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CAL-B accelerated novel synthetic protocols for 3,3′-arylidenebis-4-hydroxycoumarins and dimethyl ((substituted phenyl) (phenylamino)methyl) phosphonates

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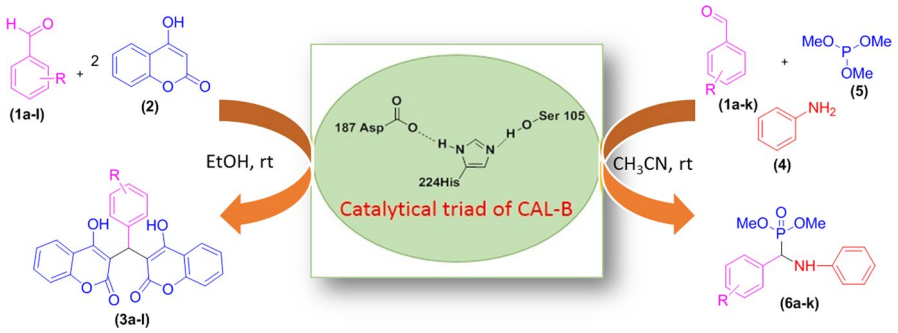
Abstract

Green protocols for the syntheses of 3,3′-arylidenebis-4-hydroxycoumarins and dimethyl ((substituted phenyl) (phenylamino)methyl) phosphonates have been first time developed using biocatalyst, CAL-B (lipase). These are carried at room temperature under stirring and are convenient and cost effective. The developed protocols are environmentally acceptable and are giving better to excellent yields of the titled products.

Graphic abstract



Keywords CAL-B · Lipase · Biocatalysts · 3,3-Arylidenebis-4-hydroxycoumarins · Dimethyl ((substituted phenyl) (phenylamino)methyl) phosphonates · Multicomponent condensation

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Introduction

Coumarins and α-amino phosphonates are gaining more importance as some of their derivatives have shown promising bioactivities. Coumarins are found naturally in various plants and are members of a class of heterocyclic compounds [1]. They are extensively employed as food and cosmetic additives [2], dye lasers [3–5] and gain stabilizing medium. They are found to possess anticoagulant, antibiotic, antitumor, anti-HIV, antihypertensive, analgesic, anti-inflammatory and anti-arrhythmia activities and are explored as precursor molecules in pharmaceutical industries [6–13]. Biscoumarins are vital organic compounds and have received considerable attention because of their broad spectrum of biological and interesting potential therapeutic activities. They often possess interesting pharmacological properties and act as antitumor, antibacterial [3–8], anticancer [9], urease and α-glucosidase inhibitory [10, 11], antifungal [12], and antiproliferative [13] agents. Dicoumarol and taxolin combination enhances synergistic inhibition of cell division of sea urchin embryos. These two compounds can be used in combination in order to reduce the high toxicity of taxol.

The distinctive nature of bioactive organophosphorus compounds has established their wide applicability in agricultural, medicinal, and industrial areas. α-Aminophosphonates are structural analogs of natural amino acids. They are considered as an important class of compounds with diverse and interesting biological activities [14–19]. Organophosphorus chemistry has provided valuable materials with potential biological activities of medicinal importance, and such products act as enzyme inhibitors [14], and are found to have HIV protease [15], antibiotic [16], herbicidal, fungicidal, insecticidal [17], plant growth regulating [18], antithrombotic [19], peptidases and proteases properties [20].

In view of these applications, several synthetic protocols have been reported to synthesize these compounds. Biscoumarins usually synthesized by carrying separately one-pot condensation of 4-hydroxycoumarins and aryl aldehydes in the presence of one of the catalysts viz. glacial acetic acid [21], acetic acid anhydride [22, 23], iodine [24], silica-supported sodium hydrogen sulfate and indion 190 resin in toluene [25], ionic liquids [26], silica-supported preyssler nanoparticles [27], tetrabutyl ammonium bromide (TBAB) [28], microwave irradiation with silica-gel support [21, 29, 30], dodecyl benzene sulfonic acid (DBSA)MW [31], phospho sulfonic acid [32], CuO–CeO_2 nanocomposite [33], starch-sulfuric acid [34], LTNPs [35], MgO-NPs [36], $BiVO_4$-NPs [37], SiO_2-OSO_3H NPs [38], P_4VPy-CuO [39], magnetic nanoparticle catalyst TrBr/[Fe_3O_4@SiO_2@$(CH_2)_3$-$ImSO_3H$]Cl [40], IL@CNTs [41], Hnmp/$ZnCl_3$ [42], [Dabco-H][AcO] [43], [TMG][Ac] [44], RHA-SO_3H [45], KF-montmorillonite [46], and PS-Zn-anthra complex [47], and Mn(pbdo)$_2$$Cl_2$/MCM-41 [48].

Mostly practiced synthetic route for obtaining α-amino organophosphonates involves one-pot condensation of anilines, aryl aldehydes and di/trimethylphosphite. Efforts are also found to be directed to accelerate this condensation using various catalysts viz. lanthanide triflate, scandium tris(dodecyl sulfate) [49], samarium diiodide along with 4-Å molecular sieves [50], heterogenous catalysts

such as $InCl_3$ [51], $TaCl_5$-SiO_2 [52] (bromodimethyl) sulfonium bromide [53], $LiClO_4$ [54], montmorillonite KSF [55], $ZrCl_4$ [56], TiO_2 [57], alumina-supported reagents [58], ionic liquids [59], $H_3PW_{12}O_{40}$ [60], Amberlite-IR120 [61], and oxalic acid [62]. Recently, a synthesis of α-amino phosphonates from ferrocene-1-carboxaldehyde, anilines and diethyl phosphite under neat condition, catalyzed by $KHSO_4$, has been reported [63].

The above referred synthetic protocols are having one or other kind of drawbacks. These are not cost effective and need non-readily available and non-biodegradable heterogeneous/homogeneous catalysts. It is also reviewed that a little attention is found to be paid on the use of biocatalysts, particularly immobilized lipases to accelerate the above condensations leading to the titled compounds. Biocatalysts/enzymes are functional proteins and now a days they are used as safer and economic catalysts for carrying organic transformations leading to biodynamic compounds. Our group has explored the use of active Baker's yeast as a whole cell source of biocatalysts for carrying various cyclocondensations leading to biodynamic heterocycles [64–72].

Recently some of the lipases are also found to be used as catalyst for carrying cost effectively value-added organic transformations [73–79].

Lipases are employed for variety of reaction viz. esterifications [73], transesterifications [74], hydrolyses [75], Bayer-Villiger oxidations [76–78], and amidations [79]. Biocatalytical promiscuity of lipases has also been reported. Lipases are well explored as biocatalysts and do catalyze hydrolysis of water soluble carboxylic esters, particularly triglycerides and phospholipids. Among lipases Candida Antartica Lipase B has been used as a biocatalyst in its pure form is as a immobilized CAL-B form to accelerate various organic reactions and biotransformations. Open and closed structures of this lipase have been thoroughly established by Benjamine et. al [80]. CAL-B is structurally similar to several other lipases and has a flexible lid. It is made up of 317 amino acids and is a member of α/β hydrolase-fold family. It consists of Serine, Hisdine, and Asparic/Glutamic catalytical triad and has secondary alcoholic binding pocket. Usually these active sites viz. Serine, Histidine, Asparic/Glutamic amino acid residues participate to display catalytic behavior to accelerate the rates of organic/ biotranformations [81]

Considering the dire need of establishing more convenient, cost-effective and eco-friendly synthetic protocols for the titled compounds, and significance of lipases as biocatalysts, here first time we have made an attempt to develop such synthetic protocols by carrying separately the above condensations in the presence of immobilized lipase, CAL-B, for obtaining the titled products 3,3'-arylidenebis-4-hydroxycoumarins and dimethyl ((substituted phenyl) (phenylamino)methyl) phosphonates conveniently and cost effectively.

Experimental

All the chemicals used were of laboratory grade. Lipase B Candida Antarctica immobilized on immobead 150 recombinant from yeast is procured from Sigma Alrich. Melting points of all the synthesized compounds were determined in open

capillary tubes and are uncorrected. ^{1}H NMR spectra were recorded with a Bruker Avance 300 spectrometer operating at 400 MHz using DMSO-d_6 solvent and tetramethylsilane (TMS) as the internal standard and chemical shift in δ ppm.^{13}C NMR spectra were recorded on Bruker Avance 75 MHz on Jeol. The purity of each compound was checked by TLC using silica-gel, $60F_{254}$ aluminum sheets as adsorbent and visualization was accomplished by iodine/ultraviolet light.

Synthesis of 3,3′-(Phenylmethylene)bis(4-hydroxy-2H-chromen-2-one) (3a)

Lipase, CAL-B (100 mg) was added to the reaction flask, containing ethanol (15 ml). Then, a mixture of benzaldehyde (1 gm/9.4 mmol) **(1a)** and 4-hydroxy coumarin (3.1 gm/18.8 mmol) (**2**) was added to the flask, and the whole reaction mass was stirred at rt. The progress of reaction was monitored by TLC using ethyl acetate: pet ether (2:8) as eluent. After stirring for 9 h, then ethyl acetate (3 × 10 ml) was added to the reaction mass and then stirred at room temperature for 10 min. and then filtered through Whatman paper. The solid residue remained on filter paper was further washed with 10 ml ethyl acetate. The obtained solid residue, CAL-B was dried and reused as a biocatalyst. Then, ethyl acetate and ethanol were removed from the collected filtrate under vacuum, and obtained crude residue remained was then crystallized using ethanol.

Similarly other derivatives of the series are prepared. The melting points and the isolated yields of the derivatives are recorded in Table 3. Melting points and spectral data of the 3,3′-arylidenebis-4-hydroxycoumarins (**3a–l**) are in good agreement with those reported in the literature [2, 15].

The scan copies of spectra of **3a** are submitted herewith as a representative of the series (**3a–l).**

Synthesis of Dimethyl (phenyl(phenylamino)methyl)phosphonate (6a)

Benzaldehyde (0.5 gm/4.7 mmol) (**1a**) and aniline (0.438 gm/4.7 mmol) (**4**) were dissolved in acetonitrile (7 ml), and then solution was stirred for few minutes. Then, trimethylphosphite (0.585 gm/4.7 mmol) (**5**) and CAL-B, lipase (50 mg) were added to the solution and then reaction mixture was stirred at room temperature. Progress of reaction was monitored by TLC. After 40 min, water (10 ml) and ethyl acetate (30 ml) were added into the reaction mass and it was then stirred for 15 min and filtered. The residue recovered, CAL-B was dried and reused. The ethyl acetate layer was separated from filtrates and washed with water, and dried over anhydrous Na_2SO_4. The solvent ethyl acetate was removed under reduced pressure and obtained diethyl (phenyl(phenylamino)methyl) phosphonates (6a). The obtained crude products were then crystalized using ethanol. Similarly other derivatives of the series were prepared (**6a–k**). Melting points and isolated yields of the derivatives are recorded in Table 4. The identity of the products was confirmed by ^{1}H and ^{13}C NMR, and HRMS, The spectral data in good agreement in those reported in the literature [82, 83].

Scan copies of spectra of **6b** are provided as a representative of the series (**6a–k).**

Spectral data of compounds (3a-l)

3′-(Phenylmethylene)bis(4-hydroxy-2H-chromen-2-one) (3a)

^{1}H NMR (DMSO-d_6, 300 MHz, δ ppm): 6.34 (s, 1H, –CH), 7.09–7.89 (m, 13H, Ar–H), 12.52 (s, 2H, 2OH).^{13}C NMR (DMSO-d_6, 75 MHz, δ ppm): 35.97, 91.01, 104.17, 115.80, 115.98, 116.35, 117.81, 123.19, 123.79, 123.90, 125.61, 126.71, 128.09, 128.54, 129.25, 131.95, 132.67, 132.82, 139.76, 152.20, 153.52, 161.88, 164.87, 165.17, 165.63. HRMS (ESI$^+$): $(M+H)^+$ calculated 413.1025, observed 413.1028.

3′-((4-Methoxyphenyl)methylene)bis(4-hydroxy-2H-chromen-2-one) (3b)

^{1}H NMR (DMSO-d_6, 300 MHz, δ ppm): 3.84 (s, 3H, OCH_3), 6.24 (s, 1H, –CH), 7.02–7.18 (m, 8H, Ar–H), 7.34–7.76 (m, 4H, Ar–H), 12.22 (s, 2H, 2OH).^{13}C NMR (DMSO-d_6, 75 MHz, δ ppm): 35.77, 56.98, 91.11, 104.23, 115.84, 115.58, 116.21, 117.68, 123.08, 123.56, 123.87, 125.48, 126.64, 128.01, 128.34, 129.15, 131.65, 132.57, 132.76, 139.45, 152.19, 153.34, 161.56, 164.45, 165.07, 165.52. HRMS (ESI$^+$): $(M+H)^+$ calculated 443.1131, observed 443.1029.

3′-(Tolylmethylene)bis(4-hydroxy-2H-chromen-2-one) (3c)

^{1}H NMR ($CDCl_3$, 300 MHz, δ ppm): 2.33 (s, 3H, CH_3), 6.06 (s, 1H, –CH), 7.08–8.05 (m, 12H, Ar–H), 11.30–11.49 (d, 2H, 2OH).^{13}C NMR ($CDCl_3$, 75 MHz, δ ppm): 21.17, 36.08, 104.29, 105.96, 116.82, 124.58, 125.04, 126.57, 129.53, 132.25, 132.98, 136.67, 152.71, 164.75, 165.89, 167.04, 169.51. HRMS (ESI$^+$): $(M+H)^+$ calculated 427.1181, observed 427.1172.

3′-((4-Hydroxyphenyl)methylene)bis(4-hydroxy-2H-chromen-2-one) (3d)

^{1}H NMR (DMSO-d_6, 300 MHz, δ ppm): 4.98 (s, 1H, OH), 6.25 (s, 1H, –CH), 6.96–7.24 (m, 8H, Ar–H), 7.27–7.66 (m, 4H, Ar–H), 12.32 (s, 2H, 2OH).^{13}C NMR (DMSO-d_6, 75 MHz, δ ppm): 35.54, 91.32, 105.87, 115.65, 116.01, 116.37, 117.58, 121.47, 123.21, 123.87, 124.76, 126.65, 128.78, 128.92, 129.47, 131.49, 132.02, 132.94, 138.19, 152.45,153.69, 161.08, 164.56, 165.69, 165.40. HRMS (ESI$^+$): $(M+H)^+$ calculated 429.0974, observed 429.0832.

3′-((3-Bromophenyl)methylene)bis(4-hydroxy-2H-chromen-2-one) (3e)

^{1}H NMR (DMSO-d_6, 300 MHz, δ ppm): 6.44 (s, 1H, –CH), 7.18–7.42 (m, 8H, Ar–H), 7.55–8.06 (m, 4H, Ar–H), 12.67 (s, 2H, 2OH).^{13}C NMR (DMSO-d_6, 75 MHz, δ ppm):36.02, 90.98, 104.64, 115.36, 115.57, 116.39, 117.65, 123.56, 123.83, 123.34, 125.46, 126.59, 127.54, 128.21, 129.49, 131.43, 132.78, 132.28,

139.54, 152.76, 153.21, 161.78, 164.23, 165.27, 165.57. HRMS (ESI^+): $(M+H)^+$ calculated 491.0130, observed 491.0028.

3′-((4-Fluorophenyl)methylene)bis(4-hydroxy-2H-chromen-2-one) (3f)

^1H NMR ($CDCl_3$, 300 MHz, δ ppm): 6.05 (s, 1H, –CH), 6.98–8.07 (m, 12H, Ar–H), 11.32–11.52 (d, 2H, 2OH).^{13}C NMR ($CDCl_3$, 75 MHz, δ ppm): 35.87, 104.14, 105.68, 115.59, 115.81, 116.58, 116.85, 117.06, 124.60, 125.15, 128.32, 128.40, 131.02, 131.05, 133.17, 152.49, 152.73, 160.69, 163.14, 164.80, 166.08, 167.02, 169.40. HRMS (ESI^+): $(M+H)^+$ calculated 431.0931, observed 431.0924.

3′-((4-Trifluromethylphenyl)methylene)bis(4-hydroxy-2H-chromen-2-one) (3 g)

^1H NMR (DMSO-d_6, 300 MHz, δ ppm):6.19 (s, 1H, –CH), 7.03–7.22 (m, 8H, Ar–H), 7.33–7.66 (m, 4H, Ar–H), 12.25 (s, 2H, 2OH).^{13}C NMR (DMSO-d_6, 75 MHz, δ ppm): 35.95, 91.09, 104.51, 115.46, 115.87, 116.89, 117.03, 123.36, 123.62, 123.89, 124.67, 126.56, 128.87, 128.87, 129.32, 130.76, 132.45, 132.76, 139.32, 152.48, 153.92, 161.23, 164.74, 166.37, 168.89. HRMS (ESI^+): $(M+H)^+$ calculated 481.0899, observed 481.0835.

3′-((4-Trifluromethoxyphenyl)methylene)bis(4-hydroxy-2H-chromen-2-one) (3 h)

^1H NMR (DMSO-d_6, 300 MHz, δ ppm):6.21 (s, 1H, –CH), 7.02–7.17 (m, 8H, Ar–H), 7.31–7.77 (m, 4H, Ar–H), 12.24 (s, 2H, 2OH).^{13}C NMR (DMSO-d_6, 75 MHz, δ ppm): 35.95, 91.76, 104.56, 115.43, 115.84, 116.65, 117.65, 123.20, 123.78, 123.87, 125.65, 126.52, 128.23, 128.34, 129.76, 131.65, 132.45, 132.79, 139.98, 152.56, 153.46, 161.72, 164.81, 165.63, 166.89. HRMS (ESI^+): $(M+H)^+$ calculated 497.0848, observed 497.0876.

3′-((4-Dimethylaminophenyl)methylene)bis(4-hydroxy-2H-chromen-2-one) (3i)

^1H NMR (DMSO-d_6, 300 MHz, δ ppm):3.09 (s, 6H, CH_3), 6.42 (s, 1H, –CH), 7.01–7.28 (m, 8H, Ar–H), 7.33–7.76 (m, 4H, Ar–H), 12.42 (s, 2H, 2OH).^{13}C NMR (DMSO-d_6, 75 MHz, δ ppm): 35.89, 50.23, 90.97, 105.52, 115.67, 116.21, 116.67, 117.38, 121.57, 123.50, 123.81, 125.42, 126.68, 128.39, 128.64, 129.78, 130.37, 132.49, 132.75, 139.59, 152.17, 153.72, 161.81, 163.78, 165.76, 167.41. HRMS (ESI^+): $(M+H)^+$calculated 456.1447, observed 456.1356.

3′-((4-Nitrophenyl)methylene)bis(4-hydroxy-2H-chromen-2-one) (3j) ^1H NMR ($CDCl_3$, 300 MHz, δ ppm):6.12 (s, 1H, –CH), 7.26–8.20 (m, 12H, Ar–H), 11.35–11.56 (d, 2H, 2OH).^{13}C NMR ($CDCl_3$, 75 MHz, δ ppm): 36.72, 103.47, 104.96, 116.43, 116.92, 116.99, 124.05, 124.69, 125.34, 125.40,127.76, 133.54, 143.55, 147.09, 152.52, 152.77, 165.01, 166.60, 167.17, 169.28. HRMS (ESI^+): $(M+H)^+$ calculated 458.0876, observed 458.0882.

3′-((4-Chlorophenyl)methylene)bis(4-hydroxy-2H-chromen-2-one) (3 k) ^{1}H NMR (DMSO-d_6, 300 MHz, δ ppm):6.34 (s, 1H, –CH), 7.29–7.45 (m, 8H, Ar–H), 7.54–7.99 (m, 4H, Ar–H), 12.57 (s, 2H, 2OH).^{13}C NMR (DMSO-d_6, 75 MHz, δ ppm):35.87, 91.56, 112.43, 115.53, 115.86, 116.71, 117.63, 123.58, 123.17, 123.49, 125.18, 126.53, 128.27, 128.83, 129.54, 131.76, 132.38, 132.76, 139.42, 152.45, 153.76, 161.98, 164.56, 165.37, 166.37. HRMS (ESI$^+$): $(M+H)^+$ calculated 447.0635, observed 447.0658.

3′-((2-Bromophenyl)methylene)bis(4-hydroxy-2H-chromen-2-one) (3 l) ^{1}H NMR (DMSO-d_6, 300 MHz, δ ppm): 6.44 (s, 1H, –CH), 7.21–7.45 (m, 8H, Ar–H), 7.52–8.06 (m, 4H, Ar–H), 12.67 (s, 2H, 2OH).^{13}C NMR (DMSO-d_6, 75 MHz, δ ppm): 35.92, 91.12, 104.43, 114.64, 115.79, 115.96, 116.91, 122.97, 123.45, 123.68, 124.89, 125.65, 128.76, 128.23, 129.45, 130.65, 131.32, 132.58, 139.71, 152.42, 153.64, 161.86, 164.09, 165.18, 165.45. HRMS (ESI$^+$): $(M+H)^+$ calculated 491.0130, observed 491.0028.

Spectral data of compounds (6a–k)

Dimethyl ((4-methoxyphenyl)(phenylamino)methyl)phosphonate (6b)

^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm):3.50 (s, 3H, –OCH_3), 3.74 (s, 3H, –OCH_3), 3.77 (s, 3H, –OCH_3), 4.72 (s, 1H, –CH), 4.79 (s, 1H, –NH), 6.58–7.40 (m, 9H, Ar–H).^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 53.93, 54.00, 54.45, 55.97, 114.12, 114.39, 114.41, 118.72, 127.54, 127.57, 129.09, 129.14, 129.37, 146.24, 146.39, 159.62. HRMS (ESI$^+$): $(M+H)^+$ calculated 322.1208, observed 322.1205.

Dimethyl (phenyl(phenylamino)methyl)phosphonate (6a)

^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 3.46 (s, 3H, –OCH_3), 3.75 (s, 3H, –OCH_3), 4.67–4.71 (d, 1H, –CH), 4.78 (s, 1H, –NH), 6.59–7.49 (m, 10H, Ar–H).^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 54.05, 55.14, 56.64, 114.09, 118.76, 127.98, 128.03, 128.29, 128.92, 129.40, 133.19, 135.78, 135.80, 146.21, 146.36. HRMS (ESI$^+$): $(M+H)^+$ calculated, 292.1102, observed, 292.1068.

Dimethyl (4-tolyl)(phenylamino)methyl)phosphonate (6c)

^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm):2.65 (s, 3H, –CH_3), 3.53 (s, 3H, –OCH_3), 3.78 (s, 3H, –OCH_3), 4.77 (s, 1H, –CH), 4.84 (s, 1H, –NH), 6.46–7.71 (m, 9H, Ar–H).^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 23.59, 54.08, 55.32, 56.62, 115.62, 118.76, 127.87, 128.52, 128.86, 128.92, 128.97, 129.42, 130.18, 135.67, 146.38, 146.84. HRMS (ESI$^+$): $(M+H)^+$ calculated, 306.1259, observed, 306.1168.

Dimethyl (4-hydroxyphenyl)(phenylamino)methyl)phosphonate (6d)

^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 3.44 (s, 3H, –OCH_3), 3.73 (s, 3H, –OCH_3), 4.79–4.86 (d, 1H, –CH), 4.91 (s, 1H, –NH), 5.46 (s, 1H, OH), 6.61–7.52 (m, 9H, Ar–H).^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 53.97, 54.34, 56.74, 114.67, 118.59,

127.24, 128.74, 128.78, 129.32, 129.69, 130.53, 133.67, 135.39, 135.47, 146.98. HRMS (ESI^+): $(M+H)^+$ calculated, 308.1051, observed, 308.0682.

Dimethyl (3-Bromophenyl)(phenylamino)methyl)phosphonate (6e)

^1H NMR ($CDCl_3$, 400 MHz, δ ppm):3.43 (s, 3H, –OCH_3), 3.78 (s, 3H, –OCH_3), 4.77–4.83 (d, 1H, –CH), 4.87 (s, 1H, –NH), 6.67–7.72 (m, 9H, Ar–H).^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 53.89, 54.23, 56.16, 114.67, 118.24, 127.82, 128.59, 128.12, 128.87, 128.36, 128.58,128.69, 135.86, 135.59, 146.79. HRMS (ESI^+): $(M+H)^+$ calculated, 370.0207, observed, 370.0158.

Dimethyl (4-Flurophenyl)(phenylamino)methyl)phosphonate (6f)

^1H NMR ($CDCl_3$, 400 MHz, δ ppm):3.28 (s, 3H, –OCH_3), 3.46 (s, 3H, –OCH_3), 4.38–4.73 (d, 1H, –CH), 4.86 (s, 1H, –NH), 6.98–7.53 (m, 9H, Ar–H).^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 54.01, 55.39, 56.57, 115.37, 118.68, 127.38, 128.72, 128.49, 128.42, 128.58, 130.27, 135.46, 135.72, 146.35, 146.64. HRMS (ESI^+): $(M+H)^+$ calculated, 310.1008, observed, 310.1068.

Dimethyl ((phenylamino)(4-(trifluoromethyl)phenyl)methyl)phosphonate (6g)

^1H NMR ($CDCl_3$, 400 MHz, δ ppm):3.55 (s, 3H, –OCH_3), 3.77 (s, 3H OCH_3), 4.83 (s, 1H, –CH), 4.89 (s, 1H, –NH), 6.55–6.75 (m, 5H, Ar–H), 7.10–7.62 (m, 4H, Ar–H).^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 53.96, 54.96, 56.45, 114.04, 119.20, 120.13, 122.84, 125.88, 125.91, 128.33, 129.53, 130.61, 130.96, 140.27, 145.80, 145.94. HRMS (ESI^+): $(M+H)^+$ calculated, 360.0976, observed, 360.0976.

Dimethyl ((phenylamino)(4-(trifluoromethoxy)phenyl)methyl)phosphonate (6h)

^1H NMR ($CDCl_3$, 400 MHz, δ ppm): 3.53 (s, 3H OCH_3), 3.71 (s, 3H, OCH_3), 4.78 (s, 1H, –CH), 4.83 (s, 1H, –NH), 6.56–7.26 (m, 5H, Ar–H), 7.49–7.52 (d, 4H, Ar–H).^{13}C NMR ($CDCl_3$,100 MHz, δ ppm):53.93, 54.51, 56.02, 114.03, 119.09, 119.34, 121.33, 121.90, 129.33, 129.39, 129.51, 134.61, 134.64, 145.90, 146.04, 149.17. HRMS (ESI^+): $(M+H)^+$ calculated 376.0925, observed 376.0921.

Dimethyl ((4-(dimethylamino)phenyl)(phenylamino)methyl)phosphonate (6i)

^1H NMR ($CDCl_3$, 400 MHz, δ ppm): 3.46 (s, 3H, OCH_3), 3.75 (s, 3H, OCH_3), 4.77–4.83 (d, 1H, –CH), 6.59–7.49 (m, 10H, Ar–H).^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 43.69, 54.02, 55.37, 56.76, 114.13, 118.47, 127.78, 128.43, 128.57, 128.73, 128.85, 129.29, 133.45, 135.76, 146.27, 146.69. HRMS (ESI^+): $(M+H)^+$ calculated, 335.1524, observed, 335.1481.

Dimethyl (4-nitrophenyl)(phenylamino)methyl)phosphonate (6j) ^1H NMR ($CDCl_3$, 400 MHz, δ ppm): 3.48 (s, 3H, OCH_3), 3.65 (s, 3H, OCH_3), 4.69 (s, 1H, –CH), 4.86 (s, 1H, –NH), 6.98–7.76 (m, 9H, Ar–H).^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm):

53.72, 54.21, 56.73, 114.64, 118.86, 127.46, 128.38, 128.57, 128.38, 128.48, 129.51, 130.53, 135.49, 146.54, 146.38. HRMS (ESI^+): $(M+H)^+$ calculated, 337.0925, observed, 337.0798.

Dimethyl (4-chlorophenyl)(phenylamino)methyl)phosphonate (6k) ^1H NMR ($CDCl_3$, 400 MHz, δ ppm): 3.52 (s, 3H, $–OCH_3$), 3.69 (s, 3H, $–OCH_3$), 4.71 (s, 1H, –CH), 4.82 (s, 1H, –NH), 6.75–7.89 (m, 9H, Ar–H).^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 53.99, 54.08, 56.64, 114.53, 118.65, 127.81, 128.49, 128.85, 128.97, 129.13, 129.67, 130.82, 135.58, 146.79, 146.93. HRMS (ESI^+): $(M+H)^+$ calculated, 326.0713, observed, 326.0687.

Results and discussion

In view to optimize reaction conditions, we separately carried the condensations of a) benzaldehyde **(1a)** (1 gm/9.4 mmol), and 4-hydroxy coumarin (**2**) (3.1 gm/18.8 mmol), and b) benzaldehyde (**1a**), (0.5 gm/4.7 mmol), aniline (**4**) (0.438 gm/4.7 mmol), and trimethyl phosphite (**5**) (0.584 gm/4.7 mmol) as model reactions in the presence of CAL-B for obtaining 3,3′-((phenyl)methylene)bis(4-hydroxy-2H-chromen-2-one) (**3a**) and dimethyl (phenyl(phenylamino)methyl)phosphonate **(6a),**

Table 1 Effect of different reaction conditions on the isolated yields of 3,3'-((phenyl)methylene)bis(4-hydroxy-2H-chromen-2-one) (**3a**)[a]

Entry	Solvent	Temp (°C)	Lipase(mg)	Time (h)	Yield (%)
1	MeOH	RT	100	9	82
2	MeCN	RT	100	9	64
3	DCM	RT	100	9	56
4	DMF	RT	100	9	59
5	1,4-Dioxane	RT	100	9	67
6	H_2O	RT	100	9	78
7	**EtOH**	RT	100	**9**	**88**
8	EtOH	RT	0	Even after 36	Trace
9	EtOH	RT	25	9	66
10	EtOH	RT	50	9	77
11	EtOH	RT	75	9	80
12	EtOH	RT	100	9	88
13	EtOH	40	100	9	91
14	EtOH	45	100	9	88
15	EtOH	50	100	9	90

After optimization, by varrying solvents, reaction temperature and amount of catalyst the best one were chosen for conducting the condensations are represented in bold form

[a]Reaction conditions: Benzaldehyde (9.4 mmol) **(1a)**, 4-hydroxy coumarin (18.8 mmol) (**2**) in solvent (15 ml)

Table 2 Effect of different reaction conditions on the isolated yields of dimethyl (phenyl(phenylamino) methyl)phosphonate (**6a**)[a]

Entry	Solvent	Temp (°C)	Lipase(mg)	Time (min)	Yield (%)
1	Neat condition	RT	50	35	82
2	EtOH	RT	50	35	79
3	MeOH	RT	50	35	74
4	**MeCN**	RT	50	**35**	**89**
5	DCM	RT	50	35	56
6	DMF	RT	50	35	59
7	H_2O	RT	50	35	68
8	MeCN	RT	0	120	Trace
9	MeCN	RT	25	35	89
10	MeCN	RT	**50**	**35**	**89**
11	MeCN	RT	75	35	90
12	MeCN	40	50	35	89
13	MeCN	45	50	35	90
14	MeCN	**50**	50	**35**	**89**

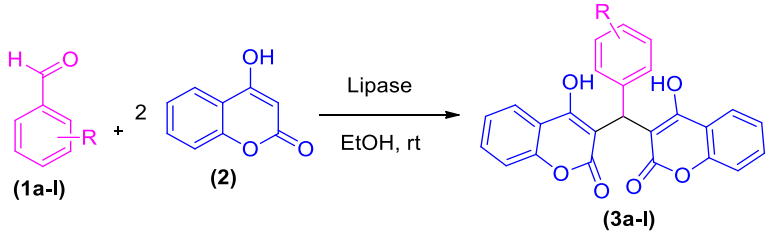
After optimization, by varrying solvents, reaction temperature and amount of catalyst the best one were chosen for conducting the condensations are represented in bold form

[a]Reaction conditions: Benzaldehyde (4.7 mmol), aniline (4.7 mmol), trimethyl phosphite (4.7 mmol), in solvents (7 ml)

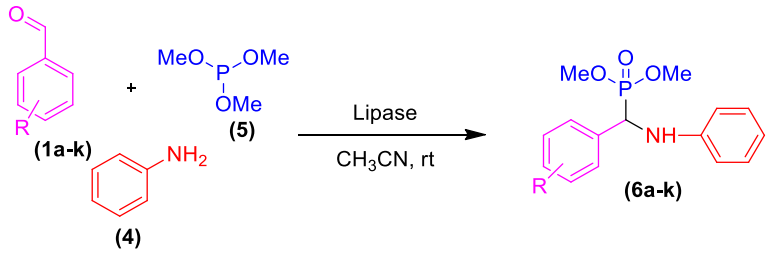
respectively, by varying the amounts of CAL-B, reaction temperature and solvents and the observed results are incorporated in Tables 1 and 2.

It was observed (Table 1) that a model reaction when carried using benzaldehyde **(1a)** (1 gm/9.4 mmol), and 4-hydroxy coumarin (**2**) (3.1 gm/18.8 mmol), in ethanol (15 ml) in the presence of CAL-B (100 mg) at room temperature gave 90% yield within 9 h and hence considered these reaction conditions as optimal conditions for conducting the condensation. It was also noted (Table 2) that the other multi-component reaction when performed using benzaldehyde (**1a**), (500 mg/4.7 mmol), aniline (**4**) (0.438 gm/4.7 mmol), and trimethyl phosphite (**5**) (0.585 gm/4.7 mmol) in acetonitrile (7 ml) in the presence of CAL-B at room temperature gave dimethyl (phenyl(phenylamino)methyl)phosphonate **(6a)** with 89% yield within 35 min. These reaction conditions are chosen as optimal conditions for this kind of condensation reaction for getting **6a–k.** It was also observed that the CAL-B retained its potential catalytic activity even after its first use and found to be reusable. The details of its isolation and reuse have been incorporated in experimental procedure.

With these inspiring observations, we carried the synthesis of substituted 3,3'-arylidenebis-4-hydroxycoumarins **(3a-l)** (Scheme 1) and dimethyl ((substituted phenyl) (phenylamino)methyl) phosphonates (**6a-k**) (Scheme 2) using the above-optimized conditions and obtained better to excellent yields of the titled products.



Scheme 1 Synthesis of substituted 3,3′-arylidenebis-4-hydroxycoumarins (**3a-l**)



Scheme 2 Synthesis of dimethyl ((substituted phenyl) (phenylamino)methyl) phosphonates (**6a-k**)

Table 3 Physical data of substituted 3,3'-arylidenebis-4-hydroxycoumarins (**3a-l**)[a]

Entry	Compound	R	Yield(%)[b]	M.P. (°C)[c]
1	**3a**	H	88	276–277
2	**3b**	4-OMe	90	234–235
3	**3c**	4-Me	87	266–268
4	**3d**	4-OH	88	255–257
5	**3e**	3-Br	79	225–228
6	**3f**	4-F	89	215–218
7	**3 g**	4-CF_3	90	227–229
8	**3 h**	4-OCF_3	86	265–267
9	**3i**	4-NMe_2	87	243–244
10	**3j**	4-NO_2	88	237–239
11	**3 k**	4-Cl	88	289–290
12	**3 l**	2-Br	88	239–241

[a]*Reaction conditions:* Substituted benzaldehydes (9.4 mmol) (**1a-l**), 4-hydroxy coumarin (18.8 mmol) (**2**), Lipase (100 mg) in ethanol (10 ml) at room temperature for 9 h

[b]Isolated yields

[c]Melting points are in good agreement with those reported in the literature [2, 15]

Table 4 Physical data of dimethyl ((substituted phenyl) (phenylamino)methyl) phosphonates (**6a-k**)[a]

Entry	Compound	R	Yield[b] (%)	M.P. (°C)[c]
1	**6a**	H	89	89–91
2	**6b**	4-OCH_3	92	130–132
3	**6c**	4-CH_3	87	59–61
4	**6d**	4-OH	78	93–95
5	**6e**	3-Br	83	63–65
6	**6f**	4-F	91	134–136
7	**6g**	4-CF_3	93	110–112
8	**6h**	4-OCF_3	88	80–82
9	**6i**	4-NMe_2	86	123–125
10	**6j**	4-NO_2	78	112–114
11	**6k**	4-Cl	92	58–60

[a]Reaction conditions: Substituted benzaldehyde (4.7 mmol), Aniline (4.7 mmol), trimethyl phosphite (4.7 mmol), Lipase (50 mg) in acetonitrile (7 ml),stirred at room temperature for 35 min

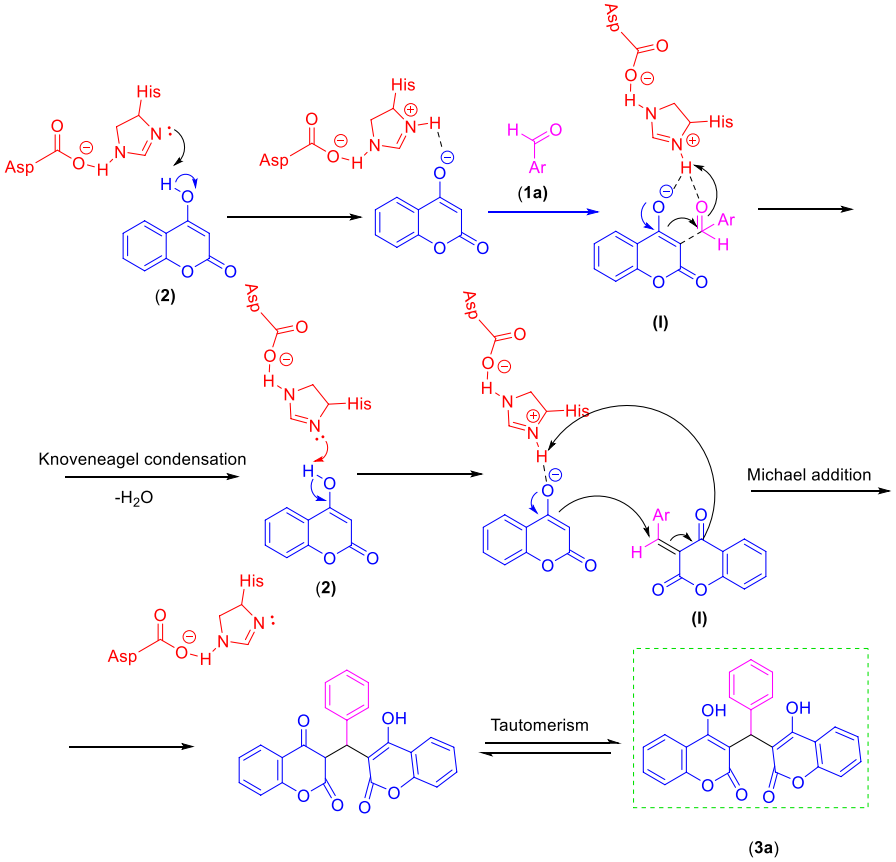
[b]Isolated yield

[c]Melting points are in good agreement with those reported in the literature [82, 83]

Physical data are summarized in Tables 3 and 4. All the synthesized compounds are known/reported and their physical constants and spectral data are in good agreement with those reported in the literature [2, 15, 82, 83].

It seems from the results recorded in Tables 1 and 2 that the condensations under reference are not found to be run satisfactorily in the absence of CAL-B, lipase and it is also observed that in the presence of lipase both the type of condensation are found to undergo rapidly, yielding reaction products at rt with better to excellent yields. Therefore, it is confirmed that lipase is displaying its catalytic role in both the condensations through the active amino acid residues. The plausible mechanism of these two types of condensations leading to titled products 3,3′-arylidenebis-4-hydroxycoumarins and dimethyl ((substituted phenyl) (phenylamino)methyl) phosphonates in presence of CAL-B has been depicted in Schemes 3 and 4.

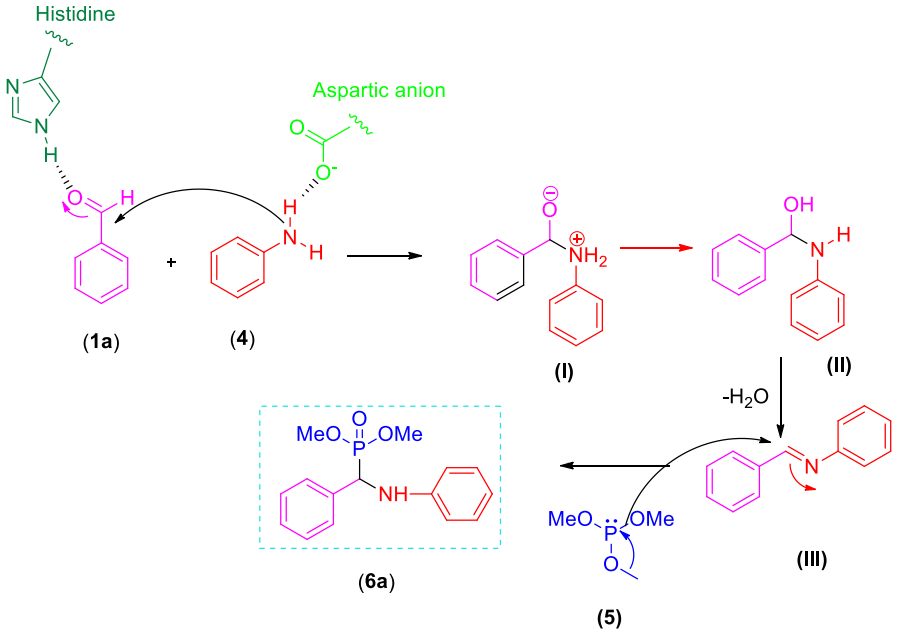
Efficient recovery and reusability of the catalyst are the valuable advantages in modern catalysis research and green chemistry. In this respect, the recovery and reusability of CAL-B were investigated for the model reactions. Consequently, the model reactions were performed. After completion of reaction, ethyl acetate was added in the reaction mixture and CAL-B was easily separated from the product by simple filtration. The obtained solid residue, CAL-B was washed with ethyl acetate and reused for next three consecutive cycles for the synthesis of **3a**. As shown in the recyclability graph of catalytic efficiency of CAL-B, the isolated yields were almost similar until the third recycling (Fig. 1). Only a slight decrease in the yield of the desired product **3a**, was noticed.



Scheme 3 Plausible mechanism for the synthesis of 3,3'-(Phenylmethylene)bis(4-hydroxy-2H-chromen-2-one) (**3a**)

Conclusion

First time an environmentally accepted, versatile, and efficient CAL-B catalyzed synthetic protocols have been developed for obtaining high yields of the 3,3′-arylidene bis-4-hydroxycoumarins and diethyl(phenyl (phenylamino)methyl) phosphonates. Catalyst lipase, CAL-B used here is biodegradable and cost-effective. These condensations leading to the title products, 3,3′-arylidene bis-4-hydroxycoumarins and diethyl(phenyl (phenylamino)methyl) phosphonates occur at room temperature in ethanol and in acetonitrile, respectively. Thus, we have opened up a new possibility for the synthesis of various heterocycles derivatives using CAL-B as catalyst. The protocols have nontedious workup in conducting and isolation of the products.



Scheme 4 Plausible mechanism for the synthesis of Dimethyl (phenyl(phenylamino)methyl)phosphonate **6a**)

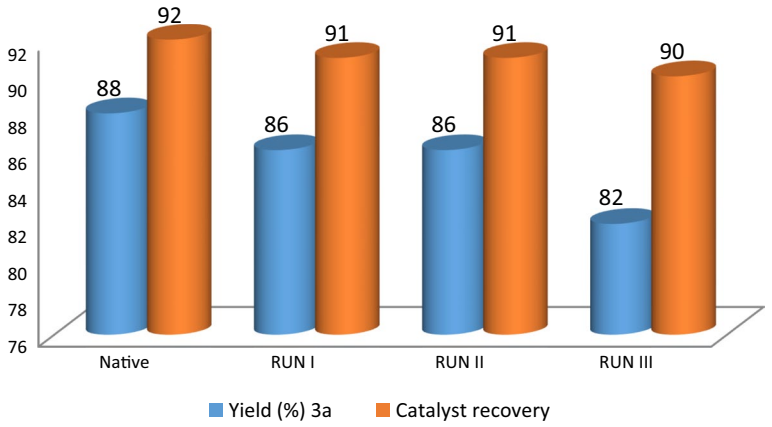


Fig. 1 Recycle and recovery of CAL-Band its effect on yield of (**3a**)

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