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Facile one-pot synthesis of a novel series of 7-aryl-8*H*-benzo[*h*]indeno[1,2-*b*]quinoline-8-one derivatives catalyzed by tribromomelamine

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Abstract Tribromomelamine, has been used as an efficient, inexpensive, and green catalyst for one-pot, three-component synthesis of 7-aryl-8*H*-benzo[*h*]indeno[1,2-*b*]quinoline-8-ones by reaction of 1,3-indanedione, aromatic aldehydes, and 1-naphthylamine under solvent-free conditions. The several advantages of this reaction include high yields, short reaction time, and high catalyst efficiency.

Keywords Indeno[1,2-*b*]quinoline-8-one · Solvent-free condition · Tribromomelamine · 1,3-Indanedione · 1-Naphthylamine

Introduction

Multicomponent reactions (MCRs) have recently become regarded as superior synthetic strategies. MCRs are very flexible and proceed through a sequence of reaction equilibria, yielding the target product. MCRs are important in combinatorial chemistry because of their suitability for synthesis of small drug-like molecules with high structural diversity. Other features of MCRs include simple procedures for formation of the final products in a one-pot process from at least three starting materials, atomic and structural economy, minimization of waste, easy construction of complex organic molecules, and avoidance of complicated purification processes. In the past decade much effort has been devoted to the development of new three and four-component MCRs [1, 2].

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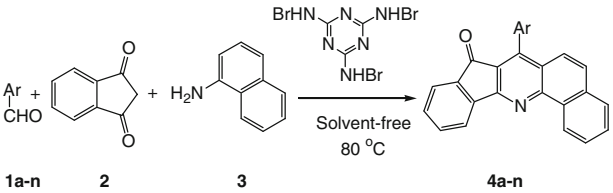
The quinoline skeleton is present in many biologically active compounds and is frequently condensed with other heterocycles [3–7]. Synthesis of a series of tetracyclic indenoquinolines and their evaluation as potential anticancer agents have been reported [8]. The design, synthesis, and biological activity of less complex quinoline derivatives with potent anti-TB activity has also recently been reported [9–13]. A new class of conformationally locked indeno[2,1-*c*]quinoline compounds with excellent antimycobacterial activity has been discovered [14]. Since the discovery of indenoisoquinolines as a novel class of potential anticancer drug candidates, extensive structural modifications have been investigated by altering the substituent on the tetracyclic pharmacophore [15]. Some indolo[2,3-*b*]quinoline derivatives have been synthesized and their antiproliferative activity has been evaluated, on the grounds that these tetracyclic heterocycles may intercalate into the DNA double helix resulting in inhibition of DNA replication and transcription [16]. Much effort has therefore been made to investigate new, simple, and direct approaches to the construction of indenoquinoline skeletons.

Many methods have been reported for synthesis of indeno[2,1-*b*]quinolineone derivatives [17–24]. Novel 7,8-dihydro-10-aryl-5*H*-indeno[1,2-*b*]quinoline-9,11-diones have been synthesized, and their application as new pH indicators has been shown to be feasible [25]. Recently, Khaligh et al. reported the synthesis of 7-aryl-8*H*-benzo[*f*]indeno[2,1-*b*]quinoline-8-one derivatives by one-pot condensation of 2-naphthylamine, aromatic aldehydes, and indane-1,3-dione in the presence of poly(4-vinylpyridinium)hydrogen sulfate [26] and 3-methyl-1-sulfonic acid imidazolium hydrogen sulfate [27] as catalysts. Many of the above procedures have their own merits. However, most of these procedures require heating under reflux for hours in organic solvents, complex steps, use of expensive catalysts, and tedious work-up. Therefore, the development of simple, efficient, clean, high-yielding, and environmentally friendly approaches using new catalysts for synthesis of indeno[2,1-*b*]quinolineones is an important task for organic chemists.

In recent years, TBM has received much attention as an inexpensive and nontoxic catalyst for a series of organic transformations [28–31], because of its cost-effectiveness, eco-friendly nature, easy handling, high reactivity, and easy work-up procedures. TBM, a homogeneous, non-hygroscopic solid catalyst, has been used in such organic transformations as the trimethylsilylation of hydroxyl groups with 1,1,1,3,3,3-hexamethyldisilazane (HMDS) [28], synthesis of 2-aryl thiazolines [29], synthesis of 1-amidoalkyl-2-naphthols [30], and acetylation and formylation reactions of alcohols [31]. TBM is stable under a variety of reaction conditions, including acidic and basic conditions. It is noteworthy that TBM is produced via a facile and clean process that does not require a complicated work-up procedure.

Prompted by these findings and because of our recent interest in the development of practical and environmentally friendly procedures for synthesis of biologically active organic compounds [32–35] by use of multi-component reactions, we have developed an efficient synthesis of 7-aryl-8*H*-benzo[*h*]indeno[1,2-*b*]quinoline-8-one derivatives by cyclocondensation reaction of 1,3-indanedione, aromatic aldehydes, and 1-naphthylamine under solvent-free conditions at 80 °C with TBM as an efficient, novel, homogeneous catalyst (Scheme 1).



Scheme 1 Synthesis of 7-aryl-8*H*-benzo[*h*]indeno[1,2-*b*]quinoline-8-ones

Experimental

Chemicals and analysis

Chemicals were purchased from Merck, Fluka, and Aldrich. All yields refer to isolated products unless otherwise stated. ^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) spectra were obtained by use of a Bruker DRX-500 Avance at ambient temperature, with TMS as internal standard. FT-IR spectra were obtained as KBr discs by use of a Shimadzu spectrometer. Mass spectra were determined on a Varian–Saturn 2000 GC–MS instrument. Elemental analysis was performed by use of a Perkin Elmer 2400 CHN elemental analyzer.

Preparation of tribromomelamine

Tribromomelamine (TBM) is readily prepared by dropwise addition of Br_2 to a solution of melamine in 5 M NaOH at room temperature (Scheme 2) [28].

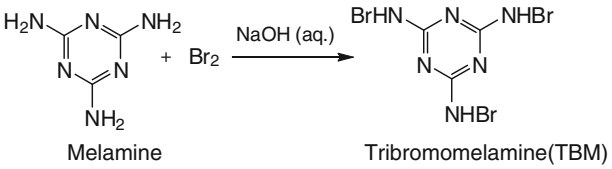
General procedure for synthesis of 7-aryl-8*H*-benzo[*h*]indeno[1,2-*b*]quinoline-8-ones (**4a–n**)

A mixture of 1,3-indanedione **1** (1 mmol), aromatic aldehyde **2** (1 mmol), 1-naphthylamine **3** (1 mmol), and tribromomelamine (10 mol%) was heated in an oil bath at 80 °C for 45–75 min. The progress of the reaction was monitored by TLC. On completion of the transformation, the reaction mixture was cooled to room temperature and hot chloroform was added. The filtrate was then collected and distilled to dryness to give the crude product, which was recrystallized from a mixture of EtOH and H_2O to give compounds **4a**–**n** in high yields (Scheme 1).

Spectral data for the synthesized compounds (**4a–n**)

*7-Phenyl-8H-benzo[h]indeno[1,2-b]quinoline-8-one (**4a**)*

IR (KBr, cm^{-1}): 3,065, 1,714, 1,621, 1,570, 1,510, 1,482, 1,080, 840, 832, 815, 750; ^{1}H NMR (500 MHz, $CDCl_3$) *δ:* 7.46–7.52 (m, 3H, Ar–H), 7.56–7.65 (m, 4H, Ar–H), 7.70–7.82 (m, 5H, Ar–H), 7.88 (d, $J = 7.7$ Hz, 1H, Ar–H), 8.18 (d, $J = 7.7$ Hz, 1H, Ar–H), 9.38 (d, $J = 8.0$ Hz, 1H, Ar–H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) *δ:*



Scheme 2 Preparation of tribromomelamine (TBM)

121.4, 123.5, 124.3, 124.8, 125.4, 126.1, 127.3, 127.7, 128.4, 129.2, 129.6, 130.2, 131.4, 133.4, 135.6, 136.0, 137.4, 143.3, 146.3, 147.3, 149.0, 160.3, 193.0 ppm; MS(ESI): *m/z* 358 $(M + H)^+$; Anal. Calcd for $C_{26}H_{15}NO$: C, 87.37; H, 4.23; N, 3.92 %. Found: C, 86.80; H, 4.69; N, 3.88 %.

*7-(4-Chlorophenyl)-8H-benzo[h]indeno[1,2-b]quinoline-8-one (**4b**)*

IR (KBr, cm^{-1}): 3,072, 1,700, 1,602, 1,591, 1,574, 1,556, 1,488, 1,083, 842, 815, 750, 741; ^1H NMR (500 MHz, $CDCl_3$) *δ:* 7.41 (d, $J = 8.0$ Hz, 2H, Ar–H), 7.48 (t, $J = 7.6$ Hz, 1H, Ar–H), 7.52–7.63 (m, 3H, Ar–H), 7.66–7.77 (m, 5H, Ar–H), 7.80 (d, $J = 7.6$ Hz, 1H, Ar–H), 8.14 (d, $J = 7.6$ Hz, 1H, Ar–H), 9.42 (d, $J = 8.0$ Hz, 1H, Ar–H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) *δ:* 122.0, 123.7, 124.2, 124.7, 125.7, 126.4, 127.0, 127.5, 128.2, 129.0, 129.5, 130.5, 131.3, 134.0, 135.4, 136.3, 138.0, 139.0, 139.6, 143.0, 146.7, 147.0, 149.5, 161.5, 192.4 ppm; MS(ESI): *m/z* 392.5 $(M + H)^+$; Anal. Calcd for $C_{26}H_{14}ClNO$: C, 79.69; H, 3.60; N, 3.57 %. Found: C, 79.58; H, 3.55; N, 3.50 %.

*7-(4-Methylphenyl)-8H-benzo[h]indeno[1,2-b]quinoline-8-one (**4c**)*

IR (KBr, cm^{-1}): 3,061, 1,707, 1,608, 1,572, 1,502, 1,344, 1,025, 840, 832, 815, 750; ^1H NMR (500 MHz, $CDCl_3$) *δ:* 2.54 (s, 3H, CH_3), 7.37 (d, $J = 8.0$ Hz, 2H, Ar–H), 7.40 (d, $J = 8.0$ Hz, 2H, Ar–H), 7.47 (t, $J = 7.40$ Hz, 1H, Ar–H), 7.56–7.74 (m, 6H, Ar–H), 7.83 (d, $J = 7.6$ Hz, 1H, Ar–H), 8.14 (d, $J = 7.2$ Hz, 1H, Ar–H), 9.40 (d, $J = 8.0$ Hz, 1H, Ar–H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) *δ:* 21.6, 122.7, 123.3, 124.0, 124.5, 125.5, 126.6, 127.5, 127.8, 128.5, 129.0, 129.7, 130.4, 131.7, 134.5, 135.3, 136.4, 138.0, 139.3, 139.5, 142.4, 146.6, 147.3, 149.5, 162.5, 192.7 ppm; MS(ESI): *m/z* 372 $(M + H)^+$; Anal. Calcd for $C_{27}H_{17}NO$: C, 87.31; H, 4.61; N, 3.77 %. Found: C, 87.22; H, 4.57; N, 3.75 %.

*7-(4-Methoxyphenyl)-8H-benzo[h]indeno[1,2-b]quinoline-8-one (**4d**)*

IR (KBr, cm^{-1}): 3,075, 2,965, 1,725, 1,605, 1,582, 1,570, 1,500, 1,495, 1,455, 1,245, 1,025, 840, 750; ^1H NMR (500 MHz, $CDCl_3$) *δ:* 3.98 (s, 3H, OCH_3), 7.15 (d, $J = 8.6$ Hz, 2H, Ar–H), 7.45 (d, $J = 8.6$ Hz, 2H, Ar–H), 7.49 (t, $J = 7.4$ Hz, 1H, Ar–H), 7.56–7.73 (m, 6H, Ar–H), 7.85 (d, $J = 7.9$ Hz, 1H, Ar–H), 8.17 (d, $J = 7.4$ Hz, 1H, Ar–H), 9.43 (d, $J = 8.0$ Hz, 1H, Ar–H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) *δ:* 54.4, 121.6, 123.3, 124.4, 124.8, 125.8, 126.3, 126.7, 127.0, 128.5, 129.4,

129.7, 130.3, 131.8, 133.7, 134.5, 136.5, 137.7, 139.5, 139.9, 142.8, 146.7, 147.7, 149.7, 161.4, 193.4 ppm; MS(ESI): *m/z* 388 $(M + H)^+$; Anal. Calcd for $C_{27}H_{17}NO_2$: C, 83.70; H, 4.42; N, 3.62 %. Found: C, 83.66; H, 4.40; N, 3.55 %.

*7-(4-Fluorophenyl)-8H-benzo[h]indeno[1,2-b]quinoline-8-one (**4e**)*

IR (KBr, cm^{-1}): 3,072, 1,709, 1,603, 1,572, 1,504, 1,155, 1,069, 852, 840, 815, 798, 772, 744; ^1H NMR (500 MHz, $CDCl_3$) *δ:* 7.20 (d, $J = 8.6$ Hz, 2H, Ar–H), 7.44–7.53 (m, 3H, Ar–H), 7.57 (d, $J = 9.1$ Hz, 1H, Ar–H), 7.62–7.77 (m, 5H, Ar–H), 7.82 (d, $J = 7.2$ Hz 1H, Ar–H), 8.11 (d, $J = 8.0$ Hz, 1H, Ar–H), 9.34 (d, $J = 8.1$ Hz, 1H, Ar–H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) *δ:* 121.7, 122.9, 123.9, 124.4, 125.4, 126.5, 126.9, 127.4, 128.2, 128.7, 129.3, 130.4, 132.0, 133.8, 134.5, 136.4, 137.7, 139.0, 142.2, 142.7, 146.5, 147.7, 149.0, 162.7, 190.8 ppm; MS(ESI): *m/z* 376 $(M + H)^+$; Anal. Calcd for $C_{26}H_{14}FNO$: C, 83.19; H, 3.76; N, 3.73 %. Found: C, 83.11; H, 3.71; N, 3.68 %.

*7-(3-Chlorophenyl)-8H-benzo[h]indeno[1,2-b]quinoline-8-one (**4f**)*

IR (KBr, cm^{-1}): 3,066, 2,925, 1,705, 1,602, 1,584, 1,575, 1,485, 1,455, 1,261, 1,025, 845, 753; ^1H NMR (500 MHz, $CDCl_3$) *δ:* 7.33–7.52 (m, 6H, Ar–H), 7.63–7.71 (m, 5H, Ar–H), 7.83 (d, $J = 7.8$ Hz, 1H, Ar–H), 8.15 (d, $J = 7.4$ Hz, 1H, Ar–H), 9.33 (d, $J = 8.0$ Hz, 1H, Ar–H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) *δ:* 122.5, 123.7, 124.5, 124.8, 125.2, 126.0, 126.8, 127.3, 127.9, 128.9, 129.3, 129.7, 132.3, 134.0, 135.2, 136.7, 137.0, 139.4, 141.2, 142.6, 146.7, 147.9, 149.5, 160.8, 191.5 ppm; MS(ESI): *m/z* 392.5 $(M + H)^+$; Anal. Calcd for $C_{26}H_{14}ClNO$: C, 79.69; H, 3.60; N, 3.57 %. Found: C, 79.60; H, 3.57; N, 3.53 %.

*7-(3-Nitrophenyl)-8H-benzo[h]indeno[1,2-b]quinoline-8-one (**4g**)*

IR (KBr, cm^{-1}): 3,057, 2,944, 1,711, 1,612, 1,582, 1,577, 1,480, 1,459, 1,272, 1,015, 822, 743; ^1H NMR (500 MHz, $CDCl_3$) *δ:* 7.37–7.55 (m, 6H, Ar–H), 7.60–7.73 (m, 5H, Ar–H), 7.86 (d, $J = 7.8$ Hz, 1H, Ar–H), 8.12 (d, $J = 7.4$ Hz, 1H, Ar–H), 9.37 (d, $J = 8.0$ Hz, 1H, Ar–H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) *δ:* 121.8, 123.8, 124.4, 124.7, 125.5, 126.0, 127.4, 127.7, 128.4, 128.8, 129.4, 129.7, 132.5, 134.0, 135.3, 135.9, 137.0, 139.5, 141.4, 142.8, 146.9, 147.4, 148.9, 160.6, 193.1 ppm; MS(ESI): *m/z* 403 $(M + H)^+$; Anal. Calcd for $C_{26}H_{14}N_2O_3$: C, 77.60; H, 3.51; N, 6.96 %. Found: C, 77.52; H, 3.47; N, 6.90 %.

*7-(3-Bromophenyl)-8H-benzo[h]indeno[1,2-b]quinoline-8-one (**4h**)*

IR (KBr, cm^{-1}): 3,074, 2,925, 1,705, 1,602, 1,580, 1,570, 1,484, 1,451, 1,266, 1,019, 837, 812, 744; ^1H NMR (500 MHz, $CDCl_3$) *δ:* 7.33–7.52 (m, 6H, Ar–H), 7.59–7.71 (m, 5H, Ar–H), 7.84 (d, $J = 7.8$ Hz, 1H), 8.10 (d, $J = 7.4$ Hz, 1H), 9.35 (d, $J = 8.0$ Hz, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) *δ:* 121.9, 123.7, 124.3, 124.9, 125.5, 126.4, 127.4, 127.8, 128.6, 129.2, 129.6, 130.0, 131.7, 133.6, 135.1, 135.7, 137.1, 139.6, 140.3, 143.0, 146.0, 147.4, 148.8, 162.4, 192.7 ppm; MS(ESI):

m/z 436.9 $(M + H)^+$; Anal. Calcd for $C_{26}H_{14}BrNO$: C, 71.57; H, 3.24; N, 3.21 %. Found: C, 71.50; H, 3.21; N, 3.17 %.

*7-(4-Nitrophenyl)-8H-benzo[h]indeno[1,2-b]quinoline-8-one (**4i**)*

IR (KBr, cm^{-1}): 3,072, 2,933, 1,715, 1,610, 1,577, 1,572, 1,480, 1,450, 1,266, 1,033, 840, 753; ^1H NMR (500 MHz, $CDCl_3$) *δ:* 7.41 (d, $J = 8.0$ Hz, 2H, Ar–H), 7.52 (t, $J = 7.6$ Hz, 1H, Ar–H), 7.55–7.63 (m, 3H, Ar–H), 7.74–7.82 (m, 5H, Ar–H), 7.90 (d, $J = 7.6$ Hz, 1H, Ar–H), 8.21 (d, $J = 7.6$ Hz, 1H, Ar–H), 9.33 (d, $J = 8.0$ Hz, 1H, Ar–H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) *δ:* 121.3, 123.9, 124.4, 124.7, 125.2, 125.9, 127.4, 127.6, 128.5, 129.4, 129.8, 130.7, 131.9, 133.7, 135.4, 135.6, 137.0, 139.4, 139.7, 143.1, 144.9, 147.4, 148.9, 162.5, 192.9 ppm; MS(ESI): *m/z* 403 $(M + H)^+$; Anal. Calcd for $C_{26}H_{14}N_2O_3$: C, 77.60; H, 3.51; N, 6.96 %. Found: C, 77.49; H, 3.44; N, 6.94 %.

*7-(2,4-Dichlorophenyl)-8H-benzo[h]indeno[1,2-b]quinoline-8-one (**4j**)*

IR (KBr, cm^{-1}): 3,080, 1,711, 1,612, 1,576, 1,478, 1,101, 1,069, 852, 815, 798, 772, 744; ^1H NMR (500 MHz, $CDCl_3$) *δ:* 7.34 (d, $J = 8.5$ Hz, 1H, Ar–H), 7.38 (d, $J = 8.5$ Hz, 1H, Ar–H), 7.46–7.49 (m, 2H, Ar–H), 7.66–7.77 (m, 6H, Ar–H), 7.85 (d, $J = 7.7$ Hz, 1H, Ar–H), 8.11 (d, $J = 7.4$ Hz, 1H, Ar–H), 9.32 (d, $J = 8.1$ Hz, 1H, Ar–H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) *δ:* 122.1, 122.9, 124.2, 124.6, 125.0, 125.8, 127.7, 127.9, 128.6, 129.4, 129.8, 130.7, 131.8, 133.6, 135.6, 136.3, 137.8, 139.6, 139.8, 143.1, 146.7, 147.6, 149.8, 160.7, 193.4 ppm; MS(ESI): *m/z* 426.9 $(M + H)^+$; Anal. Calcd for $C_{26}H_{13}Cl_2NO$: C, 73.25; H, 3.07; N, 3.29 %. Found: C, 73.17; H, 3.03; N, 3.25 %.

*7-(4-Bromophenyl)-8H-benzo[h]indeno[1,2-b]quinoline-8-one (**4k**)*

IR (KBr, cm^{-1}): 3,060, 1,705, 1,606, 1,570, 1,550, 1,480, 1,010, 995, 840, 810, 760, 740; ^1H NMR (500 MHz, $CDCl_3$) *δ:* 7.32 (d, $J = 8.2$ Hz, 2H, Ar–H), 7.46 (t, $J = 7.5$ Hz, 1H, Ar–H), 7.51 (d, $J = 8.4$ Hz, 1H, Ar–H), 7.62–7.76 (m, 7H, Ar–H), 7.82 (d, $J = 7.8$ Hz, 1H, Ar–H), 8.13 (d, $J = 7.7$ Hz, 1H, Ar–H), 9.36 (d, $J = 8.0$ Hz, 1H, Ar–H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) *δ:* 122.6, 123.3, 124.5, 124.9, 125.4, 126.0, 126.9, 127.3, 128.0, 128.7, 129.0, 129.7, 131.8, 134.2, 135.6, 136.1, 137.8, 139.4, 139.7, 143.0, 146.5, 147.7, 149.7, 160.5, 193.2 ppm; MS(ESI): *m/z* 436.9 $(M + H)^+$; Anal. Calcd for $C_{26}H_{14}BrNO$: C, 71.57; H, 3.24; N, 3.21 %. Found: C, 71.48; H, 3.18; N, 3.19 %.

*7-(2-Methoxyphenyl)-8H-benzo[h]indeno[1,2-b]quinoline-8-one (**4l**)*

IR (KBr, cm^{-1}): 3,078, 1,714, 1,608, 1,582, 1,573, 1,471, 1,045, 832, 808, 792, 755, 734; ^1H NMR (500 MHz, $CDCl_3$) *δ:* 3.74 (s, 3H, OCH_3), 7.17 (d, $J = 8.4$ Hz, 1H, Ar–H), 7.24 (t, $J = 7.4$ Hz, 1H, Ar–H), 7.35 (d, $J = 7.5$ Hz, 1H, Ar–H), 7.45–7.56 (m, 3H, Ar–H), 7.62–7.77 (m, 5H, Ar–H), 7.81 (d, $J = 7.8$ Hz, 1H), 8.11 (d, $J = 7.4$ Hz, 1H, Ar–H), 9.35 (d, $J = 8.0$ Hz, 1H, Ar–H) ppm; ^{13}C NMR (125 MHz,

$CDCl_3$) *δ:* 55.2, 122.5, 123.3, 124.2, 124.9, 125.9, 126.7, 127.3, 127.5, 128.0, 128.9, 129.5, 130.2, 131.9, 134.1, 135.3, 136.3, 137.5, 139.5, 139.9, 143.2, 146.5, 147.6, 149.7, 160.6, 193.3 ppm; MS(ESI): *m/z* 388 $(M + H)^+$; Anal. Calcd for $C_{27}H_{17}NO_2$: C, 83.70; H, 4.42; N, 3.62 %. Found: C, 83.64; H, 4.37; N, 3.59 %.

*7-(2-Chlorophenyl)-8H-benzo[h]indeno[1,2-b]quinoline-8-one (**4m**)*

IR (KBr, cm^{-1}): 3,064, 1,714, 1,611, 1,577, 1,570, 1,466, 1,043, 822, 811, 777, 750, 734; ^1H NMR (500 MHz, $CDCl_3$) *δ:* 7.17–7.23 (m, 2H, Ar–H), 7.33–7.42 (m, 3H, Ar–H), 7.46 (d, $J = 8.0$ Hz, 1H, Ar–H), 7.49–7.63 (m, 5H, Ar–H), 7.79 (d, $J = 7.7$ Hz, 1H, Ar–H), 8.05 (d, $J = 7.4$ Hz, 1H, Ar–H), 9.31 (d, $J = 8.0$ Hz, 1H, Ar–H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) *δ:* 123.0, 123.8, 124.4, 124.7, 125.9, 126.7, 127.3, 127.8, 128.4, 129.4, 129.9, 130.7, 131.9, 133.8, 135.4, 136.5, 137.2, 139.6, 139.8, 143.2, 146.7, 147.6, 149.8, 160.8, 193.4 ppm; MS(ESI): *m/z m/z* 392.5 $(M + H)^+$; Anal. Calcd for $C_{26}H_{14}ClNO$: C, 79.69; H, 3.60; N, 3.57 %. Found: C, 79.55; H, 3.53; N, 3.56 %.

*7-(3,4-Dichlorophenyl)-8H-benzo[h]indeno[1,2-b]quinoline-8-one (**4n**)*

IR (KBr, cm^{-1}): 3,085, 1,715, 1,605, 1,570, 1,470, 1,100, 1,065, 852, 840, 798, 772, 755; ^1H NMR (500 MHz, $CDCl_3$) *δ:* 7.34 (d, $J = 8.5$ Hz, 1H, Ar–H), 7.38 (d, $J = 8.5$ Hz, 1H, Ar–H), 7.47–7.52 (m, 2H, Ar–H), 7.65–7.80 (m, 6H, Ar–H), 7.88 (d, $J = 7.7$ Hz, 1H, Ar–H), 8.12 (d, $J = 7.4$ Hz, 1H, Ar–H), 9.37 (d, $J = 8.1$ Hz, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) *δ:* 122.4, 123.4, 124.1, 124.8, 125.7, 126.8, 127.4, 127.9, 128.7, 129.2, 129.7, 130.7, 131.6, 133.7, 135.5, 136.7, 137.8, 139.4, 139.9, 143.8, 146.7, 147.7, 148.5, 161.1, 193.1 ppm; MS(ESI): *m/z* 426.9 $(M + H)^+$; Anal. Calcd for $C_{26}H_{13}Cl_2NO$: C, 73.25; H, 3.07; N, 3.29 %. Found: C, 73.19; H, 3.01; N, 3.22 %.

Results and discussion

Our efforts to develop an efficient and environmentally benign method for synthesis of 7-aryl-8*H*-benzo[*h*]indeno[1,2-*b*]quinoline-8-one derivatives focused initially on three-component cyclocondensation of 1,3-indanedione (1 mmol) with 4-chlorobenzaldehyde (1 mmol) and 1-naphthylamine (1 mmol) as model reaction.

In an initial endeavor, the model reaction was conducted in the presence of TBM (10 mol%) with a variety of solvents (1,4-dioxane, CH_3CN, CH_3OH, C_2H_5OH, and $CHCl_3$) under reflux (Table 1, entries 1–5). The reaction was also performed in the absence of solvent at 80 °C (Table 1, entry 6). The results indicated the solvents had a significant effect on product yield. The best conversion was observed when the reaction was performed under solvent-free conditions at 80 °C (Table 1, entry 6).

To further optimize the yield of the reaction, we performed experiments at room temperature, 50, 60, 70, 80, and 90 °C (Table 1, entries 6–11). As shown in Table 1, we found that high temperature could improve the reaction yield and shorten the reaction time. On the basis of these results we selected solvent-free conditions for

Table 1 Optimization of the reaction conditions for synthesis of **4b**

Entry	Catalyst	Amount (mol%)	Solvent	Temperature (°C)	Time (min)	Yield (%)[a]
1	TBM	10	1,4-Dioxane	Reflux	120	50
2	TBM	10	CH_3CN	Reflux	120	48
3	TBM	10	MeOH	Reflux	100	69
4	TBM	10	EtOH	Reflux	90	76
5	TBM	10	$CHCl_3$	Reflux	120	33
6	TBM	10	Solvent-free	80	45	95
7	TBM	10	Solvent-free	rt	120	50
8	TBM	10	Solvent-free	50	90	64
9	TBM	10	Solvent-free	60	75	77
10	TBM	10	Solvent-free	70	60	85
11	TBM	10	Solvent-free	90	45	95
12	TBM	0	Solvent-free	80	120	23
13	TBM	2	Solvent-free	80	90	47
14	TBM	5	Solvent-free	80	60	64
15	TBM	15	Solvent-free	80	45	95
16	PFPAT	10	Solvent-free	80	120	55
17	LiBr	10	Solvent-free	80	90	48
18	*p*-TSA	10	Solvent-free	80	90	72

Reaction conditions: 1,3-indanedione (1 mmol), 4-chlorobenzaldehyde (1 mmol) and 1-naphthylamine (1 mmol), solvent 5 mL

[a] Isolated yields

one-pot reaction of 1,3-indanedione, aromatic aldehydes, and 1-naphthylamine at 80 °C to give corresponding substituted 7-aryl-8*H*-benzo[*h*]indeno[1,2-*b*]quinoline-8-one derivatives (Table 1, entry 6). When 0, 2, 5, 10, and 15 mol% of TBM were used, the yields were 21, 44, 67, 95, and 95 %, respectively, at 80 °C (Table 1, entries 6 and 12–15). Because use of 15 mol% of TBM did not significantly increase the yield (Table 1, entry 15), 10 mol% of TBM was sufficient (Table 1, entry 6). Among the different catalysts tested (pentafluorophenylammonium triflate (PFPAT), LiBr, *p*-toluene sulfonic acid, and TBM) TBM was the most efficient in terms of reaction time and product yield (Table 1, entries 6 and 16–18).

To evaluate the scope of this catalytic transformation, the optimized reaction conditions were subsequently applied to the reaction of 1,3-indanedione and 1-naphthylamine with a variety of different aromatic aldehydes (Table 2, entries 1–14). A wide range of aromatic aldehydes bearing either electron-donating or electron-withdrawing substituents reacted successfully with 1,3-indanedione and 1-naphthylamine to give the corresponding 7-aryl-8*H*-benzo[*h*]indeno[1,2-*b*]quinoline-8-one derivatives in high yields and with short reaction times. The yields of indeno[1,2-*b*]quinolines were strongly affected by the electronic nature and position of the substituent on the aromatic aldehydes. Aldehydes with electron-withdrawing

Table 2 Synthesis of 7-aryl-8*H*-benzo[*h*]indeno[1,2-*b*]quinoline-8-one derivatives in the presence of TBM (10 mol%)

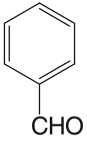
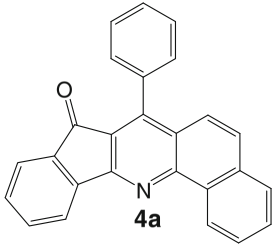
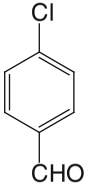
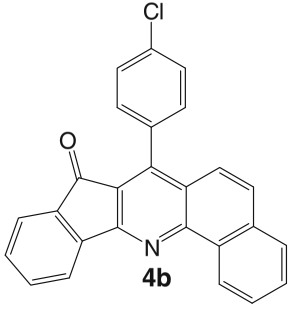
Entry	Aldehyde	Product	Time (min)	Yield (%)[a]	M.p (°C)
1		 **4a**	60	92	202–204
2		 **4b**	45	95	224–226

Table 2 continued

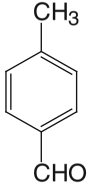
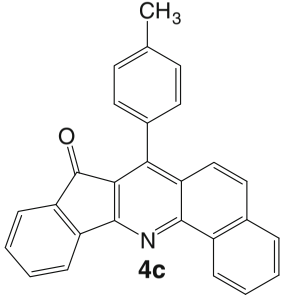
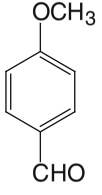
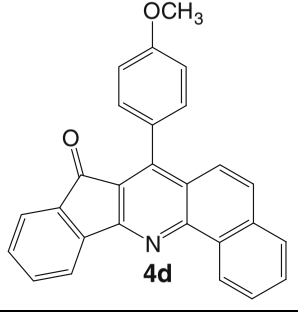
Entry	Aldehyde	Product	Time (min)	Yield (%)[a]	M.p (°C)
3		 **4c**	75	87	206–208
4		 **4d**	75	86	233–235

Table 2 continued

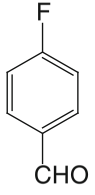
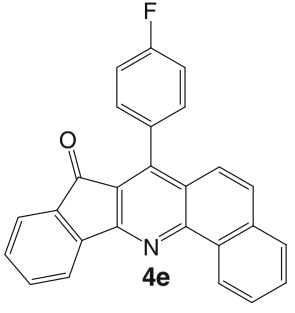
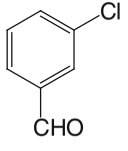
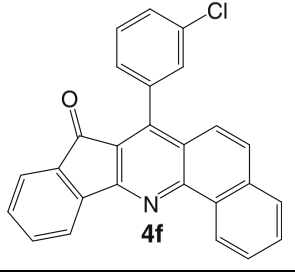
Entry	Aldehyde	Product	Time (min)	Yield (%)[a]	M.p (°C)
5		 **4e**	40	94	216–218
6		 **4f**	50	92	230–232

Table 2 continued

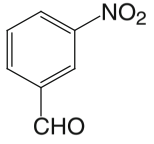
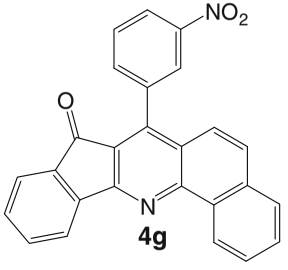
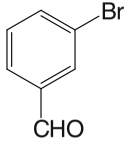
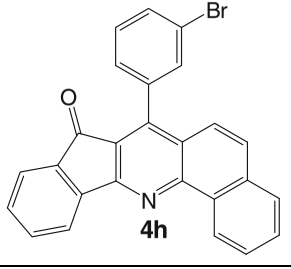
Entry	Aldehyde	Product	Time (min)	Yield (%)[a]	M.p (°C)
7		 **4g**	50	91	222–224
8		 **4h**	50	92	236–238

Table 2 continued

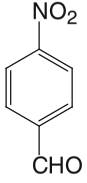
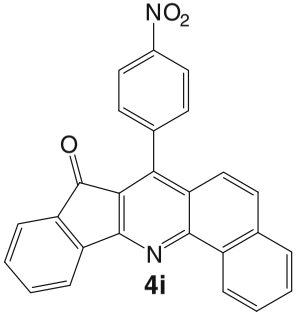
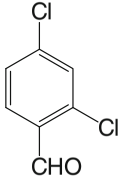
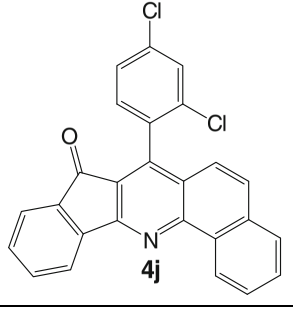
Entry	Aldehyde	Product	Time (min)	Yield (%)[a]	M.p (°C)
9		 **4i**	45	93	210–212
10		 **4j**	60	87	220–222

Table 2 continued

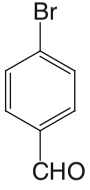
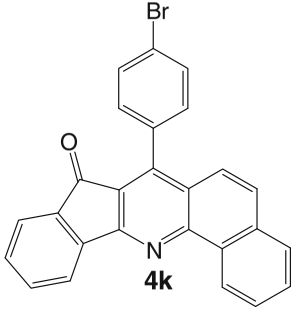
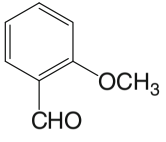
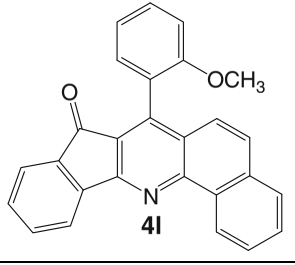
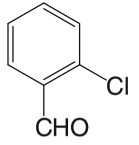
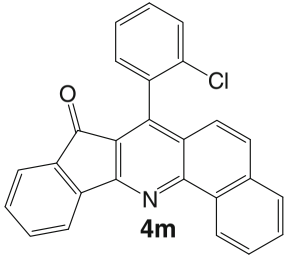
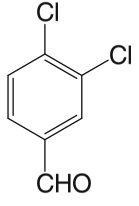
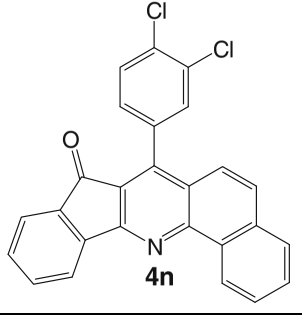
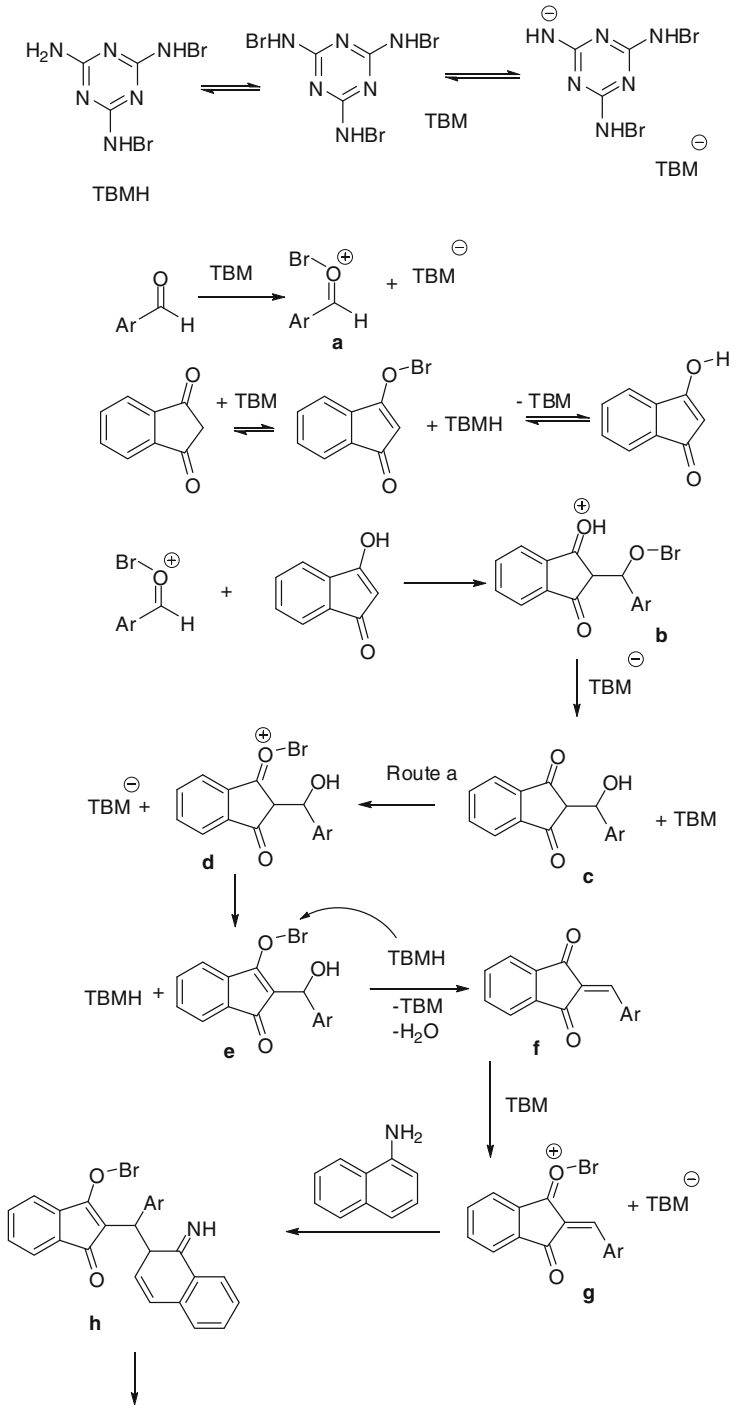
Entry	Aldehyde	Product	Time (min)	Yield (%)[a]	M.p (°C)
11		 **4k**	45	92	218–220
12		 **4l**	80	84	208–210

Table 2 continued

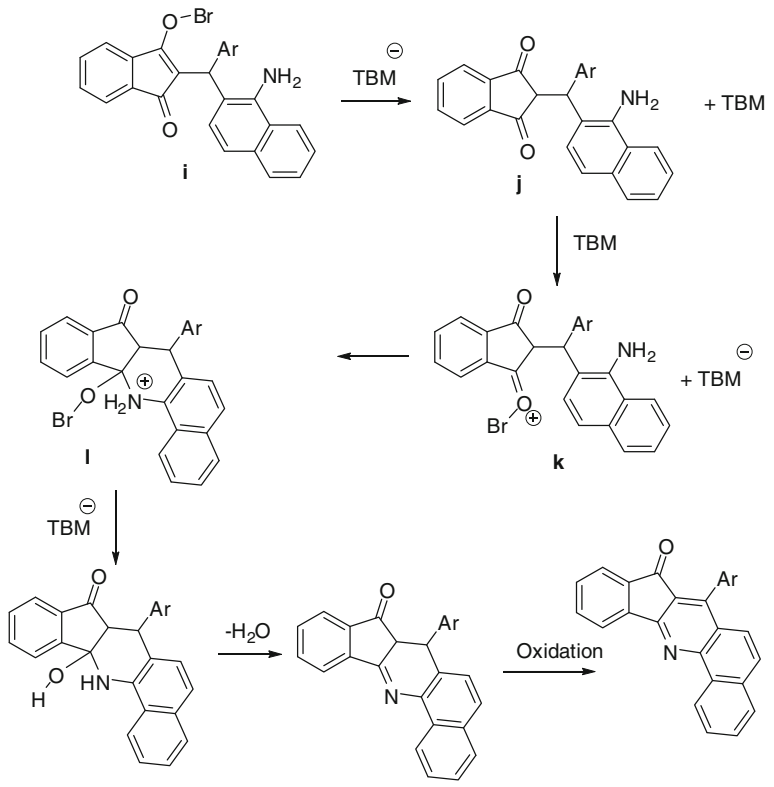
Entry	Aldehyde	Product	Time (min)	Yield (%)[a]	M.p (°C)
13		 **4m**	70	87	232–234
14		 **4n**	60	92	212–214

Reaction conditions: 1,3-indanedione (1 mmol), benzaldehyde (1 mmol) and 1-naphthylamine (1 mmol) under solvent-free conditions at 80 °C

[a] Isolated yields



Scheme 3 Plausible mechanism for synthesis of 7-aryl-8*H*-benzo[*h*]indeno[1,2-*b*]quinoline-8-ones

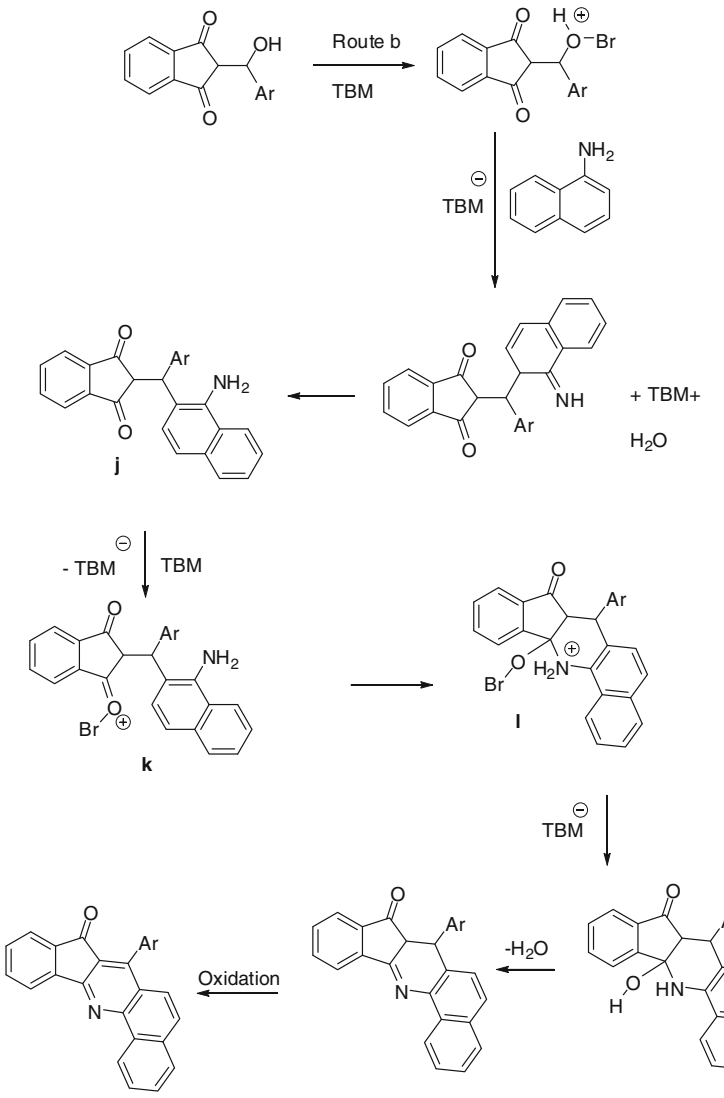


Scheme 3 continued

substituents provided the desired indeno[1,2-*b*]quinolines in good yields (Table 2, entries 2, 5, 9, and 11) whereas yields were slightly lower for aldehydes with electron-donating substituents (entries 3, 4, and 12). Aldehydes with *ortho* substituents gave slightly lower yields than those with *para* substituents (Table 2, entries 12 and 13). Aliphatic aldehydes were not good substrates, the reactions did not proceed.

A mechanistic rationale portraying the probable sequence of events in the formation of 7-aryl-8*H*-benzo[*h*]indeno[1,2-*b*]quinoline-8-one using TBM as catalyst is given in Scheme 3. In this reaction, the tribromomelamine could act as a bifunctional catalyst [30] which would activate both the carbonyl oxygen of the aldehyde and the acidic hydrogen of 1,3-indanedione. Because tribromomelamine contains Br atoms that are attached to N atoms, it is likely that Br^+ would be released in situ, and that this species would act as a catalyst in the reaction medium, leading to a substantial increase in the electrophilicity of the aldehyde (intermediate **a**).

It is proposed that tribromomelamine produces two different species, N_2,N_4-dibromo-1,3,5-triazine-2,4,6-triamine (TBMH) and the anion remaining after



Scheme 3 continued

release of Br^+ from TBM (TBM^-). The reaction proceeds by attack of 1,3-indanedione on the activated carbonyl to afford intermediate **b**. This reaction proceeds until formation of intermediate **c**. The reaction could continue via two different routes. In route a, Michael addition results in formation of intermediates **d**, **e**, **f**, **g**, and **h**. Route b proceeds via nucleophilic attack on the sp^3 carbon atom, as revealed in Scheme 3. Subsequent processes include cyclization, water removal, and aromatization, leading to formation of 7-aryl-8*H*-benzo[*h*]indeno[1,2-*b*]quinoline-8-ones.

Table 3 Effects of the different catalysts used for synthesis of 7-aryl-8*H*-benzo[*h*]indeno[1,2-*b*]quinoline-8-ones by condensation of 1,3-indanedione, benzaldehyde, and 1-naphthylamine

Entry	Catalyst (amount)	Solvent	Temperature (°C)	Time (h)	Yield (%)	Ref.
1	$[Fe(HSO_4)_3]$ (10 mol%)	DMSO	90	4	92	[24]
2	$H_6P_2W_{18}O_{62}\cdot 18H_2O$ (10 mol%)	Acetic acid	Reflux	4	90	[21]
3	AMPS (15 mol%)	CH_3CN	Reflux	2	90	[23]
4	P(4-VPH)HSO_4 (20 mg)	EtOH	Reflux	2	86	[26]
5	TBM (10 mol%)	Solvent-free	80	0.75	94	This work

Comparison of the reaction times and yields of this TBM-catalyzed synthesis of 7-aryl-8*H*-benzo[*h*]indeno[1,2-*b*]quinoline-8-one derivatives with those of methods reported in the literature reveals the merit of this method for synthesis of the desired products. In comparison with other catalysts used for the model reaction, TBM had much greater activity, which resulted in short reaction times under mild reaction conditions (Table 3). As shown in Table 3, compared with other reported catalysts (ferric hydrogensulfate $[Fe(HSO_4)_3]$ [24], $H_6P_2W_{18}O_{62}\cdot 18H_2O$ [21], cross-linked poly(2-acrylamido-2-methyl propane sulfonic acid (AMPS) [23], and poly(4-vinylpyridinium)hydrogen sulfate [26]) TBM was superior in terms of yield and reaction time.

Conclusions

An economic, rapid, and environmentally benign procedure has been developed for one-pot synthesis of 7-aryl-8*H*-benzo[*h*]indeno[1,2-*b*]quinoline-8-one derivatives by three-component reaction of 1,3-indanedione with aromatic aldehydes and 1-naphthylamine, under solvent-free conditions, with tribromomelamine as homogeneous catalyst. The method has several advantages, including short reaction times, high yields, facile workup, and the absence of any hazardous organic solvents, which makes it a useful and attractive procedure for synthesis of these compounds. The procedure is also advantageous in the sense that, because it is solvent-free, it is environmentally friendly.

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