



Research Article



An efficient synthesis of bis-indolyloxindoles from (phenylimino) indolin-2-ones and 1H-indole catalyzed by Citric acid

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Keywords 3, 3-di (indolyl) indolin-2-ones, 1H-indole (phenylimino) indolin-2-ones, Citric acid.

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ABSTRACT

Citric acid efficiently catalyzes the reaction of (phenylimino) indolin-2-ones with 1*H*-indole in CH₂Cl₂ at room temperature to afford 3, 3-di (indolyl) indolin-2-ones in excellent yields.

Keywords 3, 3-di (indolyl) indolin-2-ones, 1*H*-indole (phenylimino) indolin-2-ones, Citric acid.

1. INTRODUCTION

The oxindole structure is featured widely in a variety of pharmacologically and biologically active compounds [1-8]. Especially, 3, 3-diaryloxindoles are known to possess mechanism-specific antibacterial, antiprotozoal, antiproliferative, and anti-inflammatory activities [9]. These compounds have also been used as laxatives [10] and lead compounds for Ca²⁺-depletion mediated inhibition of translation initiation [11]. The parent compound, trisindoline is a natural product and has been isolated by Kabayshi *et al* [12].

Tabatabaeian *et al* reported the Ru (III)-catalyzed synthesis of 3,3-di(indolyl)indolin-2-ones by the reaction of (phenylimino)indolin-2-ones and indoles [13]. The use of mild acids with low cost is essential to develop an efficient method for the synthesis of 3, 3-di (indolyl)oxindoles from (phenylimino)indolin-2-ones and indoles. In some of the protocols, sulfonic acids have been used as catalyst [14]. A few other methods have also been reported for the synthesis of this class compounds from different other materials [15-16]. Furthermore, there have been no reports on the use of Citric acid for the synthesis of 3, 3-di (indolyl) oxindoles from (phenylimino) indolin-2-ones.

As a part of our continuing interest in the development of new synthetic methodologies [20-21] we herein, disclose our results on the Citric acid catalyzed synthesis of 3,3-di(indolyl)oxindoles from (phenylimino)indolin-2-ones and 1*H*-indole.

2. MATERIALS AND METHOD

General ¹H NMR and ¹³C NMR spectra were recorded in CDCl₃ on 200 MHz or 300 MHz or 500 MHz spectrometer at ambient temperature. The coupling constant *J* is given in Hz. The chemical shifts are reported in ppm on scale downfield from TMS as internal standard and signal patterns are indicated as follows: *s* = singlet, *d* = doublet, *t* = triplet, *q* = quartet, *sex* = sextet, *m* = multiplet, *br* = broad. FTIR spectra were recorded on KBr pellets CHCl₃/neat (as mentioned) and reported in wave number (cm⁻¹). Optical rotations were measured on digital polarimeter using a 1 mL cell with a 1 dm path length. For low (MS) and High (HRMS) resolution, *m/z* ratios are reported as values in atomic mass units. Mass analysis was performed in ESI mode.

All reagents were used without further purification unless specified otherwise. Solvents were distilled prior to use. THF, toluene and diethyl ether were distilled from Na and benzophenone ketyl; MeOH

from Mg and I₂; CH₂Cl₂ from CaH₂. All air or moisture-sensitive reactions were conducted under nitrogen or argon atmosphere in flame-dried or oven-dried glassware with magnetic stirring. Column chromatography was carried out using silica gel (60-120 mesh or 100- 200 mesh) packed in glass columns. Technical grade ethyl acetate and petroleum ether used for column chromatography were distilled prior to use.

General procedure for the preparation of

3, 3-di (1H-indol-3-yl) indolin-2-ones (3a-l):

To mixture of (phenylimino) indolin-2-ones (**1a**) (1 mmol), and 1H-indole (**2**) (2 mmol) in anhydrous CH₂Cl₂ (10 mL) was added Citric acid (10 mol %) under nitrogen atmosphere in a 50-mL flask and stirred at room temperature 2-3 min. After completion as monitored by TLC, the reaction mixture was diluted washed with water (3 x 15 mL) and extracted with ethyl acetate; the combined organic layers were concentrated to afford the crude mixture. The crude mixture was purified by hexane/AcOEt flash chromatography to afford the pure products **3a-l**.

Physical and spectral data

3, 3-Di (1H-indol-3-yl) indolin-2-one (3a, C₂₄H₁₇N₃O)

White solid; yield 80%; m.p.: 317–319 °C; IR (KBr): ν 3429 (NH), 3326 (NH), 3040, 1709, 1613, 1471, 1106, 930, 736 cm⁻¹; ¹H NMR (500 MHz, DMSO-*d*₆): δ = 10.82 (s, 2H, NH), 10.50 (s, 1H, NH), 7.43 (d, *J* = 8.1 Hz, 2H), 7.33 - 7.28 (m, 4H), 7.01 (d, *J* = 8.0 Hz, 3H), 6.96 (t, *J* = 7.5 Hz, 1H), 6.71 (s, 2H), 6.80 (t, *J* = 7.5 Hz, 2H) ppm; ¹³C NMR (125 MHz, DMSO-*d*₆): δ = 178.7, 141.3, 136.9, 134.6, 127.8, 125.7, 124.9, 124.2, 121.4, 120.9, 120.7, 118.2, 114.3, 111.6, 109.5, 52.5 ppm; MS (ESI, MeOH): *m/z* = 364 ([M+H]⁺).

3, 3-Di (1H-indol-3-yl)-5-methylindolin-2-one (3b, C₂₅H₁₉N₃O)

White solid; yield: 80%; m.p.: 306-307 °C; IR (KBr): ν 3375 (NH), 3325 (NH), 3041, 1704, 1489, 1100, 809, 736 cm⁻¹; ¹H NMR (500 MHz, DMSO-*d*₆): δ = 10.93 (s, 2H, NH), 10.50 (s, 1H, NH), 7.35 (d, *J* = 8.1 Hz, 2H), 7.24 (d, *J* = 7.9 Hz, 2H), 7.05 - 7.00 (m, 4H), 6.90 - 6.88 (m,

1H), 6.85 (s, 2H), 6.83 - 6.80 (m, 2H), 2.19 (s, 3H, -CH₃) ppm; ¹³C NMR (125 MHz, DMSO-*d*₆): δ = 178.5, 138.6, 136.8, 134.5, 130.0, 128.2, 125.8, 125.5, 124.5, 121.0, 120.8, 118.0, 114.5, 111.2, 109.1, 52.7, 20.1 (-CH₃) ppm; MS (ESI, MeOH): *m/z* = 378 ([M+H]⁺).

3,3-Di(1H-indol-3-yl)-5,7-dimethylindolin-2-one (3c, C₂₆H₂₁N₃O)

White solid; yield 81%; m.p.: 296-297 °C; IR (KBr): ν 3457 (NH), 3337 (NH), 1680, 1456, 1101, 850, 742 cm⁻¹; ¹H NMR (500 MHz, DMSO-*d*₆): δ = 10.92 (s, 2H, NH), 10.51 (s, 1H, NH), 7.35 (d, *J* = 8.2 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 7.35 - 7.00 (m, 2H), 6.85 - 6.81 (m, 6H), 2.30 (s, 3H, CH₃), 2.16 (s, 3H, CH₃) ppm; ¹³C NMR (125 MHz, DMSO-*d*₆): δ = 179.3, 137.3, 137.1, 134.2, 130.1, 129.3, 125.5, 124.1, 122.5, 121.1, 120.7, 118.5, 118.2, 114.7, 111.6, 52.9, 20.8, 18.6 ppm; MS (ESI, MeOH): *m/z* = 392 ([M+H]⁺).

3, 3-Di (1H-indol-3-yl)-5-methoxyindolin-2-one (3d, C₂₅H₁₉N₃O₂)

White solid; yield 82%; m.p.: 288-290 °C; IR (KBr): ν 3364, 3048, 1689, 1487, 1148, 1015, 858, 742 cm⁻¹; ¹H NMR (500 MHz, DMSO-*d*₆): δ = 10.95 (s, 2H, NH), 10.42 (s, 1H, NH), 7.35 (d, *J* = 8.0 Hz, 2H), 7.22 (d, *J* = 8.1 Hz, 2H), 7.02 - 7.02 (m, 2H), 6.92 - 6.90 (m, 1H), 6.88 (s, 2H), 6.84 - 6.81 (m, 4H), 3.61 (s, 3H, OCH₃) ppm; ¹³C NMR (125 MHz, DMSO-*d*₆): δ = 178.4, 154.5, 136.7, 135.9, 134.6, 125.3, 124.4, 120.9, 120.6, 118.1, 114.2, 112.1, 112.1, 115.7, 109.9, 55.4, 53.2 (OCH₃) ppm; MS (ESI, MeOH): *m/z* = 394 ([M+H]⁺).

3, 3-Di (1H-indol-3-yl)-5-fluoroindolin-2-one (3e, C₂₄H₁₆FN₃O)

White solid; yield 78%; m.p.: 239-240 °C; IR (KBr): ν 3436, 3316, 1696, 1481, 1104, 861, 734 cm⁻¹; ¹H NMR (500 MHz, DMSO-*d*₆): δ = 10.95 (s, 2H, NH), 10.62 (s, 1H, NH), 7.34 (d, *J* = 8.1 Hz, 2H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.05 - 7.21 (m, 5H), 6.91 (s, 2H), 6.84 (t, *J* = 7.5 Hz, 2H) ppm; ¹³C NMR (125 MHz, DMSO-*d*₆): δ = 178.7, 157.9, 137.6, 136.8, 136.4, 125.6, 124.5, 121.2, 120.4, 118.2, 114.1, 113.4, 112.2, 111.6, 110.4, 53.0 ppm; MS (ESI, MeOH): *m/z* = 382 ([M+H]⁺).

3, 3-Di (1H-indol-3-yl)-5-chloroindolin-2-one (3f, C₂₄H₁₆ClN₃O)

White solid, yield 80%; m.p.: 290-291 °C; IR (KBr): ν 3440, 3362, 3037, 1699, 1476, 1105, 817, 736 cm⁻¹; ¹H NMR (500 MHz, DMSO-*d*₆): δ = 10.35 (s, 1H, NH), 10.25 (s, 2H, NH), 7.39 (d, *J* = 8.1 Hz, 2H), 7.31 (d, *J* = 8.3 Hz, 1H), 7.19 - 7.21 (m, 3H), 7.05 - 7.01 (m, 3H), 6.89 (s, 2H), 6.84 (t, *J* = 7.5 Hz, 2H) ppm; ¹³C NMR (125 MHz, DMSO-*d*₆): δ = 178.3, 140.3, 136.9, 136.6, 127.8, 125.5, 125.4, 124.6, 124.4, 121.0, 120.5, 118.4, 113.5, 111.7, 111.1, 52.8 ppm; MS (ESI, MeOH): *m/z* = 398 ([M+H]⁺).

3, 3-Di (1H-indol-3-yl)-5-bromoindolin-2-one (3g, C₂₄H₁₆BrN₃O)

White solid; yield 75%; m.p.: 304-306 °C; IR (KBr): ν 3355 (NH), 3123 (NH), 3075, 1693, 1615, 1475, 745 cm⁻¹; ¹H NMR (500 MHz, DMSO-*d*₆): δ = 10.14 (s, 1H, NH), 10.03 (s, 2H, NH), 7.47 (s, 3H), 7.32 (d, *J* = 2 Hz, 1H), 7.26 (d, *J* = 8 Hz, 2H), 7.05 (t, *J* = 8 Hz, 2H), 6.99 (d, *J* = 8 Hz, 1H), 6.91 - 6.87 (m, 2H), 6.86 - 6.82 (m, 2H) ppm; ¹³C NMR (125 MHz, DMSO-*d*₆): δ = 178.2, 140.7, 136.9, 130.6, 127.2, 125.3, 124.32, 121.0, 120.7, 120.4, 118.3, 113.5, 113.1, 111.4, 111.5, 52.8 ppm; MS (ESI, MeOH): *m/z* = 444 ([M+H]⁺).

3, 3-Di (1H-indol-3-yl)-6-bromoindolin-2-one (3h, C₂₄H₁₆BrN₃O)

White solid; yield 72%; m.p.: 309 - 311 °C; IR (KBr): ν 3405 (NH), 3110 (NH), 3030, 1710, 1608, 1452, 1115, 744 cm⁻¹; ¹H NMR (500 MHz, DMSO-*d*₆): δ = 11.00 (s, 2H, NH); 10.74 (s, 1H, NH), 7.36 (d, *J* = 8.0 Hz, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.10 - 7.16 (m, 3H), 7.02 (t, *J* = 7.6 Hz, 2H), 6.84 (d, *J* = 2.4 Hz, 2H), 6.81 (t, *J* = 7.6 Hz, 2H) ppm; ¹³C NMR (125 MHz, DMSO-*d*₆): δ = 178.4, 143.1, 136.7, 133.9, 126.8, 125.5, 124.4, 124.1, 121.0, 120.8, 120.2, 118.6, 113.7, 112.5, 111.8, 52.2 ppm; MS (ESI, MeOH): *m/z* = 444 ([M+H]⁺).

3, 3-Di (1H-indol-3-yl)-5-nitroindolin-2-one (3i, C₂₄H₁₆N₄O₃)

Yellow solid; yield 70%; m.p.: 281-282 °C; IR (KBr): ν 3366, 3112, 1710, 1697, 1626, 1470, 1335, 735 cm⁻¹; ¹H

NMR (500 MHz, DMSO-*d*₆): δ = 11.33 (s, 1H, NH), 11.09 (s, 2H, NH), 8.25 (d, *J* = 8.7 Hz, 1H), 7.90 (s, 1H), 7.39 (d, *J* = 8.1 Hz, 2H), 7.20 - 7.22 (m, 3H), 7.04 (t, *J* = 7.8 Hz, 2H), 6.96 (s, 2H), 6.83 (t, *J* = 7.3 Hz, 2H); ¹³C NMR (125 MHz, DMSO-*d*₆): δ = 179.0, 147.5, 142.5, 137.9, 136.1, 126.2, 125.6, 125.4, 122.1, 121.2, 119.4, 119.4, 113.6, 112.7, 110.2, 52.4 ppm; MS (ESI, MeOH): *m/z* = 409 ([M+H]⁺).

3, 3-Di (1H-indol-3-yl)-1-methylindolin-2-one (3j, C₂₅H₁₉N₃O)

White solid; yield 78%; m.p.: 277-279 °C; IR (KBr): ν 3360 (NH), 3118 (NH), 3047, 2950, 1695, 1670, 1611, 1472, 734 cm⁻¹; ¹H NMR (500 MHz, DMSO-*d*₆): δ = 10.17 (s, 2H, NH), 7.56 (d, *J* = 8 Hz, 2H), 7.35 - 7.31 (m, 2H), 7.24 (d, *J* = 8 Hz, 2H), 7.12 - 7.15 (m, 1H), 7.05 - 7.00 (m, 3H), 6.91 (t, *J* = 7.6 Hz, 2H), 6.83 (t, *J* = 7.4 Hz, 2H), 3.32 (s, 3H, N-CH₃); ¹³C NMR (125 MHz, DMSO-*d*₆): δ = 176.95, 142.69, 136.95, 133.69, 127.88, 125.62, 124.55, 124.29, 122.07, 120.91, 120.71, 118.26, 114.05, 111.55, 108.46, 52.17, 26.17 (NCH₃) ppm; MS (ESI, MeOH): *m/z* = 378 ([M+H]⁺).

3, 3-Di (1H-indol-3-yl)-1-benzylindolin-2-one (3k, C₃₁H₂₃N₃O)

White solid; Yield 80%; m.p.: 198-200 °C; IR (KBr): ν 3410, 3120, 1702, 1472, 734 cm⁻¹; ¹H NMR (500 MHz, DMSO-*d*₆): δ = 9.81 (s, 2H), 7.35-7.37 (m, 4H), 7.24 - 7.33 (m, 5H), 7.10 - 7.13 (m, 3H), 6.98 - 7.03 (m, 3H), 6.87 (s, 2H), 6.74 (t, *J* = 7.2 Hz, 2H), 5.01 (s, 2H, CH₂) ppm; ¹³C NMR (125 MHz, DMSO-*d*₆): δ = 177.93, 142.57, 137.78, 137.41, 134.63, 129.44, 128.75, 128.47, 128.37, 126.44, 125.65, 125.26, 125.10, 123.12, 121.94, 121.66, 119.18, 119.18, 119.18, 114.83, 112.54, 110.21, 53.12, 43.84 ppm; MS (ESI, MeOH): *m/z* = 454 ([M+H]⁺).

3, 3-Di (1H-indol-3-yl)-N-acetylindolin-2-one (3l, C₂₆H₁₉N₃O₂)

White solid; yield 72%; m.p.: 310-312 °C; IR (KBr): ν 3420 (NH), 3323 (NH), 3052, 1747, 1720, 1460, 1371, 1349, 1299, 1267, 1245, 1170, 764, 750, 748 cm⁻¹; ¹H NMR (500 MHz, DMSO-*d*₆): δ = 11.05 (s, 2H, NH),

7.38 - 6.86 (m, 14H), 2.06 (s, 3H, CH₃) ppm; ¹³C NMR (125 MHz, DMSO-*d*₆): δ = 176.95, 142.69, 136.95, 133.69, 127.88, 125.62, 124.55, 124.29, 122.07, 120.91, 120.71, 118.26, 114.05, 111.55, 108.46, 52.17, 23.05 ppm; MS (ESI, MeOH): *m/z* = 406 ([M+H]⁺).

3. RESULTS AND DISCUSSION

Initially, we have studied the reaction of 3-(phenylimino) indolin-2-one (**1a**) with 1*H*-indole (**2**) in presence of 10 mol% of Citric acid in CH₂Cl₂ at room temperature. The reaction went to completion in 2-3 min and the product 3, 3-di (1*H*-indol-3-yl) indolin-2-one **3a** was isolated in 85% yield (Table 1, entry 1).

Encouraged by the results obtained with **1a** and **2**, we turned our attention to various substituted 3-(phenylimino) indolin-2-ones. Interestingly, 5-methyl-3-(phenylimino) indolin-2-one (**1b**) underwent smooth reaction with **2** to afford the corresponding 3, 3-di (1*H*-indol-3-yl)-5-methylindolin-2-one (**3b**) in 80% yield (Table 1, entry 2). The scope of this reaction is exemplified with a disubstituted compound, 5, 7-dimethyl-3-(phenylimino) indolin-2-one (**1c**) with **2** to produce the desired product (**3c**) in 81% yield (Table 1, entry 3).

Thus, 1*H*-indole was used as a representative starting material and the reactions were performed with various substituted (phenylimino)indolin-2-ones such as 5-methoxy, 5-fluoro, 5-chloro, 5-bromo, 6-bromo, 5-nitro derivatives to obtain the corresponding products in good yields (Table 1, entries 4-9). In all cases, the reactions proceeded smoothly to furnish the desired product in good to excellent yields. This method was further extended to N-methyl, N-Benzyl, N-Acetyl (phenylimino) indolin-2-ones to produce the desired products (Table 1, entries 10-12) in good yields. However, in the absence of the catalyst, the reaction did not yield any product even at reflux temperature. Lowering of the reaction temperature was detrimental to the efficiency of this procedure. The reaction conditions are mild and no side products or decomposition of the products were observed.

All products were characterized by ¹H, ¹³C-NMR spectroscopy and mass spectroscopy. The reaction mechanism for product formation may be explained as follows. Initially, Citric acid activates the (phenylimino)indolin-2-ones **1a** to generate the Citric acid-(phenylimino)indolin-2-one carbenium ion (**1a**₁), which subsequently reacts with 2 equivalents of 1*H*-indole (**2**) to furnish the 3,3-di(1*H*-indol-3-yl)indolin-2-one (**3a**). To know the efficacy of the Citric acid catalysis, (phenylimino)indolin-2-ones (**1**) was treated with 1*H*-indole (**2**) in the presence of 10 mol% Citric acid in CH₂Cl₂ at room temperature for 2-3 min, the corresponding 3,3-di(1*H*-indol-3-yl)indolin-2-ones **3** were obtained in excellent yields. The scope and generality of this process is illustrated with respect to various (phenylimino) indolin-2-ones and 1*H*-indole and the results are summarized in Table 1.

4. CONCLUSIONS

We have described a simple, convenient and efficient protocol for the synthesis of 3,3-di(1*H*-indol-3-yl)indolin-2-ones from (phenylimino)indolin-2-ones by the activation with *citric acid* catalyst. This method offers significant advantages such as low cost, high conversions, short reaction times and mild reaction conditions which makes it useful and attractive strategy.

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Scheme 1: Synthesis of 3, 3-di (1*H*-indol-3-yl) indolin-2-one

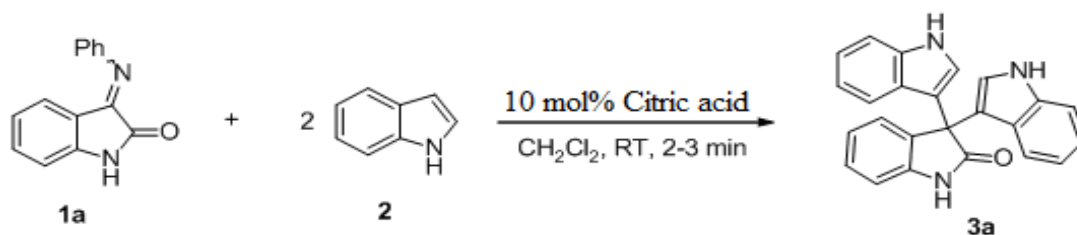
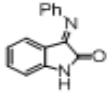
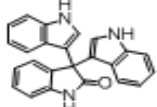
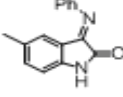
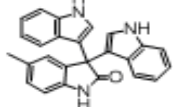
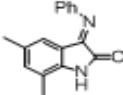
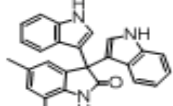
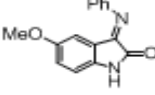
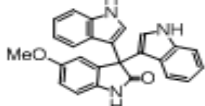
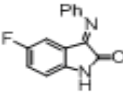
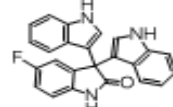
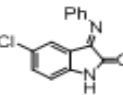
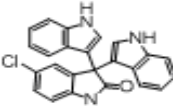
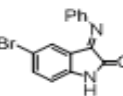
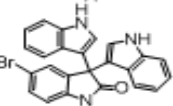
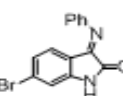
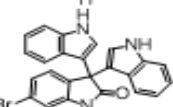
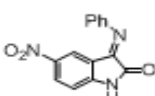
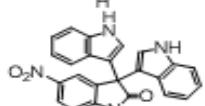
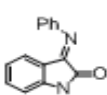
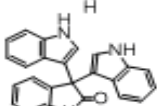
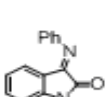
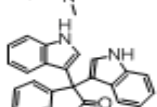
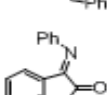
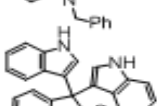


Table 1: catalyzed synthesis of bis-indolyloxindoles from phenylimino)indolin-2-ones and 1*H*-indole

Entry	Isatin-imine (1)	Indole (2)	Product (3) ^a	Yield (%) ^b
a				85
b				80
c				81
d				82
e				78
f				80
g				75
h				72
i				70
j				78
k				80
l				72

^a The reaction time was 2-3 min. All products were characterized by ¹H and ¹³C-NMR, IR and mass spectroscopy.

^b Yield of isolated product.