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$Bi(NO_3)_3$–Al_2O_3-Mediated Efficient Synthesis of 4-Aryl-2,6-dicoumarinylpyridines Under Solventless Conditions

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A new efficient and eco-friendly methodology has been developed for the synthesis of 4-aryl-2,6-dicoumarinylpyridines from coumarinylchalcones and urea, using Bi(III) nitrate–Al_2O_3 as catalyst. Coumarinylchalcones were in turn prepared from salicylaldehyde and ethylacetoacetate by the tandem reaction with aldehydes on the surface of Bi(III) nitrate–Al_2O_3 in the presence of the co-catalyst Zn(II) chloride.

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Introduction

Coumarins are well documented for their photosensitizing[1] and a wide range of other biological activities.[2] They also find industrial[3] and analytical applications.[4] Their 3- and 4-heteroaryl derivatives are associated with monoamine reductase inhibiting activity,[5] and bactericidal,[6] fungicidal,[7] and CNS-depressant activities.[8] For obvious reasons, the synthesis of pyridylcoumarins has gained considerable attention.[9] Symmetrically substituted triarylpyridines too are pharmacologically potent compounds.[10] These products also display photodynamic activity[11] and show fluorescence and scintillation properties.[12] Moreover, these products are structurally related to the photodynamic 2,4,6-triaryl-selenopyrylium, -telluropyrylium, and -thiopyrylium cell-specific cancer therapeutic agents.[11] We envisaged that, by virtue of their synergistic photodynamic activity, the suitably substituted pyridine derivatives bearing one or more coumarin pharmacophores might prove pharmacodynamically more efficacious than the aforementioned products and might avoid the metal toxicity. Traditionally, coumarin derivatives are synthesized by the Pechman condensation,[13] Knoevenagel's reaction,[14] or the Wittig reaction[15] or their modified versions involving Lewis acids[16] or cation-exchange resins.[17] However, these methodologies fail to bring about the substitutions in the pyridine nucleus. Although several approaches to the synthesis of triarylpyridines have emerged,[18] these products are mostly prepared by Krohnke[19] or modified Krohnke synthesis.[20]

In both cases, although improvements in the percentage yield of the products has been registered, each synthesis is complicated by one or more drawbacks, such as the involvement of multistage laborious processes, stringent and environmentally hazardous reaction conditions, the use of expensive rare-earth Lewis acids and their substrate selectivity, and the requirement of stoichiometric amount of reagents. Recently,[21] we observed that Bi(III) nitrate, immobilized on Al_2O_3, efficiently converted chalcones and urea into 2,4,6-triarylpyridines. We now report the preparation of 4-aryl-2,6-dicoumarinylpyridines from coumarinylchalcones using the same reagents, under solventless conditions.

Results and Discussion

Our protocol for the synthesis of 4-aryl-2,6-dicoumarinylpyridines consisted of 3-acetylcoumarin, an aldehyde, urea, and Bi(III) nitrate immobilized on alumina. As we have been interested in exploring the catalytic efficiency of the readily available non-toxic, air- and moisture-resistant Bi(III) nitrate immobilized on neutral alumina, in the synthesis of heterocyclic products, we first prepared 3-acetylcoumarin by heating an equimolar mixture of salicylaldehyde and ethylacetoacetate on the surface of 5% w/w Bi(III) nitrate–Al_2O_3 in the absence of solvent. 3-Acetylcoumarin was obtained but in low yield and the reaction proceeded with the formation of a multicomponent mixture. Therefore, it occurred to us that the use of a co-catalyst might help in arresting the side reactions. As our primary goal has been to make use of biocompatible metal salts as catalysts, we chose Zn(II) chloride as a co-catalyst in the cycloaddition reaction of salicylaldehyde. After several experiments for optimization, the optimum concentration of Zn(II) chloride, as the co-catalyst, was found to be 2.5% w/w. 3-Acetylcoumarin **3**[17] was obtained in 85% yield (Scheme 1).

Next, we attempted further condensation of the 3-acetylcoumarin with the aromatic aldehydes, using the modified bismuth(III) nitrate–Al_2O_3–$ZnCl_2$ catalyst. The reaction mixture was heated at 120 ± 5°C, in a hot-air oven, for 4–5 h, when coumarinylchalcones **5a**–**g** (Scheme 2) were obtained in 65–75% yield (Table 1). Encouraged by these observations, we conducted the tandem reactions of salicylaldehyde, ethylacetoacetate, and aldehydes **4a**–**g** on the surface of bismuth(III) nitrate–Al_2O_3–$ZnCl_2$ (5%, 2.5% w/w) catalyst, at a temperature of 120 ± 5°C. The coumarinylchalcones were obtained in nearly the same percentage yield as in the two-stage reaction. Although the exact role of the co-catalyst zinc(II) chloride in the presence

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of bismuth(III) nitrate in the reaction is not understood, the formation of 3-acetylcoumarin may involve a Mukaiyama-type aldol condensation of salicylaldehyde with ethylacetoacetate followed by cyclization. The 3-acetylcoumarin may then undergo further aldol condensation with the aldehydes (Fig. 1) to give **5a**–**g**.

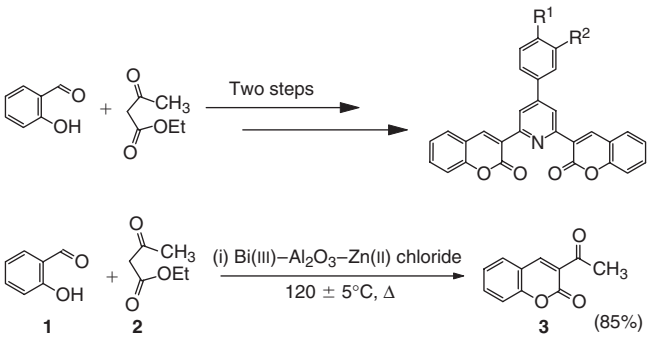
In the next step, the coumarinylchalcones and urea (2:1 mol ratio), in chloroform solution, were adsorbed on 5% w/w Bi(III) nitrate–Al_2O_3 catalyst (Scheme 3). After the mixture was dried in air, the reaction mixture was heated at 120 ± 5°C in a thermostatically controlled hot-air oven. On completion of the reaction (5–6 h), as evidenced from the TLC of the aliquots drawn out at 0.5-h intervals from a simultaneously run separate experiment, the products **7a**–**g** were extracted with hot chloroform and were purified by column chromatography on silica gel, using petroleum spirits (bp 40–60°C)/benzene graded solvent systems. The products **7a**–**g** were obtained in 65–75% yield (Table 2) and were characterized as 4-aryl-2,6-dicoumarinylpyridines by spectroscopic methods (HREIMS, IR, ^{1}H NMR, ^{13}C NMR, DEPT 135°).

All these reactions afforded minor quantities of the aldehydes from which the coumarinylchalcones were initially prepared.

The IR spectra of the compounds showed absorption bands at ν_{max} 3000–2990, 1723–1736, 1620, 1600, and 1450 cm^{-1}. The ^{1}H NMR spectra of the compounds displayed characteristic resonance signals at δ 7.20–7.30 (s, 2H), due to the protons of the pyridine ring. The ^{13}C NMR spectrum exhibited the characteristic resonance signals at δ 91.8, 112, 115.9, 129.3, 151.9, 160.7–161.5.

In order to generalize this reaction, we carried out the reactions of coumarinylchalcones **5a**–**c** with acetamide **6b**, benzamide **6c** and thiourea **6d**, using the aforementioned procedure (Scheme 3).These reaction also yielded minor quantities of aldehydes from which the chalcones were initially prepared. The percentage yield of the 4-aryl-2,6-dicoumarinylpyridines thus obtained are given in Table 2.

Mechanistically, the reaction seems to follow the pathway involving the homomolecular Michael addition of two coumarinylchalcones followed by the heteroannulation with urea and simultaneous retro-aldol disproportionation. Subsequent dehydration and catalytic oxidation may lead to the formation of the pyridinium ion, which on hydrolysis may afford 4-aryl-2,6-dicoumarinylpyridines (Fig. 2).[21]



Scheme 1. Preparation of 3-acetylcoumarin from salicylaldehyde and ethylacetoacetate in the solid state.

Conclusions

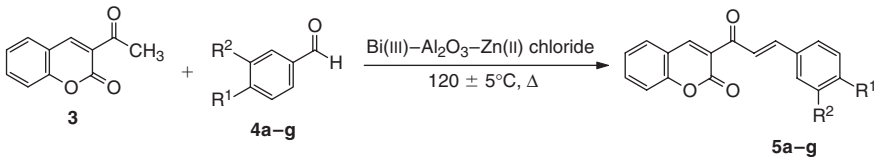
We have thus developed a simple two-stage straightforward, ecofriendly and efficient procedure for the synthesis of coumarins, coumarinylchalcones, and 4-aryl-2,6-dicoumarinylpyridines, using for the first time the biocompatible immobilized bismuth(III) nitrate as a catalyst in the presence and absence of the co-catalyst zinc(II) chloride. This procedure has an added advantage that the catalysts are non-toxic and biocompatible. Further work on the use of these catalysts in the preparation of bioactive heterocyclic compounds is in progress.

Experimental

Melting points are uncorrected and were determined on Perfit melting point apparatus. IR spectra were recorded from KBr disks. ^{1}H NMR, ^{13}C NMR, and DEPT 135° spectra were recorded on a 200 MHz Bruker AcDPX-200 spectrometer, and chemical shifts were determined from expanded peak segregated graphs. HREIMS was recorded at 70 eV. TLC was performed on 0.5-mm thick plates using silica gel G adsorbent. Column chromatography was performed on silica gel (60–120 mesh) using graded solvent systems of petroleum spirits (bp 40–60°C) and benzene (9:1; 7:3; 3:7; 1:9 v/v). The products were crystallized from chloroform/petroleum spirits (bp 40–60°C).

Table 1. Percentage yield of coumarinylchalcones 5a–g

Product	% yield (stepwise)	% yield (tandem)
5a	65	64
5b	75	73
5c	70	71
5d	72	70
5e	71	70
5f	73	72
5g	69	68



4a: $R^1 = R^2 = H$
4b: $R^1 = OCH_3$; $R^2 = H$
4c: $R^1 = Cl$; $R^2 = H$
4d: $R^1 = Br$; $R^2 = H$
4e: $R^1 = R^2 = Cl$
4f: $R^1 = R^2 = Br$
4g: $R^1 = R^2 = -OCH_2O-$

Scheme 2. Coumarinylchalcones **5a**–**g** from 3-acetylcoumarin and substituted aromatic aldehydes.

Preparation of Catalyst

Bismuth(III) nitrate (2.5 g) in 50% methanol (100 mL) was added to neutral alumina (50 g) and the mixture was stirred at room temperature for 12 h. The mixture was air-dried and then heated at 110 ± 5°C, in a thermostatic hot-air oven, for 6 h. In the second case, the catalyst 5% w/w bismuth(III) nitrate, prepared as above, was treated with zinc(II) chloride (1.25 g) in $CHCl_3$ (100 mL), and the mixture was stirred for 4 h. The solvent was removed under pressure. The mixture was reactivated at 110 ± 5°C for 4 h. The activated bismuth(III) nitrate–zinc(II) chloride–Al_2O_3 mixture was cooled in a dessicator and preserved. The catalyst was reactivated at 110 ± 5°C for 0.5 h each time before use.

General Procedure for the Synthesis of 3-Acetylcoumarins

Salicylaldehyde (1 mol) and ethylacetoacetate (1 mol) were adsorbed on the bismuth(III) nitrate–zinc(II) chloride–Al_2O_3 catalyst in proportion by weight of the substrates. The mixture was dried in air and heated at 120 ± 5°C in a thermostatically controlled hot-air oven. The reaction was monitored by TLC of aliquots drawn out from a simultaneously run separate experimental flask, under identical reaction conditions. The reaction was complete in 30 min. On completion of the reaction, the product was extracted with chloroform and recrystallized from ethanol.

Table 2. Percentage yield of coumarinylpyridines with amino derivatives

Product	Yield with different amino compounds			
	6a	**6b**	**6c**	**6d**
7a	70	67	65	68
7b	75	71	74	73
7c	68	64	64	67
7d	65	–	–	–
7e	69	–	–	–
7f	71	–	–	–
7g	67	–	–	–

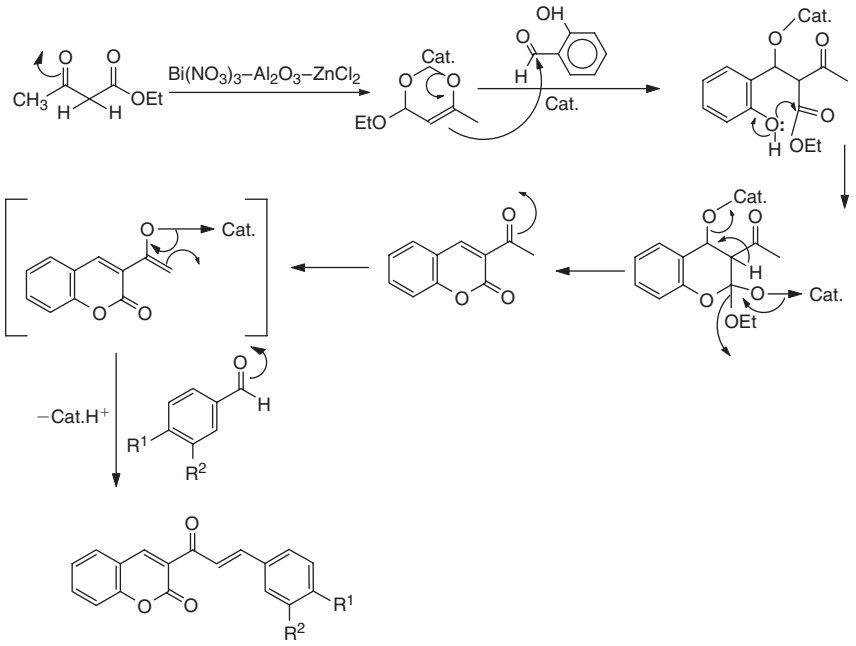
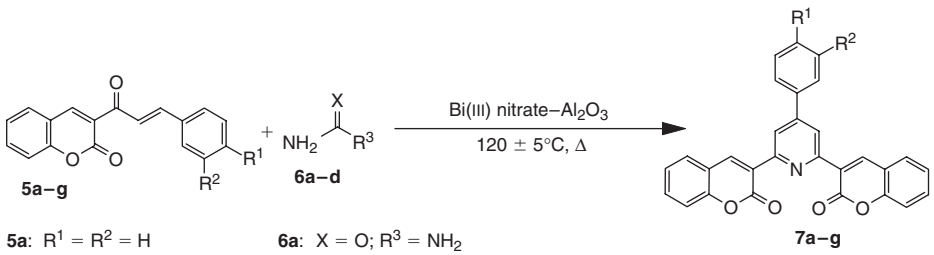


Fig. 1. Probable mechanism for the formation of 3-acetylcoumarin and coumarinylchalcones.



5a: $R^1 = R^2 = H$
5b: $R^1 = OCH_3$; $R^2 = H$
5c: $R^1 = Cl$; $R^2 = H$
5d: $R^1 = Br$; $R^2 = H$
5e: $R^1 = R^2 = Cl$
5f: $R^1 = R^2 = Br$
5g: $R^1 = R^2 = -OCH_2O-$

6a: X = O; $R^3 = NH_2$
6b: X = O; $R^3 = CH_3$
6c: X = O; $R^3 = C_6H_5$
6d: X = S; $R^3 = NH_2$

Scheme 3. 4-Aryl-2,6-dicoumarinylpyridines from coumarinylchalcones and urea derivatives.

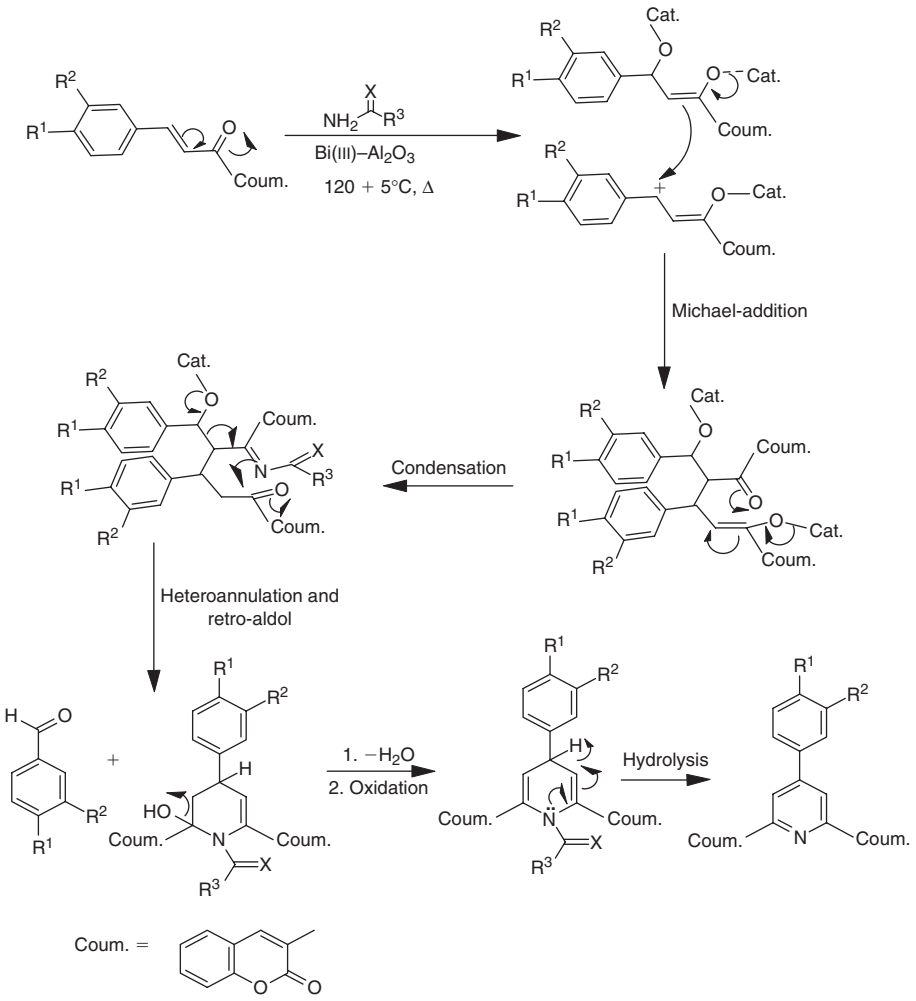


Fig. 2. Probable mechanism of the formation of 4-aryl-2,6-dicoumarinylpyridines.

*General Procedure for the Synthesis of Coumarinylchalcones **5a–g***

A mixture of 3-acetylcoumarin and appropriate benzaldehyde **4a–g** (1:1 mol ratio) were absorbed on Bi(III) nitrate–Al_2O_3–$ZnCl_2$, in proportion by weight of the substrates. The mixture was thoroughly mixed and charged into a stoppered flask. The flask was heated at $120 \pm 5°C$ in a thermostatically controlled hot-air oven. Separate experiments were run, simultaneously, to monitor the reaction by comparative TLC of the chloroform extracts of the aliquots, drawn out from reaction flask at 0.5-h intervals, using pet. ether/benzene (7:3; 1:1 v/v) graded solvent systems. The plates were developed first by exposure to iodine vapour followed by spraying with Ce^{IV} ions, when the products were observed as pink spots. On completion of the reaction (4–5 h), the products were extracted with chloroform in a Soxhlet extractor. The solvent was distilled off. The products were purified by column chromatography, using petroleum spirits (bp 40–60°C)/C_6H_6 graded solvent systems and finally by crystallization from chloroform/petroleum spirits.

*General Procedure for the Tandem Reactions for the Preparation of **5a–g***

A mixture of salicylaldehyde (1 mol) and ethylacetoacetate (1 mol) were adsorbed on the catalyst by weight of the substrates. The mixture was heated in a hot-air oven, under the same conditions as described above. To this mixture, the appropriate aromatic aldehyde (1 mol) was added and the mixture was again heated for 4–5 h. The resulting products were isolated by the same procedure as described above and were confirmed by mp and mixed mp with the products formed in the stepwise reaction.

*General Procedure for the Synthesis of **7a–g***

Coumarinylchalcones **5a–g** (2 mmol) and the substrate carrying the terminal amino group viz. urea **6a**, acetamide **6b**, benzamide **6c**, and thiourea **6d** (1 mmol) in 10 mL chloroform solution were adsorbed on the surface of the catalyst Bi(III) nitrate–Al_2O_3 in proportion by weight of the substrates. The solvent was evaporated in air and the air-dried mixture was charged in a stoppered flask. The flask was then heated at $120 \pm 5°C$ in a thermostatically controlled hot-air oven. The reaction was monitored by comparative TLC of the chloroform extracts of the aliquots drawn out at 0.5-h intervals from the reaction flask (petroleum spirits (bp 40–60°C)/C_6H_6 (19:1 and 3:7 v/v) were used as a graded solvent system for TLC). The plates were developed first by exposure to iodine vapour followed by spraying with Ce(IV) ions, when dark blue spots against a pale white background were observed. On completion of the reaction (5–6 h), the products were extracted with $CHCl_3$ in a Soxhlet extractor, freed from the solvent, and purified by column chromatography, by using the petroleum spirits (bp 40–60°C)/C_6H_6 graded solvent system

described above, and finally crystallized from $CHCl_3$/petroleum spirits (bp 40–60°C).

Spectroscopic Data for Compounds

4-Aryl-2,6-dicoumarinylpyridine ***7a***

Colourless crystals (0.620 g), mp 165°C. ν_{max} 3000, 1730, 1716, 1610, 1495, 1450, 1395, 1278, 1210, 1050, 999, 876 cm^{-1}. δ_H (200 MHz, $CDCl_3$) 6.80 (dd, *J* 8.02, 2.3, 4H, H5′, H7′, H5‴, H7‴), 7.12–7.26 (m, 5H, ArH), 7.46 (d, *J* 1.8, 2H, H3, H5), 7.56 (dd, *J* 8.0, 2.1, 2H, H6′, H6‴), 8.17 (dd, *J* 8.1, 2.3, 2H, H8′, H8‴), 8.88 (s, 2H, H4′, H4‴). δ_C ($CDCl_3$) 91.2 (C3′), 113.1 (C4a′), 114.5 (C3″, C5″), 115.3 (C4), 117.8 (C8a), 119.8 (C5), 122.4 (C4′), 122.5 (C5′), 122.8 (C1″), 125.0 (C6′), 130.7 (C2″, C6″), 132.5 (C7′), 136.8 (C4″), 153.1 (C8a′), 154.0 (C2, C6), 161.2 (C2′). *m/z* 443.1153 (calc. for $C_{29}H_{17}NO_4$: 443.1158) 415, 387, 295, 203, 155, 79.

4-(4-Methoxyphenyl)-2,6-dicoumarinylpyridine ***7b***

Colourless crystals (0.709 g), mp 180°C. ν_{max} 3020, 1730, 1716, 1606, 1550, 1495, 1420, 1359, 1157, 1028, 1010, 990, 870, 755 cm^{-1}. δ_H (200 MHz, $CDCl_3$) 3.80 (s, 3H, OCH_3), 6.89 (dd, *J* 8.0, 2.3, 4H, H5′, H7′, H5‴, H7‴), 6.95 (dd, *J* 8.1, 2H, H3″, H5″), 7.48 (s, *J* 2.3, 2H, H3, H5), 7.56 (dd, *J* 8.0, 2.1, 2H, H6′, H6‴), 7.69 (dd, *J* 8.1, 2.3, 2H, H2″, H6″), 8.19 (dd, *J* 8.1, 2.3, 2H, H8′, H8‴), 8.88 (s, 2H, H4′, H4‴). δ_C ($CDCl_3$) 55.10 (OCH_3), 91.80 (C3′), 113.1 (C4a′), 114.8 (C3″, C5″), 112.3 (C4), 117.8 (C8a′), 119.8 (C3, C5), 122.7 (C5′), 125.3 (C6′), 130.9 (C2″, C6″), 130.0 (C1″), 138.9 (C4′), 132.5 (C7′), 153.1 (C8a′), 154.0 (C2, C6), 161.3 (C2′). *m/z* 473.1260 (calc. for $C_{30}H_{19}NO_5$: 473.1264) 445, 417, 325, 233, 185, 79.

4-(4-Chlorophenyl)-2,6-dicoumarinylpyridine ***7c***

Colourless needles (0.648 g), mp 185°C. ν_{max} 3000, 1728, 1710, 1608, 1550, 1490, 1420, 1355, 1152, 1030, 1010, 980, 870, 755 cm^{-1}. δ_H (200 MHz, $CDCl_3$) 6.89 (dd, *J* 8.0, 2.3, 4H, H5′, H7′, H5‴, H7‴), 7.32 (s, 2H, H3, H5), 7.48 (dd, *J* 8.5, 3.2, 2H, H3″, H5″), 7.56 (dd, *J* 8.0, 2.3, 2H, H6′, H6‴), 7.73 (dd, *J* 8.1, 2.3, 2H, H2″, H6″), 8.12 (dd, *J* 8.5, 3.2, 2H, H8′, H8‴), 8.13 (s, 2H, H4′, H4‴). δ_C ($CDCl_3$) 91.8 (C3′), 113.1 (C4a′), 115.9 (C4), 116.8 (C4″), 117.8 (C8′), 119.8 (C5), 122.7 (C5′), 125.3 (C6′), 128.2 (C3″), 132.5 (C7′), 129.3 (C3), 133.9 (C2″, C6″), 139.4 (C1″), 152.8 (C6), 153.1 (C8a′), 154.0 (C2). *m/z* 477.0730 (calc. for $C_{29}H_{16}ClNO_4$: 477.0739, 479.0739), 449, 421, 329, 237, 189, 79.

4-(4-Bromophenyl)-2,6-dicoumarinylpyridine ***7d***

Colourless needles (0.677 g), mp 170°C. ν_{max} 2990, 1730, 1728, 1610, 1545, 490, 1387, 1359, 1227, 1072, 1018, 925, 720 cm^{-1}. δ_H ($CDCl_3$, 200 MHz) 7.19 (d, *J* 8.0, 2H, H3″, H5″), 7.30 (d, *J* 8.0, 2H, H5′, H5‴), 7.24 (s, 2H, H3, H5), 7.59 (d, *J* 8.0, 2H, H2″, H6″), 7.50 (dd, *J* 8.0, 3.2, 4H, H6′, H7′, H6‴, H7‴), 8.08 (dd, *J* 8.0, 3.2, 2H, H8′, H8‴), 8.88 (s, 2H, H4′, H4‴). δ_C ($CDCl_3$) 91.6 (C3′), 110.4 (C4″), 113.2 (C4), 113.5 (C4a′), 117.5 (C8′), 119.9 (C5), 122.9 (C5′), 125.6 (C6′), 126.3 (C3″, C5″), 129.8 (C3), 132.7 (C7′), 137.8 (C1″), 138.7 (C4′), 152.6 (C6), 153.1 (C8a′), 161.5 (C2′). *m/z* 521.0856 (calc. for $C_{29}H_{16}BrNO_4$: 521.0863, 523.0243), 494, 466, 374, 282, 234, 79.

4-(3,4-Dichlorophenyl)-2,6-dicoumarinylpyridine ***7e***

Colourless crystals (0.705 g), mp 175°C. ν_{max} 3050, 1735, 1710, 1605, 1545, 1490, 1382, 1350, 1148, 1090, 1018, 927, 730 cm^{-1}. δ_H ($CDCl_3$, 200 MHz) 7.19 (s, 1H, H6″), 7.26 (d, 1H, *J* 8.0, H3″), 7.32 (dd, *J* 8.0, 3.2, 2H, H5′, H5‴), 7.38 (s, 2H, H3, H5), 7.50 (dd, *J* 8.0, 3.2, 4H, H6′, H6‴, H7′, H7‴), 8.09 (dd, *J* 8.0, 3.2, 2H, H8′, H8‴), 8.18 (d, *J* 8.0, 1H, H2″), 8.78 (s, 2H, H4′, H4‴). δ_C ($CDCl_3$) 91.6 (C3′), 110.3 (C4″), 112.8 (C4), 113.4 (C4a′), 116.8 (C6″), 117.4 (C8′), 122.9 (C5′), 125.3 (C5″), 125.6 (C6′), 125.7 (C3″), 127.1 (C2″), 129.1 (C3), 132.5 (C7′), 136.5 (C1″), 152.6 (C6), 153.1 (C8a′), 154.2 (C2), 161.5 (C2′). *m/z* 511.0270 (calc. for $C_{29}H_{15}Cl_2NO_4$: 511.0320, 515.0320), 484, 456, 364, 272, 224, 79.

4-(3,4-Dibromophenyl)-2,6-dicoumarinylpyridine ***7f***

Colourless needles (0.850 g), mp 190°C. ν_{max} 3020, 1605, 1545, 1490, 1385, 1350, 1142, 1096, 920, 700 cm^{-1}. δ_H (200 MHz, $CDCl_3$) 7.19 (s, 1H, H6″), 7.20 (d, *J* 8.0, 1H, H3″), 7.33 (dd, *J* 8.0, 3.2, 2H, H5′, H5‴), 7.36 (s, 2H, H3, H5), 7.50 (dd, *J* 8.0, 3.2, 4H, H6′, H6‴, H7′, H7‴), 7.80 (d, *J* 8.0, 1H, H2″), 8.09 (dd, *J* 8.0, 3.2, 2H, H8′, H8‴), 8.80 (s, 2H, H4′, H4‴). δ_C ($CDCl_3$) 91.6 (C3′), 113.4 (C4a′), 116.7 (C4″), 117.4 (C8′), 117.8 (C4), 119.8 (C3″), 120.4 (C5), 122.9 (C5′), 125.6 (C6′), 126.7 (C5″), 129.1 (C3), 130.5 (C1″), 132.5 (C7′), 135.5 (C6″), 138.7 (C4′), 144.2 (C2″), 152.6 (C6), 153.1 (C8a′), 154.1 (C2), 161.1 (C2′). *m/z* 599.0564 (calc. for $C_{29}H_{15}Br_2NO_4$: 599.0569, 602.9329), 573, 545, 453, 361, 313, 79.

4-(3,4-Dioxymethylenephenyl)-2,6-dicoumarinylpyridine ***7g***

Colourless crystals (0.652 g), mp 195°C. ν_{max} 3056, 1730, 1710, 1610, 1549, 1450, 1385, 1350, 1260, 1096, 1050, 980, 926, 765 cm^{-1}. δ_H (200 MHz, $CDCl_3$) 6.01 (s, 2H, OCH_2O), 6.90 (s, 1H, H2″), 7.26 (d, *J* 8.5, 3H, H3, H5, H3″), 7.32 (dd, *J* 8.0, 3.2, 2H, H5′, H5‴), 7.50 (dd, *J* 8.0, 3.2, 4H, H6′, H6‴, H7′, H7‴), 7.53 (dd, *J* 8.5, 3.2, 1H, H6″), 8.09 (dd, *J* 8.0, 3.2, 2H, H8′, H8‴), 8.86 (s, 2H, H4′, H4‴). δ_C ($CDCl_3$) 91.6 (C3′), 101.0 (OCH_2O), 113.4 (C4a′), 114.5 (C4), 117.4 (C8′), 119.8 (C5), 122.7 (C5′), 124.1 (C5″), 125.3 (C2″), 125.6 (C6′), 129.1 (C6″), 132.5 (C7′), 133.1 (C8a′), 138.5 (C4′), 139.4 (C1″), 152.6 (C6), 154.2 (C2), 157.2 (C4″), 157.3 (C3″), 162.2 (C2). *m/z* 487.1043 (calc. for $C_{30}H_{17}NO_6$: 487.1050) 459, 431, 339, 247, 199, 79.

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