79% yield, mp = 102–105 °C). ¹H NMR (400 MHz, CDCl₃) δ 3.73 (s, 3H), 3.77 (s, 3H), 5.18 (s, 1H), 6.65 (d, *J* = 8.7 Hz, 2H), 6.71–6.74 (m, 3H), 6.78 (t, *J* = 7.2 Hz, 1H), 6.90–6.99 (m, 2H), 7.02 (d, *J* = 8.7 Hz, 2H), 7.11–7.15 (m, 1H), 7.30 (d, *J* = 8.1 Hz, 1H), 7.37–7.46 (m, 4H), 8.07 (s, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 55.2, 55.3, 71.6, 110.6, 112.1, 112.2, 113.1 (2C), 113.6 (2C), 119.0, 119.8, 120.5, 121.5, 122.1, 125.4, 125.5, 127.5, 128.4 (2C), 130.9 (2C), 132.4, 135.4, 137.0,



136.8, 159.0, 159.1, 159.5, 200.6. HRMS (ESI-TOF) m/z : calcd for $C_{30}H_{25}N_2O_3$ $[M + H]^+$ 461.1865, found 461.1851.

2-(4-Bromophenyl)-2-(2-(4-bromophenyl)-5,6-dimethyl-1H-indol-3-yl)-5,6-dimethylindolin-3-one (2j). Yellow solid (196 mg, 64% yield, mp = 192–195 °C). 1H NMR (400 MHz, $CDCl_3$) δ 2.16 (s, 3H), 2.21 (s, 3H), 2.30 (s, 3H), 2.31 (s, 3H), 4.94 (s, 1H), 6.66 (d, J = 8.7 Hz, 2H), 6.94 (d, J = 8.4 Hz, 2H), 7.11 (s, 1H), 7.16 (s, 1H), 7.25 (d, J = 8.4 Hz, 2H), 7.28 (d, J = 8.7 Hz, 2H), 7.36 (d, J = 8.7 Hz, 2H), 7.85 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.2, 20.3 (2C), 21.3, 71.7, 111.1, 112.1, 113.4, 118.8, 121.0, 121.5, 122.4, 125.0, 125.4, 126.3, 128.9, 129.0 (2C), 130.6 (2C), 131.1 (2C), 131.3 (2C), 131.9, 132.0, 134.5, 134.9, 139.7, 148.2, 158.5, 199.3. HRMS (ESI-TOF) m/z : $[M + H]^+$ calcd for $C_{32}H_{27}Br_2N_2O$ 613.0490, found 615.0433.

2-Methyl-2-(2-methyl-1H-indol-3-yl)indolin-3-one (2k). Yellow solid (145 mg, 71% yield, mp = 151–153 °C). 1H NMR (400 MHz, $CDCl_3$) δ 1.95 (s, 3H), 2.45 (s, 3H), 5.05 (s, 1H), 6.89–6.92 (m, 2H), 6.96–7.00 (m, 1H), 7.07–7.11 (m, 1H), 7.24–7.28 (m, 1H), 7.42 (dd, J = 8.1, 1.0 Hz, 1H), 7.52–7.56 (m, 1H), 7.73 (dd, J = 8.1 Hz, 1.0 Hz, 1H), 7.90 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.6, 25.1, 67.14, 109.5, 110.4, 111.4, 112.4, 119.1, 119.5, 119.7, 121.2, 125.3, 127.4, 132.6, 134.9, 137.4, 159.5, 204.3. HRMS (ESI-TOF) m/z : calcd for $C_{18}H_{17}N_2O$ $[M + H]^+$ 277.1341, found 277.1334.

Typical procedure for the synthesis of (4)

To a stirred solution of 2-phenylindole **1** (0.5 mmol) in CH_3CN (3.0 mL) was added lutidine (1.0 mmol), $Cu(OAc)_2$ (30 mol%) and *m*-CPBA (0.5 mmol) successively, followed by substituted indole **3** (1.1 equiv.) at room temperature and progress of the reaction was monitored by TLC. Once the reaction was over, it was quenched with water (3.0 mL) and stirred with EtOAc (10 mL). The organic layer was separated, and the aqueous layer was again extracted with EtOAc (5.0 mL). The combined organic extracts were washed with brine and dried over anhydrous Na_2SO_4 , followed by concentrated in the vacuum after filtration. Purification through silica-gel column chromatography by eluting the mixture of hexane/EtOAc gave corresponding product **4** as mainly yellow solid with 62–75% yields.

2-(4-Fluorophenyl)-2-(1H-indol-3-yl)indolin-3-one (4ab). Yellow solid (114 mg, 67% yield, mp = 206–210 °C). 1H NMR (400 MHz, $CDCl_3$) δ 5.36 (s, 1H), 6.90–7.06 (m, 5H), 7.15–7.13 (m, 3H), 7.41 (d, J = 8.2 Hz, 1H), 7.50–7.60 (m, 3H), 7.72 (d, J = 7.7 Hz, 1H), 8.20 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 70.7, 111.7, 113.0, 115.1, 115.3, 115.5, 119.5 (2C), 119.9, 120.2, 122.7, 123.6, 125.46, 125.6, 128.5, 128.6, 135.3, 136.9, 137.6 (2C), 160.5, 200.3. HRMS (ESI-TOF) m/z : calcd for $C_{22}H_{16}FN_2O$ $[M + H]^+$ 343.1246, found 343.1236.

2-(4-Chlorophenyl)-2-(1H-indol-3-yl)indolin-3-one (4ad). Yellow solid (118 mg, 66% yield, mp = 123–1126 °C). 1H NMR (400 MHz, $CDCl_3$) δ 5.35 (s, 1H), 6.91 (t, J = 8.2 Hz, 2H), 6.98–7.03 (m, 1H), 7.12–7.13 (m, 2H), 7.17–7.21 (m, 1H), 7.24–7.26 (m, 2H), 7.37 (d, J = 8.2 Hz, 1H), 7.49–7.53 (m, 3H), 7.69 (d, J = 7.7 Hz, 1H), 8.26 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 70.7, 111.7, 113.1, 115.1, 119.4 (2C), 119.9, 120.1, 122.6, 123.6, 125.3, 125.6, 128.2 (2C), 128.5 (2C), 133.6, 136.9, 137.7, 138.1, 160.5,

200.1. HRMS (ESI-TOF) m/z : calcd for $C_{22}H_{16}ClN_2O$ $[M + H]^+$ 359.0951, found 359.0951.

2-(3-Bromophenyl)-2-(1H-indol-3-yl)indolin-3-one (4ae). Yellow solid (137 mg, 68% yield, mp = 135–138 °C). 1H NMR (400 MHz, $CDCl_3$) δ 5.38 (s, 1H), 6.92–9.97 (m, 2H), 7.01–7.05 (m, 1H), 7.15–7.23 (m, 4H), 7.38–7.44 (m, 2H), 7.48–7.52 (m, 1H), 7.52–7.56 (m, 1H), 7.72 (d, J = 7.7 Hz, 1H), 7.81 (t, J = 3.6 Hz, 1H), 8.30 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 70.7, 111.8, 113.2, 115.0, 119.4, 119.4, 120.0, 120.2, 122.5, 122.7, 123.7, 125.3, 125.6, 126.0, 129.4, 130.0, 130.8, 136.9, 137.8, 142.0, 160.5, 199.9. HRMS (ESI-TOF) m/z : calcd for $C_{22}H_{16}BrN_2O$ $[M + H]^+$ 403.0446, found 403.0441.

2-(1H-Indol-3-yl)-2-(*p*-tolyl)indolin-3-one (4ag). Yellow solid (122 mg, 69% yield, mp = 103–107 °C). 1H NMR (400 MHz, $CDCl_3$) δ 2.31 (s, 3H), 5.39 (s, 1H), 6.86–6.91 (m, 2H), 6.95–7.01 (m, 1H), 7.09–7.11 (m, 3H), 7.14–7.19 (m, 2H), 7.34 (d, J = 8.1 Hz, 1H), 7.43 (d, J = 8.2 Hz, 2H), 7.47–7.51 (m, 1H), 7.69 (d, J = 7.3 Hz, 1H), 8.29 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.1, 71.2, 111.7, 112.8, 115.5, 119.5, 119.5, 119.8, 119.9, 122.4, 123.8, 125.6 (2C), 126.7 (2C), 129.2 (2C), 136.5, 136.9, 137.4, 137.5, 160.5, 200.9. HRMS (ESI-TOF) m/z : calcd for $C_{23}H_{18}N_2O$ $[M + H]^+$ 339.1497, found 339.1492.

2-(2-Hydroxyphenyl)-2-(1H-indol-3-yl)indolin-3-one (4ak). Yellow solid (105 mg, 62% yield, mp = 107–111 °C). 1H NMR (400 MHz, $CDCl_3$) δ 2.08 (s, 1H), 5.42 (s, 1H), 6.90–7.01 (m, 6H), 7.09 (d, J = 7.9 Hz, 1H), 7.12–7.16 (m, 1H), 7.23–7.31 (m, 2H), 7.56–7.60 (m, 1H), 7.71 (dd, J = 7.9 Hz, 1.6 Hz, 1H), 7.76 (d, J = 7.8 Hz, 1H), 8.39 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 71.6, 111.8, 122.5, 113.4, 113.7, 118.8, 119.0, 120.1, 120.2, 120.7, 124.0, 124.5, 124.9, 125.6, 128.1, 129.9, 136.8, 138.7, 156.0, 160.1, 171.3, 204.0. HRMS (ESI-TOF) m/z : calcd for $C_{22}H_{17}N_2O_2$ $[M + H]^+$ 341.1290, found 341.1286.

2-(5-Methoxy-1H-indol-3-yl)-2-phenylindolin-3-one (4ba). Yellow solid (128 mg, 72% yield, mp = 91–94 °C). 1H NMR (400 MHz, $CDCl_3$) δ 3.63 (s, 3H), 5.39 (s, 1H), 6.58 (d, J = 2.2 Hz, 1H), 6.85 (dd, J = 8.8 Hz, 2.4 Hz, 1H), 6.92 (t, J = 7.4 Hz, 1H), 6.96 (d, J = 8.2 Hz, 1H), 7.12 (d, J = 2.6 Hz, 1H), 7.26–7.34 (m, 4H), 7.51–7.55 (m, 1H), 7.62 (dd, J = 8.0 Hz, 1.5 Hz, 2H), 7.72 (d, J = 7.7 Hz, 1H), 8.14 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.5, 71.2, 101.8, 112.3, 112.3, 112.8, 115.4, 119.6, 119.7, 124.4, 125.5, 126.0, 126.84 (2C), 127.7, 128.4 (2C), 131.9, 137.5, 139.3, 154.2, 160.5, 200.1. HRMS (ESI-TOF) m/z : calcd for $C_{23}H_{19}N_2O_2$ $[M + H]^+$ 355.1446, found 355.1429.

2-(4-Fluorophenyl)-2-(5-methoxy-1H-indol-3-yl)indolin-3-one (4bb). Yellow solid (137mg, 74% yield, mp = 201–204 °C). 1H NMR (400 MHz, $CDCl_3$) δ 3.65 (s, 3H), 5.37 (s, 1H), 6.55 (d, J = 2.3 Hz, 1H), 6.85 (dd, J = 8.8 Hz, 2.4 Hz, 1H), 6.91–7.03 (m, 4H), 7.09 (d, J = 2.6 Hz, 1H), 7.27 (d, J = 9.6 Hz, 1H), 7.52–7.60 (m, 3H), 7.72 (d, J = 7.7 Hz, 1H), 8.19 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.6, 70.7, 101.7, 112.3, 112.4, 113.1, 115.1, 115.2, 115.3, 119.7, 119.9, 124.4, 125.5, 125.9, 128.6, 128.7, 132.0, 135.1, 137.7, 154.1, 160.5, 162.5 (d, J = 246 Hz), 200.6. HRMS (ESI-TOF) m/z : calcd for $C_{23}H_{18}FN_2O_2$ $[M + H]^+$ 373.1352, found 373.1334.

2-(5-Methoxy-1H-indol-3-yl)-2-(3-methoxyphenyl)indolin-3-one (4bh). Yellow solid (140 mg, 75% yield, mp = 91–95 °C). 1H NMR (400 MHz, $CDCl_3$) δ 3.62 (s, 3H), 3.74 (s, 3H), 5.32 (s, 1H),



6.59 (d, $J = 2.4$ Hz, 1H), 6.80–6.84 (m, 2H), 6.89 (t, $J = 7.7$ Hz, 1H), 6.93 (d, $J = 8.2$ Hz, 1H), 7.11 (d, $J = 2.7$ Hz, 1H), 7.16–7.21 (m, 2H), 7.23–7.25 (m, 1H), 7.27 (s, 1H) 7.48–7.52 (m, 1H), 7.69 (d, $J = 7.7$ Hz, 1H), 8.01 (s, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 55.2, 55.6, 71.1, 101.9, 112.2, 112.3, 112.8 (2C), 112.9, 115.5, 119.3, 119.6, 119.9, 124.4, 125.5, 126.0, 129.3, 131.9, 137.4, 141.0, 154.0, 159.6, 160.4, 200.4. HRMS (ESI-TOF) m/z : calcd for $\text{C}_{24}\text{H}_{21}\text{N}_2\text{O}_3$ $[\text{M} + \text{H}]^+$ 385.1552, found 385.1535.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was supported by an OPERA-grant of BITS Pilani and DST-SERB (EMR/2016/005599). SV thanks to SERB-NPDF grant (PDF/2017/001791) for Research Fellowship. The authors are also grateful for generous support from the DST-FIST (SR/FST/CSI-270/2015) for HRMS facility to the Department of Chemistry at BITS-Pilani.

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- The X-ray crystallographic structure for **2g** has been deposited at the Cambridge Crystallographic Data Centre (CCDC), under deposition numbers CCDC 1832862.†

