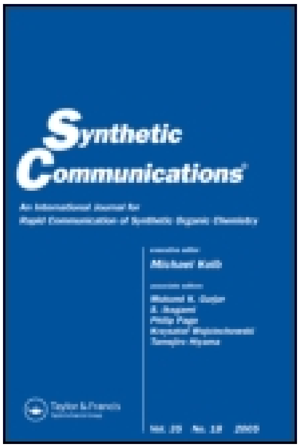


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# Cation-Exchange Resins: Efficient Heterogeneous Catalysts for Facile Synthesis of Dibenzoxanthene from β-Naphthol and Aldehydes

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# Cation-Exchange Resins: Efficient Heterogeneous Catalysts for Facile Synthesis of Dibenzoxanthene from β-Naphthol and Aldehydes

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**Abstract:** *β*-Naphthol reacts with alkyl and aryl aldehydes in the presence of Indion-130 to give 14-alkyl/aryl-14H[*a,j*]dibenzoxanthenes in good yield.

**Keywords:** Cation exchange resins, dibenzoxanthenes, Indion-130

## INTRODUCTION

Despite their wide range of biological,[1] pharmaceutical,[2] and synthetic applications,[3] the synthesis of dibenzoxanthenes have received of little attention. The synthesis may be achieved by cycloacylation of carbamates,[4] trapping of benzynes by phenol,[5] cyclocondensation of 2-hydroxyaromatic aldehyde with 2-tetralone,[6] and intramolecular phenyl carbonyl coupling reaction of benzaldehyde and acetophenone.[7] Other methods involve reaction of *β*-naphthol with aldehydes,[8] aldehyde acetal,[9] formamide,[10] carbon monoxide,[11] and 2-naphthol-1-methanol.[12] The reaction of *β*-naphthol with aldehydes can be catalyzed by a Brønsted acid such as $H_2SO_4$,[8a] HCl,[8b] or *p*-TSA.[8c] Theses conventional catalysts are often

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toxic, corrosive, and difficult to separate and recover from the products, despite their higher catalytic activity. There are no reports on the use of heterogeneous solid acids such as clays, zeolites, and ion-exchange resins for the synthesis of dibenzoxanthenes.

In this communication, we report for the first time a facile and efficient synthetic strategy for preparing 14-alkyl/aryl-14H[*a,j*]dibenzoxanthenes in excellent yield using cation-exchange resins as heterogeneous catalysts (Scheme 1).

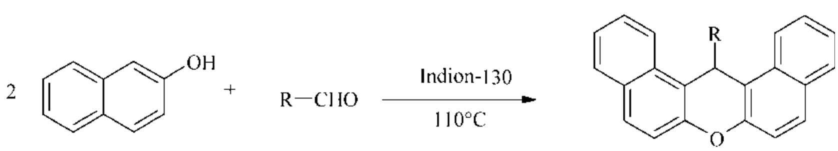


## RESULTS AND DISCUSSION

Different heterogeneous acidic catalysts were used for condensation of *β*-naphthol with 4-chlorobenzaldehyde (Scheme 1). All the catalysts were of analytical grade procured from firms of repute: Amberlyst 15 and Mont. K-10 were obtained from Fluka (USA); Amberlyst 36 from Rohm and Hass (USA); Indion-130 and Indion- 140 from Ion Exchanged India Ltd. (India); and silica from S. D. Fine Chem Ltd. (India). Among these, Indion-130, Indion-140, and Amberlyst-15 were found to be efficient and gave 86–94% yield of the product in 12–18 min. Amberlyst-36 and silica were not very effective and gave 38 and 28% yield of the product in 45 min and 120 min, respectively. K-10 was totally ineffective for the transformation.

Various aldehydes were reacted with *β*-naphthol in the presence of Indion-130 to obtain 14-alkyl/aryl-14H[*a,j*]dibenzoxanthenes under these reaction conditions (Table 1). The nature of the substituent on the aromatic ring had a profound effect on the yield of the product. The electron-donating group needed a longer reaction time to give satisfactory yield than the electron-withdrawing group present on aldehyde. For example, 4-chlorobenzaldehyde reacted rapidly with *β*-naphthol to give the product in excellent yield within 12 min, whereas aliphatic aldehydes (propanal and isobutyraldehyde) needed 50–60 min for comparable yields.

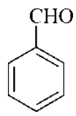
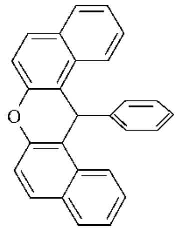
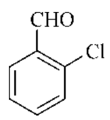
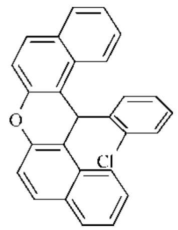
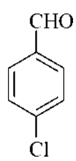
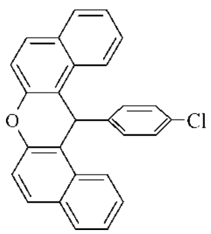
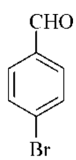
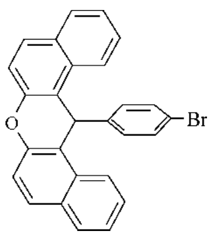
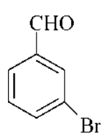
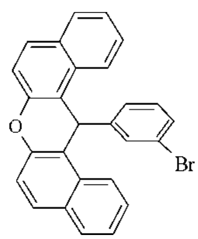
The reusability of the catalyst was checked by separation, drying, and reloading the same catalyst for the new run. We found that the catalyst could be reused several times. For example, the yield of **3c** was 89%, 86%, and 81% in three successive runs.




1 2 3

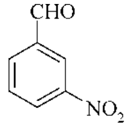
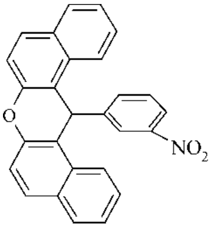
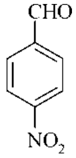
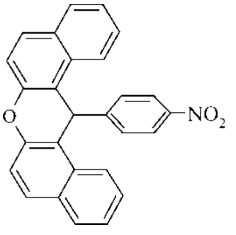
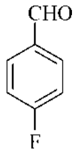
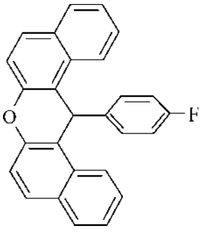
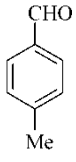
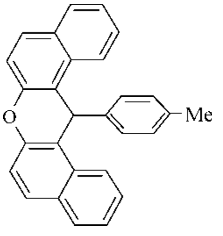
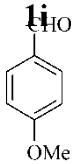
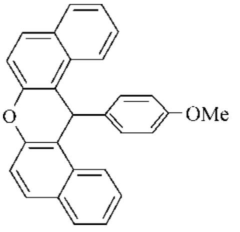
***Scheme 1.***

***Table 1.*** Condensation reactions between $\beta$-naphthol and aldehydes in the presence of Indion-130[a]

| Entry | Aldehyde **1** | Product **3** | Yield (%)[b] | Time (min) | M.p (°C) [lit.] |
|---|---|---|---|---|---|
| **1** |  **1a** |  | 91 | 20 | 184–185 [185[9]] |
| **2** |  **1b** |  | 88 | 12 | 213–214 [215[8c]] |
| **3** |  **1c** |  | 94 | 12 | 289–290 [289[8c]] |
| **4** |  **1d** |  | 92 | 18 | 296–297 [297[9]] |
| **5** |  **1e** |  | 90 | 20 | 192–193 [192[8c]] |

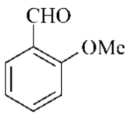
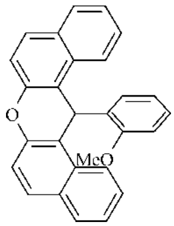
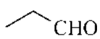
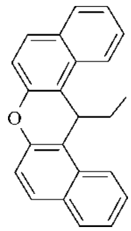
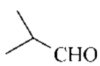
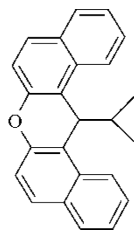
(*continued*)

*Table 1.* Continued

| Entry | Aldehyde **1** | Product **3** | Yield (%)$^b$ | Time (min) | M.p (°C) [lit.] |
|---|---|---|---|---|---|
| **6** |  **1f** |  | 84 | 12 | 209–210 [211[8c]] |
| **7** |  **1g** |  | 92 | 12 | 310–311 [310[9]] |
| **8** |  **1h** |  | 92 | 18 | 238–239 [239[8c]] |
| **9** |  **1i** |  | 89 | 40 | 229–230 [229[9]] |
| **10** |  **1j** |  | 89 | 55 | 204–205 [204[8c]] |

(*continued*)

*Table 1.* Continued

| Entry | Aldehyde **1** | Product **3** | Yield (%)$^b$ | Time (min) | M.p (°C) [lit.] |
|---|---|---|---|---|---|
| 11 |  **1k** |  | 78 | 55 | 261–262 [260[8c]] |
| 12 |  **1l** |  | 86 | 50 | 151–152 [151–152[8b]] |
| 13 |  **1m** |  | 76 | 60 | 151–152 [151–152[8b]] |

$^a$β-Naphthol; 5 mmol; aldehydes, 2.5 mmol; Indion-130, 0.25 g; temperature 110°C.
$^b$Isolated yield.

In conclusion, a reliable, rapid, and environmentally benign method for synthesizing dibenzoxanthenes has been developed that involves the use of recyclable cation-exchange resin.

## EXPERIMENTAL

### General Procedure

β-Naphthol (5 mmol), aldehyde (2.5 mmol), and Indion-130 (0.25 g) were heated at 110°C and monitored by TLC. The reaction mixture was cooled, triturated with methylene chloride (15 ml), filtered, and evaporated. The residue was crystallized from ethanol and characterized by IR, $^1$H NMR and MS in comparison with literature data.

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