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Total Synthesis of Proposed Auranthine

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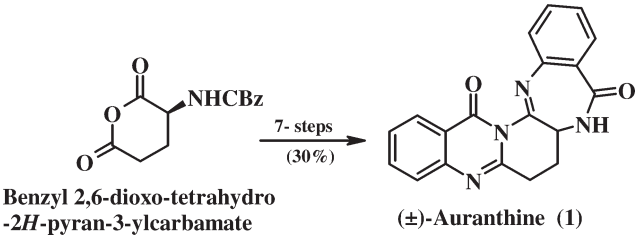

Starting from CBz-protected glutamic anhydride and Boc-protected *o*-aminobenzyl amine, the first total synthesis of proposed structure of auranthine has been reported. An intramolecular aza-Wittig reaction involving a lactam carbonyl group that delivered the diazepine core unit was the key step in the synthesis.

Quinazolinone is a building block for a large number of structurally diverse alkaloids boasting a wide range of biological activities, several of which are now in clinical use.[1] In the course of isolating nephrotoxins, a new fungal metabolite, (−)-auranthine, was isolated from *Penicillium aurantiogriseum* but the configuration at the asymmetric center was not determined.[2] Structurally, auranthine bears a close resemblance to the novel microbial metabolite (−)-asperlicin, a potent neuropeptide antagonist[3] (Figure 1). A look at the structure of auranthine reveals that (−)-glutamic acid and anthranilamide could be potential building blocks for constructing this structurally intriguing alkaloid. However, studies on the total synthesis of **1** by Bergman and coworkers indicate that the instability of the potential intermediate **2** and the presence of an active methylene group in the product were the major impediments in accessing it.[4]

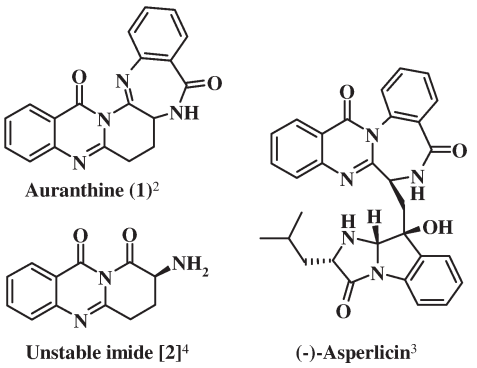

FIGURE 1. Auranthine, (−)-asperlicin, and unstable imide intermediate.

Auranthine is a structurally unique quinazoline alkaloid that contains an unusually positioned diazepine moiety, a feature that has largely rendered its total synthesis a challenge to date.[5] On the basis of our continuing interest in the chemistry of cyclic anhydrides and their applications in natural product synthesis,[6] we herein report a facile synthesis of the target compound (Scheme 1).

Starting the synthesis of auranthine (**1**) from CBz-protected (*S*)-glutamic anhydride **4**, we could foresee that our major challenges would lie in the following: (i) regioselective nucleophilic ring-opening of the unsymmetrical anhydride **4** with an aromatic amine, (ii) intramolecular cyclization reaction involving the lactam carbonyl using an aromatic amine/azide that would deliver the diazepine ring system, and (iii) the smooth pool of enantiomeric purity throughout the synthesis. As per the literature reports,[7] the nucleophilic regioselective ring-opening of an anhydride **4** in DMSO with the amine **3** exclusively furnished the expected anilic acid **5** in 92% yield. Carrying out the reaction in a polar solvent such as DMSO brings about intermolecular hydrogen bonding of the hydrogen atom on an amide nitrogen with the solvent, rather than the five-membered intramolecular hydrogen bonding with an adjacent carbonyl group of anhydride **4**. The incoming nucleophile, the primary aromatic amine, thus exclusively attacks on an unhindered carbonyl group of anhydride **4** to form the product **5**. Diazomethane esterification of anilic acid **5** provided the methyl ester **6** in 97% yield. Cleaving the Boc-protection in **6** resulted in instantaneous intramolcular dehydrative cyclization to **7**, which upon an

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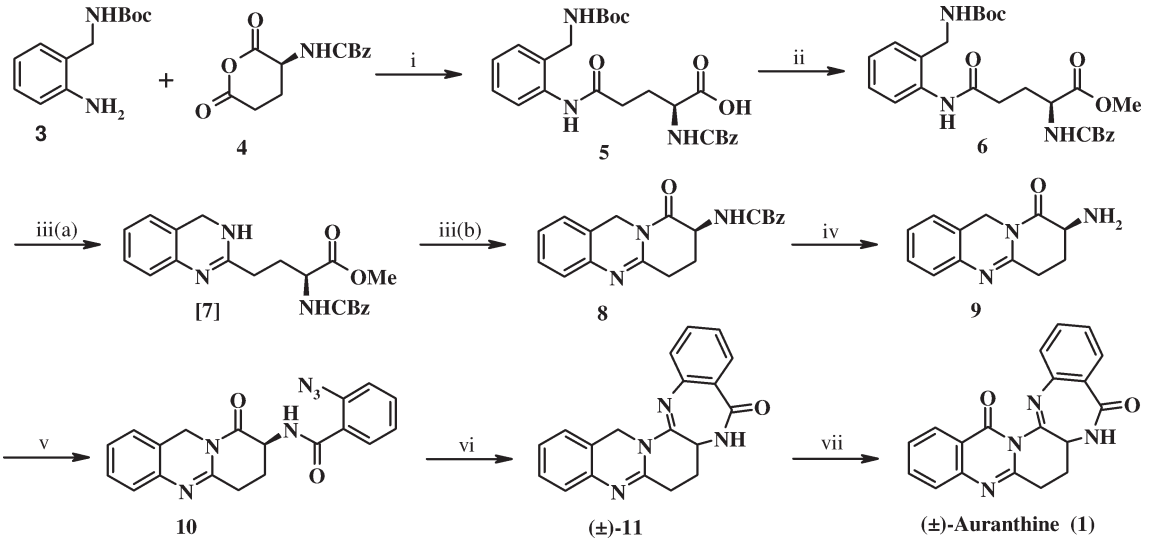
SCHEME 1. Synthesis of Proposed Auranthine via an Intramolecular Aza-Wittig Reaction with the Lactam Carbonyl Group[a]



[a]Reagents, conditions, and yields: (i) CH_3SOCH_3, 25 °C, 30 min (92%); (ii) CH_2N_2, Et_2O, 0 to 25 °C, 30 min (97%); (iii) (a) CF_3COOH, CH_2Cl_2, 25 °C, 8 h, (b) dry toluene, reflux, 8 h (78%); (iv) 30% HBr in AcOH, 25 °C, 2 h (82%); (v) *o*-azidobenzoic acid, *N*-ethyl-*N*′-(3-dimethylaminopropyl)carbodimide hydrochloride (EDCI), CH_2Cl_2, 25 °C, 18 h (89%); (vi) sealed tube, *n*-Bu_3P, dry *p*-xylene, 25 °C, 1 h, then 200 °C, 48 h (74%); (vii) $KMnO_4$, dry acetone, reflux, 3 h (79%).

immediate refluxing in toluene effected another intramolecular cyclization to afford the lactam **8** in 78% yield.[6a] Compound **8** on treatment with hydrobromic acid gave the amine **9**, which was used in the next step without further purification. The EDCI driven dehydrative coupling between the amine **9** and *o*-azidobenzoic acid provided the azido compound **10** in 89% yield. We reduced the azide group in compound **10** to the corresponding amine using catalytic hydrogenation and attempted an intramolecular dehydrative cyclization under a variety of reaction conditions including microwave irradiation, but all our attempts met with failure. At this stage, we decided to use the intramolecular aza-Wittig reaction for the transformation of azide **10** to the potential auranthine precursor **11**.[8−10] The intramolecular aza-Wittig reaction with triphenylphosphine in refluxing *p*-xylene, however, was not successful. Instead, using tributylphosphine-driven aza-Wittig reaction in refluxing *p*-xylene gave the required product **11**, but in only 4−5% yield, after 48 h. We were delighted to find that the same reaction in a sealed tube at 200 °C for 48 h regioselectively furnished the desired auranthine precursor **11** in 74% yield, however, unfortunately, with the nearly complete racemization (by specific rotation). The structure of aza-Wittig product **11** was unambiguously confirmed on the basis of X-ray crystallographic data. The higher reaction temperature and the longer reaction time were essential for the formation of compound **11** in an acceptable yield for two reasons, viz. (i) the stabilized nitrogen ylide formed is in conjugation with a suitably ortho-substituted amide carbonyl group and (ii) the nitrogen ylide has to react with the less reactive lactam carbonyl group to form the seven-membered cyclized product. Herein, in the conversion of **10** to **11**, the formation of a corresponding four-membered betaine-type intermediate must be a high-energy process. Hence, during the course of the reaction, the starting material and/or product suffer from a thermal racemization process.[11] Finally, the $KMnO_4$-induced[12] chemoselective oxidation of the benzylic methylene group of quinazolinopyridobenzodiazepine **11** to the corresponding carbonyl group, keeping the allylic methylene group intact, provided auranthine (**1**), in 79% yield. Starting from anhydride **4**, the overall yield of auranthine (**1**) in seven steps was 30%. The analytical and spectral data obtained for tetrahydroquinazolinopyridobenzodiazepindione **1** were in complete agreement with those of the assigned structure.[2] Finally, the structure of synthetic auranthine was unequivocally confirmed on the basis of X-ray crystallographic data. However, the ^{1}H NMR spectrum of synthetic **1** in benzene-d_6 was not in agreement with the ^{1}H NMR spectrum of natural product.[2] We were unable to obtain a ^{13}C NMR spectrum of the synthetic auranthine in benzene-d_6 for comparison due to solubility issues.[13] Hence what we have accomplished is the synthesis of the proposed structure of auranthine.

In summary, starting from a cyclic anhydride we have accomplished an efficient total synthesis of the proposed

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(9) To the best of our knowledge until today only one aza-Wittig reaction with an amide carbonyl group is reported to design the seven-membered diazepine nucleus, wherein in the starting material the lone pair on an amide nitrogen atom is in cross conjugation with an ortho-substituted ester unit.[10]

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(13) The solubility of synthetic auranthine in benzene-d_6 was very weak (< 1 mg/mL), hence we were unable to record the ^{13}C NMR spectrum of **1** even after overnight scanning.

structure of auranthine. The intramolecular aza-Wittig reaction involving a lactam carbonyl group is the key step in the present synthesis. We strongly believe that the present approach will be useful to design several desired bioactive natural and unnatural diazepine analogues and congeners.

Experimental Section

(*S*)-2-(Benzyloxycarbonylamino)-5-(2-((*tert*-butoxycarbonylamino)methyl)phenylamino)-5-oxopentanoic Acid (5). To a stirred solution of anhydride **4** (5.00 g, 19.01 mmol) in DMSO (25 mL) was added a solution of *tert*-butyl 2-aminobenzylcarbamate **3** (4.60 g, 22.91 mmol) in DMSO (10 mL) in a dropwise fashion over a period of 5 min and the resulting reaction mixture was further stirred at room temperature for 25 min. The reaction mixture was diluted with ethyl acetate (200 mL) and washed with brine, 1 N HCl, water, and again with brine and the organic layer was dried over Na_2SO_4. Concentration of the organic layer in vacuo followed by silica gel column chromatographic purification of residue with petroleum ether−ethyl acetate (3:7) as an eluent afforded the acid **5** as a white solid (8.49 g, 92%). Mp 93−95 °C; $[\alpha]^{25}_D$ +14.6 (*c* 0.90 $CHCl_3$); ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.39 (s, 9H), 2.19 (br s, 2H), 2.61 (br s, 2H), 4.20 (br d, J = 4 Hz, 2H), 4.39 (br d, J = 2 Hz, 1H), 4.68 (br s, 1H), 5.06 (s, 2H), 5.27 (br quintet, J = 4 Hz, 1H), 6.10 (br d, J = 4 Hz, 1H), 6.95−7.45 (m, 8H), 7.95 (br d, J = 6 Hz, 1H), 9.70 (br s, 1H); ^{1}H NMR (CD_3OD, 200 MHz) δ 1.41 (s, 9H), 2.03 (sextet, J = 8 Hz, 1H), 2.32 (sextet, J = 8 Hz, 1H), 2.58 (t, J = 8 Hz, 2H), 4.17 (s, 2H), 4.24 (dd, J = 8 and 4 Hz, 1H), 5.08 (s, 2H), 7.07−7.40 (m, 8H), 7.58 (d, J = 8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 28.3 (3 CH_3), 29.7 (CH_2), 33.1 (CH_2), 41.4 (CH_2), 53.9 (CH), 66.9 (CH_2), 80.7 (C), 123.6 (CH), 124.9 (CH), 127.8 (CH), 128.0 (2 CH), 128.4 (2 CH), 128.7 (CH), 129.7 (C), 130.2 (CH), 135.9 (C), 136.3 (C), 156.4 (C), 157.3 (C), 172.4 (C), 174.9 (C); ESIMS (*m*/*z*) 486 $[M + H]^+$, 508 $[M + Na]^+$, 524 $[M + K]^+$; IR (Nujol) ν_{max} 3330, 1691, 1660 cm^{-1}. Anal. Calcd for $C_{25}H_{31}N_3O_7$: C, 61.84; H, 6.44; N, 8.65. Found: C, 61.96; H, 6.44; N, 8.97.

(*S*)-Methyl 2-(Benzyloxycarbonylamino)-5-(2-((*tert*-butoxycarbonylamino)methyl)phenylamino)-5-oxopentanoate (6). An ether solution of diazomethane was added dropwise to a suspension of acid **5** (5.00 g, 10.30 mmol) in diethyl ether (50 mL) at 0 °C until the acid dissolved with persistence of light yellow color and the reaction mixture was stirred at room temperature for 30 min. The solvent was removed under reduced pressure and silica gel column chromatographic purification of the resulting residue with petroleum ether−ethyl acetate (6:4) as an eluent afforded the pure ester **6** as a white solid (4.99 g, 97%). Mp 71−73 °C; $[\alpha]^{25}_D$ +13.2 (*c* 1.64 $CHCl_3$); ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.41 (s, 9H), 2.00−2.40 (m, 2H), 2.58 (t, J = 8 Hz, 2H), 3.73 (s, 3H), 4.24 (br s, 2H), 4.44 (br q, J = 6 Hz, 1H), 5.09 (s, 2H), 5.15 (m, 1H), 5.85 (br d, J = 8 Hz, 1H), 7.04 (t, J = 8 Hz, 1H), 7.13 (dt, J = 8 and 2 Hz, 1H), 7.17−7.42 (m, 6H), 8.15 (d, J = 8 Hz, 1H), 9.54 (br s, 1H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 27.8 (CH_2), 28.2 (3 CH_3), 33.1 (CH_2), 41.5 (CH_2), 52.4 (CH_3), 53.7 (CH), 66.9 (CH_2), 80.6 (C), 122.6 (CH), 124.2 (CH), 128.0 (2 CH), 128.4 (2 CH), 128.70 (C), 128.73 (CH), 128.8 (CH), 130.3 (CH), 136.2 (C), 136.5 (C), 156.2 (C), 157.3 (C), 171.0 (C), 172.5 (C); ESIMS (*m*/*z*) 500 $[M + H]^+$, 522 $[M + Na]^+$, 538 $[M + K]^+$; IR ($CHCl_3$) ν_{max} 3330, 1715, 1683 cm^{-1}. Anal. Calcd for $C_{26}H_{33}N_3O_7$: C, 62.51; H, 6.66; N, 8.41. Found: C, 62.20; H, 6.96; N, 8.36.

(*S*)-Benzyl 9-Oxo-7,8,9,11-tetrahydro-6*H*-pyrido[2,1-*b*]quinazolin-8-ylcarbamate (8). To a stirred solution of ester **6** (4.00 g, 8.02 mmol) in dry DCM (50 mL) was added trifluoroacetic acid (5.95 mL, 10.00 mmol) and the reaction mixture was stirred at room temperature for 8 h. The reaction mixture was basified slowly with a saturated solution of $NaHCO_3$ and extracted with DCM (3 × 100 mL). The combined organic layer was washed with brine and dried over Na_2SO_4. The solvent was removed under reduced pressure, the resulting crude product was immediately dissolved in dry toluene (50 mL), and the reaction mixture was refluxed for 8 h under argon atmosphere. The reaction mixture was allowed to cool to room temperature and the solvent was removed in vacuo. Silica gel column chromatographic purification of the resulting residue with petroleum ether−ethyl acetate (1:1) as an eluent afforded the pure **8** as an off-white solid (2.18 g, 78%). Mp 145−147 °C; $[\alpha]^{25}_D$ −38.7 (*c* 0.82 $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.83 (dq, J = 8 and 4 Hz, 1H), 2.45−2.62 (br m, 1H), 2.87 (dt, J = 8 and 2 Hz, 1H), 2.97−3.05 (m, 1H), 4.25−4.40 (br m, 1H), 4.73 (d, J = 16 Hz, 1H), 5.05 (d, J = 16 Hz, 1H), 5.14 (s, 2H), 5.75 (br s, 1H), 7.05 (d, J = 8 Hz, 1H), 7.10−7.40 (m, 8H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 25.0 (CH_2), 30.1 (CH_2), 42.9 (CH_2), 53.0 (CH), 67.1 (CH_2), 121.6 (C), 125.5 (CH), 125.7 (CH), 126.9 (CH), 128.1 (2 CH), 128.2 (CH), 128.5 (2 CH), 128.7 (CH), 136.1 (C), 139.0 (C), 150.0 (C), 156.0 (C), 169.2 (C); ESIMS (*m*/*z*) 350 $[M + H]^+$, 372 $[M + Na]^+$; HRMS (EI) calcd for $C_{20}H_{19}N_3O_3$ 349.1426, found 349.1420; IR (Nujol) ν_{max} 3265, 1726, 1679 cm^{-1}. Anal. Calcd for $C_{20}H_{19}N_3O_3$: C, 68.75; H, 5.48; N, 12.03. Found: C, 68.46; H, 5.44; N, 11.70.

(*S*)-8-Amino-7,8-dihydro-6*H*-pyrido[2,1-*b*]quinazolin-9(11*H*)-one (9). Compound **8** (1.00 g, 2.87 mmol) was stirred in 30% HBr in AcOH (10 mL) at room temperature for 2 h. The reaction mixture was concentrated under reduced pressure and the resulting hydrobromide salt was neutralized with a saturated solution of $NaHCO_3$. The reaction mixture was extracted with DCM (3 × 100 mL) and the organic layer was washed with brine and dried over Na_2SO_4. Concentration of organic layer in vacuo afforded the amine **9** as an off-white solid (0.51 g, 82%). The amine **9** was immediately used for the next step without any purification. Mp 115−118 °C; $[\alpha]^{25}_D$ −27.1 (*c* 0.42 MeOH); ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.70−1.95 (m, 3H), 2.20−2.37 (m, 1H), 2.68−3.08 (m, 2H), 3.58 (dd, J = 12 and 4 Hz, 1H), 4.92 (q, J = 16 Hz, 2H), 7.00−7.32 (m, 4H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 26.7 (CH_2), 30.5 (CH_2), 42.7 (CH_2), 52.9 (CH), 121.8 (C), 125.4 (CH), 125.7 (CH), 126.7 (CH), 128.6 (CH), 139.0 (C), 151.2 (C), 173.3 (C); ESIMS (*m*/*z*) 216 $[M + H]^+$; HRMS (EI) calcd for $C_{12}H_{13}N_3O$ 215.1059, found 215.1073; IR (neat) ν_{max} 3447, 3358, 1690, 1665, 1620 cm^{-1}.

(*S*)-2-Azido-*N*-(9-oxo-7,8,9,11-tetrahydro-6*H*-pyrido[2,1-*b*]-quinazolin-8-yl)benzamide (10). To the stirred mixture of *o*-azidobenzoic acid (0.38 g, 2.32 mmol) and EDCI (0.54 g, 2.79 mmol) in DCM (20 mL) was added amine **9** (0.50 g, 2.32 mmol) in DCM (15 mL) and the reaction mixture was further stirred at room temperature for 18 h. The reaction mixture was diluted with DCM (100 mL) and washed with water, a saturated solution of $NaHCO_3$, and brine and dried over Na_2SO_4. The solvent was removed under reduced pressure and silica gel column chromatographic purification of the resulting residue with petroleum ether−ethyl acetate (3:7) as an eluent furnished the pure azide **10** as an off-white solid (0.76 g, 89%). Mp 177−178 °C; $[\alpha]^{25}_D$ +55.6 (*c* 0.50 $CHCl_3$); ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.70−2.10 (m, 1H), 2.65−2.80 (m, 1H), 2.85−3.18 (m, 2H), 4.76 (dd, J = 18 and 6 Hz, 1H), 4.80 (d, J = 16 Hz, 1H), 5.12 (d, J = 16 Hz, 1H), 7.04−7.34 (m, 6H), 7.55 (dt, J = 8 and 2 Hz, 1H), 8.20 (dd, J = 8 and 2 Hz, 1H), 8.53 (br d, J = 4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 24.7 (CH_2), 30.2 (CH_2), 42.9 (CH_2), 52.6 (CH), 118.5 (CH), 121.6 (C), 124.0 (C), 125.2 (CH), 125.5 (CH), 125.7 (CH), 126.9 (CH), 128.7 (CH), 132.3 (CH), 132.8 (CH), 137.5 (C), 139.0 (C), 150.3 (C), 164.5 (C), 169.6 (C); ESIMS (*m*/*z*) 383 $[M + Na]^+$; HRMS (EI) calcd for $C_{19}H_{16}N_6O_2$ 360.1335, found 360.1338; IR (Nujol) ν_{max} 3298, 2127, 1697, 1657, 1620 cm^{-1}.

6,7,7a,8-Tetrahydro-16*H*-quinazolino[3′,2′:1,6]pyrido[2,3-*b*]-[1,4]benzodiazepin-9-one (11). To a stirred mixture of compound **10** (0.40 g, 1.11 mmol) in dry *p*-xylene (5 mL) was added *n*-Bu_3P (0.33 mL, 1.33 mmol) at room temperature under argon atmosphere in a sealed tube and the stirring was

continued for 1 h. The reaction mixture was heated at 200 °C in a sealed tube for 48 h and then allowed to cool to room temperature. Precipitated product was filtered off and washed with *n*-hexane and then recrystalization from DCM afforded **11** as an off-white solid (0.26 g, 74%). Mp 273−275 °C; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.75−2.14 (m, 1H), 2.15−2.43 (m, 1H), 2.70−2.90 (m, 1H), 3.00−3.20 (m, 1H), 4.07 (q, J = 4 Hz, 1H), 4.88 (d, J = 18 Hz, 1H), 5.33 (d, J = 16 Hz, 1H), 7.08−7.33 (m, 6H), 7.55 (dt, J = 8 and 2 Hz, 1H), 7.99 (dd, J = 8 and 2 Hz, 1H), 8.70 (br d, J = 4 Hz, 1H); ^{1}H NMR (DMSO-d_6, 400 MHz) δ 1.95−2.05 (m, 1H), 2.14−2.26 (m, 1H), 2.58 (ddd, J = 16, 4, and 4 Hz, 1H), 2.90 (ddd, J = 12, 12, and 4 Hz, 1H), 4.03 (q, J = 4 Hz, 1H), 4.83 (d, J = 16 Hz, 1H), 5.19 (d, J = 16 Hz, 1H), 7.10 (d, J = 8 Hz, 1H), 7.13 (t, J = 8 Hz, 1H), 7.20−7.27 (m, 4H), 7.55 (dt, J = 8 and 2 Hz, 1H), 7.81 (d, J = 8 Hz, 1H), 8.68 (br d, J = 4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.8 (CH_2), 28.0 (CH_2), 44.1 (CH_2), 45.6 (CH), 122.7 (C), 124.2 (CH), 124.7 (CH), 126.0 (CH), 126.2 (CH), 126.6 (C), 126.9 (CH), 128.3 (CH), 130.0 (CH), 131.9 (CH), 139.8 (C), 145.5 (C), 151.8 (C), 156.0 (C), 168.4 (C); ESIMS (m/z) 317 $[M + H]^+$, 339 $[M + Na]^+$; HRMS (EI) calcd for $C_{19}H_{16}N_4O$ 316.1324, found 316.1315; IR (Nujol) ν_{max} 3435, 1661, 1636, 1612 cm^{-1}.

6,7,7a,8-Tetrahydroquinazolino[3′,2′:1,6]pyrido[2,3-*b*][1,4]benzodiazepin-9,16-dione (Auranthine, 1). To a stirred solution of compound **11** (64 mg, 0.20 mmol) in dry acetone (5 mL) was added $KMnO_4$ (64 mg, 0.40 mmol) and the reaction mixture was refluxed for 3 h under argon atmosphere. The reaction mixture was allowed to cool to room temperature and filtered off and the residue was washed with acetone. Concentration of filtrate in vacuo followed by silica gel column chromatographic purification of residue with dichloromethane−methanol (9:1) as an eluent furnished the final product aurnthine (**1**) (52 mg, 79%). Mp 188−189 °C (ethyl acetate); ^{1}H NMR (benzene-d_6, 500 MHz) δ 1.40−1.43 (m, 1H), 1.50−1.58 (m, 2H), 2.33−2.39 (m, 1H), 2.98−3.04 (m, 1H), 6.01 (br s, 1H), 6.95 (t, J = 10 Hz, 2H), 7.07−7.25 (m, 2H), 7.34 (d, J = 10 Hz, 1H), 7.61 (d, J = 10 Hz, 1H), 8.34 (d, J = 10 Hz, 1H), 8.39 (d, J = 10 Hz, 1H); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.00 (dq, J = 12 and 4 Hz, 1H), 2.59−2.68 (m, 1H), 2.73 (dt, J = 12, and 4 Hz, 1H), 3.16 (ddd, J = 16, 4, and 4 Hz, 1H), 4.11−4.19 (m, 1H), 7.19 (br d, J = 4 Hz, 1H), 7.38 (t, J = 8 Hz, 1H), 7.39 (d, J = 8 Hz, 1H), 7.50 (t, J = 8 Hz, 1H), 7.60 (dt, J = 8 and 4 Hz, 1H), 7.64 (d, J = 8 Hz, 1H), 7.79 (t, J = 8 Hz, 1H), 8.09 (d, J = 8 Hz, 1H), 8.33 (d, J = 8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 24.3 (CH_2), 30.2 (CH_2), 48.8 (CH), 122.0 (C), 126.0 (C), 126.89 (CH), 126.94 (CH), 127.46 (CH), 127.54 (CH), 128.2 (CH), 130.7 (CH), 132.5 (CH), 135.2 (CH), 143.4 (C), 145.6 (C), 151.2 (C), 152.9 (C), 159.6 (C), 168.6 (C); ESIMS (m/z) 331 $[M + H]^+$, 353 $[M + Na]^+$, 369 $[M + K]^+$; IR (Nujol) ν_{max} 3400, 1716, 1664, 1601 cm^{-1}. Anal. Calcd for $C_{19}H_{14}N_4O_2$: C, 69.08; H, 4.27; N, 16.96. Found: C, 69.02; H, 4.27; N, 16.87.

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Supporting Information Available: ^{1}H NMR, ^{13}C NMR, and DEPT spectra of compounds **1**, **5**, **6**, and **8**−**11**, ^{1}H NMR spectrum of natural auranthine, X-ray crystallographic data (CIF), and the ORTEP diagrams for compounds **11** and **1**. This material is available free of charge via the Internet at http://pubs.acs.org.