Tetrahedron Letters 59 (2018) 3895–3901

Contents lists available at ScienceDirect

Tetrahedron Letters

journal homepage: www.elsevier.com/locate/tetlet

Resorcinarene supramolecular organocatalyst for functionalized *1*-tetralone synthesis in aqueous medium

Pampa Maity, Chhanda Mukhopadhyay *

Department of Chemistry, University of Calcutta, 92 APC Road, Kolkata 700009, India

ARTICLE INFO

Article history:
Received 28 July 2018
Revised 1 September 2018
Accepted 13 September 2018
Available online 17 September 2018

Keywords:
Aqueous medium
Resorcin[4]arene
Fluorenone
1-Tetralone
Supramolecular organocatalyst

ABSTRACT

An efficient, straightforward and environmentally benign process has been developed for the synthesis of fluorenone and 1-tetralone derivatives using cyclic *1,3*-dione, malononitrile and dialkylacetylenedicarboxylate as starting materials in aqueous medium. The reaction is favoured in presence of resorcin[4]arene which is effective as a reusable organocatalyst. The catalyst has been easily synthesized and characterized by ^{1}H, ^{13}C NMR, IR, XRD and HRMS analyses. Resorcin[4]arene afforded the resulted products in a shorter time and in good yields. The recyclability of the catalyst was established up to 6th cycle by FT-IR and SEM images.

Introduction

The fluorenones and *1*-tetralones based compounds are nowadays in demand because of their biological activity [1] as well as their availability in natural products [2]. They are also the key to starting and intermediate materials in the synthesis of various drugs [3]. Several synthetic approaches such as Friedel–Crafts reaction [4], radical cyclization process [5], transition-metalcatalyzed cross-couplings reaction [6] and even intramolecular dehydro Diels–Alder reactions [7] have often been introduced for the construction of such scaffolds. However, tedious synthetic procedures, usage of metal-based catalysts, costly synthetic approaches hinder their potential commercialization. Thus, an efficient straightforward synthetic strategy is highly desirable that could transform the easily available substrates into the desired fluorenones and *1*-tetralones based products. In this regard, macrocyclic molecules with network structure could come up as forerunners because of their easy synthetic protocols, high yield and tailorable pore interiors [8]. The operational simplicity, ease of handling, nontoxic nature of the macromolecule could make them potential organocatalyst for the aforementioned synthetic protocols [9]. Resorcinarene macrocycles are conventional supramolecular hosts for different alkali and metal cations [10] as well as small organic molecules [11].

The pre-designed cavity containing aromatic rings offer electron-richness inside the pore that can hold the small organic guest molecules through cation$\cdots\pi$ and CH$\cdots\pi$ interactions [12]. In this regard, resorcinarene based supramolecular frameworks could prove better because of the framework nature. The hydrogen-bonded architecture is ideal for docking the substrates into its two-dimensional array. The resorcinarene framework is thus expected to provide the much-desired platform to integrate multiple components within one place that can result in the catalytic product. Unlike classical catalysts such as inorganic acids, bases and organobases, the resorcinarene based frameworks are less toxic, environmentally compatible and recyclable [13]. These unique features make them attractive for further modification of their structure and make them suitable for the desired catalysis. Notably, *1*-tetralone and fluorenone derivatives have been synthesized in aqueous medium in presence of resorcin[4]arene from the easily available substrates cyclic-*1,3*-dione, malononitrile and dialkylacetylenedicarboxylate. From an ecological point of view, water is undoubtedly the most obvious material of choice for any 'clean' reaction in academic and scientific research [14].

Results and discussion

The organocatalyst, resorcin[4]arene, has been synthesized following a simpler and greener approach without following any time consuming reflux condition. Firstly, equimolar quantities of resorcinol and 4-hydroxy benzaldehyde have been ground together in presence of catalytic amount of *p*-toluenesulfonic acid (PTSA).

---

* Corresponding author.
E-mail address: cmukhop@yahoo.co.in (C. Mukhopadhyay).

https://doi.org/10.1016/j.tetlet.2018.09.037
0040-4039/© 2018 Elsevier Ltd. All rights reserved.

The resulted viscous paste-like material was kept for few minutes to yield a sticky solid that further hardens on standing. The product was washed several times with water and recrystallized from dimethyl sulfoxide (DMSO) solvent. The single-crystal X-ray diffraction analysis delineates that resorcin[4]arene has been crystallized in the triclinic system with a *P*-1 space group and forms two-dimensional hydrogen-bonded structures. The structure clearly reveals that each resorcin[4]arene is linked with neighbouring four resorcinarene units via O—H···O intermolecular hydrogen bonds (Fig. 1).

In particular, two-dimensional hydrogen-bonded frameworks have been formed through O1—H1···O6 and O3—H3···O1hydrogen bonding interactions (Fig. 1e and f). It was observed that the hydroxyl (—OH) groups present at the *para*-position of the benzene unit (i.e. 4-hydroxy benzene unit, O1) hold two types of hydrogen bonding interactions: 1) one with the —OH group of resorcinol unit (O3—H3···O1; *D* = 2.76 Å, *d* = 2.00 Å, θ = 153.6°) 2) another one with the —OH group of 4-hydroxy benzene unit (O1—H1···O6; *D* = 2.74 Å, *d* = 2.07 Å, θ = 139.4°). As a result, a significant number (8H-bonding per unit of resorcinarene) of intermolecular

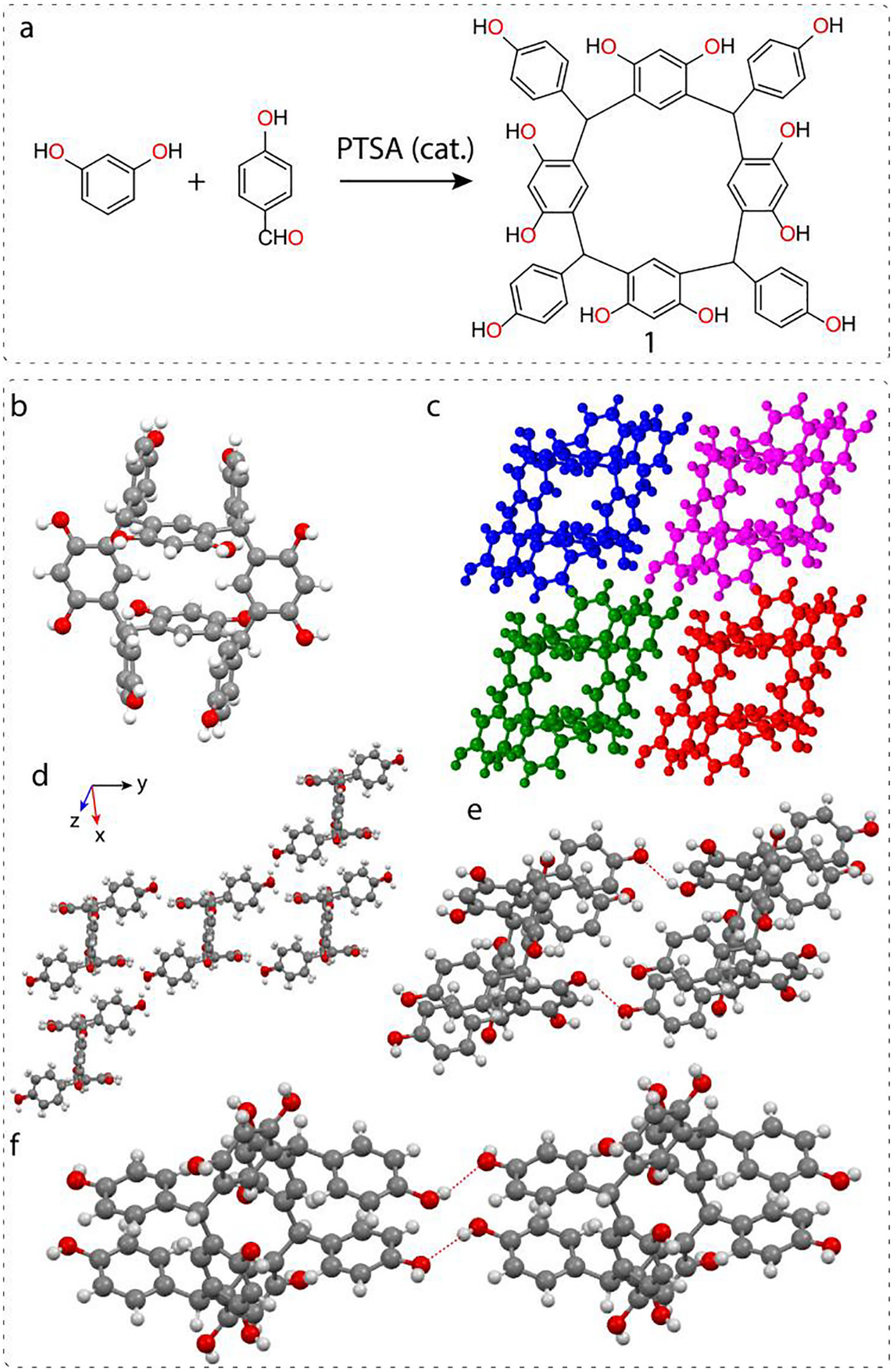

Fig. 1. Synthesis and crystallographic details of as-synthesized resorcin[4]arene. a) Schematic representation of the synthesis of resorcin[4]arene. b) and c) Single crystal structure of **1** (CCDC no 1843050). d) Two-dimensional resorcinarene structure where each unit is surrounded by four other resorcinarene units. e) and f) Hydrogen bonding interaction present in the framework **1**.