Palladium-Mediated Synthesis of Calothrixin B

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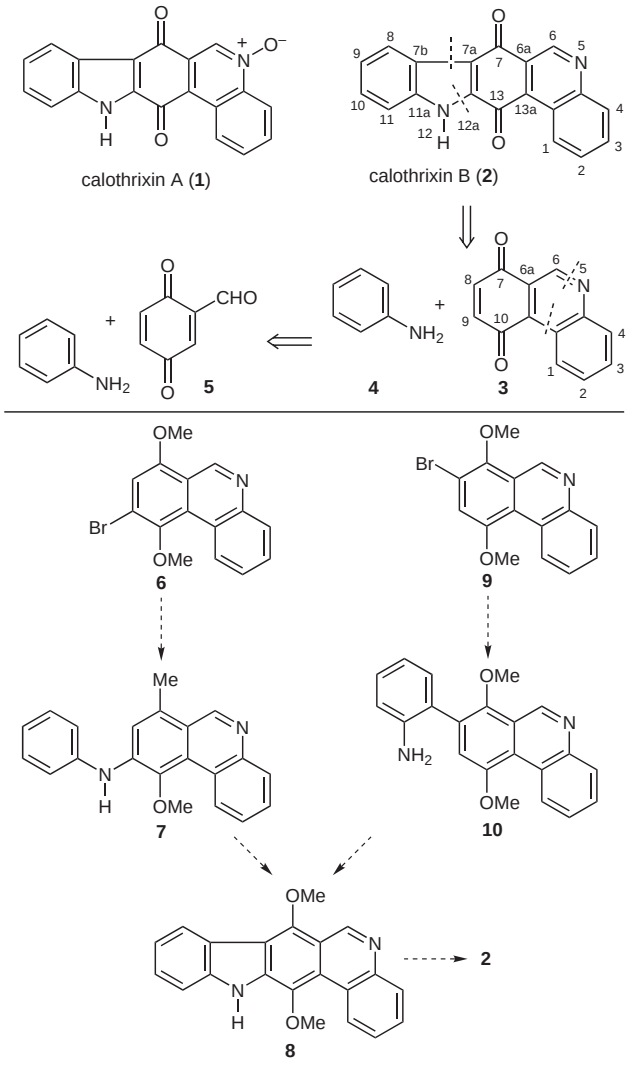
Abstract: An efficient synthesis of the indolo[3,2-*j*]phenanthridine alkaloid calothrixin B is described. The relative ease and high yields of this synthesis make this an attractive route for the preparation of calothrixin B derivatives for structure–activity relationship studies.

Key words: cyclizations, palladium-catalyzed reactions, fused-ring systems, natural products, quinones

The indolophenanthridines calothrixin A (**1**) and calothrixin B (**2**) continue to attract scientific interest due to their potent biological activities against cancer cell lines and *P. falciparum*.[1] A number of different strategies have been reported in the construction of the novel pentacyclic system.[2] The shortest route to date is that reported by Kelly,[2a] while the best overall yields obtained so far was the synthesis reported by our group in 2002.[2b,c] Although all the synthetic routes to date are amenable to the synthesis of analogues and derivatives, in practice, difficulties exist due to the lack of availability of the required starting materials and/or the sequences involved. For ease of analogue and derivative synthesis, the chemistries involved in the synthetic sequence should be robust, tolerant of a wide range of functional groups as well as amenable to simple synthetic manipulations. In the design of such a synthetic route, we aimed to maximize the use of palladium-mediated coupling reactions as these reactions are amenable to small-compound library synthesis.

Our retrosynthetic strategy is outlined in Scheme 1. Disconnection of the C7a–C7b bond and the N12–C12a bond in calothrixin B gives the phenanthridine **3** and aniline (**4**). Further disconnection of the phenanthridine at the N5–C6 and C10a–C10b bonds yields another aniline unit and 2-formyl-1,4-benzoquinone (**5**). Our plan was firstly to construct the requisite phenanthridine **3** or its equivalent, with a halogen group at the 8- or 9-position of the ring. This halogen moiety would then allow us to effect the regioselective coupling of aniline to the phenanthridine, and a subsequent ring-closing step would then lead to the desired indolo[3,2-*j*]phenanthridine ring system. This plan translates to two convergent synthetic strategies, utilizing synthetic intermediates which differ only in the position of the halogen functionality. For example, 9-bromo-7,10-dimethoxyphenanthridine (**6**) can be used as a synthetic precursor in palladium-catalyzed Buchwald–Hartwig amination reactions with aniline to access the anilinophenanthridine **7** while the deployment of the regioisomeric 8-bromo-7,10-dimethoxyphenanthridine (**9**) would enable the exploitation of palladium-catalyzed C–C biaryl coupling methods. In both instances, the regioisomeric compounds **7** and **10** can be further transformed to the indolophenanthridine **8**. Oxidative demethylation of **8** would then lead to the natural product, calothrixin B (**2**). The results of our synthetic investigations are described below.

The synthesis of the target phenanthridines **6** and **9** began with the preparation of the benzoic acids **11** and **12**, following the procedures of Rubenstein.[3] The benzoic acids **11** and **12** were then converted into the acid chloride



Scheme 1

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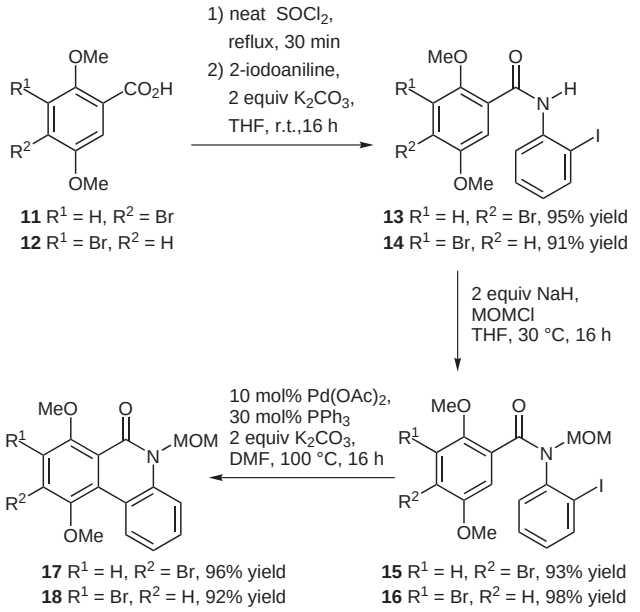
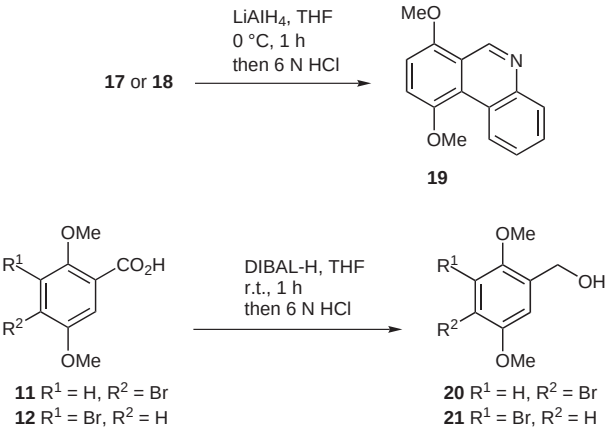
and coupled to 2-iodoaniline to furnish the amides **13** and **14** in 95% and 91% yields, respectively. The secondary amides **13** and **14** were converted into the corresponding tertiary amides **15** and **16** using NaH and MOMCl at 30 °C. We found that the maintenance of the reaction temperature was important to ensure full conversion of the starting material. The use of tertiary amides has been reported to facilitate intramolecular biaryl coupling.[4] Thus in the subsequent intramolecular Heck cyclization of the tertiary amides **15** and **16** using $Pd(OAc)_2$ (10 mol%) and PPh_3 (30 mol%) in the presence of K_2CO_3 at 100 °C, the respective phenanthridinones **17** (96% yield) and **18** (92% yield) were obtained as the sole products in the respective reactions (Scheme 2).



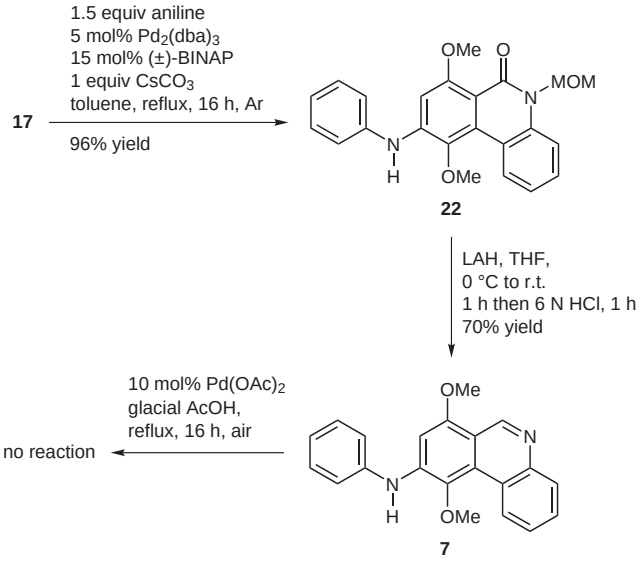
Scheme 2

With the phenanthridinones **17** and **18** in hand, attempts were made to reduce the amide functionality to the imine using lithium aluminum hydride. In each case, the debrominated phenanthridine **19** was obtained. Not surprisingly the use of milder reducing agents, such as $NaBH_4$, left the amide functionality untouched but debromination of the substrate was observed. DIBAL-H effected the reduction of the benzoic acids **11** and **12** to the corresponding alcohols **20** and **21** (Scheme 3), leaving the bromo substituent intact, but the phenanthridinones **17** and **18** did not react under these conditions. These difficulties prompted us to postpone the reduction of the phenanthridinone systems to the phenanthridines to a later stage in the synthesis.

9-Bromophenanthridinone **17** was subjected to treatment with aniline and catalytic $Pd_2(dba)_3$, (±)-2,2′-bis(diphenylphosphino)-1,1′-binaphthyl [(±)-BINAP] and a base under Buchwald–Hartwig amination conditions[5] and pleasingly the anilinophenanthridinone **22** was isolated in 96% yield. The anilinophenanthridinone **22** was then reduced with $LiAlH_4$ to obtain the anilinophenanthridine **7** in 70% yield. However, attempts to cyclize the anilinophenanthridine using catalytic $Pd(OAc)_2$ in refluxing glacial AcOH[6] in the presence of molecular oxygen only resulted in the recovery of the starting material (Scheme 4). An attempt to oxidatively cleave the methyl ethers of **22** using CAN to access the corresponding quinone for alternative ring-closing procedures gave a complex reaction mixture. Consequently this route was abandoned.



Scheme 3



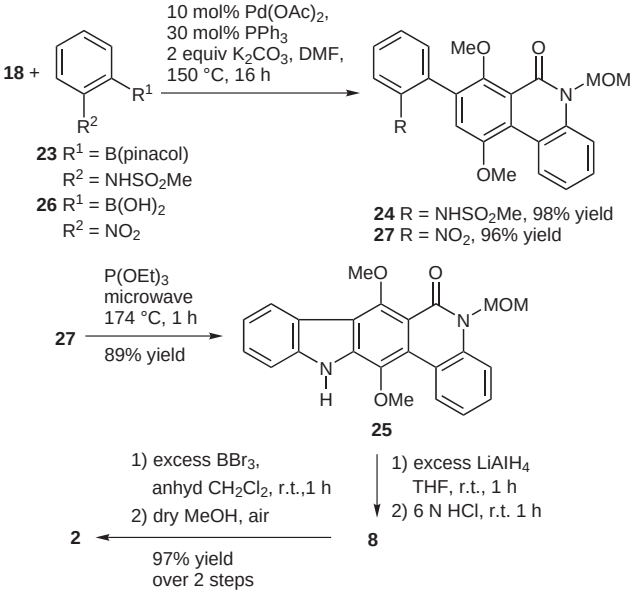
Scheme 4

We then turned our attention to the second strategy employing the regioisomeric 8-bromophenanthridinone **18** as a precursor for a palladium catalyzed C–C coupling. In this strategy, a Suzuki coupling reaction was executed. Our initial attempts utilized pinacol *N*-mesyl-2-aminophenylboronic ester **23** (1.2 equiv) with the phenanthridinone **18**. This gave the desired coupled product **24** in 98% isolated yield. Alternatively, precursor **16** can also be used to synthesize the aminophenylphenanthridinone **24** in a one-pot procedure. Here, an intramolecular Heck coupling reaction of **16** was followed by an intermolecular Suzuki coupling to boronic ester **23** at 150 °C to yield the

aminophenylphenanthridinone **24** in 94% yield. Subsequent numerous attempts to convert the aminophenylphenanthridinone **24** into the desired intermediate **25** failed. For example, attempts to generate a reactive nitrene intermediate by treating **24** with phenyliodine(III) bis(trifluoroacetate) (PIFA) at room temperature yielded complex mixtures. Attempts to selectively oxidize the methyl ether functionalities of aminophenylphenanthridinone **24** with CAN also resulted in a complex mixture, presumably due to the greater propensity of the aniline ring system to undergo single-electron-transfer reactions.

As there are many reports on the synthesis of carbazoles using the Cadogan reaction[7] we envisaged that an appropriate Cadogan precursor will allow access to the indolophenanthridinone skeleton. Hence the nitro derivative **27** was synthesized using nitrophenylboronic acid **26** under similar Suzuki conditions as described for the synthesis of **24**.

The nitrophenylphenanthridinone **27** was then cyclized to the indolophenanthridinone **25** in 40% isolated yield under the standard conditions for the Cadogan reaction.[8] The yields of the indolophenanthridinone **25** was increased to 89% when the Cadogan reaction was carried out in a sealed tube at 174 °C under microwave conditions[9] using the Biotage Initiator™ EXP microwave reactor. The subsequent steps to the synthesis of calothrixin B were readily accomplished by the reduction of the amide group of the phenanthridinone to 7,10-dimethoxyindolo[3,2-*j*]phenanthridine (**8**) using $LiAlH_4$. Cleavage of the methyl ether groups of **8** was accomplished with excess BBr_3, following which the reaction was quenched by the addition of anhydrous methanol and stirred in the presence of molecular oxygen. The red precipitate formed was calothrixin B (**2**) and after purification, calothrixin B was obtained in 97% yield. The ^1H NMR spectrum of the product obtained was identical to the natural product, calothrixin B (**2**).[1] Thus the total synthesis of calothrixin B was achieved in seven steps in 68% overall yield (Scheme 5).[10]



Scheme 5

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(10) **3-Bromo-*N*-(2-iodophenyl)-2,5-dimethoxybenzamide (14)**: 3-Bromo-2,5-dimethoxybenzoic acid (**12**, 1 g, 3.8 mmol) was dissolved in $SOCl_2$ (25 mL) and refluxed for 30 min under argon. The reaction mixture was cooled to r.t., and the solvent was quickly removed in vacuo. The residue was dissolved in anhyd THF (20 mL) and kept under argon. To this solution were added 2-iodoaniline (0.84 g, 3.8 mmol) and anhyd K_2CO_3 (1.05 g, 7.6 mmol). The reaction mixture was stirred for a further 16 h. The reaction was quenched with sat. $NaHCO_3$ solution (10 mL) and the organic layer was separated. The aqueous layer was further extracted with EtOAc (2 × 20 mL). The combined organic layer was dried with $MgSO_4$, filtered, and the solvent was removed in vacuo to obtain the crude product. Flash chromatography on silica gel (EtOAc–hexanes, 2:3) gave the title compound as a cream-colored solid (1.61 g, 3.5 mmol, 91% yield); R_f 0.83 (EtOAc–hexanes, 2:3); mp 99–101 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 3.82 (s, 3 H, OMe), 3.96 (s, 3 H, OMe), 6.91 (m, 1 H, ArH), 7.30–7.43 (m, 2 H, ArH), 7.66 (s, 1 H, ArH), 7.86 (m, 1 H, ArH), 8.49 (d, *J* = 8 Hz, 1 H, ArH), 10.11 (s, 1 H, NH). ^{13}C NMR (75 MHz, $CDCl_3$; rotamer 1): δ = 55.8 (OMe), 62.8 (OMe), 99.6, 111.9, 117.8, 121.0, 126.0, 129.5, 130.4, 132.1, 139.9, 140.4, 147.3, 155.3, 168.0 (CO). ^{13}C NMR (75 MHz, $CDCl_3$; rotamer 2): δ = 55.9, 62.7, 89.4, 115.0, 118.2, 122.4, 123.6, 128.0, 129.0, 130.0, 139.2, 139.3, 148.6, 156.3, 162.4. MS (EI): *m*/*z* (%) = 463 (100) $[M^+]$, 461 (100) $[M^+]$, 459 (95) $[M – H]^+$, 458 (90) $[M – H]^+$, 446 (68), 444 (68). Two molecular ion peaks $[M^+]$ and two

$[M - OMe]^+$ peaks were observed due to ^{81}Br and ^{79}Br isotopes. HRMS (EI): *m*/*z* calcd for $C_{15}H_{13}{}^{79}BrINO_3$: 460.9124; found: 460.9127. FTIR (KBr): 724 (w), 755 (w), 784 (w), 863 (w), 992 (m), 1042 (m), 1239 (m), 1295 (m), 1420 (m), 1471 (s), 1525 (m), 1599 (m), 1678 (m), 1713 (m), 2853 (m), 2925 (m), 3436 (br) cm^{-1}.

3-Bromo-*N*-(2-iodophenyl)-2,5-dimethoxy-*N*-methoxymethylbenzamide (16): To a solution of 3-bromo-*N*-(2-iodophenyl)-2,5-dimethoxybenzamide (**14**, 0.88 g, 1.9 mmol) in anhyd THF (10 mL) under nitrogen were added MOMCl (0.30 mL, 3.9 mmol) and NaH (0.10 g, 4.1 mmol). The reaction mixture was stirred for 16 h at 30 °C following which the reaction mixture was poured into a sat. $NaHCO_3$ solution (20 mL) to quench the reaction. The organic layer was separated and the aqueous layer was further re-extracted with CH_2Cl_2 (3 × 15 mL). The combined organic layers were dried with $MgSO_4$, filtered and the solvent was removed in vacuo to yield the crude product. Column chromatography on silica gel (EtOAc–hexanes, 2:3) gave the desired compound as a viscous yellow oil which solidified upon standing (0.93 g, 1.8 mmol, 98% yield). Two distinct sets of methoxy signals (three methoxy signals per set) in a ratio of 4:1 were observed in the ^1H NMR spectrum which suggested the presence of rotamers, but the aromatic hydrogen signals overlapped. The ^{13}C NMR spectrum showed distinct sets of signals for each rotamer; the carbon resonances of each rotamer are reported below.

R_f 0.72 (EtOAc–hexanes, 2:3); mp 40–42 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 3.62 (s, 3 H, OMe), 3.66, 3.78 (s, 3 H, OMe), 3.80, 3.93 (s, 3 H, OMe), 4.60 (d, *J* = 10 Hz, 1 H, CH_aH_b), 5.87 (d, *J* = 10 Hz, 1 H, CH_aH_b), 6.88–6.91 (m, 2 H, ArH), 7.00–7.08 (m, 1 H, ArH), 7.20 (m, 1 H, ArH), 7.36–7.39 (m, 1 H, ArH), 7.74 (d, *J* = 8 Hz, 1 H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$; rotamer 1): δ = 55.6 (OMe), 56.7 (OMe), 62.3 (OMe), 76.6 (CH_2), 99.5, 109.5, 117.1, 119.9, 128.8, 129.9, 131.3, 132.7, 139.2, 141.8, 146.1, 155.3, 168.2 (CO). ^{13}C NMR (75 MHz, $CDCl_3$; rotamer 2): δ = 55.6 (OMe), 56.7 (OMe), 62.8 (OMe), 76.6 (CH_2), 99.5, 111.7, 112.5, 117.6, 120.8, 129.3, 129.9, 131.6, 132.0, 139.7, 147.1, 155.2, 167.8 (CO). MS (EI): *m*/*z* (%) = 507 (15) $[M^+]$, 505 (15) $[M^+]$, 380 (42) $[M - I]^+$, 378 (42) $[M - I]^+$, 245 (97), 243 (100), 45 (92). Two molecular ion peaks $[M^+]$ and two $[M - I]^+$ peaks were observed due to ^{81}Br and ^{79}Br isotopes. HRMS (EI): *m*/*z* calcd for $C_{17}H_{17}{}^{79}BrINO_4$: 504.9380; found: 504.9380. FTIR (KBr): 648 (w), 681 (w), 725 (w), 747 (w), 856 (w), 911 (w), 994 (m), 1018 (m), 1044 (s), 1082 (s), 1225 (s), 1278 (m), 1306 (m), 1374 (m), 1420 (s), 1473 (s), 1562 (w), 1598 (m), 1669 (s), 2831 (w), 2937 (m), 3436 (br) cm^{-1}. Anal. Calcd for $C_{17}H_{17}BrINO_4$: C, 40.34; H, 3.39; N, 2.77. Found: C, 40.66; H, 3.48; N, 2.48.

8-Bromo-7,10-dimethoxy-5-methoxymethylphenanthridin-6-one (18): To a solution of the tertiary benzamide **16** (0.18 g, 0.35 mmol) in degassed anhyd DMF (15 mL) were added PPh_3 (28 mg, 0.11 mmol), anhyd K_2CO_3 (97 mg, 0.70 mmol) and $Pd(OAc)_2$ (8 mg, 0.035 mmol). The reaction mixture was stirred at 100 °C under an argon atmosphere for 16 h following which the reaction mixture was cooled to r.t. and filtered through Celite. An aliquot of acetone (10 mL) was filtered through the Celite, and the combined filtrates were removed under reduced pressure to yield the crude product. Purification via column chromatography on silica gel (EtOAc–hexanes, 1:1) gave the desired compound as a brown solid (0.12 g, 0.32 mmol, 92% yield); R_f 0.74 (EtOAc–hexanes, 1:1); mp 102–104 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 3.51 (s, 3 H, OMe), 3.95 (s, 3 H, OMe), 4.03 (s, 3 H, OMe), 5.77 (s, 2 H, CH_2), 7.25–7.29 (m, 2 H, ArH), 7.49 (s, 1 H, ArH), 7.52–7.58 (m, 1 H, ArH), 9.13 (d, *J* = 8 Hz, 1 H, ArH). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 56.4 (OMe), 56.7 (OMe), 61.7 (OMe), 74.2 (CH_2), 115.1, 118.1, 118.4, 119.9, 121.3, 122.5, 125.4, 128.7, 129.3, 136.7, 152.0, 153.4, 159.5 (CO). MS (EI): *m*/*z* (%) = 379 (90) $[M^+]$, 377 (86) $[M^+]$, 347 (50), 345 (48), 336 (52), 334 (68), 319 (100), 317 (88), 304 (73). HRMS (EI): *m*/*z* calcd for $C_{17}H_{16}{}^{79}BrNO_4$: 377.0263; found: 377.0265. HRMS (EI): *m*/*z* calcd for $C_{17}H_{16}{}^{81}BrNO_4$: 379.0242; found: 379.0252. FTIR (KBr): 758 (w), 1052 (s), 1076 (s), 1224 (m), 1276 (w), 1297 (w), 1363 (w), 1458 (s), 1655 (s), 2824 (w), 2932 (w), 2962 (w), 3435 (br) cm^{-1}. Anal. Calcd for $C_{17}H_{16}BrNO_4$: C, 53.99; H, 4.26; N, 3.70. Found: C, 53.84; H, 4.56; N, 3.68.

8-(Nitrophenyl-2-yl)-7,10-dimethoxy-5-methoxymethylphenanthridin-6-one (27): To a rigorously degassed solution of the 8-bromophenanthridinone **18** (0.1 g, 0.26 mmol) in DMF (10 mL) were added K_2CO_3 (73 mg, 0.53 mmol), PPh_3 (21 mg, 0.082 mmol, 30 mol%), and $Pd(OAc)_2$ (6 mg, 0.026 mmol, 10 mol%). To the reaction mixture was added nitrophenyl-2-boronic acid (**26**, 2 equiv). The reaction mixture was stirred at 150 °C for 16 h under argon. The reaction mixture was cooled to r.t. and sat. $NaHCO_3$ (10 mL) was added. The solvent was then removed under reduced pressure, and the residue was partitioned between $CHCl_3$ (20 mL) and sat. $NaHCO_3$ (20 mL). The aqueous layer was further extracted with $CHCl_3$ (2 × 20 mL) and the combined organic layer was dried with $MgSO_4$, filtered, and the solvent was removed in vacuo to obtain the crude product. Purification by column chromatography on silica gel gave the desired product as a yellow solid (0.106 g, 0.25 mmol, 96% yield); R_f 0.34 (EtOAc–hexanes, 1:2); mp 146–148 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 3.51 (s, 3 H, OMe), 3.56 (s, 3 H, OMe), 4.02 (s, 3 H, OMe), 5.78 (br s, 2 H, NCH_2), 7.18 (s, 1 H, ArH), 7.26 (app. t, *J* = 7 Hz, 1 H, ArH), 7.50 (app. t, *J* = 7 Hz, 1 H, ArH), 7.52 (m, 3 H, ArH), 7.69 (app. t, *J* = 7 Hz, 1 H, ArH), 8.05 (d, *J* = 7 Hz, 1 H, ArH), 9.20 (d, *J* = 8 Hz, 1 H, ArH). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 56.4 (OMe), 56.7 (OCMe), 61.6 (OMe), 74.1 (CH_2), 115.1, 116.5, 118.5, 120.3, 122.5, 124.3, 126.1, 128.7, 128.8, 129.3, 132.3, 132.4, 132.5, 132.7, 136.9, 149.2, 151.9, 153.2, 160.2 (CO). MS (EI): *m*/*z* (%) = 420 (40) $[M^+]$, 405 (25) $[M - OMe]^+$, 393 (30), 381 (45), 343 (56), 331 (52), 293 (100), 281 (77), 269 (43), 243 (85), 231 (97), 219 (80). HRMS (EI): *m*/*z* calcd for $C_{23}H_{20}N_2O_6$: 420.1321; found: 420.1363. Anal. Calcd for $C_{23}H_{20}N_2O_6$: C, 65.71; H, 4.79; N, 6.66. Found: C, 65.30; H, 4.97; N, 6.25.

Intramolecular Cyclization of the Nitrophenylphenanthridinone 27 via Microwave-Assisted Cadogan Reaction: A solution of 8-(nitrophenyl-2-yl)-7,10-dimethoxy-5-methoxymethylphenanthridin-6-one (**27**, 0.10 g, 0.24 mmol) in triethylphosphite (1 mL) was heated at 174 °C for 1 h in a sealed vessel using the Biotage Initiator™ EXP microwave reactor. The reaction mixture was cooled to r.t. and the solvent was removed in vacuo. The residue was partitioned between $CHCl_3$ (10 mL) and sat. $NaHCO_3$ (10 mL). The organic layer was dried with $MgSO_4$, filtered, and the solvent was removed. Purification via column chromatography on silica gel (EtOAc–hexanes, 1:1) gave the desired product **25** as a yellow solid (82 mg, 0.21 mmol, 89% yield); R_f 0.21 (EtOAc–hexanes, 1:3). ^1H NMR (400 MHz, $CDCl_3$): δ = 3.55 (s, 3 H, OMe), 3.90 (s, 3 H, OMe), 4.20 (s, 3 H, OMe), 5.82 (br s, 2 H, NCH_2), 7.28–7.36 (m, 2 H, ArH), 7.48 (m, 3 H, ArH), 7.59 (d, *J* = 8 Hz, 1 H, ArH), 8.42 (d, *J* = 8 Hz, 1 H, ArH), 8.67 (br s, 1 H, NH), 9.17 (d, *J* = 8 Hz, 1 H, ArH). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 56.6 (OMe), 60.2 (OMe), 61.6 (OMe), 73.8 (CH_2), 110.7, 111.3, 115.3, 118.8, 118.9, 121.0, 122.8, 122.8, 123.7, 125.0,

126.9, 127.4, 129.0, 136.6, 137.8, 138.3, 139.9, 155.7, 161.1 (CO). MS (ESI): *m*/z (%) = 412 (38) $[M + Na]^+$, 390 (100) $[M + H]^+$. HRMS (ESI): *m*/*z* $[M+ H]^+$ calcd for $C_{23}H_{20}N_2O_4$: 389.1496; found: 389.1499.

$LiAlH_4$-Mediated Reduction of the Pentacyclic Lactam 25 to 7,10-dimethoxyindolo[3,2-*j*]phenanthridine (8): To a solution of the lactam **25** (10 mg, 0.026 mmol) in anhyd Et_2O (1 mL) at 0 °C were added freshly crushed pellets of $LiAlH_4$ (3 mg, 0.08 mmol). The reaction mixture was warmed to r.t. and stirred for a further 1 h. The reaction was stopped by the careful addition of distilled H_2O (1 mL). The reaction was then acidified to pH 1 using 6 N HCl. The mixture was stirred for a further 1 h. The reaction mixture was then made basic by the slow addition of 1 M NaOH until a clear biphasic solution was obtained. The organic layer was separated, and the aqueous layer was further extracted with EtOAc (10 mL). The combined organic layer was dried with $MgSO_4$ and filtered. The solvent was removed in vacuo to obtain the crude product; R_f 0.86 (EtOAc–hexanes, 1:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.07 (s, 3 H, OMe), 4.16 (s, 3 H, OMe), 7.01 (app. t, *J* = 7 Hz, 1 H, ArH), 7.48 (m, 2 H, ArH), 7.70 (app. t, *J* = 7 Hz, 1 H, ArH), 7.92 (d, *J* = 8 Hz, 1 H, ArH), 8.02 (d, *J* = 8 Hz, 1 H, ArH), 8.09 (d, *J* = 8 Hz, 1 H, ArH), 8.95 (d, *J* = 8 Hz, 1 H, ArH), 9.57 (br s, 1 H, ArH), 11.07 (br s, 1 H, NH).

Conversion of 8 into Calothrixin B (2): To a solution of the crude dimethyl ether **8** in anhyd CH_2Cl_2 (1 mL) at 0 °C was added 1 M BBr_3 (0.1 mL). The reaction mixture was warmed to r.t. and stirred for 1 h. The reaction was stopped by the addition of anhyd MeOH (1 mL) and stirred in the presence of air for 1 h. The solvent was carefully removed in vacuo, and the residue was partitioned between sat. $NaHCO_3$ (10 mL) and EtOAc (10 mL). The organic layer was dried with $MgSO_4$ and filtered, and the solvent was removed under reduced pressure. Purification by column chromatography on silica gel yielded calothrixin B as a red solid (7.5 mg, 0.025 mmol, 97% yield over 2 steps from **25**); R_f 0.47 (EtOAc–hexanes, 1:2); mp >>300 °C (Lit.[1] >>300 °C). ^{1}H NMR (400 MHz, DMSO-*d*): δ = 7.40 (app. t, *J* = 7 Hz, 1 H, ArH), 7.47 (app. t, *J* = 7 Hz, 1 H, ArH), 7.62 (d, *J* = 8 Hz, 1 H, ArH), 7.89 (app. t, *J* = 8 Hz, 1 H, ArH), 7.96 (app. t, *J* = 8 Hz, 1 H, ArH), 8.17 (d, *J* = 8 Hz, 1 H, ArH), 8.18 (d, *J* = 8 Hz, 1 H, ArH), 9.58 (d, *J* = 9 Hz, 1 H, ArH), 9.62 (s, 1 H, ArH).