Synthetic Routes to Pyrroloiminoquinone Alkaloids. A Direct Synthesis of Makaluvamine C

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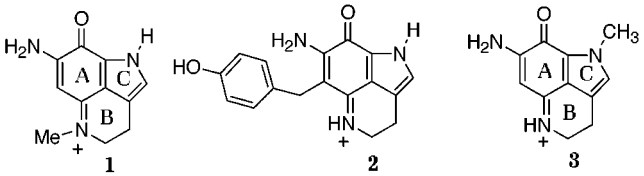
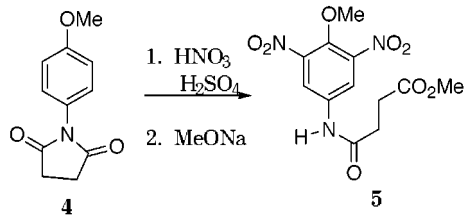
Makaluvamine C is a pyrroloiminoquinone which has been isolated from marine sponges. This molecule has been synthesized in 13 steps from *p*-anisidine. The key steps in this synthesis include an intramolecular nucleophilic aromatic substitution mediated by potassium *tert*-butoxide, the selective reduction of a dinitro ester using catalytic hydrogenation, and the novel use of Fremy's salt to synthesize an iminoquinone from an amino phenol. The synthesis of makaluvamine C has been achieved from *p*-anisidine in 13.1% overall yield.

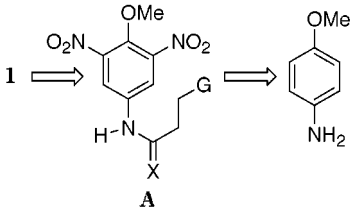
A number of biologically active alkaloids possessing the pyrroloiminoquinone nucleus have been isolated in recent years.[1] Recently, the makaluvamines, a group of potent antineoplastic agents, have been isolated from marine sponges. This novel class of metabolites has been shown to be topoisomerase II inhibitors.[2] Several pyrroloiminoquinones are cytotoxic against human colon tumor cell line HCT-116.[3] Representative members of this class include makaluvamine C (**1**),[2] veiutamine (**2**),[4] and makaluvamine A (**3**).[2]



Several syntheses and synthetic approaches have been reported.[5] In most cases the tricyclic skeleton was generated from an indole. There are also reports which start from a quinoline or tetrahydroquinoline precursor. Recently, we reported a synthetic route to a tricyclic precursor to makaluvamine A (**3**) or veiutamine (**2**).[6] Our synthetic plan was based on the intramolecular nucleophilic aromatic substitution[7] of a dinitroanisole. Although an approach using an intermolecular substitution has been reported, our synthetic plan is strategically quite distinct from that of existing syntheses.[8] We now report that a modification of our previous approach has led to a direct total synthesis of makaluvamine C (**1**).

Initial efforts to prepare **A** from picric acid proved to be cumbersome. Both O-alkylation of the phenol and selective reduction of the nitro group in the 4-position were difficult to achieve on a large scale. We eventually converted *p*-anisidine and succinic anhydride in boiling toluene into imide **4**[9] in 91% yield. Imide **4** is cleanly nitrated to produce a dinitro imide in 86% yield which reacts rapidly with sodium methoxide in methanol to generate ester **5** in 96% yield. The imide moiety was important for efficient nitration. Nitration of the mono amide of succinic acid was not as selective.





The key intramolecular nucleophilic aromatic substitution was attempted with various bases (LDA, NaOMe, KOtBu) at different temperatures. The resulting dark red σ complex was oxidized in situ with ceric ammonium nitrate (CAN). The best conditions involved deprotonation of the amide ester **5** with potassium *tert*-butoxide from −78 to −30 °C followed by CAN oxidation at −30 °C. This provided lactam ester **6** in 53% yield. We felt that this cyclization would proceed via a dianion, favoring six-membered ring formation. Confirmation of this ex-

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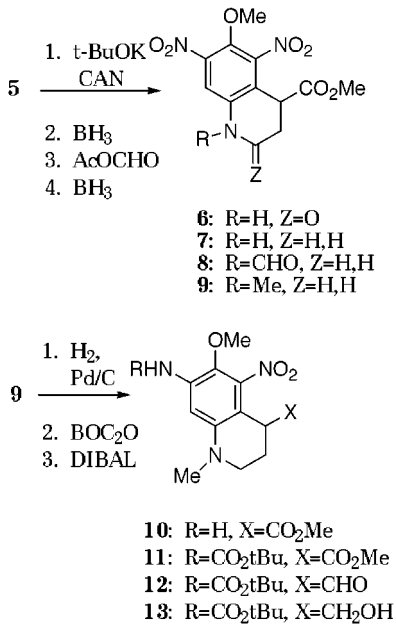
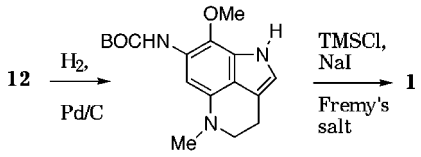
Scheme 1



pectation came from the 2D-COSY experiment on compound **7** which confirmed the tetrahydroquinoline structure. Lactam ester **6**, the product of the intramolecular nucleophilic substitution reaction, was treated with BH_3 in THF to afford the amine **7** in 84% yield. To achieve the substitution pattern for makaluvamine C, the amine was methylated by formylation with formic acetic anhydride followed by borane reduction to **9** in 88% overall yield (Scheme 1).[10]

In our previous approach, both nitro groups were reduced simultaneously by catalytic hydrogenation. Fortunately, hyrdogenation for a short time afforded selective reduction of the less hindered nitro group in 90% yield. This furnished the opportunity to protect the amine as its BOC derivative **11** in 92% yield. The ability to protect the amine before the indole was introduced proved to be a key factor in the synthesis of **1**. The reduction of the ester **11** with DIBAL produced the aldehyde **12** and the alcohol **13** in a 2.35:1 ratio in a combined yield of 97%. Alcohol **13** could be oxidized to **12** using the Dess−Martin periodinane reagent.

Hydrogenation of aldehyde **12** required 21 h to go to completion and afforded indole **14** in 76% yield. This compound could be purified by chromatography and was stable to storage in the refrigerator. The corresponding amino indole was much less stable. Indole **14** was treated with CAN, a reagent previously employed to generate the pyrroloiminoquinone framework.[11] Unfortunately, this oxidation produced only decomposition. Attempted demethylation of **14** with butanethiolate in HMPA led to recovered starting material.[12] Treatment of **14** with aqueous trifluoroacetic acid resulted in decomposition. However, treatment of **14** with chlorotrimethylsilane and sodium iodide in acetonitrile[13] followed by in situ oxidation of the resulting amine with Fremy's salt afforded makaluvamine C in 73% yield.[14] This represents a novel use of Fremy's salt to synthesize iminoquinones.[15] The NMR and ^{13}C NMR spectra in DMSO were identical to those reported.[16] Additionally, our compound was identical to an authentic sample provided by Professor Ireland by TLC analysis in two different solvent systems.[17]



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A synthesis of makaluvamine C has been achieved in 13 steps from *p*-anisidine in 13.1% overall yield. The key steps include an intramolecular nucleophilic aromatic substitution reaction, the selective reduction of a dinitro ester, and an oxidation using Fremy's salt. This synthesis of makaluvamine C is a flexible one which should make possible the synthesis of quantities of **1** plus other members of the makaluvamine family.

Experimental Section

Proton NMR spectra were measured at 300 MHz unless otherwise mentioned. ^{13}C NMR spectra were recorded at 75 MHz. High-resolution mass spectra (HRMS) were EI spectra. Sgc refers to silica gel flash chromatography. Organic extracts were dried over sodium sulfate.

2-(4-Methoxyphenyl)succinimide (4). A mixture of *p*-anisidine (31.31 g, 0.254 mol) and succinic anhydride (24.19 g, 0.242 mol) in dry toluene (150 mL) was boiled for 36 h. Toluene (100 mL) was then added, and 200 mL was distilled out to effect azeotropic removal of water. The residue was cooled and filtered to give the product as a blue-colored solid which is sufficiently pure for the next step (45.15 g, 91%). An analytical sample was prepared by recrystallization from hot ethanol and Norit to afford **4** as a colorless solid: mp 163−164 °C (lit.[9] mp 162−163 °C); ^1H NMR (CD_3COCD_3) δ 2.82 (s, 4 H), 3.82 (s, 3 H), 6.95−7.22 (m, 4 H); ^{13}C NMR (CD_3COCD_3) δ 29.2, 55.8, 114.8, 126.8, 129.1, 160.2, 177.5. Anal. Calcd for $C_{11}H_{11}NO_3$: C, 64.38; H, 5.40; N, 6.83. Found: C, 64.35; H, 5.44; N, 6.86.

Methyl *N*-(4-Methoxy-3,5-dinitrophenyl)succinimidate (5). To a three-necked round-bottomed flask, fitted with a mechanical stirrer, an internal thermometer, and an addition funnel, were added the imide **4** (10.31 g, 50 mmol) and concentrated sulfuric acid (41 mL). The resultant vigorously stirred solution was cooled in an ice−salt bath. After the temperature drops below −5 °C, an ice cold mixture of fuming HNO_3 (19 mL) and concentrated H_2SO_4 (30 mL) was added dropwise through the addition funnel at such a rate that the internal temperature will not rise above 0 °C. The reaction mixture was vigorously stirred for 10 min after the end of the addition and was loaded into a separatory funnel. This was added dropwise into a mechanically stirred ice−water mixture. The resultant mixture was extracted into EtOAc (4 × 400 mL), and the combined organic extracts were washed with water (2 × 200 mL) and brine (200 mL) and dried. The solvent was evaporated to yield the dinitro imide (12.69 g, 86%) as a yellow powder which was sufficiently pure for the next step. A sample

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(17) TLC data: R_f 0.43 in 1:3 MeOH:$CHCl_3$; R_f 0.46 in 1:1 MeOH:HOAc.

for analytical purposes was obtained by recrystallization from ethyl acetate: mp 174 °C; ^{1}H NMR (CD_3COCD_3) δ 2.94 (s, 4 H), 4.11 (s, 3 H), 8.30 (s, 2 H); ^{13}C NMR (CD_3COCD_3) δ 29.3 (2C), 65.3, 128.3 (2C), 129.7, 145.9, 147.2 (2C), 176.7 (2C); IR (Nujol) cm^{-1} 1707, 1531. Anal. Calcd for $C_{11}H_9N_3O_7$: C, 44.76; H, 3.07; N, 14.23. Found: C, 44.78; H, 3.02; N, 13.98.

To a stirred solution of dinitro imide (2.00 g, 6.8 mmol) in dry THF (75 mL) and MeOH (15 mL) in a room-temperature water bath was added NaOMe (0.44 g, 8.15 mmol) in one portion. After 15 min at the same temperature, a saturated aqueous NH_4Cl solution (50 mL) was added and the resultant mixture was concentrated in vacuo to remove THF and MeOH. The aqueous layer was extracted with EtOAc (4 × 100 mL), and the combined organic extracts were washed with water (70 mL) and brine (70 mL) and dried. The residue obtained after evaporation of solvent was filtered through a short column of silica gel with hexane−ethyl acetate (1:1) to yield the amide ester **5** (2.13 g, 96% yield) as a yellow powder. An analytical sample was obtained by recrystallization from ethyl acetate: mp 128−129 °C; ^{1}H NMR ($CDCl_3$) δ 2.68−2.72 (m, 2 H), 2.78−2.82 (m, 2 H), 3.76 (s, 3 H), 4.03 (s, 3 H), 8.28 (s, 2 H), 8.35 (brs, 1 H); ^{13}C NMR ($CDCl_3$ and CD_3COCD_3) δ 28.5 (2C), 31.4, 51.8, 64.7, 119.3 (2C), 135.0, 142.3, 145.1, 170.8, 173.0; IR (neat film) cm^{-1} 3351, 1732. Anal. Calcd for $C_{12}H_{13}N_3O_8$: C, 44.04; H, 4.00; N, 12.84. Found: C, 44.03; H, 3.96; N, 12.66.

Methyl 1,2,3,4-Tetrahydro-6-methoxy-2-oxo-5,7-dinitroquinoline-4-carboxylate (6). To a suspension of *t*-BuOK (0.214 g, 1.9 mmol) in dry THF (7 mL) at −78 °C was added a cooled (−78 °C) solution of dinitro ester **5** (0.208 g, 0.64 mmol) in dry THF (8 mL) via a cannula under a positive pressure of argon over 20 min. The resultant dark brown reaction mixture was stirred and warmed to −35 °C over 4 h under argon, at which temperature the reaction was stirred for a further 2 h. The reaction mixture was recooled to −78 °C, and ceric ammonium nitrate (0.348 g, 0.64 mmol) was added in three lots over 2 min. The resultant mixture was stirred for 3 h while warming to −40 °C slowly. The mixture was diluted with ethyl acetate (100 mL) and filtered through a pad of Celite and silica gel. The filtrate was evaporated, and the residue was chromatographed on silica gel. Elution with 1:1 hexane−ethyl acetate afforded the cyclized dinitro ester **6** (0.111 g, 53% yield): ^{1}H NMR ($CDCl_3$) δ 2.82 (dd, J = 6.9, 16.8 Hz, 1 H), 3.13 (dd, J = 1.8, 16.8 Hz, 1 H), 3.73 (s, 3 H), 4.01 (s, 3 H), 4.16 (dd, J = 1.8, 6.9 Hz, 1 H), 7.55 (s, 1 H), 9.06 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 31.7, 38.5, 53.7, 65.5, 114.4, 119.3, 134.6, 142.2, 144.0, 147.2, 169.1, 169.3; IR (neat) cm^{-1} 3321, 1736, 1698. Anal. Calcd for $C_{12}H_{11}N_3O_8$: C, 44.32; H, 3.41; N, 12.92. Found: C, 44.35; H, 3.28; N, 12.62.

Methyl 1,2,3,4-Tetrahydro-6-methoxy-5,7-dinitroquinoline-4-carboxylate (7). To a solution of dinitroamide ester **6** (51.6 mg, 0.16 mmol) in dry THF (4 mL) at 0 °C was added 1 M BH_3·THF (0.8 mL, 0.8 mmol) dropwise under argon. The resultant mixture was warmed to 20 °C while being stirred over 12 h at which point TLC showed the disappearance of the starting material. The reaction mixture was cooled to 0 °C, and wet ether was added to quench excess BH_3. The product was extracted into ether (4 × 15 mL), and the combined extracts were washed with water and brine and dried. The residue obtained after evaporation of solvents was chromatographed on a short silica gel column. The amine ester **7** (41.5 mg, 84% yield) was obtained by elution with 2:1 hexanes−ethyl acetate. A yellow oil solidified upon standing: ^{1}H NMR 400 MHz ($CDCl_3$) δ 1.85−1.98 (m, 1 H), 2.28−2.38 (m, 1 H), 3.28−3.43 (m, 2 H), 3.72 (s, 3 H), 3.85−3.87 (m, 1 H), 3.90 (s, 3 H), 4.5 (br s, 1 H), 7.16 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 23.0, 37.7, 38.3, 53.0, 65.1, 111.4, 114.5, 136.1, 141.3, 143.5, 148.1, 172.1; IR (neat) cm^{-1} 3415, 1734, 1539; MS *m*/*z* 311, 294, 252, 235, HRMS *m*/*z* 311.07490, calcd for $C_{12}H_{13}N_3O_7$ 311.07535.

Methyl *N*-Methyl-1,2,3,4-tetrahydro-6-methoxy-5,7-dinitroquinoline-4-carboxylate (9). A solution of 96% formic acid (1.23 mL, 32.5 mmol) was added dropwise to acetic anhydride (2.51 mL, 26.6 mmol) at 0 °C under argon. After the addition, the mixture was heated to 60 °C for 2 h and cooled to room temperature. To this stirred reagent of acetic formic anhydride was added dry THF (2 mL) followed by a solution of amine ester **7** (0.23 g, 0.74 mmol) in dry THF (4 mL). A TLC control revealed the reaction to be complete at the end of 4 h. The solvent was removed, and the residue was left on a high vacuum pump for 10 min.

The residue obtained above was dissolved in dry THF (6 mL) and cooled in an ice bath. To this stirred mixture was added 1 M BH_3·THF (2.96 mL, 2.96 mmol) dropwise, and at the end of addition, TLC showed complete consumption of starting material. The reaction mixture was quenched by careful dropwise addition of moist ether, followed by water and extracted with ether (4 × 20 mL). The combined organic extract were washed with water and brine and dried. The residue obtained after evaporation of solvent was chromatographed on silica gel to afford the product **9** (0.212 g, 88% yield) as reddish orange solid: mp 99−100 °C; ^{1}H NMR ($CDCl_3$) δ 1.94−2.07 (m, 1 H), 2.30−2.38 (m, 1 H), 3.01 (s, 3 H), 3.23−3.31 (m, 1 H), 3.37−3.47 (m, 1 H), 3.71 (s, 3 H), 3.82−3.85 (m, 1 H), 3.90 (s, 3 H), 7.18 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 23.5, 38.7, 39.4, 46.6, 53.0, 65.0, 107.7, 116.0, 135.3, 142.6, 143.6, 148.0, 171.9; IR (neat) cm^{-1} 1735, 1540; MS *m*/*z* 325, 308, 291, 266, 249, 219, 189, 160, 132; HRMS *m*/*z* 325.09090, calcd for $C_{13}H_{15}N_3O_7$ 325.09100. Anal. Calcd for $C_{13}H_{15}N_3O_7$: C, 48.00; H, 4.65; N, 12.92. Found: C, 48.34; H, 4.67; N, 12.73.

Methyl *N*-Methyl-7-amino-1,2,3,4-tetrahydro-6-methoxy-5-nitroquinoline-4-carboxylate (10). A suspension of amino ester **9** (0.1046 g, 0.32 mmol) and 10% Pd−C (10 mg) in ethanol (9 mL) was stirred under an atmosphere of hydrogen. The progress of the reaction was followed by TLC, and the reaction was complete after about 2 $^1/_2$ h. The reaction was then filtered on a Celite pad and washed with with ethyl acetate. The filtrate was evaporated, and the residue was purified by sgc to afford the monoreduction product **10** (0.0852 g, 90% yield): ^{1}H NMR ($CDCl_3$) δ 1.92−2.06 (m, 1 H), 2.16−2.24 (m, 1 H), 2.88 (s, 3 H), 3.05−3.15 (m, 1 H), 3.25−3.35 (m, 1 H), 3.67 (s, 3 H), 3.71−3.74 (m, 1 H), 3.76 (s, 3 H), 3.88 (brs, 2 H), 6.08 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 24.6, 37.9, 39.6, 47.0, 52.4, 61.8, 99.8, 100.4, 129.6, 141.1, 143.4, 146.5, 173.9; IR (neat) cm^{-1} 3374, 1736, 1530; MS *m*/*z* 295, 280, 236, 189, 161; HRMS *m*/*z* 295.11750, calcd for $C_{13}H_{17}N_3O_5$ 295.11682.

Methyl *N*-Methyl-7-BOC-amino-1,2,3,4-tetrahydro-6-methoxy-5-nitroquinoline-4-carboxylate (11). A solution of the amine **10** (0.0303 g, 0.1 mmol) and $(BOC)_2O$ (0.0448 g, 0.21 mmol) in dry dioxane (3 mL) was boiled under an argon atmosphere. After 24 h, TLC showed a small amount starting material, and more BOC_2O (0.0448 g, 0.21 mmol) was added. The reaction mixture was refluxed for a further 24 h at which time the TLC showed a clean conversion. Evaporation of solvent followed by chromatography of the residue on silica gel afforded **11** (0.0373 g, 92% yield) as reddish orange solid: ^{1}H NMR ($CDCl_3$) δ 1.52 (s, 9 H), 1.92−2.60 (m, 1 H), 2.20−2.28 (m, 1 H), 2.97 (s, 3 H), 3.12−3.20 (m, 1 H), 3.28−3.39 (m, 1 H), 3.67 (s, 3 H), 3.76 (s, 3 H), 3.74−3.78 (m, 1 H), 6.88 (s, 1 H), 7.58 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 24.3, 28.5 (3 C), 38.1, 39.7, 47.0, 52.5, 63.1, 81.4, 103.2, 104.0, 130.5, 133.1, 143.3, 145.8, 152.6, 173.4; IR (neat) cm^{-1} 1737, 1537. MS *m*/*z* 395, 339, 280, 234, 57; HRMS *m*/*z* 395.16975, calcd for $C_{18}H_{25}N_3O_7$ 395.16925.

***N*-Methyl-7-BOC-amino-1,2,3,4-tetrahydro-6-methoxy-5-nitroquinoline-4-carboxaldehyde (12).** To a stirred solution of ester **11** (0.0358 g, 0.091 mmol) in dry toluene (3 mL) was added a precooled (−78 °C) solution of 1 M DIBAL in CH_2Cl_2 (0.54 mL, 0.54 mmol) in dry toluene (3 mL) via a cannula over 30 min. The resultant mixture was stirred at the same temperature for 3 h, and another batch of 1 M DIBAL in CH_2Cl_2 (0.27 mL, 0.27 mmol) was added over 10 min. After a further 30 min at −78 °C, the reaction mixture was quenched by careful addition of a −78 °C solution of MeOH (0.5 mL) in toluene (3 mL) over 30 min. A saturated aqueous solution of potassium sodium tartrate (15 mL) was added at −78 °C, and the resultant mixture was extracted with ether (4 × 15 mL). The combined organic extracts were washed with water and brine and dried. The residue after evaporation of solvent was chromatographed on silica gel and eluted with 1:3 ethyl

acetate−hexane to afford the aldehyde **12** (22.5 mg, 68% yield): ^{1}H NMR ($CDCl_3$) δ 1.53 (s, 9 H), 1.86−2.0 (m, 1 H), 2.39−2.47 (m, 1 H), 2.94 (s, 3 H), 3.13−3.18 (m, 2 H), 3.52−3.55 (m, 1 H), 3.79 (s, 3 H), 6.90 (s, 1 H), 7.60 (s, 1 H), 9.64 (d, J = 0.6 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 21.4, 28.5, 39.6, 45.3, 47.2, 63.2, 81.5, 102.4, 103.2, 130.5, 133.4, 143.9, 146.1, 152.6, 200.2; IR (neat) cm^{-1} 1731. MS *m*/*z* 365, 336, 309, 280, 236, 57; HRMS *m*/*z* 365.15876, calcd for $C_{17}H_{23}N_3O_6$ 365.15864.

Further elution with 1:2 ethyl acetate−hexane afforded the alcohol **13** (9.7 mg, 29.2% yield). The combined yield is 97%. **13**: ^{1}H NMR ($CDCl_3$) δ 1.52 (s, 9 H), 1.7−1.9 (m, 1 H), 2.1−2.23 (m, 1 H), 2.90−2.95 (m, 1 H), 2.95 (s, 3 H), 3.13−3.21 (m, 1 H), 3.37−3.43 (m, 1 H), 3.55−3.62 (m, 1 H), 3.71−3.78 (m, 1 H), 3.75 (s, 3 H), 6.83 (s, 1 H), 7.47 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 22.2, 28.4 (3 C), 34.7, 39.2, 46.0, 63.1, 64.5, 81.2, 102.3, 106.9, 129.6, 132.2, 143.1, 146.0, 152.6; IR (neat) cm^{-1} 3431, 1728, 1532; MS *m*/*z* 367, 311, 280, 57; HRMS *m*/*z* 367.174566, calcd for $C_{17}H_{25}N_3O_6$ 367.17430.

7-BOC-amino-8-methoxy-5-methyl-1,3,4,5-tetrahydropyrrolo[4,3,2-*de*]quinoline (14). A mixture of 10% Pd−C (3 mg) and the aldehyde **12** (22.5 mg, 0.06 mmol) in ethanol (3 mL) was stirred under an atmosphere of H_2 for 21 h. The mixture was filtered on a Celite mat and washed with ethyl acetate. The filtrate was evaporated, and the residue was purified by sgc to afford compound **14** (14.8 mg, 76% yield) as a slightly decomposing colorless oil, which was used for the next step as soon as possible: ^{1}H NMR (CD_3COCD_3) δ 1.50 (s, 9 H), 2.88 (s, 3 H), 2.97 (dt, J = 0.9, 6 Hz, 2 H), 3.20 (t, J = 6 Hz, 2 H), 3.83 (s, 3 H), 6.73 (t, J = 0.9 Hz, 1 H), 6.90 (s, 1 H), 7.27 (s, 1 H), 9.80 (s, 1 H); ^{13}C NMR (CD_3COCD_3) δ 24.1, 28.7, 38.5, 53.6, 60.7, 79.6, 93.8, 111.5, 116.1, 117.6, 127.1, 127.2, 129.0, 140.1 154.1; IR (neat) cm^{-1} 3421, 3356, 1700, 1539; MS *m*/*z* (EI) 317.2 (M^+), 261, 202; HRMS *m*/*z* 317.17346, calcd for $C_{17}H_{23}N_3O_3$ 317.17394.

Makaluvamine C (1). To a mixture of **14** (6 mg, 0.0189 mmol), NaI (11.3 mg, 0.0756 mmol), and dry CH_3CN (0.35 mL) under argon was added TMSCl (9.59 μL, 0.0756 mmol). The reaction mixture was stirred for 45 min resulting in a cloudy appearance. Monobasic phosphate buffer (0.5 mL, pH 7) was added at which time the reaction mixture turned to a clear yellow solution. To this solution was added Fremy's salt (11.1 mg, 0.0413 mmol) in one portion, and the resultant reddish orange mixture was stirred for 2 h. The reaction mixture was extracted with $CHCl_3$ (4 × 2 mL), and the organic layer was dried to yield makaluvamine C (2.8 mg, 73%): ^{1}H NMR (CD_3SOCD_3) δ 2.93 (t, J = 7.5 Hz, 2 H), 3.32 (s, 3 H), 3.91 (t, J = 7.5 Hz, 2 H), 5.64 (s, 1 H), 7.30 (d, J = 2.7 Hz, 1 H), 8.68 (br s, 1 H), 9.29 (br s, 1 H), 13.03 (br s, 1 H); ^{13}C NMR (CD_3SOCD_3) δ 18.9, 39.0, 52.7, 85.4, 118.1, 123.3, 123.4, 126.7, 155.8, 156.5, 167.5.

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Supporting Information Available: ^{1}H and ^{13}C NMR data for compounds which lack elemental analyses (14 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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