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A Scalable Total Syntheses of some Natural and Unnatural Lamellarins: Application of a One-Pot Domino process for Regioselective Access to the Central 1,2,4-Trisubstituted Pyrrole Core

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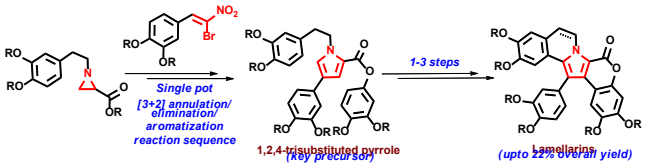


Abstract: A short and scalable total syntheses of lamellarin G trimethyl ether, lamellarin D trimethyl ether, lamellarin H, lamellarin η, dihydrolamellarin η and lamellarin U has been realized in 4-6 linear steps with an overall yield upto 22%. Highlights of the synthesis includes a single step access to the central 1,2,4-trisubstituted pyrrole core in a highly regioselective manner via a one-pot [3+2] cycloaddition/elimination/aromatization sequence based domino process. Subsequent, palladium mediated double C-H oxidative coupling in a single pot operation provides access to the pentacyclic coumarin fused pyrrolo-dihydroisoquinoline core present in lamellarins.

Introduction

Pyrroles are among the most prevalent *N*-heterocycles which manifests in numerous molecules of natural origin[1] and human imagination for diverse applications ranging from pharmaceutics[2] to material science.[3] As far as natural products are concerned a significant number of biologically interesting and structurally fascinating pyrrole containing alkaloids has been produced by marine organisms.[1c] One such family of pyrrole alkaloids first isolated from marine prosobranch mollusk *Lamellaria sp.* by Faulkner and co-workers in 1985 is the huge lamellarins family.[4] With more than 50 siblings of the family reported till date, they have been classified into Type I, II and III.[1c]

Typically, the Type I and II lamellarins as depicted in **Figure 1** display a pentacyclic coumarin fused pyrrolo-dihydroisoquinoline/pyrrolo-isoquinoline ring system respectively. On the other hand, the Type III lamellarins are relatively simple non-fused, 3,4-diarylated-pyrrole-2-carboxylates. Differing with respect to the substitution pattern on the arylated central pyrrole core, lamellarins are believed to biogenetically derived from L-DOPA which perhaps is also considered responsible for the genesis of other closely related marine alkaloids such as ningalins A-D,[5a] lukianols A and B,[5b] rigidin A-E,[5c] polycitrins A and B,[5d] polycitone A & B,[5d,e] storniamides A-D[5f] among few others, reported over the past three decades.[1c]

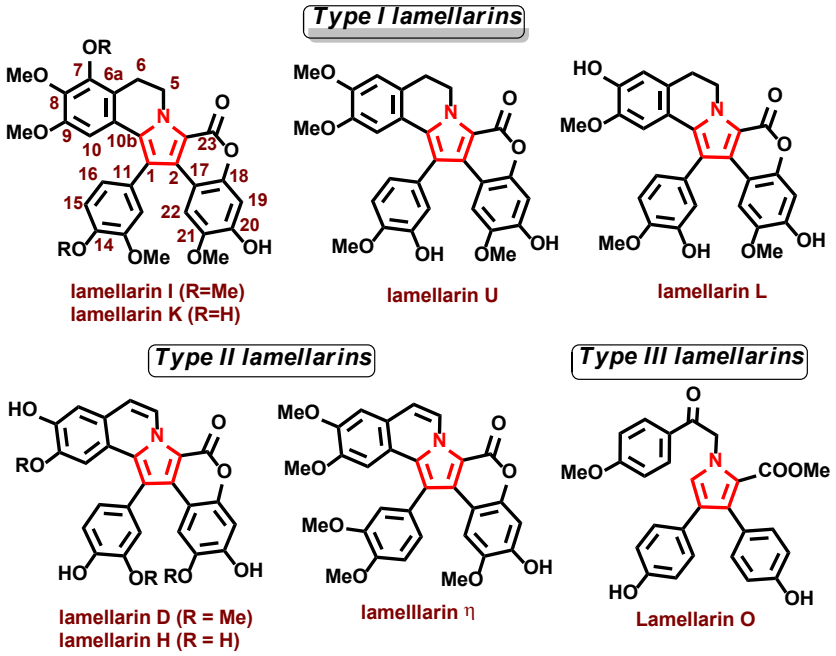


Figure 1. Representative members belonging to the bioactive lamellarin alkaloid family.

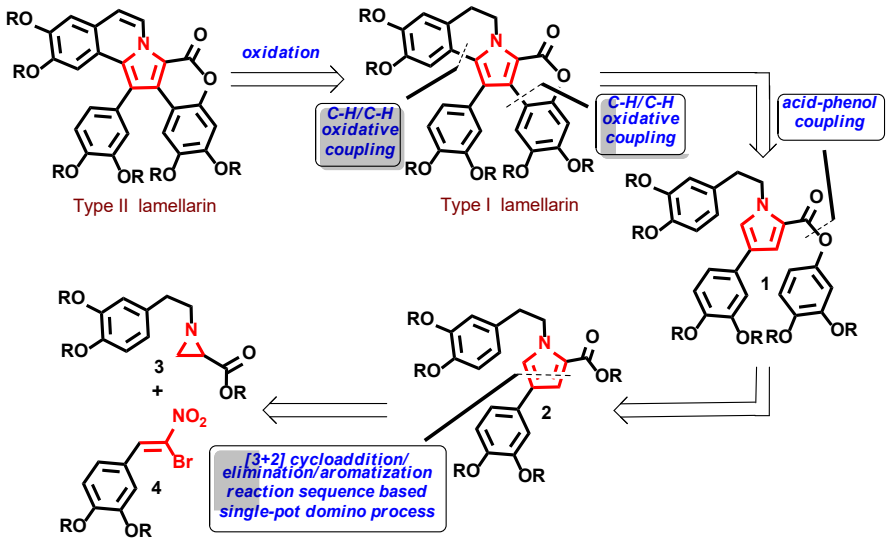
The marine pyrrole alkaloids (MPAs) captured in **Figure 1** besides structurally fascinating also exhibits interesting bioactivity profile including antitumor activity, multi-drug resistant (MDR) reversal activity in cancer cells, HIV integrase inhibitor activity, antibacterial and antioxidant activity among others.[1c,6] In view of their aforementioned remarkable structural & biological attributes these MPAs have been hot targets for total and diversity-oriented synthesis in the eyes of synthetic and medicinal chemists over the past two decades. A vast repertoire of synthetic endeavors towards the lamellarins family has been documented in the

literature leading to systematic reviews by Iwao,[6b] Opatz[7a] and Alvarez[7b] of the notable synthetic and SAR developments in the arena.

Despite the existence of several total synthesis endeavors involving traditional[6b,7,8] as well as recently developed methods[9] for accessing the multisubstituted central pyrrole core and subsequently the pentacyclic lamellarins scaffold we realized that there still subsists considerable scope for the development of new synthetic approaches. In particular, approaches which are general, amenable for diversity creation as well as simple in terms of operational procedure involving cheap and readily accessible bench-top stable starting materials in addition to the exclusion of expensive reagents and transition-metal catalyst are compelling. Therefore, in view of our on-going interest towards the development of metal/acid/base free synthetic methods for regioselective access to pyrroles[10] and other N-heterocycle based scaffolds[11] as well as keeping in mind the few lacunes in the existing synthetic strategies we were motivated to fabricate a simple and concise route for the total synthesis of some natural and unnatural type I & type II lamellarins. Gratifyingly, our efforts in this direction has culminated in the development of one of the rare approaches[9a-c,f] which comprises of single step reaction to access the central 1,2,4-trisubstituted pyrrole core in a highly regioselective manner unlike many others which uses multiple steps.[9d,e, 12] Also, subsequent elaboration to the pentacyclic coumarin fused pyrrolo-dihydroisoquinoline core present in lamellarins is accomplished in a single-pot operation.

Results and discussion

The contours of the general retrosynthetic plan which we envisioned for quick access to some of the type I & type II lamellarin alkaloids is as captured in **Scheme 1**. Since, a simple oxidation of the isoquinoline core in type I lamellarin was expected to deliver the type II lamellarin core, our initial focus was to gain access to the pentacyclic type I lamellarin core. In order to accomplish this task, an iterative oxidative C-H coupling of pyrrole with that of peripheral phenyl rings in

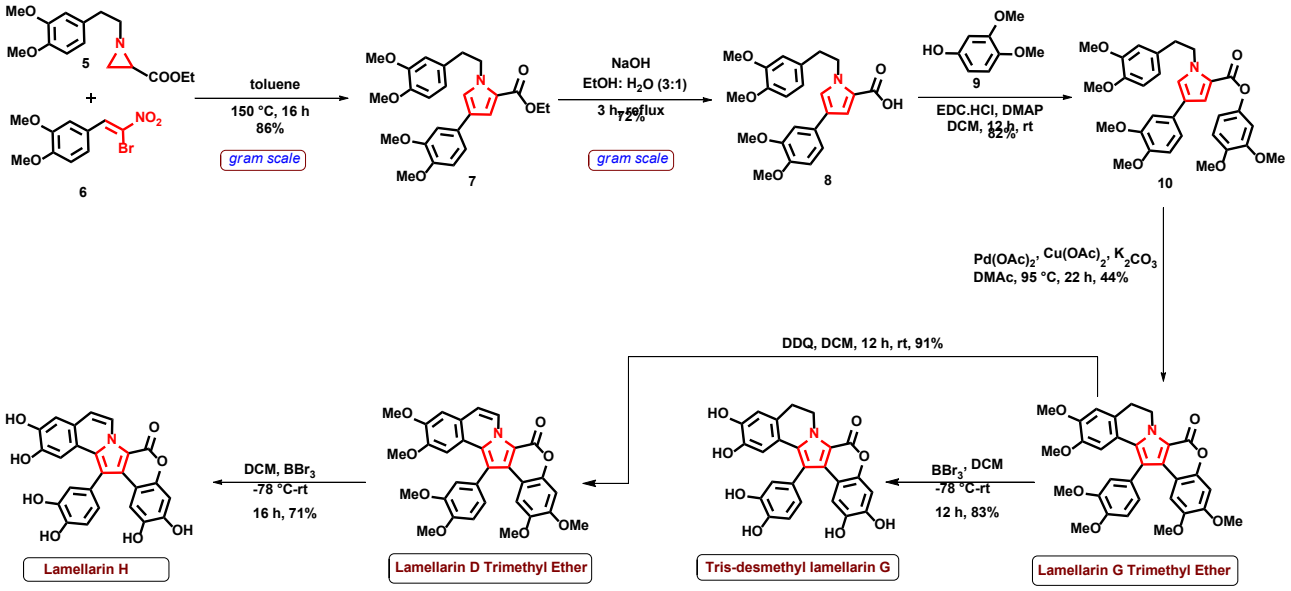


Scheme 1. A general retrosynthetic plan towards some natural and unnatural lamellarins.

pyrrole-2-carboxylate **1** was chosen as the preferred reaction. The key intermediate **1** was synthetically planned to be derived from 1,4-disubstituted pyrrole-2-carboxylate (**2**). While the acquisition of **2** was conceptualized from readily accessible starting materials like *N*-substituted aziridine ester **3** and *β*-bromo-*β*-nitrostyrene **4**, through the one-pot domino process for regioselective access to 1,2,4-trisubstituted pyrrole developed in our laboratory.[10]

Therefore towards the realization of the retrosynthetic plan, we commenced our synthetic journey as captured in **Scheme 2** with the annulation of aziridine ester **5**[10] with *β*-bromo- *β*-nitrostyrene **6**[10] under our optimized condition to access the 1,2,4-trisubstituted pyrrole ester **7** which was then easily elaborated to **10** via EDC· HCl mediated coupling of pyrrole-2-carboxylic acid **8** with phenol **9**.[13] Having **10** in hand, the next key task was to establish two C-C bonds in a consecutive manner between the central pyrrole core and the appended phenyl rings in the ester functionality as well as the phenyl ring of phenethyl substitution at the pyrrole-N-atom. After scouting several conditions for the desired task we opted for Greaney *et al.* reported strategy based on catalytic Pd-mediated C-H oxidative coupling of arenes in presence of $Cu(OAc)_2$.[14] However, in view of exploration of same strategy by Itami group in context of lamellarins synthesis,[15] we straightaway exposed **10** to their optimized condition to arrive at lamellarin G

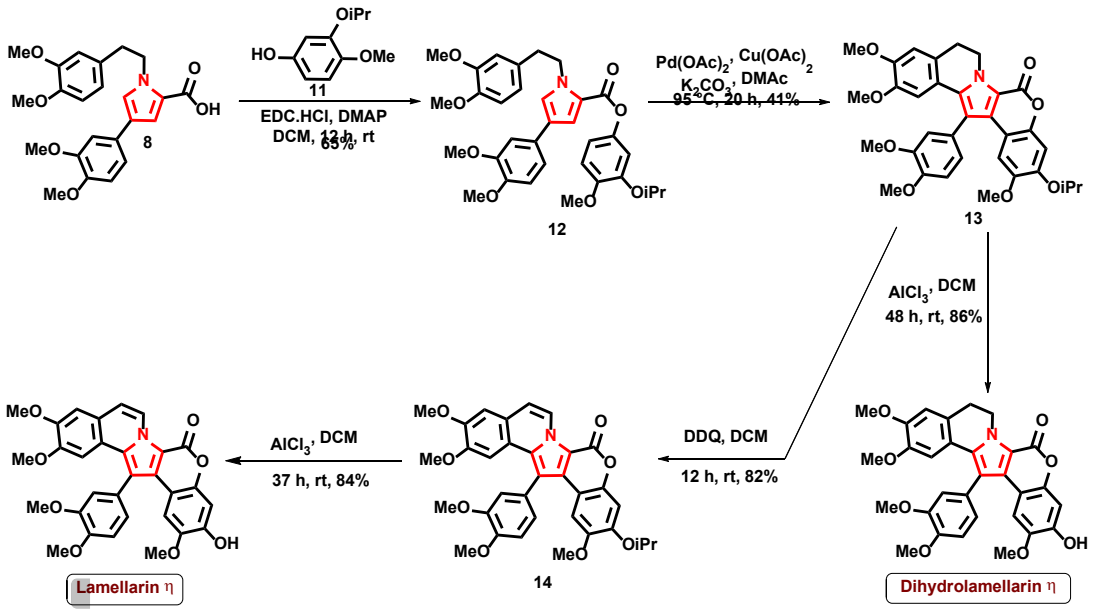
trimethyl ether in 44% yield. Then, subjection of lamellarin G trimethyl ether to dehydrogenation using DDQ readily introduced the C_5, C_6 double bond to offer lamellarin D trimethyl ether in excellent yield. While, exposure of both lamellarin G and lamellarin D trimethyl ethers to global methyl ether deprotection of the peripheral phenyl rings using BBr_3 smoothly furnished tris-desmethyl lamellarin G and lamellarin H respectively. While, tris-desmethyl lamellarin G has not been reported before, the NMR spectral data of the presently synthesized trimethyl ethers of lamellarin G & D as well as lamellarin H were in good agreement with those reported in the literature.[12e, 16]



Scheme 2. Total synthesis of several natural and unnatural lamellarins.

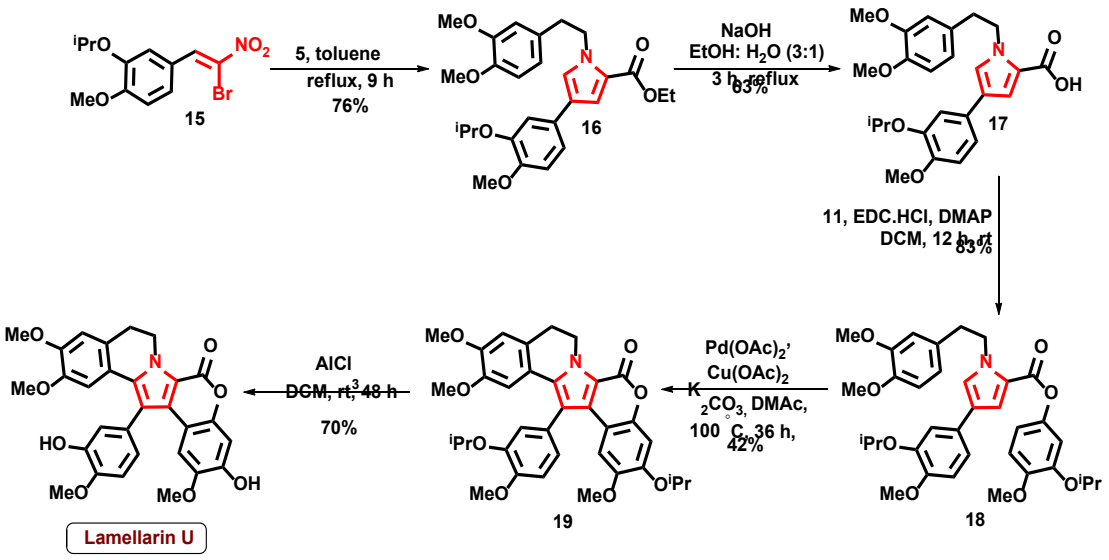
Similarly, the synthesis of lamellarin η and dihydrolamellarin η was realized as depicted in **Scheme 3**. Pyrrole-2-carboxylic acid, **8** was coupled with **11**[12b] using EDC· HCl to arrive at **12** which on exposure to Pd-mediated C-H oxidative coupling condition[14, 15] delivered the pentacyclic intermediate **13**. Then, it was just a matter of selective stripping of the isopropyl group from the fused coumarin domain of **13** to access dihydrolamellarin η. And for this purpose $AlCl_3$ proved to be a better option among other investigated conditions, offering dihydrolamellarin η in reasonably good yield. On the other hand, first oxidation of the pentacyclic intermediate **13** using DDQ to arrive at **14** and then followed by $AlCl_3$ mediated

selective isopropyl group deprotection from the fused coumarin domain of **14** readily furnished lamellarin η. Also, the NMR spectral data of the presently synthesized dihydrolamellarin η and lamellarin η were found to be in good agreement with the reported data.[17]



Scheme 3. Total synthesis of dihydrolamellarin η and lamellarin η.

Next attention was turned towards the synthesis of lamellarin U and as highlighted in **Scheme 4**, a similar reaction sequence as employed for the other lamellarins described above was adopted. Applying our reported condition[10] for the annulation of azirdine-2-carboxylate **5** with *β*-bromo-*β*-nitrostyrene **15** smoothly furnished the 1,4-disubstituted pyrrole-2-carboxylate **16** in good yield. Saponification on **16** followed by coupling of the resultant acid **17** with phenol **11**[12b] delivered the key intermediate **18** for executing the Pd-mediated C-H/C-H oxidative coupling[14, 15] of arenes to access the pentacyclic isoquinoline-coumarin fused pyrrole **19** in decent yield. Towards the end game the isopropyl phenyl ethers were deprotected using $AlCl_3$ to expose the phenolic –OH groups and access the natural product lamellarin U. To our delight, the NMR spectral data of the synthetic lamellarin U was found to be in close agreement with the one reported in the literature.[18]



Scheme 4. Total synthesis of lamellarin U.

Conclusion

In summary, we have demonstrated a concise and general route for the total syntheses of several natural and unnatural lamellarins in 4-6 steps starting from very cheap and readily accessible starting materials. The synthetic route comprises of two key single-pot transformations which provides rapid acquisition of the pentacyclic coumarin fused pyrrolo-dihydroisoquinoline core present in the lamellarin alkaloids. Lamellarin G trimethyl ether, lamellarin D trimethyl ether and lamellarin H have been accessed with an overall yield of 22% (4 steps), 20% (5 steps) and 14% (6 steps) respectively. While, dihydrolamellarin η, lamellarin η and lamellarin U has been synthesized with an overall yield of 14% (5 steps), 11% (6 steps) and ~12% (5 steps). In view of the relatively simple operational procedure of the steps involved it is a very much scalable synthetic approach. A further exploration of the present synthetic strategy towards the synthesis of other pyrrole alkaloids is under investigation and shall be communicated in due course of time.

Experimental Section

General Method: All the reagents were purchased from commercial suppliers and used without further purification. While most of the desired solvents supplied by commercial suppliers were

dried using the standard drying procedures.[19] All the moisture and air sensitive reactions were performed under a flow of nitrogen or argon atmosphere using flame-dried or oven-dried glassware with magnetic stirring. All purifications were done using column chromatography with 100-200 mesh size SiO_2-gel as the stationary phase. Distilled EtOAc and petroleum ether were typically used for column chromatography. The ^1H & $^{13}C\{^1H\}$ NMR spectra were recorded on 400 MHz Bruker spectrometer using $CDCl_3$ (H: δ = 7.26 and C: δ = 77.0 ppm) or TMS (δ = 0.0) residual solvent peaks as internal standard and DMSO-d_6 ((H: δ = 2.50 and C: δ = 39.52±0.06 ppm). The following abbreviations are used for spin multiplicity: s = singlet, d = doublet, t = triplet, q = quartet, p = quintet/pentet, sept. = septet, dd = doublet of doublet, ddd= doublet of doublet of doublet, td = triplet of doublet, dq = doublet of quartet and m = multiplet. The chemical shifts are reported as δ values (ppm) and the coupling constants (*J*) values are reported in Hz. High Resolution Mass Spectra (HRMS) were obtained using electron spray ionization (ESI) technique and TOF mass analyser. IR spectra were recorded on a Bruker FT/IR-460 Plus spectrometer. Melting points were determined on a Buchi M-560 apparatus and are uncorrected. Progress of the reactions were monitored using precoated SiO_2-gel GF254 TLC plates while spot visualizations were done under UV light and using spot developing stains like *p*-anisaldehyde, ceric ammonium molybdate, ninhydrin or $KMnO_4$.

Gram Scale Synthesis of Ethyl 1-(3,4-dimethoxyphenethyl)-4-(3,4-dimethoxyphenyl)-1H-pyrrole-2-carboxylate (7):- As per our optimized procedure,[10] using **5** [ethyl 1-(3,4-dimethoxyphenethyl)aziridine-2-carboxylate] (1.6 g, 5.7 mmol, 1 equiv.) and **6** [(*Z*)-4-(2-bromo-2-nitrovinyl)-1,2-dimethoxybenzene][10] (1.3 g, 5.7 mmol, 1 equiv.) with a reaction time of 16 h, **7** was was obtained after flash column chromatography as pale yellow oil (2.16 g, 86% yield); R_f = 0.7 (20% EtOAc + pet. ether). **IR** (neat): ν_{max} 2935, 2835, 1697, 1589, 1564, 1515, 1465, 1419, 1250, 1195, 1092, 1027, 801, 762 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.19 (d, J = 2 Hz, 1H), 6.97 (dd, J_1 = 2 Hz, J_2 = 8.6 Hz, 1H), 6.93 (d, J = 2.0 Hz, 1H), 6.85 (d, J = 8.4 Hz, 1H),

6.81 (d, J = 2 Hz, 1H), 6.79 (d, J = 8 Hz, 1H), 6.71 (dd, J_1 = 1.6 Hz, J_2 = 8 Hz, 1H), 6.55 (d, J = 3.2 Hz, 1H), 4.52 (t, J = 7.2 Hz, 2H), 4.34 (q, J = 7.2 Hz, 2H), 3.92 (s, 3H), 3.89 (s, 3H), 3.85 (s, 3H), 3.78 (s, 3H), 3.02 (t, J = 7.2 Hz, 2H), 1.40 (t, J =7.2 Hz, 3H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 161.1, 149.1, 148.8, 147.7, 147.6, 131.0, 127.7, 125.4, 123.8, 122.2, 120.9, 117.4, 115.1, 112.1, 111.6, 111.2, 108.7, 59.99, 55.97, 55.87, 55.86, 55.75, 51.2, 37.8, 14.5. **HRMS** (ES) m/z calcd for $C_{25}H_{30}NO_6$ $(M+H)^+$: 440.2068; found: 440.2088.

1-(3,4-dimethoxyphenethyl)-4-(3,4-dimethoxyphenyl)-1H-pyrrole-2-carboxylic acid (8):- To a solution of **7** (1.5 g, 3.42 mmol, 1 equiv.) in ethanol : water (3:1, 40 mL), crushed NaOH pellets (0.68 g, 17 mmol, 5 equiv.) was added at rt and the reaction was then allowed to reflux for 3 h, until completion of the saponification process was indicated by TLC analysis. The reaction was worked up by removing the volatiles under reduced pressure and then neutralization of the resultant residue by 1N HCl. The aqueous phase was subjected to extraction with EtOAc (4 × 30 mL). Drying of the organic phase over Na_2SO_4 and then removal of solvent under reduced pressure gave a crude residue which was subjected to SiO_2-gel column chromatography to access pure acid **8** as a yellow solid (1.01 g, 72% yield); R_f = 0.4 (50% EtOAc + pet. ether); m.p. 164-166 °C. **IR** (neat): ν_{max} 2935, 1666, 1565, 1515, 1463, 1254, 1140, 1094, 1026, 802, 763 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34 (d, J = 2 Hz, 1H), 6.97 (dd, J_1 = 2 Hz, J_2 = 8.4 Hz, 1H), 6.92 (d, J = 2 Hz, 1H), 6.87 (d, J = 2 Hz, 1H), 6.86 (d, J = 8.4 Hz, 1H 2H), 6.80 (d, J = 8.4 Hz, 1H), 6.70 (dd, J_1 = 2 Hz, J_2 = 7.8 Hz, 1H), 6.58 (d, J = 2 Hz, 1H), 4.52 (t, J = 7.2 Hz, 2H), 3.92 (s, 3H), 3.89 (s, 3H), 3.85 (s, 3H), 3.80 (s, 3H), 3.05 (t, J = 7.2 Hz, 2H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 165.7, 149.2, 148.9, 147.8, 147.7, 130.8, 127.3, 126.9, 124.4, 120.9, 120.8, 117.5, 117.3, 112.1, 111.6, 111.3, 108.8, 56.0, 55.91, 55.88, 55.7, 51.6, 37.8. **HRMS** (ES) m/z calcd for $C_{23}H_{26}NO_6$ $(M+H)^+$: 412.1755; found: 412.1773.

3,4-dimethoxyphenyl 1-(3,4-dimethoxyphenethyl) 4-(3,4-dimethoxyphenyl)-1H-pyrrole-2-carboxylate (10):- In an dry 25 mL round bottom flask under nitrogen atmosphere, **8** (0.617 g, 1.5 mmol, 1 equiv.) and **9** [3,4-dimethoxyphenol] (0.23 g, 1.5 mmol, 1 equiv.) were taken and dichloromethane (10 mL) was added. Then, EDC.HCl (0.306 g, 1.7 mmol, 1.1 equiv.) and DMAP (0.21 g, 1.7 mmol, 1.1 equiv.) were added sequentially at rt and the reaction was allowed to stir at rt for 12 h until complete consumption of starting materials was indicated by TLC analysis. The reaction was worked up by removing the solvent under reduced pressure and subjection of the resultant residue to SiO_2-gel flash column chromatography to access **10** as a pale yellow oil (0.673 g, 82% yield); R_f = 0.3 (30% EtOAc + pet. ether). **IR** (neat): ν_{max} 3059, 2999, 2936, 2835, 1715, 1604, 1589, 1563, 1514, 1465, 1419, 1231, 1189, 1154, 1050, 1027, 764, 734 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 (d, J = 2 Hz, 1H), 7.02 (dd, J_1 = 2 Hz, J_2 = 8 Hz, 1H), 6.98 (d, J = 2.0 Hz, 1H), 6.95 (d, J = 2 Hz, 1H), 6.93-6.87 (m, 2H), 6.80-6.77 (m, 3H), 6.71 (dd, J_1 = 2.0 Hz, J_2 = 8 Hz, 1H), 6.57 (d, J = 2.0 Hz, 1H), 4.56 (t, J = 7.2 Hz, 2H), 3.94 (s, 3H), 3.91 (s, 6H), 3.90 (s, 3H), 3.86 (s, 3H), 3.78 (s, 3H), 3.06 (t, J = 7.2 Hz, 2H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 159.7, 149.5, 149.3, 148.8, 147.84, 147.77, 146.9, 144.2, 130.8, 127.4, 126.5, 124.4, 121.2, 121.0, 117.5, 116.4, 113.3, 112.2, 111.7, 111.3 (2C), 108.8, 106.1, 56.2, 56.0, 55.99, 55.90 (2C), 55.8, 51.3, 37.8. **HRMS** (ES) m/z calcd for $C_{31}H_{34}NO_8$ $(M+H)^+$: 548.2279; found: 548.2309.

Lamellarin G trimethyl ether: Using the earlier reported procedure,[17] an oven dried schlenk tube was charged with **18** (0.54 g, 1 mmol, 1 equiv.), $Pd(OAc)_2$ (0.45 g, 2 mmol, 2 equiv.) and $Cu(OAc)_2$ (1.09 g, 6 mmol, 6 equiv.) under N_2 atmosphere. Then, dimethylacetamide (3 mL) followed by K_2CO_3 (0.28 g, 2 mmol, 2 equiv.) was added maintaining the inert atmosphere and the reaction was allowed to stir at 95 °C for 22 h. Upon reaction completion indication by TLC analysis, the reaction was filtered through celite and the celite bed was washed with EtOAc (4 ×

15 mL). The filtrate were combined and subjected to solvent removal under reduced pressure to arrive at a crude residue which was purified by SiO_2-gel flash column chromatography to access lamellarin G trimethyl ether as a white solid (0.24 g, 44% yield); R_f = 0.5 (50% EtOAc + pet. ether); m.p. 234-236 °C. Also, the spectroscopic data of our synthesized lamellarin G trimethyl ether compares favourably with the previously reported data.[16a] **IR** (neat): ν_{max} 1702, 1513, 1485, 1462, 1414, 1338, 1269, 1240, 1214, 1165, 1040 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.11 (dd, J_1 = 2.0 Hz, J_2 = 8 Hz, 1H), 7.07 (d, J = 8 Hz, 1H), 7.04 (d, J = 2 Hz, 1H), 6.90 (s,1H), 6.76 (s, 1H), 6.71 (s, 1H), 6.66 (s, 1H), 4.86-4.73 (m, 2H), 3.95 (s, 3H), 3.89 (s, 3H), 3.88 (s, 3H), 3.86 (s, 3H), 3.45 (s, 3H), 3.36 (s, 3H), 3.12 (t, J = 7.2 Hz, 2H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 155.6, 149.7, 149.0, 148.84, 148.81, 147.5, 146.1, 145.5, 136.0, 128.2, 128.0, 126.6, 123.6, 120.0, 114.8, 114.0, 113.8, 111.8, 111.0, 110.3, 108.6, 104.5, 100.5, 56.24, 56.16, 56.1, 55.94, 55.5, 55.2, 42.4, 28.7. **HRMS** (ES) m/z calcd for $C_{31}H_{30}NO_8$ $(M+H)^+$: 544.1966; found: 544.1994.

Lamellarin D trimethyl ether: To a solution of lamellarin G trimethyl ether (120 mg, 0.22 mmol, 1 equiv.) in DCM (5 mL), DDQ (125 mg, 0.55 mmol, 2.5 equiv.) was added at rt. The reaction was then allowed to stir at room temperature for 12 h until complete consumption of starting material was indicated by TLC analysis. Subjection of the crude reaction mixture to SiO_2-gel flash column chromatography afforded lamellarin D trimethyl ether as white solid (108 mg, 91% yield); R_f = 0.5 (50% EtOAc + pet. ether); m.p. 278-280 °C. Also, the spectroscopic data of our synthesized lamellarin D trimethyl ether compares favourably with the previously reported data.[16b] **IR** (neat): ν_{max} 2924, 2853, 1699, 1512, 1491, 1463, 1429, 1416, 1225, 1167, 1088, 1045, 1010, 970, 941 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.26 (d, J = 7.6 Hz, 1H), 7.25 (dd, J_1 = 1.6 Hz, J_2 = 8 Hz, 1H), 7.19-717 (m, 3H), 7.12 (s, 1H), 7.08 (d, J = 7.6 Hz, 1H), 6.97 (s,1H), 6.76 (s, 1H), 4.02 (s, 3H), 4.01 (s, 3H), 3.92 (s, 3H), 3.90 (s, 3H), 3.49 (s, 3H), 3.48 (s,

3H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 155.5, 150.2, 149.9, 149.6, 149.2, 149.1, 146.8, 145.6, 134.5, 129.5, 128.2, 124.9, 124.1, 123.4, 119.1, 114.4, 112.4, 112.0, 111.0, 109.9, 107.9, 107.4, 105.3, 105.1, 100.6, 56.3, 56.2, 56.1, 56.0, 55.5, 55.2. **HRMS** (ES) m/z calcd for $C_{31}H_{28}NO_8$ $(M+H)^+$: 542.1809; found: 542.1833.

Lamellarin H: To a cold solution of lamellarin D trimethyl ether (54 mg, 0.1 mmol, 1 equiv.) in DCM (5 ml) at -78 °C, BBr_3 (1M solution in DCM, 2 mL, 2 mmol, 20 equiv.) was added dropwise over 10 min. and after stirring at the same temperature for almost 20 min., the reaction was allowed to warm to rt and stirred for another 12 h until formation of a prominent new spot was indicated by TLC analysis. The reaction was worked up by quenching it with MeOH (5 mL) followed by removal of the volatiles under reduced pressure. To the resultant residue H_2O (3mL) was added and extracted with EtOAc (3 × 15 mL). Drying of the organic phase over Na_2SO_4 and then removal of solvent under reduced pressure gave a crude residue which was subjected to SiO_2-gel flash column to access lamellarin H as a white solid (32.5 mg, 71% yield); R_f = 0.3 (80% EtOAc + pet. ether); m.p. >300 °C. Also, the spectroscopic data of our synthetic lamellarin H compares favourably with the previously reported data.[12e] **IR** (neat): ν_{max} 1676, 1558, 1472, 1417, 1260, 1191, 1155, 1080, 1033, 955, 849, 752 cm^{-1}; **^{1}H NMR** (400 MHz, DMSO-d_6) δ 10.00 (s,1H), 9.77 (s, 1H), 9.43 (s, 1H), 9.22 (s, 1H), 9.21 (s, 1H), 8.99 (d, J = 7.6 Hz, 1H), 8.92 (s, 1H), 7.15 (d, J = 8 Hz, 1H), 7.14 (s, 1H), 6.99 (d, J = 8 Hz, 1H), 6.96 (s, 1H), 6.83 (s, 1H), 6.79 (d, J = 2 Hz, 1H), 6.71 (dd, J_1 = 2.0 Hz, J_2 = 8 Hz, 1H), 6.57 (s, 1H); **^{13}C{^{1}H} NMR** (100 MHz, DMSO-d_6) δ 155.0, 148.1, 147.3, 147.0, 146.7, 146.0, 145.7, 142.6, 134.4, 129.3, 125.9, 124.2, 121.9, 121.6, 118.6, 118.0, 117.5, 113.0, 111.9 (2C), 110.1, 110.0, 109.2, 106.8, 103.8. **HRMS** (ES) m/z calcd for $C_{25}H_{16}NO_8$ $(M+H)^+$: 458.0870; found: 458.0889.

Tris-desmethyl Lamellarin G:- :- Applying the above described procedure for global phenyl methyl ether deprotection on lamellarin G trimethyl ether (30 mg, 0.055 mmol), tris-desmethyl lamellarin G was obtained as white solid (22 mg, 83% yield); R_f = 0.8 (EtOAc); m.p. >300 °C. **IR** (neat): ν_{max} 1643, 1477, 1427, 1391, 1345, 1281, 1233, 1156, 1031, 865, 473, 449, 438 cm^{-1}; **^{1}H NMR** (400 MHz, DMSO-d_6) δ 9.55 (s, 1H), 9.37 (s, 1H), 9.10 (s, 2H), 8.82 (s, 1H), 8.63 (s, 1H), 6.87 (d, J = 8 Hz, 2H), 6.72 (s, 1H), 6.67 (d, J = 2 Hz, 1H), 6.66 (s, 1H), 6.59 (dd, J_1 = 1.6 Hz, J_2 = 8 Hz, 1H), 6.50 (s, 1H), 6.44 (s, 1H), 4.63-4.47 (m, 2H), 2.92 (t, J = 6.4 Hz, 2H); **^{13}C{^{1}H} NMR** (100 MHz, DMSO-d_6) δ 154.9, 146.5, 146.4, 146.3, 145.6, 145.1, 144.0, 142.4, 136.4, 127.9, 126.2, 125.8, 121.7, 118.9, 117.9, 117.2, 115.5, 115.1, 113.8, 112.6, 109.7, 109.3, 103.6, 42.4, 28.3. **HRMS** (ES) m/z calcd for $C_{25}H_{18}NO_8$ $(M+H)^+$: 460.1027; found: 460.1044.

3-isopropoxy-4-methoxyphenyl-1-(3,4-dimethoxy phenethyl)-4-(3,4-dimethoxyphenyl)-1H-pyrrole-2-carboxylate (12): Following similar procedure as described for synthesis of **10,** using **8** (411 mg, 1 mmol, 1 equiv.) and 3-isopropoxy-4-methoxyphenol, **11** (182 mg, 1 mmol, 1 equiv.), **12** was obtained as pale yellow oil (373 mg, 65% yield); R_f = 0.5 (30% EtOAc + pet. ether). **IR** (neat): ν_{max} 2974, 2934, 2853, 1714, 1605, 1515, 1466, 1260, 1186, 1156, 1069, 1049, 1028, 801, 763, 734 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40 (d, J = 2 Hz, 1H), 7.00 (dd, J_1 = 2 Hz, J_2 = 8.2 Hz, 1H), 6.96 (d, J = 2 Hz, 1H), 6.93 (d, J = 2 Hz, 1H), 6.89 (d, J = 8.4 Hz, 1H), 6.85 (d, J = 8 Hz, 1H), 6.78-6.74 (m, 3H), 6.89 (dd, J_1 = 1.6 Hz, J_2 = 8.4 Hz, 1H), 6.55 (d, J = 1.6 Hz, 1H), 4.57-4.51 (m, 3H), 3.92 (s, 3H), 3.88 (s, 3H), 3.85 (s, 3H), 3.83 (s, 3H), 3.76 (s, 3H), 3.03 (t, J = 7.2 Hz, 2H), 1.39 (d, J = 6.4 Hz, 6H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 159.6, 149.2, 148.8, 148.1, 147.8 (2C), 147.7, 144.1, 130.8, 127.4, 126.5, 124.3, 121.2, 121.0, 117.4, 116.4, 113.6, 112.2, 112.0, 111.6, 111.2, 109.7, 108.8, 71.5, 56.4, 56.0, 55.9 (2C), 55.8, 51.3, 37.8, 22.0 (2C). **HRMS** (ES) m/z calcd for $C_{33}H_{38}NO_8$ $(M+H)^+$: 576.2592; found: 576.2618.

14-(3,4-dimethoxyphenyl)-3-isopropoxy-2,11,12-trimethoxy-8,9-dihydro-6H-chromeno[4',3':4,5] pyrrolo[2,1-a]isoquinolin-6-one (13): Applying similar procedure for the oxidative coupling as described for lamellarin G trimethyl ether, on **12** (287.5 mg, 0.5 mmol), **13** was obtained as white solid (118 mg, 41% yield); R_f = 0.4 (50% EtOAc + pet. ether); m.p. 207-210 °C. **IR** (neat): ν_{max} 2924, 1645, 1515, 1414, 1261, 1239, 1214, 1164, 1112, 1037, 492, 472, 461 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.18 (d, J = 8.4 Hz, 1H), 7.08 (d, J = 2.0 Hz, 1H), 7.05 (s,1H), 7.04 (dd, J_1 = 2 Hz, J_2 = 8 Hz, 1H), 6.98 (s, 1H), 6.65 (s, 1H), 6.57 (s, 1H), 4.71-4.57 (m, 3H), 3.81 (s, 3H), 3.76 (s, 3H), 3.71 (s, 3H), 3.30 (s, 3H), 3.22 (s, 3H), 3.12 (t, J = 7.2 Hz, 2H), 1.24 (d, J = 6 Hz, 3H), 1.23 (d, J = 6 Hz, 3H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 155.6, 149.6, 148.9, 148.7, 147.4, 147.0, 146.5, 145.9, 135.8, 128.2, 128.0, 126.6, 123.5, 120.0, 114.7, 113.9, 113.7, 111.8, 110.9, 110.3, 108.6, 104.8, 103.4, 71.4, 56.2, 56.1, 55.9, 55.5, 55.1, 42.3, 28.6, 21.8 (2C). **HRMS** (ES) m/z calcd for $C_{33}H_{34}NO_8$ $(M+H)^+$: 572.2279; found: 572.2292.

14-(3,4-dimethoxyphenyl)-3-isopropoxy-2,11,12-trimethoxy-6H-chromeno[4',3':4,5]pyrrolo[2,1-a]isoquinolin-6-one (14): To a solution of **13** (57.5 mg, 0.1 mmol, 1 equiv.) in DCM (2.5 mL), DDQ (57 mg, 0.25 mmol, 2.5 equiv.) was added at rt. The reaction was then allowed to stir at room temperature for 12 h until complete consumption of starting material was indicated by TLC analysis. Subjection of the crude reaction mixture to SiO_2-gel flash column chromatography afforded **14** as white solid (47 mg, 82% yield); R_f = 0.4 (50% EtOAc + pet. ether); m.p. 229-230 °C. **IR** (neat): ν_{max} 1639, 1510, 1463, 1430, 1416, 1267, 1224, 1179, 1104, 1042, 751, 451, 438 cm^{-1}; **^{1}H NMR** (400 MHz, DMSO-d_6) δ 9.05 (d, J = 7.2 Hz, 1H), 7.41 (s, 1H), 7.30 (d J = 7.6 Hz, 1H), 7.26 (d, J = 8.4 Hz, 1H), 7.20 (d, J = 1.2 Hz, 1H), 7.14 (dd, J_1 = 1.6 Hz, J_2 = 8 Hz, 1H), 7.11 (s, 1H), 7.08 (s, 1H), 6.67 (s, 1H), 4.69-4.63

(m, 1H), 3.86 (s, 3H), 3.85 (s, 3H), 3.74 (s, 3H), 3.32 (s, 6H), 1.25 (dd, J_1 = 2.4 Hz, J_2 = 5.8 Hz, 6H); **^{13}C{^{1}H} NMR** (100 MHz, DMSO-d_6) δ 154.8, 150.5, 150.4, 149.53, 149.49, 148.1, 146.63, 146.61, 134.2, 129.1, 127.5, 124.9, 124.1, 122.7, 118.8, 115.1, 113.5, 113.3, 111.5, 109.6, 108.7, 107.3, 105.9, 105.2, 103.7, 71.0, 56.5, 56.3, 56.1, 55.3, 55.0, 22.2, 22.1. **HRMS** (ES) m/z calcd for $C_{33}H_{32}NO_8$ $(M+H)^+$: 570.2122; found: 570.2127.

Lamellarin η: In an oven round bottom flask, under N_2 atmosphere **14** (57 mg, 0.1 mmol, 1 equiv.) was dissolved in DCM (2.5 mL) before adding anhydrous $AlCl_3$ (133 mg, 1 mmol, 10 equiv.) in small portions over 10 min. The reaction was stirred at rt for 48 h until complete consumption of starting material was indicated by TLC analysis. The reaction was worked up by quenching it with water (5 mL) followed by extraction with EtOAc (3 × 10 mL). Drying of the organic phase over Na_2SO_4 and then removal of solvent under reduced pressure gave a crude residue which was subjected to SiO_2-gel flash column to access lamellarin η as a white solid (43.5 mg, 84% yield); R_f = 0.2 (50% EtOAc + pet. ether); m.p. 261-263 °C. Also, the spectroscopic data of our synthesized lamellarin η compares favourably with the previously reported data.[17] **IR** (neat): ν_{max} 3054, 2986,1714, 1606, 1422, 1326, 1264, 1165, 1123, 895 cm^{-1}; **^{1}H NMR** (400 MHz, DMSO-d_6) δ 9.86 (s, 1H), 9.06 (d, J = 7.2 Hz, 1H), 7.42 (s, 1H), 7.31 (d, J = 7.2 Hz, 1H), 7.27 (d, J = 8.4 Hz, 1H), 7.20 (d, J = 2 Hz, 1H), 7.15 (dd, J_1 = 1.6 Hz, J_2 = 8.4 Hz, 1H), 7.08 (s, 1H), 6.86 (s, 1H), 6.66 (s, 1H), 3.86 (s, 3H), 3.85 (s, 3H), 3.74 (s, 3H), 3.33 (s, 6H); **^{13}C{^{1}H} NMR** (100 MHz, DMSO-d_6) δ 154.4, 150.0, 149.9, 149.0, 149.0, 147.9, 146.3, 144.6, 133.7, 128.9, 127.2, 124.4, 123.7, 122.2, 118.3, 114.6, 113.0, 112.7, 110.8, 108.2 (2C), 106.6, 105.6, 104.8, 103.8, 56.0, 55.9, 55.6, 55.1, 54.5. **HRMS** (ES) m/z calcd for $C_{30}H_{26}NO_8$ $(M+H)^+$: 528.1653; found: 528.1660.

Dihydrolamellarin η: Applying the above described procedure for selective isopropyl group deprotection, on **13** (57 mg, 0.1 mmol, 1 equiv.), dihydrolamellarin η was obtained as white solid (46 mg, 86% yield); R_f = 0.3 (50% EtOAc + pet. ether); m.p. 237-239 °C. Also, the spectroscopic data of our synthesized dihydrolamellarin η compares favourably with the previously reported data.[17] **IR** (neat): ν_{max} 2931, 1666, 1547, 1516, 1486, 1462, 1415, 1338, 1245, 1216, 1163, 1042, 956, 861, 734 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.11 (dd, J_1 = 1.6 Hz, J_2 = 8 Hz, 1H), 7.07 (d, J = 8 Hz, 1H), 7.05 (d, J = 1.6 Hz, 1H), 6.96 (s, 1H), 6.76 (s, 1H), 6.70 (s, 1H), 6.63 (s, 1H), 5.72 (s, 1H), 4.86-4.72 (m, 2H), 3.96 (s, 3H), 3.89 (s, 3H), 3.86 (s, 3H), 3.48 (s, 2H), 3.36 (s, 3H), 3.12 (t, J = 6.8 Hz, 2H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 155.6, 149.8, 149.0, 148.9, 147.5, 146.5, 145.5, 143.3, 135.9, 128.2, 128.2, 126.7, 123.6, 120.1, 114.6, 114.0, 113.7, 111.9, 111.0, 110.3, 108.7, 104.0, 103.5, 56.3, 56.2, 55.9, 55.8, 55.2, 42.4, 28.7.

Ethyl 1-(3,4-dimethoxyphenethyl)-4-(3-isopropoxy-4-methoxyphenyl)-1H-pyrrole-2-carboxylate (16):- As per our optimized procedure,[10] using **5** (388 mg, 1.22 mmol, 1 equiv.) and **15** [(*Z*)-4-(2-bromo-2-nitrovinyl)-2-isopropoxy-1-methoxybenzene] (342.5 mg, 1.22 mmol, 1 equiv.) with a reaction time of 9.5 h, **16** was obtained after flash column chromatography as pale yellow oil (436 mg, 76% yield); R_f = 0.7 (30% EtOAc + pet. ether). **IR** (neat): ν_{max} 2365, 2356, 1698, 1563, 1513, 1465, 1418, 1385, 1248, 1194, 1139, 1091, 1028 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.16 (d, J = 2 Hz, 1H), 6.97-6.95 (m, 2H), 6.84 (d, J = 8.8 Hz, 1H), 6.78 (d, J = 1.6 Hz, 1H), 6.78 (d, J = 8.0 Hz, 1H), 6.69 (dd, J_1 = 1.6 Hz, J_2 = 8.4 Hz, 1H), 6.53 (d, J = 2 Hz, 1H), 4.57 (sept, J = 6.0 Hz, 1H), 4.50 (t, J = 7.2 Hz, 2H), 4.32 (q, J = 7.2 Hz, 2H), 3.85 (s, 3H), 3.84 (s, 3H), 3.77 (s, 3H), 3.00 (t, J = 7.2 Hz, 2H), 1.39 (t, J =7.2 Hz, 3H), 1.38 (d, J = 6.0 Hz, 6H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 161.1, 149.1, 148.8, 147.6, 147.4, 131.0, 127.6, 125.4, 123.8, 122.1, 120.9, 118.0, 115.1, 113.6, 112.3, 112.1, 111.1, 71.5, 60.0, 56.1, 55.9, 55.8,

51.2, 37.8, 22.2 (2C), 14.5. **HRMS** (ES) m/z calcd for $C_{27}H_{34}NO_6$ $(M+H)^+$: 468.2381; found: 468.2381.

1-(3,4-dimethoxyphenethyl)-4-(3-isopropoxy-4-methoxyphenyl)-1H-pyrrole-2-carboxylic acid (17):- To a solution of **16** (404 mg, 0.86 mmol, 1 equiv.) in ethanol : water (3:1, 12 mL), crushed NaOH pellets (173 mg, 4.3 mmol, 5 equiv.) was added at rt and the reaction was then allowed to reflux for 3 h, until completion of the saponification process was indicated by TLC analysis. The reaction was worked up by removing the volatiles under reduced pressure and then neutralization of the resultant residue by 1N HCl. The aqueous phase was subjected to extraction with EtOAc (4 × 15 mL). Drying of the organic phase over Na_2SO_4 and then removal of solvent under reduced pressure gave a crude residue which was subjected to SiO_2-gel column chromatographyto access pure acid **17** as a yellow solid (240 mg, 63% yield); R_f = 0.5 (50% EtOAc + pet. ether); m.p. 161-163 °C. **IR** (neat): ν_{max} 2374, 2364, 1667, 1564, 1514, 1456, 1419, 1383, 1357, 1297, 1253, 1190, 1139, 1097, 1026 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.31 (d, J = 2.0 Hz, 1H), 6.86 (d, J = 8.8 Hz, 2H), 6.84 (d, J = 1.6 Hz, 1H), 6.78 (d, J = 8.0 Hz, 1H), 6.69 (dd, J_1 = 1.6 Hz, J_2 = 8.0 Hz, 1H), 6.57 (d, J = 1.6 Hz, 1H), 4.56 (sept, J = 6.0 Hz, 1H), 4.51 (t, J = 7.2 Hz, 2H), 3.86 (s, 3H), 3.84 (s, 3H), 3.80 (s, 3H), 3.03 (t, J = 7.2 Hz, 2H), 1.38 (d, J = 6.0 Hz, 6H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 165.6, 149.3, 148.8, 147.7, 147.4, 130.8, 127.2, 126.8, 124.3, 121.1, 120.8, 118.0, 117.1, 113.6, 112.4, 112.0, 111.2, 71.6, 56.1, 55.9, 55.7, 51.6, 37.8, 22.2 (2C). **HRMS** (ES) m/z calcd for $C_{25}H_{30}NO_6$ $(M+H)^+$: 440.2068; found: 440.2095.

3-isopropoxy-4-methoxyphenyl 1-(3,4-dimethoxyphenethyl)-4-(3-isopropoxy-4-methoxyphenyl)-1H-pyrrole-2-carboxylate (18):- In an dry 25 mL round bottom flask under nitrogen atmosphere, **17** (0.210 g, 0.478 mmol, 1 equiv.) and **11** [3-isopropoxy-4-

methoxyphenol] (0.087 g, 0.478 mmol, 1 equiv.) were taken and dichloromethane (5 mL) was added. Then, EDC.HCl (0.182 g, 0.956 mmol, 2 equiv.) and, DMAP (0.116 g, 0.956 mmol, 2 equiv.) were added sequentially at rt and the reaction was allowed to stir at rt for 12 h until complete consumption of starting materials was indicated by TLC analysis. The reaction was worked up by removing the solvent under reduced pressure and subjection of the resultant residue to SiO_2-gel flash column chromatography to access **26** as a pale yellow oil (0.237 g, 83% yield); R_f = 0.6 (40% EtOAc + pet. ether). **IR** (neat): ν_{max} 2976, 2934, 1715, 1604, 1563, 1513, 1467, 1419, 1385, 1335, 1261, 1185, 1156, 1068, 1049, 989 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39 (d, J = 2.0 Hz, 1H), 7.02-7.00 (m, 2H), 6.92 (d, J = 2.0 Hz, 1H), 6.90 (d, J = 8.4 Hz, 1H), 6.87 (d, J = 8.8 Hz, 1H), 6.78-6.74 (m, 3H), 6.70 (dd, J_1 = 2.0 Hz, J_2 = 8 Hz, 1H), 6.56 (d, J = 1.6 Hz, 1H), 4.63-4.48 (m, 4H), 3.87 (s, 3H), 3.86 (s, 3H), 3.84 (s, 3H), 3.76 (s, 3H), 3.03 (t, J = 7.2 Hz, 2H), 1.40 (d, J = 6.0 Hz, 6H), 1.39 (d, J = 6.0 Hz, 6H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 159.7, 149.3, 148.8, 148.1, 147.8, 147.7, 147.5, 144.0, 130.8, 127.3, 126.4, 124.3, 121.2, 121.0, 118.0, 116.3, 113.61, 113.57, 112.4, 112.1, 112.0, 111.2, 109.7, 71.6, 71.5, 56.4, 56.1, 55.9, 55.8, 51.3, 37.8, 22.2 (2C), 22.0 (2C). **HRMS** (ES) m/z calcd for $C_{35}H_{42}NO_8$ $(M+H)^+$: 604.2905; found: 604.2921.

3-isopropoxy-14-(3-isopropoxy-4-methoxyphenyl)-2,11,12-trimethoxy-8,9-dihydro-6H-chromeno[4',3':4,5]pyrrolo[2,1-a]isoquinolin-6-one (19): Applying similar procedure for the oxidative coupling as described for lamellarin G trimethyl ether, on **18** (0.212 g, 0.351 mmol), **19** was obtained as a white solid (0.088 g, 42% yield); R_f = 0.5 (50% EtOAc + pet. ether); m.p. 229-230 °C. **IR** (neat): ν_{max} 1704, 1620, 1484, 1439, 1415, 1269, 1240, 1211, 1165, 1136, 1041, 851 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.08 (d, J = 1.6 Hz, 1H), 7.07 (s,1H), 7.04 (s, 1H), 6.91 (s, 1H), 6.75 (s, 1H), 6.71 (s, 1H), 6.66 (s, 1H), 4.86-4.72 (m, 2H), 4.57-4.48 (m, 2H), 3.92 (s, 3H), 3.88 (s, 3H), 3.43 (s, 3H), 3.36 (s, 3H), 3.11 (t, J = 6.8 Hz, 2H), 1.38 (d, J = 6 Hz, 6H),

1.34 (d, J = 6.0 Hz, 3H), 1.32 (d, J = 6.0 Hz, 3H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$)δ 155.7, 150.0, 148.9, 148.0, 147.4, 147.0, 146.5, 146.0, 135.9, 128.3, 127.9, 126.6, 123.7, 120.1, 117.8, 114.9, 113.7, 112.6, 111.0, 110.4, 108.6, 104.9, 103.4, 71.4, 71.3, 56.3, 55.9, 55.5, 55.1, 42.4, 28.7, 22.0, 21.9, 21.8 (2C). **HRMS** (ES) m/z calcd for $C_{35}H_{38}NO_8$ $(M+H)^+$: 600.2592; found: 600.2618.

Lamellarin U: In an oven dried round bottom flask, under N_2 atmosphere **19** (60 mg, 0.1 mmol, 1 equiv.) was dissolved in DCM (2.5 mL) before adding anhydrous $AlCl_3$ (133 mg, 1 mmol, 10 equiv.) in small portions over 10 min. The reaction was stirred at rt for 48 h until complete consumption of starting material was indicated by TLC analysis. The reaction was worked up by quenching it with water (5 mL) followed by extraction with EtOAc (3 × 10 mL). Drying of the organic phase over Na_2SO_4 and then removal of solvent under reduced pressure gave a crude residue which was subjected to SiO_2-gel flash column to access lamellarin U as a white solid (36.5 mg, 70% yield); R_f = 0.3 (80% EtOAc + pet. ether); m.p. 201-203 °C. Also, the spectroscopic data of our synthesized lamellarin U compares favourably with the previously reported data.[18] **IR** (neat): ν_{max} 2365, 2355, 1679, 1549, 1513, 1486, 1461, 1414, 1273, 1247, 1212, 1164, 1044, 766, 723 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.13 (d, J = 2.0 Hz, 1H), 7.03 (d, J = 8.0 Hz, 1H), 6.99 (dd, J_1 = 1.6 Hz, J_2 = 8.2 Hz, 1H), 6.92 (s, 1H), 6.75 (s, 1H), 6.72 (s, 1H), 6.69 (s, 1H), 5.84 (s, 1H), 5.76 (s, 1H), 4.81 (dt, J_1 = 6.6 Hz, J_2 = 13.2 Hz, 1H), 4.72 (dt, J_1 = 6.8 Hz, J_2 = 13.2 Hz, 1H), 3.97 (s, 3H), 3.89 (s, 3H), 3.51 (s, 3H), 3.39 (s, 3H), 3.09 (t, J = 6.8 Hz, 2H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 155.7, 148.9, 147.4, 146.43, 146.40, 146.37, 145.4, 143.2, 135.9, 128.7, 128.2, 126.7, 123.1, 120.1, 117.5, 114.5, 113.6, 111.3, 110.9, 110.3, 108.8, 104.2, 103.3, 56.3, 55.9, 55.6, 55.1, 42.4, 28.7.

Associated Content:

Supporting Information:

Copies of $^{1}H/^{13}C$ NMR spectra for all the compounds reported herein.

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Notes

The authors declare no competing financial interest.

DEDICATION

This work is dedicated to Prof. Goverdhan Mehta (Univ. of Hyderabad, India) on the occassion of his 76th birthday.

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