



## ORIGINAL ARTICLE

# Pentafluorophenylammonium triflate: An effective and reusable organocatalyst for the one-pot preparation of 2,4-diaryl-5*H*-indeno[1,2-*b*]pyridin-5-one derivatives



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## KEYWORDS

Pentafluorophenylammonium triflate (PFPAT);  
Chalcones;  
Indeno[1,2-*b*]pyridines;  
1,3-Indandione

**Abstract** A new one-pot and efficient three-component condensation of 1,3-diphenyl-2-propen-1-ones (chalcones), 1,3-indandione, and ammonium acetate using pentafluorophenylammonium triflate (PFPAT) as catalyst for the synthesis of substituted 2,4-diaryl-5*H*-indeno[1,2-*b*]pyridin-5-one is described. The present methodology offers several advantages, such as good yields, atom economy, short reaction times and a recyclable catalyst with a very easy work up.

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## 1. Introduction

5*H*-Indeno[1,2-*b*]pyridin-5-ones (4-azafluorenones) are the naturally occurring alkaloids isolated from the root of the plant *Polyalthia debilis* (Pierre) belonging to the family of Annonaceae. Azafluorenone, being the core structural unit in a wide range of natural products, has attracted much research in recent times (Mueller et al., 2009). Representative members of this class of compounds are onychine (a), polyfothine (b), isoursuline (c), and cyathocaline (d) (Fig. 1). These compounds

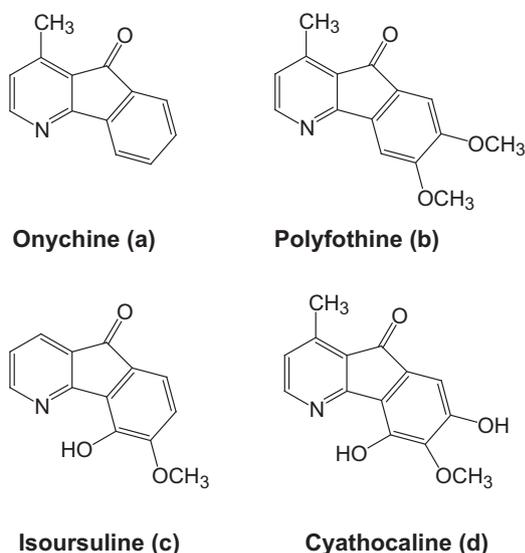
show powerful antimicrobial, DNA damaging, and anti-malarial effects against *Plasmodium falciperum* and also acts as a DNA modifying agent (Kraus and Kempema, 2010; Wijeratne et al., 1995). Azafluorenone derivatives have been reported to possess activities of aldose reductase inhibition (Wang and Wei, 2012) and cytotoxic activity (Prachayasittikul et al., 2009). Roots of *Polyalthia cerasoides* has led to the isolation of the new compound, 6,8-dihydroxy-7-methoxy-1-methyl-azafluorenone. This compound exhibited potent cytotoxic activities (Pumsalid et al., 2010). Koyama et al. (2005) reported structure–activity relations of azafluorenone and aza-anthraquinone as antimicrobial compounds. Correlations among reduction potential, hydrophobic parameter, and antimicrobial activity were discussed. Due to their crucial importance in chemistry, biology and industry, a general and flexible method of preparation of azafluorenones is important.

Several methods are available describing the synthesis of 5*H*-indeno[1,2-*b*]pyridin-5-ones: Dhara et al. (2013) synthe-

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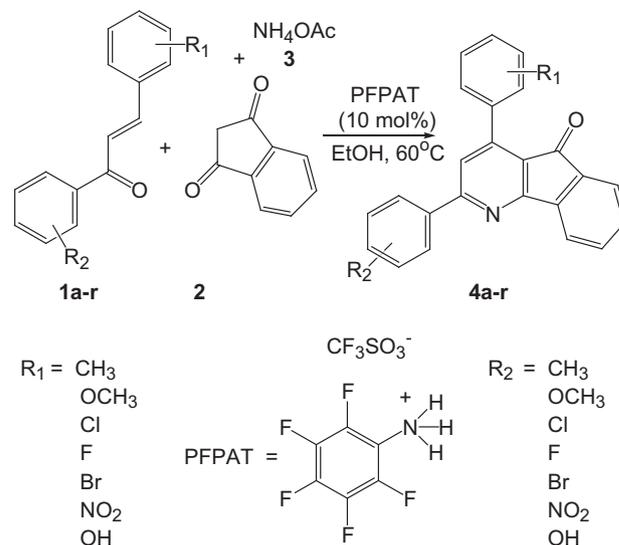




**Figure 1** Some naturally occurring bioactive azafluorenones.

sized azafluorenone via oxidative intramolecular Heck cyclization using Pd(0). [Tapaswi and Mukhopadhyay, 2011](#) reported the synthesis of indeno[1,2-*b*]pyridines using ceric ammonium nitrate as catalyst. [Marquise et al. \(2013\)](#) reported the synthesis of azafluorenones and related compounds by a route involving cyclization of the ketones. [Li et al. \(2013\)](#) reported a novel three-component [5 + 1] heterocyclization leading to 2-azafluorenone synthesis and its ployfunctionalisations. [Tu et al. \(2007\)](#) developed the synthesis of substituted indeno[1,2-*b*]pyridines by the multi-component reaction of aldehydes, 1,3-indandione and aromatic ketones in the presence of ammonium acetate under microwave irradiation. [Addla et al. \(2012\)](#) reported the synthesis of novel 1-benzyl 2-butyl-4-chloroimidazole embodied 4-azafluorenones via the molecular hybridization approach in very good yields using one pot condensation of 1-benzyl-2-butyl-4-chloroimidazole-5-carboxaldehyde, 1,3-indanedione, aryl/heteroaryl methyl ketones and ammonium acetate and studied their antimicrobial evaluation. [Mukhopadhyay et al. \(2010\)](#) reported the synthesis of several indeno[1,2-*b*]pyridine derivatives by the multi-component reaction of 1,3-indandione, aldehydes, 2-acetylthiophene or 2-acetylfluorene and ammonium acetate at room temperature using L-proline (15 mol%) as catalyst. [Padwa et al. \(2000\)](#) reported the synthesis of several alkaloids employing the Pummerer reaction of imidosulfoxides bearing tethered alkenyl groups. Most of these methodologies suffer from one or more serious drawbacks such as laborious and complex work-up and purification, strong basic and acidic conditions, multistep reactions and occurrence of side reactions, low yields, and the use of expensive reagents. In addition, most of the earlier-reported methodologies require elevated temperature created by microwave-oven irradiation.

Considering the novel route for the synthesis of heterocyclic compounds based on the development of environmentally friendly procedures for the synthesis of biologically active molecules, such as 4,6-diphenyl-3,4-dihydropyrimidine-2(*H*)-thione ([Aswin et al., 2013](#)), 1,4-dihydropyridine ([Mansoor et al., 2013](#)), polyhydroquinoline derivatives ([Mansoor et al., 2012a](#)) and 2-amino-4,6-diphenylnicotinonitrile ([Mansoor](#)



**Scheme 1** Synthesis of various 2,4-diaryl-5*H*-indeno[1,2-*b*]pyridin-5-one derivatives.

[et al., 2012b](#)) by multicomponent reactions, we now describe the synthesis of 2,4-diaryl-5*H*-indeno[1,2-*b*]pyridin-5-one derivatives using PFPAT as an efficient organo-catalyst. These compounds were synthesized using chalcones, 1,3-indandione and ammonium acetate ([Scheme 1](#)).

## 2. Experimental

### 2.1. Apparatus and analysis

Chemicals were purchased from Merck, Fluka and Aldrich Chemical Companies. All yields refer to isolated products unless otherwise stated.  $^1\text{H}$  NMR (500 MHz) and  $^{13}\text{C}$  NMR (125 MHz) spectra were obtained using Bruker DRX-500 Avance at an ambient temperature, using TMS as internal standard. FT-IR spectra were obtained as KBr disks on Shimadzu spectrometer. Mass spectra were determined on a Varion – Saturn 2000 GC/MS instrument. Elemental analysis was measured by means of Perkin Elmer 2400 CHN elemental analyzer flowchart.

### 2.2. Preparation of the catalyst (PFPAT)

To a solution of 2,3,4,5,6-pentafluoroaniline (25 mmol) in toluene (25 mL),  $\text{CF}_3\text{SO}_3\text{H}$  (25 mmol) was added at 0–5 °C. The reaction mixture was stirred at the same temperature for 30 min. After this time, the solvent was evaporated *in vacuo*, the crude product was collected and washed with hexane to give the pure catalyst in 92% yield ([Funatomi et al., 2006](#)).

### 2.3. General experimental procedure for the synthesis of indeno[1,2-*b*]pyridine derivatives

In a 25 mL round-bottomed flask, 1,3-diphenyl-2-propen-1-ones (1 mmol), 1,3-indandione (1 mmol), and ammonium acetate (1.3 mmol) were stirred in the presence of 10 mol% of PFPAT in ethanol (5 mL) at 60 °C for the stipulated time.

The progress of the reaction was monitored by TLC. After completion of the reaction, the reaction mixture was diluted with water (10 mL) and extracted with ethyl acetate (3 × 10 mL). The organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, concentrated and recrystallized from hot ethanol to afford pure product.

### 3. Results

To find out the suitable conditions for the reaction, we studied the standard reaction of 1,3-diphenyl-2-propen-1-one (**1a**), 1,3-indandione (**2**), and ammonium acetate (**3**) as a model reaction using PFPAT (10 mol%) as catalyst (Scheme 1). In order to optimize the conditions, we studied the reaction in various conditions.

Among various catalysts tested, PFPAT (10 mol%) was found to be an effective catalyst wherein the product was obtained in good yield under mild conditions (Table 1). With PFPAT (10 mol%) as catalyst, next the effect of various solvents was screened (Table 2). Ethanol was found to be the best solvent under these conditions (Table 2, entry 5). Under the optimized set of reaction conditions a number of 1,3-diaryl-2-propen-1-one derivatives (**1**) were allowed to react with 1,3-indandione (**2**) and ammonium acetate (**3**) in the presence PFPAT (10 mol%) as catalyst (Scheme 1). The results are given in Table 3. The IR, <sup>1</sup>H NMR, <sup>13</sup>C NMR, mass and elemental analysis data of the synthesized compounds are given below.

3.1. Spectral data for the synthesized compounds are presented below (4a–r)

#### 3.1.1. 4-(4-Fluorophenyl)-2-(4-methylphenyl)-5H-indeno[1,2-b]pyridin-5-one (**4a**)

IR (KBr, cm<sup>-1</sup>): 3051, 2948, 2839, 1714, 1600, 1508, 1362, 1252, 1155, 828, 757; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ: 2.16 (s, 3H, CH<sub>3</sub>), 7.08–7.33 (m, 8H, ArH), 7.60 (s, 1H, Py-H), 7.72–7.88 (m, 4H, ArH) ppm; <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ: 18.0, 121.1, 123.3, 123.6, 123.9, 127.4, 128.3, 128.5, 129.0, 129.5, 129.7, 131.4, 131.9, 135.4, 135.7, 139.9, 141.4, 142.2, 142.8, 146.4, 147.4, 162.5, 163.9, 191.6 ppm; MS(ESI): *m/z* 366 (M+H)<sup>+</sup>; Anal. Calcd for C<sub>25</sub>H<sub>16</sub>FNO: C, 82.19; H, 4.38; N, 3.83%. Found: C, 82.11; H, 4.35; N, 3.80%.

#### 3.1.2. 3.1.2.4-(4-Methoxyphenyl)-2-(4-methylphenyl)-5H-indeno[1,2-b]pyridin-5-one (**4b**)

IR (KBr, cm<sup>-1</sup>): 3049, 2953, 2844, 1718, 1604, 1509, 1365, 1254, 1154, 826, 755; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ: 2.20 (s, 3H, CH<sub>3</sub>), 3.72 (s, 3H, OCH<sub>3</sub>), 7.13–7.29 (m, 8H, ArH), 7.74 (s, 1H, Py-H), 7.85–7.96 (m, 4H, ArH) ppm; <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ: 18.2, 55.0, 121.5, 123.7, 123.9, 123.9, 127.9, 128.6, 129.4, 129.8, 129.9, 131.1, 135.3, 135.6, 139.4, 141.7, 142.5, 146.7, 147.8, 162.2, 163.6, 191.3 ppm; MS(ESI): *m/z* 378 (M+H)<sup>+</sup>; Anal. Calcd for C<sub>26</sub>H<sub>19</sub>NO<sub>2</sub>: C, 82.76; H, 5.04; N, 3.71%. Found: C, 82.72; H, 5.00; N, 3.66%.

**Table 1** Synthesis of 4-(4-fluorophenyl)-2-(4-methylphenyl)-5H-indeno[1,2-b]pyridin-5-one. Effect of catalysis<sup>a</sup>.

Entry	Catalyst	Amount of catalyst (mol%)	Time (h)	Yield (%) <sup>b</sup>
1	None	–	3.0	32
2	FeCl <sub>3</sub>	20	3.0	65
3	InCl <sub>3</sub>	20	3.0	68
4	BiCl <sub>3</sub>	10	3.0	72
5	La(OTf) <sub>3</sub>	10	3.0	76
6	Nd(OTf) <sub>3</sub>	10	3.0	60
7	Yb(OTf) <sub>3</sub>	10	3.0	80
8	PFPAT	10	1.5	92
9	PFPAT	5	1.5	81
10	PFPAT	2	1.5	72
11	PFPAT	15	1.5	90

<sup>a</sup> Reaction conditions: chalcone **1a** (1 mmol), 1,3-indandione (1 mmol), and ammonium acetate (1.3 mmol) heating at 60 °C in the presence of PFPAT (10 mol%) in 5 ml ethanol.

<sup>b</sup> Isolated yields.

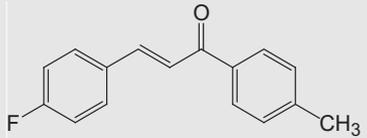
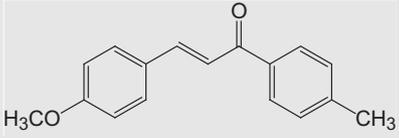
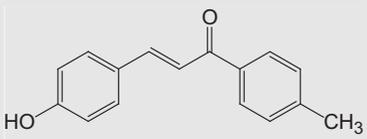
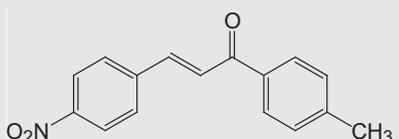
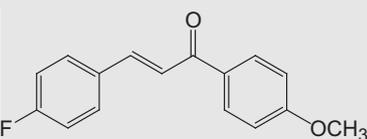
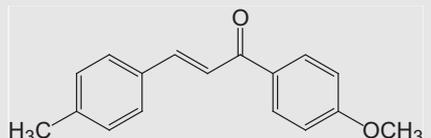
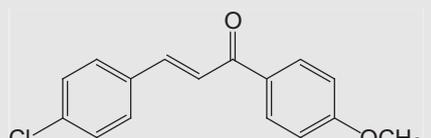
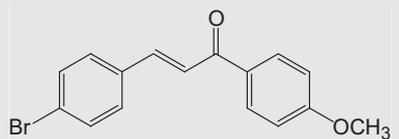
**Table 2** Synthesis of 4-(4-fluorophenyl)-2-(4-methylphenyl)-5H-indeno[1,2-b]pyridin-5-one. Effect of solvent.<sup>a</sup>

Entry	Solvent	Amount of catalyst (mol%)	Time (h)	Yield (%) <sup>b</sup>
1	Acetonitrile	10	1.5	68
2	1,4-Dioxane	10	1.5	63
3	Cyclohexane	10	1.5	48
4	Methanol	10	1.5	84
5	Ethanol	10	1.5	92
6	None	10	1.5	58

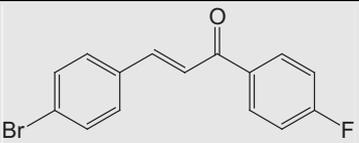
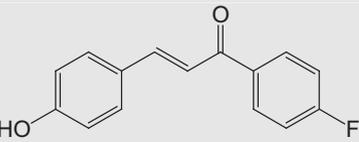
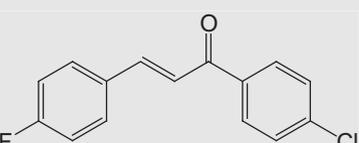
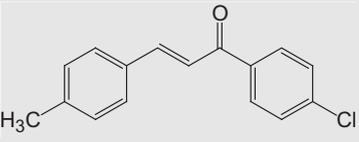
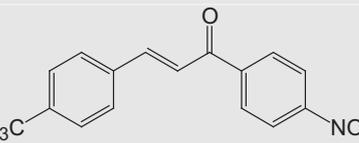
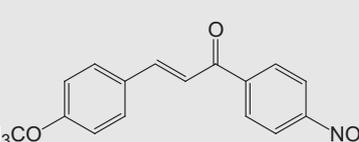
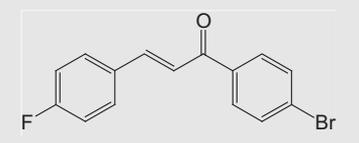
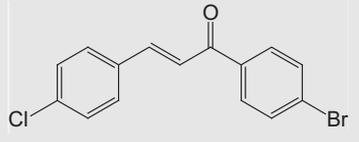
<sup>a</sup> Reaction conditions: chalcone **1a** (1 mmol), 1,3-indandione (1 mmol), and ammonium acetate (1.3 mmol) heating at 60 °C in the presence of PFPAT (10 mol%) with various solvents (5 ml).

<sup>b</sup> Isolated yields.

**Table 3** Synthesis of various 2,4-diaryl-5*H*-indeno[1,2-*b*]pyridin-5-one derivatives.<sup>a</sup>

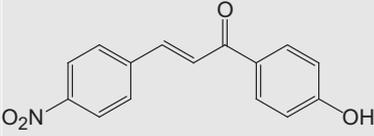
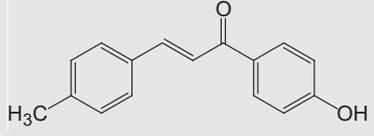
Entry	Chalcones	Product	Time (h)	Yield (%) <sup>b</sup>	Mp (°C)
1		<b>4a</b>	1.5	92	236–238
2		<b>4b</b>	2.0	83	224–226
3		<b>4c</b>	1.5	93	244–246
4		<b>4d</b>	1.5	94	217–219
5		<b>4e</b>	1.5	92	228–230
6		<b>4f</b>	2.0	83	206–208
7		<b>4g</b>	1.5	89	202–204
8		<b>4h</b>	1.5	88	214–216

**Table 3** (continued)

Entry	Chalcones	Product	Time (h)	Yield (%) <sup>b</sup>	Mp (°C)
9		<b>4i</b>	1.5	89	198–200
10		<b>4j</b>	1.5	91	226–228
11		<b>4k</b>	1.5	91	216–218
12		<b>4l</b>	2.0	84	210–212
13		<b>4m</b>	2.0	83	202–204
14		<b>4n</b>	2.0	82	246–248
15		<b>4o</b>	1.5	88	196–198
16		<b>4p</b>	1.5	89	206–208

(continue on next page)

**Table 3** (continued)

17		<b>4q</b>	1.5	95	234–236
18		<b>4r</b>	2.0	84	218–220

<sup>a</sup> Reaction conditions: chalcones **1a–r** (1 mmol), 1,3-indandione (1 mmol), and ammonium acetate (1.3 mmol) heating at 60 °C in the presence of PFPAT (10 mol%) in ethanol.

<sup>b</sup> Isolated yield.

### 3.1.3. 4-(4-Hydroxyphenyl)-2-(4-methylphenyl)-5H-indeno[1,2-b]pyridin-5-one (**4c**)

IR (KBr,  $\text{cm}^{-1}$ ): 3362, 3045, 2942, 2833, 1707, 1604, 1512, 1366, 1256, 1151, 824, 753;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$ : 2.26 (s, 3H,  $\text{CH}_3$ ), 7.18–7.45 (m, 8H, ArH), 7.69 (s, 1H, Py–H), 7.79–7.92 (m, 4H, ArH), 9.22 (s, 1H, OH) ppm;  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$ : 18.7, 121.0, 123.4, 123.5, 123.9, 128.0, 128.7, 129.1, 129.5, 129.7, 131.6, 135.2, 135.7, 139.0, 141.6, 142.4, 146.6, 147.6, 162.0, 163.4, 191.0 ppm; MS(ESI):  $m/z$  364 ( $\text{M} + \text{H}$ )<sup>+</sup>; Anal. Calcd for  $\text{C}_{25}\text{H}_{17}\text{NO}_2$ : C, 82.64; H, 4.68; N, 3.86%. Found: C, 82.60; H, 4.64; N, 3.84%.

### 3.1.4. 4-(4-Nitrophenyl)-2-(4-methylphenyl)-5H-indeno[1,2-b]pyridin-5-one (**4d**)

IR (KBr,  $\text{cm}^{-1}$ ): 3042, 2939, 2830, 1706, 1602, 1504, 1369, 1250, 1154, 827, 756;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$ : 2.19 (s, 3H,  $\text{CH}_3$ ), 7.22–7.40 (m, 8H, ArH), 7.76 (s, 1H, Py–H), 7.84–7.97 (m, 4H, ArH) ppm;  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$ : 17.6, 120.9, 123.3, 123.5, 123.7, 127.8, 128.8, 129.2, 129.5, 129.9, 131.7, 135.7, 135.7, 139.7, 142.1, 142.9, 147.1, 148.1, 162.0, 163.1, 191.2 ppm; MS(ESI):  $m/z$  393 ( $\text{M} + \text{H}$ )<sup>+</sup>; Anal. Calcd for  $\text{C}_{25}\text{H}_{16}\text{N}_2\text{O}_3$ : C, 76.53; H, 4.08; N, 7.14%. Found: C, 76.43; H, 4.02; N, 7.10%.

### 3.1.5. 4-(4-Fluorophenyl)-2-(4-methoxyphenyl)-5H-indeno[1,2-b]pyridin-5-one (**4e**)

IR (KBr,  $\text{cm}^{-1}$ ): 3049, 2946, 2837, 1713, 1611, 1513, 1367, 1245, 1152, 822, 752;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$ : 3.66 (s, 3H,  $\text{OCH}_3$ ), 7.06–7.33 (m, 8H, ArH), 7.62 (s, 1H, Py–H), 7.73–7.85 (m, 4H, ArH) ppm;  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$ : 55.9, 121.1, 123.1, 123.4, 123.8, 127.6, 128.1, 128.6, 128.9, 129.6, 129.9, 131.2, 131.7, 135.4, 135.6, 139.8, 142.3, 142.7, 143.1, 147.3, 148.3, 162.1, 163.8, 191.8 ppm; MS(ESI):  $m/z$  382 ( $\text{M} + \text{H}$ )<sup>+</sup>; Anal. Calcd for  $\text{C}_{25}\text{H}_{16}\text{FNO}_2$ : C, 78.74; H, 4.20; N, 3.67%. Found: C, 78.76; H, 4.24; N, 3.69%.

### 3.1.6. 4-(4-Methylphenyl)-2-(4-methoxyphenyl)-5H-indeno[1,2-b]pyridin-5-one (**4f**)

IR (KBr,  $\text{cm}^{-1}$ ): 3040, 2937, 2828, 1704, 1608, 1509, 1365, 1257, 1147, 821, 750;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$ : 2.22

(s, 3H,  $\text{CH}_3$ ), 3.74 (s, 3H,  $\text{OCH}_3$ ), 7.28–7.55 (m, 8H, ArH), 7.71 (s, 1H, Py–H), 7.80–7.94 (m, 4H, ArH) ppm;  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$ : 17.9, 55.2, 121.5, 123.6, 123.7, 123.9, 127.5, 128.5, 129.0, 129.6, 129.8, 131.5, 135.0, 135.5, 139.5, 142.0, 142.9, 147.2, 148.3, 161.8, 162.9, 192.5 ppm; MS(ESI):  $m/z$  378 ( $\text{M} + \text{H}$ )<sup>+</sup>; Anal. Calcd for  $\text{C}_{26}\text{H}_{19}\text{NO}_2$ : C, 82.76; H, 5.04; N, 3.71%. Found: C, 82.79; H, 5.00; N, 3.74%.

### 3.1.7. 4-(4-Chlorophenyl)-2-(4-methoxyphenyl)-5H-indeno[1,2-b]pyridin-5-one (**4g**)

IR (KBr,  $\text{cm}^{-1}$ ): 3051, 2949, 2844, 1719, 1602, 1511, 1366, 1255, 1144, 817, 746;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$ : 3.70 (s, 3H,  $\text{OCH}_3$ ), 7.20–7.48 (m, 8H, ArH), 7.68 (s, 1H, Py–H), 7.77–7.93 (m, 4H, ArH) ppm;  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$ : 55.5, 121.7, 123.5, 123.9, 124.2, 128.2, 128.8, 129.3, 129.4, 129.9, 131.3, 135.3, 135.6, 139.6, 142.1, 143.1, 147.3, 148.1, 161.7, 163.5, 192.2 ppm; MS(ESI):  $m/z$  398 ( $\text{M} + \text{H}$ )<sup>+</sup>; Anal. Calcd for  $\text{C}_{25}\text{H}_{16}\text{ClNO}_2$ : C, 75.48; H, 4.02; N, 3.52%. Found: C, 75.38; H, 4.05; N, 3.56%.

### 3.1.8. 4-(4-Bromophenyl)-2-(4-methoxyphenyl)-5H-indeno[1,2-b]pyridin-5-one (**4h**)

IR (KBr,  $\text{cm}^{-1}$ ): 3053, 2954, 2846, 1712, 1609, 1515, 1365, 1255, 1147, 820, 749;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$ : 3.67 (s, 3H,  $\text{OCH}_3$ ), 7.30–7.52 (m, 8H, ArH), 7.62 (s, 1H, Py–H), 7.83–7.99 (m, 4H, ArH) ppm;  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$ : 55.0, 121.2, 123.3, 123.8, 123.9, 127.9, 128.4, 129.4, 129.6, 129.8, 131.7, 135.7, 135.9, 139.5, 142.2, 142.9, 147.3, 147.5, 162.0, 163.0, 191.1 ppm; MS(ESI):  $m/z$  442.9 ( $\text{M} + \text{H}$ )<sup>+</sup>; Anal. Calcd for  $\text{C}_{25}\text{H}_{16}\text{BrNO}_2$ : C, 67.88; H, 3.62; N, 3.17%. Found: C, 67.78; H, 3.58; N, 3.14%.

### 3.1.9. 4-(4-Bromophenyl)-2-(4-fluorophenyl)-5H-indeno[1,2-b]pyridin-5-one (**4i**)

IR (KBr,  $\text{cm}^{-1}$ ): 3041, 2940, 2831, 1711, 1603, 1503, 1365, 1253, 1145, 819, 747;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.14–7.44 (m, 8H, ArH), 7.72 (s, 1H, Py–H), 7.85–7.98 (m, 4H, ArH) ppm;  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$ : 121.7, 123.6, 123.7, 123.8, 127.2, 128.3, 128.8, 129.2, 129.4, 129.7, 130.8,

131.4, 134.5, 135.3, 139.5, 141.3, 142.3, 142.6, 146.3, 147.5, 162.6, 163.8, 191.9 ppm; MS(ESI):  $m/z$  430.9 (M + H)<sup>+</sup>; Anal. Calcd for C<sub>24</sub>H<sub>13</sub>BrFNO: C, 66.99; H, 3.02; N, 3.26%. Found: C, 66.84; H, 3.02; N, 3.20%.

3.1.10. 4-(4-Hydroxyphenyl)-2-(4-fluorophenyl)-5H-indeno[1,2-b]pyridin-5-one (**4j**)

IR (KBr, cm<sup>-1</sup>): 3358, 3048, 2945, 2836, 1719, 1608, 1508, 1367, 1258, 1143, 820, 750; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ: 7.19–7.39 (m, 8H, ArH), 7.64 (s, 1H, Py-H), 7.73–7.93 (m, 4H, ArH), 9.28 (s, 1H, OH) ppm; <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ: 121.9, 123.0, 123.5, 123.8, 127.2, 127.7, 128.7, 129.3, 129.6, 130.3, 130.9, 131.6, 135.4, 135.8, 139.9, 141.2, 142.3, 142.7, 146.4, 147.5, 162.4, 163.5, 191.4 ppm; MS(ESI):  $m/z$  368 (M + H)<sup>+</sup>; Anal. Calcd for C<sub>24</sub>H<sub>14</sub>FNO<sub>2</sub>: C, 78.47; H, 3.81; N, 3.81%. Found: C, 78.40; H, 3.80; N, 3.84%.

3.1.11. 4-(4-Fluorophenyl)-2-(4-chlorophenyl)-5H-indeno[1,2-b]pyridin-5-one (**4k**)

IR (KBr, cm<sup>-1</sup>): 3045, 2944, 2833, 1714, 1602, 1512, 1364, 1254, 1152, 825, 754; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ: 7.15–7.40 (m, 8H, ArH), 7.73 (s, 1H, Py-H), 7.80–7.95 (m, 4H, ArH) ppm; <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ: 121.3, 123.4, 123.7, 123.9, 127.4, 128.0, 128.5, 129.2, 129.4, 129.7, 130.5, 131.8, 135.6, 135.7, 139.9, 141.6, 142.4, 142.8, 146.6, 147.6, 162.1, 163.7, 192.0 ppm; MS(ESI):  $m/z$  386 (M + H)<sup>+</sup>; Anal. Calcd for C<sub>24</sub>H<sub>13</sub>ClFNO: C, 74.72; H, 3.37; N, 3.63%. Found: C, 74.66; H, 3.32; N, 3.58%.

3.1.12. 4-(4-Methylphenyl)-2-(4-chlorophenyl)-5H-indeno[1,2-b]pyridin-5-one (**4l**)

IR (KBr, cm<sup>-1</sup>): 3054, 2955, 2845, 1718, 1606, 1504, 1366, 1260, 1156, 829, 758; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ: 2.23 (s, 3H, CH<sub>3</sub>), 7.23–7.52 (m, 8H, ArH), 7.63 (s, 1H, Py-H), 7.70–7.88 (m, 4H, ArH) ppm; <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ: 17.6, 122.0, 123.4, 123.7, 124.2, 127.3, 128.4, 129.4, 129.6, 130.5, 131.4, 135.4, 135.6, 139.6, 141.9, 142.9, 146.9, 147.8, 162.6, 163.6, 191.6 ppm; MS(ESI):  $m/z$  382 (M + H)<sup>+</sup>; Anal. Calcd for C<sub>25</sub>H<sub>16</sub>ClNO: C, 78.65; H, 4.19; N, 3.67%. Found: C, 78.55; H, 4.15; N, 3.65%.

3.1.13. 4-(4-Methylphenyl)-2-(4-nitrophenyl)-5H-indeno[1,2-b]pyridin-5-one (**4m**)

IR (KBr, cm<sup>-1</sup>): 3047, 2942, 2835, 1715, 1607, 1507, 1365, 1255, 1155, 822, 758; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ: 2.22 (s, 3H, CH<sub>3</sub>), 7.28–7.49 (m, 8H, ArH), 7.75 (s, 1H, Py-H), 7.79–7.97 (m, 4H, ArH) ppm; <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ: 18.3, 121.7, 123.5, 123.8, 123.9, 128.0, 128.6, 129.5, 129.7, 129.9, 131.3, 135.3, 135.6, 139.9, 141.5, 142.5, 146.4, 147.9, 162.3, 163.3, 191.3 ppm; MS(ESI):  $m/z$  393 (M + H)<sup>+</sup>; Anal. Calcd for C<sub>25</sub>H<sub>16</sub>N<sub>2</sub>O<sub>3</sub>: C, 76.53; H, 4.08; N, 7.14%. Found: C, 76.50; H, 4.04; N, 7.10%.

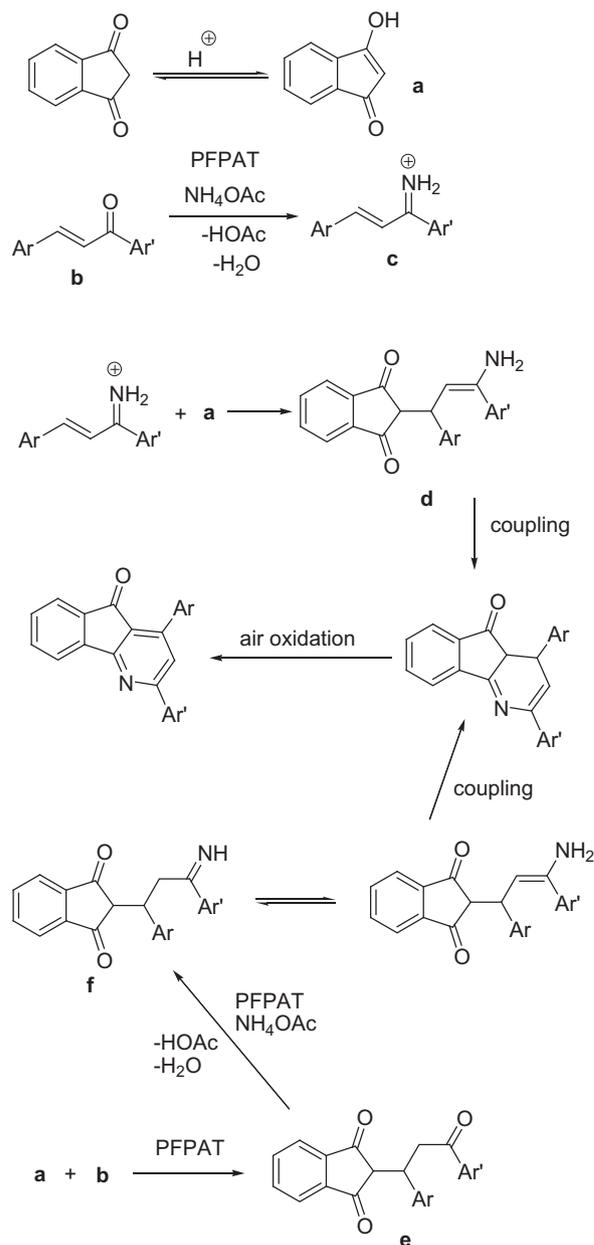
3.1.14. 4-(4-Methoxyphenyl)-2-(4-nitrophenyl)-5H-indeno[1,2-b]pyridin-5-one (**4n**)

IR (KBr, cm<sup>-1</sup>): 3050, 2949, 2839, 1719, 1602, 1514, 1370, 1262, 1146, 818, 745; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ: 3.66 (s, 3H, OCH<sub>3</sub>), 7.30–7.47 (m, 8H, ArH), 7.65 (s, 1H, Py-H), 7.73–7.94 (m, 4H, ArH) ppm; <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ: 55.0, 121.0, 123.0, 123.5, 123.9, 127.8, 128.8, 129.3, 129.7,

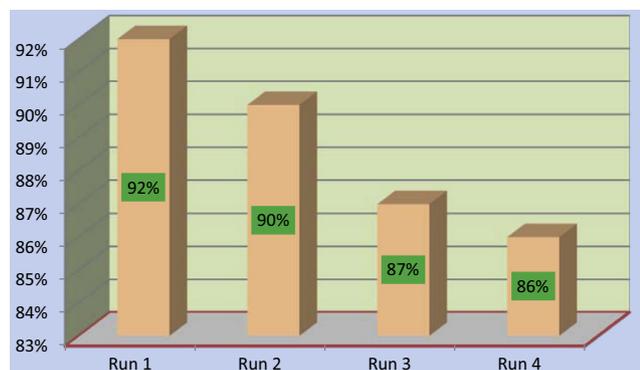
129.9, 131.0, 135.0, 135.3, 139.9, 142.0, 142.8, 147.1, 148.5, 162.2, 163.4, 191.6 ppm; MS(ESI):  $m/z$  409 (M + H)<sup>+</sup>; Anal. Calcd for C<sub>25</sub>H<sub>16</sub>N<sub>2</sub>O<sub>4</sub>: C, 73.53; H, 3.92; N, 6.86%. Found: C, 73.44; H, 3.90; N, 6.84%.

3.1.15. 4-(4-Fluorophenyl)-2-(4-bromophenyl)-5H-indeno[1,2-b]pyridin-5-one (**4o**)

IR (KBr, cm<sup>-1</sup>): 3044, 2948, 2838, 1714, 1600, 1500, 1355, 1244, 1149, 825, 751; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ: 7.35–7.51 (m, 8H, ArH), 7.69 (s, 1H, Py-H), 7.79–7.96 (m, 4H, ArH) ppm; <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ: 121.5, 123.5, 123.8, 124.4, 127.0, 127.6, 128.6, 129.6, 129.8, 130.0, 131.2, 131.7, 135.2, 135.7, 139.6, 141.4, 142.7, 143.0, 146.5, 148.4, 162.4, 163.6, 191.8 ppm; MS(ESI):  $m/z$  430.9 (M + H)<sup>+</sup>; Anal.



**Scheme 2** Mechanism for the formation of 2,4-diaryl-5H-indeno[1,2-b]pyridin-5-one derivatives.



**Figure 2** Recyclability of PFPAT for the synthesis of 4-(4-fluorophenyl)-2-(4-methylphenyl)-5H-indeno[1,2-b]pyridin-5-one.

Calcd for  $C_{24}H_{13}BrFNO$ : C, 66.99; H, 3.02; N, 3.26%. Found: C, 66.94; H, 3.06; N, 3.29%.

### 3.1.16. 4-(4-Chlorophenyl)-2-(4-bromophenyl)-5H-indeno[1,2-b]pyridin-5-one (**4p**)

IR (KBr,  $cm^{-1}$ ): 3046, 2947, 2836, 1710, 1606, 1502, 1356, 1248, 1145, 822, 751;  $^1H$  NMR (500 MHz,  $CDCl_3$ )  $\delta$ : 7.10–7.36 (m, 8H, ArH), 7.71 (s, 1H, Py-H), 7.83–7.96 (m, 4H, ArH) ppm;  $^{13}C$  NMR (125 MHz,  $CDCl_3$ )  $\delta$ : 121.8, 123.6, 123.7, 123.9, 128.2, 128.8, 129.0, 129.4, 129.7, 131.5, 135.0, 135.7, 139.7, 142.3, 143.0, 146.6, 147.6, 162.0, 163.0, 191.0 ppm; MS(ESI):  $m/z$  447 (M+H) $^+$ ; Anal. Calcd for  $C_{24}H_{13}BrClNO$ : C, 64.52; H, 2.91; N, 3.14%. Found: C, 64.57; H, 2.90; N, 3.12%.

### 3.1.17. 4-(4-Nitrophenyl)-2-(4-hydroxyphenyl)-5H-indeno[1,2-b]pyridin-5-one (**4q**)

IR (KBr,  $cm^{-1}$ ): 3364, 3042, 2943, 2834, 1712, 1602, 1511, 1364, 1256, 1149, 822, 755;  $^1H$  NMR (500 MHz,  $CDCl_3$ )  $\delta$ : 7.19–7.40 (m, 8H, ArH), 7.67 (s, 1H, Py-H), 7.78–7.98 (m, 4H, ArH), 9.44 (s, 1H, OH) ppm;  $^{13}C$  NMR (125 MHz,  $CDCl_3$ )  $\delta$ : 121.2, 123.2, 123.6, 123.8, 127.9, 128.5, 129.0, 129.5, 129.7, 131.7, 135.6, 135.9, 139.4, 141.9, 142.4, 146.4, 148.4, 161.5, 162.5, 191.9 ppm; MS(ESI):  $m/z$  395 (M+H) $^+$ ; Anal. Calcd for  $C_{24}H_{14}N_2O_4$ : C, 73.09; H, 3.55; N, 7.11%. Found: C, 73.00; H, 3.54; N, 7.08%.

### 3.1.18. 4-(4-Methylphenyl)-2-(4-hydroxyphenyl)-5H-indeno[1,2-b]pyridin-5-one (**4r**)

IR (KBr,  $cm^{-1}$ ): 3359, 3043, 2941, 2830, 1707, 1604, 1509, 1363, 1253, 1148, 824, 759;  $^1H$  NMR (500 MHz,  $CDCl_3$ )  $\delta$ : 2.27 (s, 3H,  $CH_3$ ), 7.17–7.37 (m, 8H, ArH), 7.63 (s, 1H, Py-H), 7.77–7.97 (m, 4H, ArH), 9.36 (s, 1H, OH) ppm;  $^{13}C$  NMR (125 MHz,  $CDCl_3$ )  $\delta$ : 18.0, 121.1, 123.3, 123.6, 123.9, 128.3, 128.8, 129.3, 129.6, 129.8, 130.7, 134.5, 135.3, 139.5, 141.7, 142.9, 146.7, 147.7, 162.6, 163.3, 191.9 ppm; MS(ESI):  $m/z$  364 (M+H) $^+$ ; Anal. Calcd for  $C_{25}H_{17}NO_2$ : C, 82.64; H, 4.68; N, 3.86%. Found: C, 82.56; H, 4.64; N, 3.84%.

## 4. Discussion

A novel and efficient procedure for the synthesis of 2,4-diaryl-5H-indeno[1,2-b]pyridin-5-one derivatives by the reaction of

1,3-diphenyl-2-propen-1-one (**1a**), 1,3-indandione (**2**), and ammonium acetate (**3**) in the presence of PFPAT as a novel organo-catalyst is described.

Our initial work started with screening of catalyst loading so as to identify optimal reaction conditions for the synthesis of 2,4-diaryl-5H-indeno[1,2-b]pyridin-5-one derivatives. First of all, a number of Lewis acid catalysts such as  $FeCl_3$ ,  $InCl_3$ ,  $BiCl_3$ ,  $La(OTf)_3$ ,  $Nd(OTf)_3$ ,  $Yb(OTf)_3$  and PFPAT have been screened using the model reaction in ethanol (Table 1). PFPAT was found to be the best catalyst under these conditions. We have studied the amount of PFPAT required for the reaction. It was found that when decreasing the amount of the catalyst from 10 to 5 mol%, the yield decreased from 92% to 81% (Table 1, entry 9). When increasing the amount of the catalyst from 10 to 15 mol%, there is no change in the yield (Table 1, entry 11). The use of 10 mol% of PFPAT maintains the yield at 92%, so this amount is sufficient to promote the reaction. In the presence of more than this amount of the catalyst, neither the yield nor the reaction time was improved (entries 10 and 11).

The reaction was performed in various solvents to identify the best solvent condition. A range of solvents like acetonitrile, 1,4-dioxane, cyclohexane, methanol and ethanol were examined (Table 2, entries 1–5). The reaction without any solvent at 60 °C was not very successful (Table 2, entry 6). Ethanol was found to be the best solvent under these conditions (Table 2, entry 5).

Encouraged by this successful three-component reaction, synthesis of diverse indeno[1,2-b]pyridine derivatives **4a–r** was undertaken. The chalcones bearing electron-withdrawing and electron donating groups were found to be equally effective to produce 2,4-diaryl-5H-indeno[1,2-b]pyridin-5-ones **4a–r** in very good yields (Table 3). As expected, satisfactory results were observed, and the results are summarized in Table 3. It is shown that in general a wide range of chalcones could react with 1,3-indandione and ammonium acetate smoothly to give **4a–r** in good to excellent yields (Table 3, entries 1–18). It is also notable that the electronic property of the aromatic ring of chalcones has some effects on the rate of the condensation process. The results summarized in Table 3 reveals that the reaction gave higher yields of 2,4-diaryl-5H-indeno[1,2-b]pyridin-5-ones and also shorter reaction time was needed when the aromatic aldehyde part of chalcones bear an electron-withdrawing substituents probably because the Michael addition is easier (Table 3, entries 1, 3–5, 7–11, 15–17). On the other hand, when the aromatic aldehyde part of chalcones bearing the electron-donating groups can afford the corresponding products with almost equally satisfactory yields a slightly longer reaction period was necessary to complete the reaction (Table 3, entries 2, 6, 12–14, 18).

To explain the formation of 2,4-diaryl-5H-indeno[1,2-b]pyridin-5-ones via the one-pot multi-component reaction, we have proposed a plausible reaction mechanism, which is illustrated in Scheme 2. According to the reported literatures (Shafiee et al., 2011; Shinde et al., 2012), two courses are possible:

- 1) First the equilibrium of diketone with its enolic form was established under acidic condition (intermediate **a**). With the same manner, the catalytic coupling of amine with  $\alpha,\beta$ -unsaturated ketone by Brønsted acid was performed to form intermediate (**b**) which is equi-

brated with its enamine form. In continuation the formation of intermediate (**d**) resulting from the condensation of intermediate (**a**) with intermediate (**c**) was established. Finally the intramolecular coupling of intermediate (**d**) followed by air oxidation resulting in the synthesis of 2,4-diaryl-5*H*-indeno[1,2-*b*]pyridin-5-ones (Scheme 2).

- 2) First the catalytic condensation of (**a**) and (**b**) was performed to form intermediate (**e**). In continuation the intermediate (**f**) was formed from the catalytic coupling of ammonium acetate with (**e**). Intermediate (**f**) is equilibrated with its enamine form (intermediate **d**). The intramolecular coupling followed by air oxidation resulting in the targeted molecules (Scheme 2).

The possibility of recycling the catalyst was examined using the model reaction under the optimized conditions. Upon completion of the reaction, the mixture was filtered and then washed with warm ethanol. The product was recrystallized from hot ethanol. The recovered catalyst was dried and reused for subsequent runs. The recycled catalyst could be reused four times without any additional treatment or appreciable reduction in the catalytic activity (Fig. 2). The yield of product **4a** obtained from the recycled catalyst for the four runs at 1.5 h are 92%, 90%, 87% and 86% respectively.

## 5. Conclusion

In conclusion, we successfully developed a facile and efficient method for preparing a variety of 2,4-diaryl-5*H*-indeno[1,2-*b*]pyridin-5-ones from the reactions of different chalcones, 1,3-indandione, and ammonium acetate in the presence of a catalytic amount of PFPAT at 60 °C in ethanol. The catalytic activity of PFPAT is remarkable and the use of the environmentally benign, non-toxic PFPAT as catalyst in the synthesis of 2,4-diaryl-5*H*-indeno[1,2-*b*]pyridin-5-ones in good yield is also significant. The present method has many obvious advantages compared to those reported in the previous literatures, including the cost-effectiveness, eco-friendly nature, simplicity of the methodology and recycling of the catalyst.

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