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Total Syntheses of (-)-Fumquinazolines A, B, and I

Supporting Material

General. NMR spectra were recorded in $CDCl_3$ at 400 MHz. Chemical shifts are reported in δ, coupling constants are reported in Hz, and IR data are reported in cm^{-1}.

***N*$_\alpha$-2,2,2-Trichloroethoxycabonyl-D-tryptophan Methyl Ester (15).** To a mixture of $NaHCO_3$ (0.84 g, 10 mmol) and 10% aqueous $NaHCO_3$ solution (10 mL) and ether (10 mL) at 0 ºC was added D-tryptophan methyl ester hydrochloride (2.55 g, 10 mmol) in several portions over 10 min. A solution of 2,2,2-trichloroethyl chloroformate (2.12 g, 10 mmol) in 10 mL of ether was then added dropwise over 1 h. The reaction mixture was stirred at rt for 4 h, and the ether layer was separated. The aqueous layer was extracted with ether (2 × 10 mL). The combined organic layers were washed with brine (20 mL), dried (Na_2SO_4), and concentrated. Flash chromatography of the residue on silica (ether) gave pure **15** (3.78 g, 96%) as a white foamy solid: mp 48-54 ºC; $[\alpha]_D$ -38.9 (*c* 0.36 in $CHCl_3$); ^{1}H NMR 8.10 (br s, 1, NH), 7.55 (d, 1, *J* = 8.0), 7.36 (d, 1, *J* = 8.0), 7.20 (dd, 1, *J* = 8.0, 7.3), 7.13 (dd, 1, *J* = 8.0 7.3), 7.10 (d, 1, *J* = 2.4); 5.56 (br d, 1, *J* = 7.9, NH), 4.80 (d, 1, *J* = 12.2), 4.75 (dt, 1, *J* = 7.9, 5.5), 4.65 (d, 1, *J* = 12.2), 3.70 (s, 3), 3.35 (d, 2, *J* = 5.5); ^{13}C NMR 171.8, 153.9, 136.1, 127.4, 122.9, 122.3, 119.8, 118.6, 111.2, 109.6, 95.4, 74.6, 54.7, 52.5, 27.9; IR (KBr) 3405 (br, NH), 1735, 1726, 1528.

***N*$_{in}$-L-Cbz-Alanyl-*N*$_\alpha$-2,2,2-Trichloroethoxycabonyl-D-tryptophan Methyl Ester (16a).** BH_3•THF in THF (1 M, 17 mmol) was added dropwise to a solution of indole **15** (3.33 g, 8.4 mmol) in trifluoroacetic acid (17 mL) at 0 ºC under N_2. The resulting mixture was stirred at 0 ºC for 1 h and concentrated under reduced pressure. The residue was dissolved in EtOAc (50 mL), which was washed with saturated $NaHCO_3$ (100 mL), dried (Na_2SO_4) and evaporated to give the foamy indoline (2.99 g, 90%).

DCC (1.57 g, 7.6 mmol) was added to a solution of *N*-Cbz-L-alanine (1.70 g, 7.6 mmol) in CH_2Cl_2 (20 mL). The mixture was stirred at rt for 5 min, and a solution of crude indoline in CH_2Cl_2 (5 mL) was added. The resulting mixture was stirred at rt for 20 min. The insoluble

byproduct was filtered off and the filtrate was evaporated at reduced pressure to give the amide as a colorless oil. The oil was dissolved in toluene (25 mL) and DDQ (1.36 g, 6.0 mmol) was added. The resulting black-red mixture was heated at 110 ºC for 1 h, and additional DDQ (0.68 g, 3.0 mmol) was added. The mixture was stirred at 110 ºC for 1 h and cooled and filtered. The filtrate was washed with saturated $NaHCO_3$ solution (2 × 30 mL), dried (Na_2SO_4), and evaporated to give a black-red oil. Flash chromatography on silica gel (50:1 CH_2Cl_2/EtOAc) gave **16a** (3.53 g, 78%) as a foamy solid: mp 63-67 ºC; $[\alpha]_D$ -54.0 (*c* 0.53 in $CHCl_3$); ^{1}H NMR 8.43 (d, 1, *J* = 8.0), 7.52 (d, 1, *J* = 8.0), 7.43-7.32 (m, 7), 7.32 (td, 1, *J* = 8.0, 1.0), 5.70 (br d, 1, *J* = 7.4, NH), 5.65 (br d, 1, *J* = 7.9, NH), 5.16 (d, 1, *J* = 12.2), 5.12 (d, 1, *J* = 12.2), 5.12 (q, 1, *J* = 6.7), 4.80 (d, 1, *J* = 12.2), 4.79-4.72 (m, 1), 4.67 (d, 1, *J* = 12.2), 3.74 (s, 3), 3.33 (dd, 1, *J* = 15.3, 6.1), 3.26 (dd, 1, *J* = 15.3, 5.5), 1.55 (d, 3, *J* = 6.7); ^{13}C NMR 171.3, 170.9, 155.5, 153.8, 136.1, 136.0, 130.4, 128.5 (2 C), 128.2 (2 C), 128.1, 125.9, 124.3, 122.4, 118.8, 117.8, 116.9, 95.2, 74.6, 67.1, 53.9, 52.8, 49.4, 27.9, 19.6; IR (KBr) 3347 (br, NH), 1720, 1701, 1528.

***N*$_{in}$-L-Cbz-Leucyl-*N*$_{\alpha}$-2,2,2-Trichloroethoxycarbonyl-D-tryptophan Methyl Ester (16b).** Reduction of indole **15** (3.33 g, 8.4 mmol) as described above gave the foamy solid indoline (2.93 g, 92%).

DCC (1.55 g, 7.5 mmol) was added to a solution of *N*-Cbz-L-leucine (1.99 g, 7.5 mmol) in CH_2Cl_2 (20 mL). The mixture was stirred at rt for 5 min, and a solution of crude indoline in CH_2Cl_2 (5 mL) was added. The resulting mixture was stirred at rt for 20 min. The insoluble byproduct was filtered off and the filtrate was evaporated at reduced pressure to give the amide as a colorless oil. The oil was dissolved in toluene (25 mL) and DDQ (1.36 g, 6.0 mmol) was added. The resulting black-red mixture was heated at 110 ºC for 1 h, and additional DDQ (0.68 g, 3.0 mmol) was added. The mixture was stirred at 110 ºC for 1 h and cooled and filtered. The filtrate was washed with saturated $NaHCO_3$ solution (2 × 30 mL), dried (Na_2SO_4) and evaporated to give a black-red oil. Flash chromatography on silica gel (50:1 CH_2Cl_2/EtOAc) gave **16b** (3.64 g, 77%) as a foamy solid: mp 63-66 ºC; $[\alpha]_D$ -52.0 (*c* 0.22 in $CHCl_3$); ^{1}H NMR 8.43 (d, 1, *J* = 8.0), 7.53 (d, 1, *J* = 8.0), 7.43 (s, 1), 7.41-7.28 (m, 7), 5.66 (br d, 1, *J* = 7.9, NH),

5.48 (br d, 1, *J* = 9.2, NH), 5.15 (d, 1, *J* = 12.2), 5.13 (m, 1), 5.10 (d, 1, *J* = 12.2), 4.80 (m, 1), 4.74 (br s, 2), 3.74 (s, 3), 3.33 (dd, 1, *J* = 15.1, 6.3), 3.28 (dd, 1, *J* = 15.1, 5.5), 1.80 (m, 1), 1.69 (m, 2), 1.08 (d, 3, *J* = 6.7), 0.94 (d, 3, *J* = 6.7); ^{13}C NMR 171.3, 171.2, 156.1, 153.9, 136.03, 135.95, 130.4, 128.5 (2 C), 128.2, 128.0 (2 C), 125.8, 124.2, 122.5, 118.8, 117.7, 116.9, 95.2, 74.6, 67.2, 54.0, 52.7, 52.0, 42.5, 27.8, 24.8, 23.1, 21.8; IR (KBr) 3336 (br, NH), 2956, 1720, 1702, 1522.

***N*$_{in}$-L-Cbz-Alanyl-2-*N*$_{\alpha}$-2,2,2-Trichloroethoxycabonyl-2-iodo-D-tryptophan Methyl Ester (17a).** To a solution of **16a** (1.20 g, 2.0 mmol) in dry CH_2Cl_2 (15 mL) was added $Hg(OTFA)_2$ (1.10 g, 2.6 mmol). The solution was stirred at rt for 20 min, washed with aqueous saturated KI solution (3 × 10 mL), dried (Na_2SO_4), filtered, and treated with iodine (760 mg, 3.0 mmol) in one portion. The resulting mixture was stirred at rt for 3 h. The red precipitate was filtered off and the filtrate was washed with aqueous $Na_2S_2O_3$ (3 M, 30 mL), dried (Na_2SO_4) and evaporated to give a yellow oil. Flash chromatography on silica gel (100:1 CH_2Cl_2/EtOAc) gave recovered **16a** (115 mg, 10%) preceded by iodide **17a** (1.23 g, 85%) as a light yellow solid: mp 67-70 ºC; $[\alpha]_D$ -18.5 (*c* 0.45 in $CHCl_3$); ^{1}H NMR 8.01 (d, 1, *J* =7.9), 7.59 (dd, 1, *J* = 7.9, 1.0), 7.40-7.25 (m, 7), 5.85 (dq, 1, *J* = 7.9, 6.7), 5.70 (br d, 1, *J* = 7.9, NH), 5.68 (br d, 1, *J* = 6.7, NH), 5.18 (d, 1, *J* = 12.2), 5.14 (d, 1, *J* = 12.2), 4.75 (q, 1, *J* = 6.7), 4.71 (d, 1, *J* = 11.6), 4.64 (d, 1, *J* = 11.6), 3.64 (s, 3), 3.33 (dd, 1, *J* = 14.4, 6.7), 3.26 (dd, 1, *J* = 14.4, 6.7), 1.40 (d, 3, *J* = 6.7); ^{13}C NMR 174.1, 171.3, 155.7, 153.7, 138.3, 136.1, 129.6, 128.6 (2 C), 128.2 (2 C), 128.1, 126.2, 125.4, 123.6, 118.5, 114.3, 95.2, 79.6, 74.6, 67.1, 53.7, 52.9, 52.4, 31.36, 19.0; IR (KBr) 3358 (br, NH), 1725, 1528.

***N*$_{in}$-L-Cbz-Leucyl-2-*N*$_{\alpha}$-2,2,2-Trichloroethoxycabonyl-2-iodo-D-tryptophan Methyl Ester (17b).** To a solution of **16b** (1.92 g, 3.0 mmol) in dry CH_2Cl_2 (20 mL) was added $Hg(OTFA)_2$ (1.67 g, 3.9 mmol). The solution was stirred at rt for 20 min, washed with aqueous saturated KI solution (3 × 10 mL), dried (Na_2SO_4), filtered and treated with iodine (1.27 g, 5.0 mmol) in one portion. The resulting mixture was stirred at rt for 3 h. The red precipitate was filtered off and the filtrate was washed with aqueous $Na_2S_2O_3$ (3 M, 30 mL), dried (Na_2SO_4) and

evaporated to give a yellow oil. Flash chromatography on silica gel (100:1 CH_2Cl_2/EtOAc) gave recovered **16b** (192 mg, 10%) preceded by iodide **17b** (1.95 g, 85%) as a light yellow solid: mp 64-69 ºC; $[\alpha]_D$ -13.2 (*c* 0.20 in $CHCl_3$); ^{1}H NMR 8.05 (d, 1, *J* = 7.9), 7.57 (d, 1, *J* = 7.9), 7.40-7.22 (m, 7), 5.87 (m, 1), 5.79 (br d, 1, *J* = 8.5, NH), 5.64 (br d, 1, *J* = 9.2, NH), 5.18 (d, 1, *J* = 12.2), 5.15 (d, 1, *J* = 12.2), 4.76 (m, 1), 4.71 (d, 1, *J* = 11.6), 4.65 (d, 1, *J* = 11.6), 3.66 (s, 3), 3.33 (dd, 1, *J* = 14.4, 6.7), 3.26 (dd, 1, *J* = 14.4, 6.7), 1.79-1.65 (m, 1), 1.57-1.47 (m, 1), 1.47-1.37 (m, 1), 0.94 (d, 3, *J* = 6.7), 0.81 (d, 3, *J* = 6.7); ^{13}C NMR 174.7, 171.3, 156.2, 153.7, 138.2, 136.0, 129.5, 128.5 (2 C), 128.2, 128.0 (2 C), 125.8, 125.2, 123.4, 118.4, 113.9, 95.1, 79.7, 74.5, 67.1, 55.3, 53.6, 52.8, 42.1, 31.2, 24.9, 22.9, 21.6; IR (KBr) 3365 (br, NH), 2957, 1720, 1522.

Methyl (αR, 2S)-2,3-Dihydro-2-methyl-3-oxo-1-[(phenylmethoxy)carbonyl]-α-[[(2,2,2-trichloroethoxy)carbonyl]amino]-1*H*-imidazo(1, 2-*a*)indole-9-propanoate (14a). To a solution of **17a** (725 mg, 1.0 mmol) in dry toluene (5 mL) was added $Pd_2(dba)_3$ (46 mg, 0.05mmol, 0.05 eq), P(*o*-tolyl)$_3$ (61 mg, 0.2 mmol, 0.2 eq) and finely ground anhydrous K_2CO_3 (414 mg, 3.0 mmol, 3 eq). The mixture was vigorously stirred and heated under N_2 at 105 ^{o}C for 1 h. Additional $Pd_2(dba)_3$ (46 mg, 0.05mmol, 0.05 eq) and P(*o*-tolyl)$_3$ (61 mg, 0.2 mmol, 0.2 eq) were added and the mixture was heated at 105 ^{o}C for an additional h. The solution was cooled and filtered, and the filtrate was evaporated at reduced pressure to give a red oil. Flash chromatography on silica gel (CH_2Cl_2) gave the deiodinated indole **16a** (80 mg, 11%) preceded by **14a** (382 mg, 64%) as a light yellow solid: mp 53-57 ºC; $[\alpha]_D$ -20.4 (*c* 0.42 in $CHCl_3$); ^{1}H NMR 7.89 (d, 1, *J* = 8.0), 7.52 (d, 1, *J* = 8.0), 7.37-7.46 (m, 5), 7.33 (td, 1, *J* = 8.0, 1.0), 7.27 (td, 1, *J* = 8.0, 1.0), 5.38 (d, 1, *J* = 12.8), 5.33 (d, 1, *J* = 12.8), 4.77 (q, 1, *J* = 6.7), 4.70 (d, 1, *J* = 12.2), 4.57 (d, 1, *J* = 12.2), 4.69–4.43 (m, 1), 3.80-3.59 (m, 1), 3.70 (s, 3), 3.43-3.26 (m, 1), 1.67 (d, 3, *J* = 6.7); ^{13}C NMR 171.9, 165.6, 154.1, 151.3, 136.4, 134.7, 129.0 (2 C), 128.9 (2 C), 128.6, 126.9, 125.1, 123.7, 118.6, 118.5, 113.2, 95.40, 95.37, 74.5, 69.0, 62.6, 54.3, 52.4, 26.4, 17.4; IR (KBr) 3352, 2952, 1730 (br), 1630, 1513. Anal. Calcd for $C_{26}H_{24}Cl_3N_3O_7$: C, 52.32; H, 4.05; N, 7.04. Found: C, 51.81; H, 3.90; N, 6.79.

Methyl (αR, 2S)-2,3-Dihydro-2-(2-methylpropyl)-3-oxo-1-[(phenylmethoxy)carbonyl]-α-[[(2,2,2-trichloroethoxy)carbonyl]amino]-1*H*-imidazo(1, 2-*a*)indole-9-propanoate (14b). To a solution of **17b** (767 mg, 1.0 mmol) in dry toluene (5 mL) was added $Pd_2(dba)_3$ (46 mg, 0.05 mmol, 0.05 eq), P(*o*-tolyl)$_3$ (61 mg, 0.2 mmol, 0.2 eq) and finely ground anhydrous K_2CO_3 (414 mg, 3.0 mmol, 3 eq). The mixture was vigorously stirred and heated under N_2 at 105 ºC for 1 h. Additional $Pd_2(dba)_3$ (46 mg, 0.05 mmol, 0.05 eq) and P(*o*-tolyl)$_3$ (61 mg, 0.2 mmol, 0.2 eq) were added and the mixture was heated at 105 ºC for an additional h. The solution was cooled and filtered, and the filtrate was evaporated at reduced pressure to give a deep-red oil. Flash chromatography on silica gel (3:1 CH_2Cl_2/hexane) gave deiodinated indole **16b** (130 mg, 17%) preceded by **14b** (428 mg, 67%) as a light yellow solid: mp 57-60 ºC; $[\alpha]_D$ -9.7 (*c* 0.20 in $CHCl_3$); ^{1}H NMR 7.89 (d, 1, *J* = 8.0), 7.52 (d, 1, *J* = 8.0), 7.46-7.37 (m, 5), 7.32 (t, 1, *J* = 8.0), 7.26 (t, 1, *J* = 8.0), 6.17 (br, 1, NH), 5.40 (d, 1, *J* = 12.8), 5.29 (d, 1, *J* = 12.8), 4.75 (m, 1), 4.63 (s, 2), 4.52 (qd, 1, *J* = 6.7, 4.3), 3.75-3.59 (m, 1), 3.70 (s, 3), 3.36-3.26 (m, 1), 2.01-1.82 (m, 3), 0.82 (d, 3, *J* = 6.7), 0.80 (d, 3, *J* = 6.7); ^{13}C NMR 171.9, 165.4, 154.2, 151.4, 136.7, 134.7, 135.5, 129.0 , 128.9 (2 C), 128.8 (2 C), 126.9, 125.0, 123.6, 118.5, 113.2, 95.3 (2 C), 74.5, 69.1, 62.6, 54.4, 52.4, 39.9, 26.3, 23.9, 23.3, 21.9; IR (KBr) 3354, 2957, 1735 (br), 1630, 1601, 1522. Anal. Calcd for $C_{29}H_{30}Cl_3N_3O_7$: C, 54.52; H, 4.73; N, 6.58. Found: C, 54.66; H, 4.63, N, 6.37.

Methyl (αR,2S,9S)]- and (αR,2S,9R)]-2,3,9,9a-Tetrahydro-9-hydroxy-9a-methoxy-2-methyl-3-oxo-1-[(phenylmethoxy)carbonyl]-α-[[(2,2,2-trichloroethoxy)carbonyl]amino]-1*H*-imidazo(1, 2-*a*)indole-9-propanoate (18a and 19a). To a solution of **14a** (382 mg, 0.64 mmol) in 4:1 MeOH/CH_2Cl_2 (5 mL) was added 7b-butyl-7b*H*-oxazirino[2,3-b][1,2]benzisothiazole 3,3-dioxide (230 mg, 0.96 mmol, 1.5 eq). The resulting mixture was stirred at rt for 12 h. After removal of the solvent under reduced pressure, the mixture was purified by flash chromatography on silica gel (30:1 CH_2Cl_2/EtOAc) to give **19a** (95 mg, 23%) as a white solid followed by **18a** (268mg, 65%) as a white solid.

Data for **18a**: mp 81-84 ºC; ^{1}H NMR 7.51 (d, 1, *J* = 7.9), 7.49-7.35 (m, 6), 7.34 (t, 1, *J* = 7.9), 7.25-7.17 (m, 1), 5.88-5.79 (br, 1, NH), 5.39-5.15 (m, 2), 4.73 (d, 1, *J* = 12.2), 4.78-4.61 (m, 1), 4.67 (d, 1, *J* = 12.2), 4.53 (q, 1, *J* = 6.7), 3.62-3.48 (br, 3), 3.21-3.07 (br, 3), 2.52-2.32 (br, 1), 2.00-1.86 (br, 1), 1.67-1.56 (br, 3); ^{13}C NMR 171.7, 166.6 (br), 153.8, 152.8 (br), 137.0 (br), 135.0, 133.6, 129.7, 128.7 (3 C), 128.5 (2 C), 126.2, 125.4 , 116.5, 95.2, 81.3 (br), 74.6, 68.6, 60.7 (br), 52.4, 51.1, 49.4, 37.8, 17.6, 16.7; IR (KBr) 3346, 1728, 1610, 1485.

Data for **19a**: mp 79-85 ºC; ^{1}H NMR 7.7.53-7.31 (m, 8), 7.26-7.19 (m, 1), 6.53 (br, 1, NH), 5.75 (br, 1), 5.31 (d, 1, *J* = 12.8), 5.26 (d, 1, *J* = 12.8), 4.81 (br s, 2), 4.53 (m, 1), 3.97 (m, 1), 3.64 (s), 3.60 (s), 3.31 (br s, 3), 1.77 (br, d, *J* = 6.7), 1.72 (br d, *J* = 6.7); IR (KBr) 3453, 1735, 1510.

Tetracyclic Lactone 20a. To 2 mL of acetic acid in an ice water bath was added $NaBH_4$ (470 mg, 12.4 mmol) in several portions. The $NaBH_4$ solution in acetic acid was warmed to 25 ºC and added to a solution of **18a** (260 mg, 0.41 mmol) in acetic acid (2 mL). The resulting mixture was stirred at 25 ºC for 3 h. The reaction mixture was diluted with CH_2Cl_2 (15 mL) and washed with water (3 × 10 mL), saturated $NaHCO_3$ solution and brine, dried (Na_2SO_4) and evaporated to give a crude mixture of hydroxy ester and lactone **20a** (233 mg). Silica gel (EM 9385, silica gel 60, 230-400 mesh, 3.0 g) was added to a solution of this mixture in CH_2Cl_2 (5 mL). The suspension was stirred at rt for 12 h and filtered. The filtrate was evaporated under reduced pressure to give a residue that was purified by flash chromatography on silica gel (50:1 CH_2Cl_2/EtOAc) to give **20a** (158 mg, 66%) as a white solid: mp 113-115 ºC; $[\alpha]_D$ +18.4 (*c* 0.54 in $CHCl_3$); ^{1}H NMR (1:1 mixture of rotamers) 7.60 (d, 1, *J* = 7.9), 5.55-7.35 (m, 6), 7.34-7.22 (m, 2), 5.96 (br s, 1), 5.69 (br, 1, NH), 5.44-5.16 (br, 2), 5.10-4.18 (m, 4), 2.74-2.05 (m, 2), 1.55 (br d, 3, *J* = 6.7); ^{13}C NMR (two rotamers, most peaks are broad, partial) 169.3, 156.0, 154.5, 131.5 (sharp), 130.1, 129.2 (sharp), 128.6 (sharp), 127.2 (sharp), 124.2, 117.1, 95.3, 84.2, 82.2, 75.2, (sharp) 69.2, 68.4, 59.4, 50.2, 36.2, 18.6, 18.3 (two quaternary carbons were not observed); IR (KBr) 3397 (br), 1800, 1734, 1608, 1521. Anal. Calcd for $C_{25}H_{22}Cl_3N_3O_7$: C, 51.52; H, 3.80; N, 7.21. Found: C, 51.53; H, 3.73, N, 7.03.

Tetracyclic Lactone 21a. To 1 mL of acetic acid in an ice water bath was added $NaBH_4$ (120 mg, 3.0 mmol) in several portions. The $NaBH_4$ solution in acetic acid was warmed to 25 ºC and added to a solution of **19a** (64 mg, 0.10 mmol) in acetic acid (1 mL). The resulting mixture was stirred at 25 ºC for 3 h. The reaction mixture was diluted with CH_2Cl_2 (10 mL) and washed with water (3×10 mL), saturated $NaHCO_3$ solution and brine, dried (Na_2SO_4) and evaporated to give crude hydroxy ester (58 mg). To a solution of this mixture in CH_2Cl_2 (2 mL) was added silica gel (EM 9385, silica gel 60, 230-400 mesh, 800 mg). The suspension was stirred at rt for 24 h. The silica gel was filtered off and the filtrate was evaporated under reduced pressure to give a residue, which was purified by flash chromatography on silica gel (50:1 CH_2Cl_2/EtOAc) to give **21a** (41 mg, 70%) as a white solid: mp 172-175 ºC; $[\alpha]_D$ +67.4 (*c* 0.52 in $CHCl_3$); ^{1}H NMR (5:1 mixture of rotamers) 7.77 (d, 1, *J* = 8.0), 7.51 (d, 1, *J* = 8.0), 7.46-7.35 (m, 5), 7.28 (t, 2, *J* = 8.0), 5.95 (s, 1), 5.66 (br d, 1, *J* = 6.7, NH), 5.26 (d, 1, *J* = 12.2), 5.21 (d, 1, *J* = 12.2), 4.80 (d, 1, *J* = 12.2), 4.71 (d, 1, *J* =12.2), 4.45 (q, 1, *J* = 6.7), 4.52-4.02 (m, 1), 2.81 (dd, 1, *J* = 13.7, 10.8), 2.26 (dd, 1, *J* = 13.7, 9.0), 1.63 (br d, 3, *J* = 6.7); ^{1}H NMR (minor rotamer, partial) 7.68 (d, 1, *J* = 7.9), 7.47 (d, 1, *J* = 7.9), 5.91 (s, 1), 5.60 (br d, 1, *J* = 6.1, NH), 5.30 (d, 1, *J* = 12.2), 5.16 (d, 1, *J* = 12.2), 4.61 (br, 1), 4.51-4.42 (br, 1), 3.93-3.81 (m, 1), 3.00-2.86 (m,1), 2.39-2.28 (m, 1), 1.59 (br d, 3, *J* = 6.7); ^{13}C NMR (major rotamer) 173.5, 169.1, 154.4, 153.8, 136.0, 135.7, 135.4, 130.8, 128.8 (2 C), 128.6, 128.4 (2 C), 127.3, 125.6, 116.2, 95.0, 89.5, 83.3, 74.8, 68.5, 59.7, 51.7, 35.1, 11.0; ^{13}C NMR (minor rotamer, partial) 129.6, 129.0, 125.1, 116.6, 89.9, 60.2, 51.3, 34.8, 16.6; IR (KBr) 3344, 1796, 1727, 1710, 1678, 1606, 1529.

Tetracyclic Lactone 21b. To a solution of **14b** (956 mg, 1.50 mmol) in 4:1 MeOH/CH_2Cl_2 (5 mL) was added dimethyldioxirane (0.1 M in acetone, 15 mL, 15 mmol) at -78 ºC. The resulting mixture was stirred at -78 ºC for 5 min. After removal of the solvent under reduced pressure, the mixture was purified by flash chromatography on silica gel (50:1 CH_2Cl_2/EtOAc) to give **18b** (391 mg, 38%) as a white solid followed by **19b** (566 mg, 55%) as a white solid.

To 5 mL of acetic acid in an ice water bath was added $NaBH_4$ (460 mg, 24 mmol) in several portions. The $NaBH_4$ solution in acetic acid was warmed to 25 ºC and added to a solution of **19b** (566 mg, 0.82 mmol) in acetic acid (5 mL). The resulting mixture was stirred at 25 ºC for 3 h, then diluted with CH_2Cl_2 (15 mL) and washed with water (3 × 10 mL), saturated $NaHCO_3$ solution and brine, dried (Na_2SO_4) and evaporated to give a crude mixture of hydroxy ester and **21b**. Flash chromatography on silica (100:1 CH_2Cl_2/EtOAc) gave by **19b** (45 mg, 9%) as a white solid followed by hydroxy ester (408 mg, 76%) as a white solid: mp 79-81 ºC; $[\alpha]_D$ +78.4 (*c* 0.22 in $CHCl_3$); ^{1}H NMR (6:1 mixture of rotamers, major rotamer), 7.52 (d, 1, *J* = 8.0), 7.46 (d, 1, *J* = 8.0), 7.43-7.35 (m, 6), 7.23 (t, 1, *J* = 8.0), 6.43 (br d, 1, *J* = 4.9, NH), 5.70 (s, 1), 5.34 (d, 1, *J* = 12.2), 5.20 (d, 1, *J* = 12.2), 4.81 (d, 1, *J* = 12.2), 4.74 (d, 1, *J* = 12.2), 4.47 (m, 1), 4.47 (s, 1, OH), 4.47-4.42 (m, 1), 3.66 (s, 3), 1.99-1.78 (m, 5), 0.92 (d, 3, *J* = 6.7), 0.85 (d, 3, *J* = 6.7); ^{1}H NMR (minor rotamer, partial), 7.59 (d, 1, *J* = 8.0), 6.27 (br, 1, NH), 5.66 (s, 1), 5.61 (d, 1, *J* = 11.6), 4.99 (d, 1, *J* = 11.6), 4.54 (m, 1), 3.63 (s, 3), 1.05 (d, 3, *J* = 6.7), 0.99 (d, 1, *J* = 6.7); ^{13}C NMR (major rotamer), 171.9, 167.0, 155.1, 154.0, 135.4, 134.9, 134.6, 130.3, 128.9, 128.8 (2 C), 128.6 (2 C), 126.6, 125.3, 117.0, 95.5, 86.6, 81.7, 74.6, 68.7, 62.8, 52.5, 51.1, 40.0, 34.3, 24.1, 23.5, 22.1; ^{13}C NMR (minor rotamer, partial) 131.3, 129.7,129.6, 38.8; IR (KBr) 3386, 2958, 1734 (br), 1609, 1560, 1508.

To a solution of hydroxy ester (328 mg, 0.50 mmol) in CH_2Cl_2 (10 mL) was added silica gel (EM 9385, silica gel 60, 230-400 mesh, 3.5 g). The suspension was stirred at rt for 5 d. The silica gel was filtered off and the filtrate was evaporated under reduced pressure to give a residue, which was purified by flash chromatography on silica gel (50:1 CH_2Cl_2/EtOAc) to give recovered hydroxy ester (55 mg, 17%), which could be recycled, preceded by **21b** (223 mg, 71%) as a white solid: mp 237-238 ºC; $[\alpha]_D$ +79.8 (*c* 0.24 in $CHCl_3$); ^{1}H NMR (5:1 mixture of rotamers, major rotamer) 7.75 (d, 1, *J* = 8.0), 7.49 (d, 1, *J* = 8.0), 7.42-7.33 (m, 5), 7.25 (t, 2, *J* = 8.0), 5.91 (s, 1), 5.56 (br d, 1, *J* = 6.7, NH), 5.26 (d, 1, *J* = 12.2), 5.15 (d, 1, *J* = 12.2), 4.77 (d, 1, *J* = 12.2), 4.68 (d, 1, *J* =12.2), 4.40 (m, 1), 4.10 (m, 1), 2.79 (dd, 1, *J* = 14.0, 10.4), 2.23 (dd, 1, *J* = 14.0, 9.4), 1.95-1.72 (m, 3), 0.90 (br d, 3, *J* = 6.7), 0.83 (d, 1, *J* = 6.7); ^{1}H NMR (minor

rotamer, partial) 7.67 (d, 1, *J* = 7.9), 7.45 (d, 1, *J* = 7.9), 5.51 (br d, 1, *J* = 6.1, NH), 5.30 (d, 1, *J* = 12.2), 5.10 (d, 1, *J* = 12.2), 4.47 (m, 1), 3.90-3.79 (m, 1), 2.90-2.78 (m,1), 2.36-2.27 (m, 1), 2.10-1.93 (m, 3), 0.96 (br d, 3, *J* = 6.7); ^{13}C NMR (major rotamer) 173.5, 168.8, 154.2, 153.8, 136.0, 135.7, 135.4, 130.8, 128.8 (3 C),128.7 (2 C), 127.2, 125.6, 116.2, 95.0, 89.6, 83.6, 74.8, 68.4, 62.3, 51.8, 40.0, 35.2, 24.1, 23.5, 22.0; ^{13}C NMR (minor rotamer, partial) 129.6, 129.1, 127.4, 125.1, 116.7, 89.9, 63.0, 51.4, 37.9, 22.3 IR (KBr) 3333, 2958, 1797, 1728, 1710, 1678, 1608, 1529. Anal. Calcd for $C_{28}H_{28}Cl_3N_3O_7$: C, 53.82; H, 4.52; N, 6.72. Found: C, 54.06; H, 4.50, N, 6.52.

Aniline Precursor to 22. To a solution of **20a** (177 mg, 0.3 mmol) in acetic acid (3.0 mL) was added zinc dust (600 mg). The mixture was stirred at rt for 30 min. The zinc dust was filtered off and the filtrate was concentrated. The residue was dissolved in EtOAc (10 mL), which was washed with saturated $NaHCO_3$ (3 × 10 mL), brine (10 mL), dried (Na_2SO_4), and evaporated under reduced pressure to give crude amine.

To a mixture of crude amine and EDAC (127 mg, 0.66 mmol) in MeCN (1 mL) was added anthranilic acid (82 mg, 0.6 mmol) in several portions over 60 min at rt with stirring. The reaction mixture was stirred for an additional 20 min, and concentrated under reduced pressure. The residue was dissolved in CH_2Cl_2 (10 mL), which was washed with water (5 mL) and saturated $NaHCO_3$ (3 × 10 mL), dried (Na_2SO_4) and concentrated. Flash chromatography on silica gel (10:1 CH_2Cl_2/EtOAc) gave the aniline (134 mg, 85%) as a white solid: mp 115-118 ºC; $[\alpha]_D$ +76.2 (*c* 0.32 in $CHCl_3$); ^{1}H NMR 7.60 (d, 1, *J* = 7.9), 7.45 (td, 2, *J* = 7.9, 1.2), 7.42-7.20 (m, 8), 7.10 (br, 1, NH), 6.70 (d, 1, *J* = 8.0), 6.73-6.62 (m, 1), 5.90 (br, 1), 5.56 (br, 2, NH), 5.48-5.20 (br, 2), 5.08 (d, 1, *J* = 11.6), 4.58 (br, 1), 2.75 (br, 1), 2.45 (br, 1), 1.52 (br d, 3, *J* = 6.7); ^{13}C NMR 172.0, 169.0 (br, 2 C), 154.4, 149.1, 133.1, 131.1, 130.7, 128.8 (br, 3 C), 128.5 (2 C), 128.3 (br), 127.6 (br), 127.2, 127.0, 124.3 (br), 117.4, 116. 6, 116.1 (br, 2 C), 89.9 (br), 84.2 (br), 68.7 (br), 59.0 (br), 48.4 (br), 36.5 (br), 17.6 (br); IR (KBr) 3361, 1795, 1726, 1642, 1612, 1586, 1513;

Diamide 22a. To a solution of the aniline (105 mg, 0.2 mmol) and EDAC (84 mg, 0.44 mmol) in MeCN (1 mL) was added *N*-Fmoc-L-alanine (124 mg, 0.40 mmol). The resulting mixture was stirred at rt for 1.5 h and concentrated. The residue was dissolved in CH_2Cl_2 (10 mL), which was washed with water (5 mL) and saturated $NaHCO_3$ (3 × 10 mL), dried (Na_2SO_4), and concentrated. Flash chromatography on silica gel gave **22a** (147 mg, 89%) as a white solid: mp 139-142 ºC; $[\alpha]_D$ +59.0 (*c* 0.34 in $CHCl_3$); ^{1}H NMR 11.55 (br, 1, NH), 8.64 (br d, 1, *J* = 7.9), 7.77-7.67 (m, 2), 7.67-7.53 (m, 4), 7.57-7.47 (m, 1), 7.47-7.13 (m, 13), 7.09 (br, 1, NH), 5.91 (br s, 1), 5.52 (br d, 1, *J* = 7.1, NH), 5.40-5.15 (m, 2), 5.06 (d, 1, *J* = 11.7), 4.54 (br, 1), 4.52-4.32 (br, 2), 4.36-4.13 (m, 2), 2.69-2.50 (br, 1), 2.47-2.24 (br, 1), 1.53 (br d, 3, *J* = 6.7), 1.51 (br d, 3, *J* = 6.7); ^{13}C NMR 173.5 (br), 171.2, 168.8, 168.6, 155.8, 144.0, 143.7 (2 C), 141.2 (2 C), 139.7 (br), 137.0, 133.5, 131.2, 129.0 (2 C), 128.8 (3 C), 128.0 (br), 127.7, 127.7, 127.1 (2 C), 127.08, 126.8 (br), 125.2, 125.1 (br), 124.7 (br), 124.3 (br), 123.1, 121.6, 120.0 (2 C), 119.0, 116.4 (br), 89.9, 84.2 (br), 68.8 (br), 67.1, 58.9 (br), 51.8, 48.3 (br), 47.2, 36.0, 19.0, 18.3 (br); IR (KBr) 3344 (br), 1796, 1725, 1692, 1657, 1603, 1586, 1546, 1513. Anal. Calcd for $C_{47}H_{41}N_5O_9 \bullet H_2O$: C, 67.39; H, 5.14; N, 8.36. Found: C, 67.82; H, 4.99, N, 8.27.

Diamide 22b To a solution of aniline (184 mg, 0.35 mmol) and EDAC (147 mg, 0.77 mmol) in MeCN (2 mL) was added *N*-Fmoc-D-alanine (218 mg, 0.70 mmol). The resulting mixture was stirred at rt for 1.5 h and concentrated. The residue was dissolved in CH_2Cl_2 (10 mL), washed with water (5 mL) and saturated $NaHCO_3$ (3 × 10 mL), dried (Na_2SO_4), and concentrated. Flash chromatography on silica gel gave **22b** (258 mg, 90%) as a white solid: mp 138-142 ºC; $[\alpha]_D$ +52.6 (*c* 0.43 in $CHCl_3$); ^{1}H NMR (6:1 mixture of rotamers) 11.71 (br, 1, NH), 8.65 (br d, 1, *J* = 8.0), 7.83-7.64 (m, 3), 7.63-7.44 (m, 4), 7.44-7.32 (m, 4), 7.32-7.14 (m, 8), 7.13-6.97 (m, 2), 5.83 (s, 1), 5.59 (br s, 1), 5.27-5.11 (m, 2), 5.09-4.96 (m, 1), 4.59 (br, 1), 4.54-4.37 (m, 1), 4.28-4.18 (m, 2), 4.18-4.06 (br, 1), 2.25 (br, 2), 1.53 (br, 3), 1.44 (br, 3); ^{1}H NMR (minor rotamer, partial) 11.08 (s, 1), 6.16 (br, 1), 5.40 (br, 1), 2.46 (br, 2); ^{13} C NMR (two rotamers) 173.5 (br), 171.2, 168.7 (br), 168.5, 155.9 (br), 144.3 (br, 2 C), 143.4, 141.1, 139.6 (br), 136.9 (br), 133.6, 133.3, 131.1, 128.9 (2 C), 128.8 (3 C), 128.0, 127.7 (2 C), 127.1, 127.0,

126.9, 126.8, 125.5, 125.1 (2 C), 124.3, 123.1, 121.7, 119.93, 119.86, 119.3, 116.3 (br), 89.8, 84.2, 68.8, 67.2, 58.9, 52.0, 48.1, 47.2, 35.6, 18.8, 18.2; IR (KBr) 3329 (br), 1796, 1726, 1692, 1656, 1603, 1586, 1546, 1513. Anal. Calcd for $C_{47}H_{41}N_5O_9$: C, 68.85; H, 5.04; N, 8.54. Found: C, 68.26; H, 5.08, N, 8.27.

Iminobenzoxazine 23a. To a solution of Ph_3P (78 mg, 0.3 mmol, 2.0 eq) in dry CH_2Cl_2 (5 mL) was added a Br_2 solution in CH_2Cl_2 (1.0 M, 0.29 mmol, 1.95 eq) under N_2. The resulting solution was stirred at rt for 15 min, and Et_3N (0.10 mL, 3 eq) and **22a** (123 mg, 0.15 mmol) were added. The resulting mixture was stirred at rt for 15 min and concentrated. The dark residue was shaken with anhydrous benzene (5 mL) and the triethylamine hydrobromide was filtered off. The filtrate was concentrated to give a dark red residue. Flash chromatography on silica gel (20:1 CH_2Cl_2/EtOAc) gave **23a** (91 mg, 76%) as a light red solid: mp 138-140 ºC; $[\alpha]_D$ +82.5 (*c* 0.34 in $CHCl_3$); ^{1}H NMR 8.13 (d, 1, *J* = 8.0), 7.78-7.72 (m, 2), 7.68-7.53 (m, 4), 7.48-7.35 (m, 8), 7.35-7.23 (m, 6), 6.02 (s, 1), 5.73 (d, 1, *J* = 8.5, NH), 5.38 (br d, 1, *J* = 11.6), 5.31 (dd, 1, *J* = 9.7, 8.5), 4.95 (br d, 1, *J* = 11.6), 4.71 (dq, 1, *J* = 8.5, 6.7), 4.64 (q, 1, *J* = 6.7), 4.46-4.34 (m, 2), 4.23 (t, 1, *J* = 6.7), 2.85 (dd, 1, *J* = 13.0, 8.5), 2.42 (dd, 1, *J* = 13.0, 9.7), 1.63 (br d, 3, *J* = 6.7), 1.62 (br d, 3, *J* = 6.7); ^{13}C NMR 173.3, 169.3, 159.4, 155.6, 154.4, 150.1, 143.9, 143.7, 141.24, 141.15, 136.5, 135.4, 134.7, 133.9, 130.8, 129.0 (br), 128.8, 128.5 (3 C), 128.4 (2 C), 127.7 (2 C), 127.0 (2 C), 126.9, 126.39, 126.36, 125.0 (2 C), 123.7, 120.0 (br, 2 C), 118.8, 116.9, 89.9, 82.9, 68.2, 67.0, 59.3, 53.6, 49.0, 47.1, 37.0, 19.4, 18.0 (br); IR (KBr) 3344 (br), 1795, 1725, 1677, 1641, 1606, 1528, 1500.

Iminobenzoxazine 23b. To a solution of Ph_3P (130 mg, 0.5 mmol, 2.0 eq) in dry CH_2Cl_2 (5 mL) was added a Br_2 solution in CH_2Cl_2 (1.0 M, 0.49 mmol, 1.95 eq) under N_2. The resulting solution was stirred at rt for 10 min, and Et_3N (0.16 mL, 3 eq) and **22b** (205 mg, 0.25 mmol) were added. The resulting mixture was stirred at rt for 15 min and concentrated. The dark residue was shaken with anhydrous benzene (5 mL) and the triethylamine hydrobromide was filtered off. The filtrate was concentrated to give a dark red residue. Flash chromatography on silica gel (20:1 CH_2Cl_2/EtOAc) gave **23b** (142 mg, 71%) as a light red solid: mp 141-143 ºC;

$[\alpha]_D$ +71.3 (*c* 0.33 in $CHCl_3$); ^{1}H NMR 8.14 (dd, 1, *J* = 7.9, 1.2), 7.76 (d, 2, *J* = 7.9), 7.49-7.58 (m, 5), 7.35-7.49 (m, 7), 7.22-7.35 (m, 6), 6.02 (s, 1), 5.51 (d, 1, *J* = 7.9, NH), 5.46-5.30 (br, 1), 5.36 (dd, 1, *J* = 9.2, 8.7), 5.08-4.91 (br, 1), 4.77 (dq, 1, *J* = 7.9, 6.7), 4.63 (q, 1, *J* = 6.7), 4.50-4.36 (m, 2), 4.26 (t, 1, *J* = 6.7), 2.83 (dd, 1, *J* = 13.4, 9.2), 2.45 (dd, 1, *J* = 13.4, 8.7), 1.58 (d, 3, *J* = 6.7), 1.57 (d, 3, *J* = 6.7); ^{13}C NMR 173.3, 169.4, 159.0, 155.8, 154.4, 150.3, 144.0, 143.7, 141.3, 141.2, 136.5, 135.5, 134.8, 133.9, 130.8, 129.1 (br), 128.6 (br, 3 C), 128.5 (2 C), 128.4, 127.7 (br, 2 C), 127.0 (br, 3 C), 126.5, 126.4, 125.2, 125.0, 124.0, 120.0 (2 C), 118.8, 117.0, 89.6, 82.9, 68.3, 67.1, 59.4, 53.7, 48.7, 47.2, 36.9, 18.7, 18.0; IR (KBr) 3309 (br), 1794, 1725, 1676, 1655, 1607, 1586, 1546, 1528.

***N*-19-Cbz-Fumiquinazoline A (25a) and 26a.** To a solution of **23a** (80 mg, 0.1 mmol) in dry EtOAc (0.5 mL) was added dry piperidine (0.1 mL, 10 eq). The resulting mixture was stirred at rt for 10 min, and concentrated under reduced pressure to give crude amidine **24a**, which was dissolved in dry MeCN (4 mL). The solution was refluxed for 2 h, cooled down, and concentrated to give a light red residue. Flash chromatography on silica gel (2:1 CH_2Cl_2/EtOAc) gave **25a** (38 mg, 65%) as a white solid followed by **26a** (11 mg, 19%) as white solid.

Data for **25a**: mp 156-160 ºC; $[\alpha]_D$ -221.6 (*c* 0.36 in $CHCl_3$); ^{1}H NMR 8.17 (d, 1, *J* = 7.9), 8.06 (br d, 1, *J* = 7.9), 7.76 (ddd, 1, *J* = 7.9, 7.9, 1.1), 7.69 (d, 1, *J* = 7.9), 7.60 (d, 1, *J* = 7.9), 7.47 (ddd, 1, *J* = 7.9, 7.9, 1.2), 7.42 (dd, 1, *J* = 7.9, 1.2), 7.36 (br m, 5), 7.32 (ddd, 1, *J* = 7.9, 7.9, 1.2), 6.81 (br, 1, NH), 5.78 (s, 1), 5.72 (dd, 1, *J* = 10.7, 8.0), 5.36-5.18 (m, 2), 5.24 (s, OH), 4.64-4.46 (m, 2), 2.29 (dd, 1, *J* = 13.7, 10.7), 1.90 (br dd, 1, *J* = 13.7, 8.0), 1.74 (br d, 3, *J* = 6.7), 1.45 (d, 3, *J* = 6.7); ^{13} NMR 170.0 (br), 167.9, 160.1, 155.8 (br), 150.9, 146.8, 136.2, 135.8, 135.6, 134.8, 130.1, 128.6 (3 C), 128.5 (2 C), 128.2, 127.50, 127.46, 127.1, 126.4, 120.1, 116.4, 87.2, 80.1, 68.3, 59.7, 51.9, 49.2, 36.7, 18.2, 17.3; IR (KBr) 3261 (br), 1721, 1690, 1607, 1603, 1571, 1547, 1512.

Data for **26a**: mp 159-163 ºC; $[\alpha]_D$ +135.0 (*c* 0.11 in $CHCl_3$); ^{1}H NMR 8.24 (dd, 1, *J* = 7.8, 1.2), 7.85 (t, 1, *J* = 7.8), 7.78-7.67 (m, 1), 7.71 (d, 1, *J* = 7.8), 7.54 (t, 1, *J* = 7.8), 7.49 (d, 1, *J* = 7.8), 7.42-7.22 (m, 6), 7.20-7.06 (m, 1), 6.67 (br, 1, NH), 5.82 (br s, 1), 5.64 (t, 1, *J* = 4.9),

5.29 (s, 1, OH), 5.28 (d, 1, *J* = 12.2), 5.12 (br d, 1, *J* = 12.2), 4.70 (qd, 1, *J* = 6.7, 4.2), 4.59 (q, 1, *J* = 6.7), 2.30 (br d, 2, *J* = 4.9), 1.63 (br d, 3, *J* = 6.7), 1.53 (d, 3, *J* = 6.7); ^{13}C NMR 167.7, 161.7, 150.7, 147.1, 136.8, 135.5, 135.4, 135.3 (br), 129.7, 128.6 (2 C), 128.5, 128.4 (2 C), 127.6 (br), 127.1, 126.9 (br, 2 C), 125.8 (br), 120.0, 116.1, 87.2, 79.8, 68.1, 59.8, 52.4, 51.1, 41.0, 24.5, 18.0 (two quaternary C were not observed); IR (KBr) 3370 (br), 1720, 1691, 1604, 1657, 1546, 1528, 1511.

***N*-19-Cbz-Fumiquinazoline B (25b) and 26b.** To a solution of **23b** (120 mg, 0.15 mmol) in dry EtOAc (0.6 mL) was added dry piperidine (0.14 mL, 10 eq). The resulting mixture was stirred at rt for 10 min, and concentrated under reduced pressure to give crude amidine **24b**, which was dissolved in dry MeCN (5 mL). The solution was refluxed for 2 h, cooled down, and concentrated to give a light red residue. Flash chromatography on silica gel (5:2 CH_2Cl_2/EtOAc) gave **25b** (60 mg, 69%) as white solid preceded by **26b** (16 mg, 18%) as a white solid.

Data for **25b**: mp 152-156 ºC; $[\alpha]_D$ +226.7 (*c* 0.24 in $CHCl_3$); ^{1}H NMR 8.13 (d, 1, *J* = 8.0), 8.04 (br d, 1, *J* = 7.3), 7.75 (ddd, 1, *J* = 8.2, 7.0, 1.0), 7.63 (d, 1, *J* = 7.9), 7.61 (d, 1, *J* = 7.9), 7.39-7.47 (m, 4), 7.29-7.38 (m, 4), 6.69, (br s, 1, NH), 5.85 (s, 1), 5.57 (dd, 1, *J* = 11.0, 3.0), 5.29 (d, 1, *J* = 11.2), 5.25 (s, 1, OH), 5.22 (d, 1, *J* = 11.2), 4.73 (m, 1), 4.55 (q, 1, *J* = 6.7), 2.26 (dd, 1, *J* = 13.4, 11.0), 2.08 (dd, 1, *J* = 13.4, 3.0), 1.61 (br d, 3, *J* = 6.7), 1.44 (d, 3, *J* = 6.7); ^{13}C NMR 170.1, 168.2, 159.9, 155.4, 150.9, 146.9, 136.2 (2 C), 135.6, 134.9, 130.0, 128.6 (2 C), 128.4, 128.1 (2 C), 127.3, 127.1, 126.8, 126.4, 126.2, 119.9, 116.5, 88.3, 81.1, 69.0, 60.6, 53.6, 52.2, 39.4, 25.8, 19.4; IR (KBr) 3344 (br), 2919, 1723, 1710, 1691, 1678, 1641, 1606, 1586, 1547, 1512.

Data for **26b**: mp 163-169 ºC; $[\alpha]_D$ +51.7 (*c* 0.40 in $CHCl_3$); ^{1}H NMR 8.22 (br d, 1, *J* = 8.0), 7.81 (t, 1, *J* = 8.0), 7.73 (d, 1, *J* = 8.0), 7.72-7.62 (br, 1), 7.51 (t, 1, *J* = 8.0), 7.49 (d, 1, *J* = 8.0), 7.44-7.21 (m, 6), 7.10-6.90 (br, 1), 6.30 (br s, 1, NH), 5.76 (dd, 1, *J* = 5.5, 4.9), 5.73 (s, 1), 5.27 (d, 1, *J* = 11.6), 5.19 (d, 1, *J* = 11.6), 4.70 (br, 1), 4.58 (q, 1, *J* = 6.7), 4.42 (br, 1, OH), 2.35 (dd, 1, *J* = 14.0, 5.5), 2.23 (dd, 1, *J* = 14.0, 4.9), 1.75 (d, 3, *J* = 6.7), 1.57 (d, 3, *J* = 6.7); ^{13}C NMR 150.9, 146.7, 136.6, 135.5, 135.3, 134.9, 129.8, 128.6 (3 C), 128.4 (2 C), 127.5 (2 C),

127.0, 126.2, 125.4, 120.3, 116.2, 87.0, 79.8, 68.4, 59.8, 52.4, 49.4, 40.0, 18.0, 17.8 (four quaternary C were not observed); IR (KBr) 3368 (br), 1721, 1687, 1604, 1570, 1547, 1528.

Fumiquinazoline A (2). To a solution of **25a** (23 mg, 0.040 mmol) in MeOH (2 mL) was added 5% Pd/C (10 mg). The suspension was stirred at rt under H_2 for 30 min. The catalyst was filtered off and the filtrate was evaporated to give crude **2**. Flash chromatography on silica gel (1:1 CH_2Cl_2/EtOAc) gave pure fumiquinazoline A (**2**) (16 mg, 90%) as a light yellow solid: mp 178-183 ºC (lit[1] 178-182 ºC); $[\alpha]_D$ -225.4 (*c* 0.36 in $CHCl_3$, lit.[1] -214.5); λ_{max} (EtOH)/nm 208 (log ε 4.58), 226 (4.47), 234 (4.42), 256 (4.17), 264 (4.13), 278 (3.97), 306 (3.39), 318 (3.24); ^{1}H NMR 8.23 (dd, 1, *J* = 7.9, 1.1), 7.75 (ddd, 1, *J* = 8.2, 7.0, 1.1), 7.67 (d, 1, *J* = 8.2), 7.61 (d, 1, *J* = 7.5), 7.52 (d, 1, *J* = 7.3), 7.49 (ddd, 1, *J* = 7.9, 1.1), 7.31 (td, 1, *J* = 7.5, 1.1), 7.16 (td, 1, *J* = 7.5, 1.1), 6.31 (br s, 1, NH), 5.97 (ddd, 1, 10.8, 6.1, 0.9), 5.49 (br d, 1, *J* = 4.8), 4.88 (q, 1, *J* = 6.7), 4.82 (s, 1, OH), 4.22 (qd, 1, *J* = 6.7, 6.1), 2.72 (br dd, 1, *J* = 6.1, 4.8, NH), 2.51 (dd, 1, *J* = 13.7, 10.8), 2.28 (dd, 1, *J* = 13.7, 6.1), 1.79 (d, 3, *J* = 6.7), 1.35 (d, 3, *J* = 6.7), ^{13}C NMR 172.2, 170.2, 160.4, 150.6, 146.8, 138.5, 136.2, 134.8, 129.8, 127.5, 127.6, 126.8, 125.6, 124.8, 120.2, 115.0, 86.3, 80.1, 59.0, 53.0, 49.2, 36.8, 18.6, 16.9; IR (KBr) 3347 (br), 1686 (br), 1607. The spectral data are identical to those previously reported.[4]

***epi*-Fumiquinazoline A 27a.** To a solution of **26a** (11 mg, 0.019 mmol) in MeOH (1 mL) was added 5% Pd/C (5 mg). The suspension was stirred at rt under H_2 for 30 min. The catalyst was filtered off and the filtrate was evaporated to give crude **27a**. Flash chromatography on silica gel (3:2 EtOAc/CH_2Cl_2) gave pure **27a** (7.3 mg, 86%) as a light yellow solid: mp 248-252 ºC; λ_{max} (EtOH)/nm 208 (log ε 4.68), 228 (4.58), 234 (4.56), 256 (4.27), 268 (4.27), 280 (4.12), 308 (3.67), 320 (3.57); ^{1}H NMR 8.29 (dd, 1, *J* = 7.8, 1.0), 7.81 (td, 1, *J* = 7.8, 1.2), 7.68 (d, 1, *J* = 7.8), 7.55 (d, 1, *J* = 7.8), 7.53 (t, 1, *J* = 7.8), 7.43 (d, 1, *J* = 7.8), 7.31 (td, 1, *J* = 7.8, 1.0), 7.13 (td, 1, *J* = 7.8, 1.0), 6.61 (br s, 1, NH), 6.02 (t, 1, *J* = 6.8), 5.52 (br d, 1, 6.8), 5.18 (s, 1, OH), 4.78 (qd, 1, *J* = 7.0, 4.2), 4.08 (qd, 1, *J* = 6.8, 6.8), 2.89 (t, 1, *J* = 6.8), 2.71 (dd, 1, *J* = 14.8, 6.8), 2.18 (dd, 1, *J* = 14.8, 6.8), 1.83 (d, 3, *J* = 7.0), 1.33 (d, 3, *J* = 6.8); IR (KBr) 3344 (br), 1703, 1678, 1603. The spectral data are identical to those previously reported.[4]

Fumiquinazoline B (3). To a solution of **25b** (46 mg, 0.080 mmol) in MeOH (2 mL) was added 5% Pd/C (15 mg). The suspension was stirred at rt under H_2 for 30 min. The catalyst was filtered off and the filtrate was evaporated to give crude **3**. Flash chromatography on silica gel (2:3 CH_2Cl_2/EtOAc) gave pure fumiquinazoline B (**3**) (32 mg, 90%) as a light yellow solid: mp 174-178 ^oC (lit[1] 174-176 ^oC); $[\alpha]_D$ –179.6 (*c* 0.50 in $CHCl_3$, lit.[1] –196.6); λ_{max} (EtOH)/nm 208 (log ε 4.74), 228 (4.63), 234 (4.59), 256 (4.30), 268 (4.19), 278 (3.97), 306 (3.39), 318 (3.24); ^{1}H NMR (0.08 M) 8.20 (dd, 1, *J* = 7.9, 1.0), 7.74 (ddd, 1, *J* = 7.9, 7.0, 1.0), 7.62 (dd, 1, *J* = 7.6, 1.2), 7.57 (dd, 1, *J* = 7.9, 1.0), 7.52 (dd, 1, *J* = 7.6, 1.2), 7.46 (ddd, 1, *J* = 7.9, 7.0, 1.0), 7.31 (td, 1, *J* = 7.6, 1.2), 7.25 (br s, 1, NH), 7.17 (td, 1, *J* = 7.6, 1.2), 5.79 (dd, 1, *J* = 11.4, 4.9), 5.45 (s, 1, OH), 5.42 (br s, 1), 4.72 (qd, 1, *J* = 7.2, 4.9), 4.15 (q, 1, *J* = 6.7), 2.72 (br s, 1, NH), 2.61 (dd, 1, *J* = 13.3, 11.4), 2.48 (dd, 1, *J* = 13.3, 4.9), 1.83 (d, 3, *J* = 7.2), 1.29 (d, 1, *J* = 6.7); ^{1}H NMR (0.01 M) 8.26 (dd, 1, *J* = 7.9, 1.2), 7.77 (ddd, 1, *J* = 7.9, 7.0, 1.2), 7.66 (d, 1, *J* = 7.6), 7.62 (d, 1, *J* = 7.9), 7.55 (d, 1, *J* = 7.6), 7.49 (dd, 1, *J* = 7.9, 7.0), 7.33 (tdd, 1, *J* = 7.6, 1.2), 7.19 (tdd, 1, *J* = 7.6,1.2), 6.48 (br s, 1, NH), 5.84 (dd, 1, *J* = 11.4, 4.9), 5.47 (dd,1, *J* = 5.5, 1.8), 5.25 (s, 1, OH), 4.78 (qd, 1, *J* = 7.2, 4.9), 4.19 (qd, 1, *J* = 6.7, 6.7), 2.62 (dd, 1, *J* = 13.3, 11.4), 2.61 (br d, 1, *J* = 6.7, NH), 2.51 (dd, 1, *J* = 13.3, 4.9), 1.87 (d, 3, *J* = 7.2), 1.33 (d, 1, *J* = 6.7); ^{13}C NMR (0.08 M) 170.6, 170.5, 160.3, 150.7, 147.0, 138.6, 136.5, 134.9, 129.7, 127.2, 126.8 (2 C), 125.5, 125.0, 120.0, 114.8, 86.4, 80.2, 59.0, 52.7, 52.0, 38.9, 24.8, 18.1; IR (KBr) 3345 (br), 1672, 1603. The spectral data are identical to those previously reported.[4]

***epi*-Fumiquinazoline B (27b).** To a solution of **26b** (15 mg, 0.025 mmol) in MeOH (1 mL) was added 5% Pd/C (5 mg). The suspension was stirred at rt under H_2 for 30 min. The catalyst was filtered off and the filtrate was evaporated to give crude **27b**. Flash chromatography on silica gel (1:1 EtOAc/CH_2Cl_2) gave pure **27b** (9.5 mg, 86%) as a light yellow solid: mp 175-178 ^oC; $[\alpha]_D$ +215.0 (*c* 0.42 in $CHCl_3$); λ_{max} (EtOH)/nm 206 (log ε 4.84), 226 (4.72), 234 (4.67), 256 (4.38), 266 (4.33), 276 (4.20), 306 (3.67), 318 (3.55); ^{1}H NMR 8.31 (dd, 1, *J* = 7.9, 1.2), 7.83 (td, 1, *J* = 7.9, 1.2), 7.75 (d, 1, *J* = 7.9), 7.56 (td, 1, *J* = 7.9, 1.2), 7.51 (d, 2, *J* = 7.8), 7.30 (t, 1, *J* = 7.8), 7.15 (td, 1, *J* = 7.8, 1.2), 6.60 (br s, 1, NH), 5.91 (dd, 1, *J* = 9.8, 5.0), 5.41 (br s,

1), 5.41 (s, 1, OH), 4.81 (q, 1, *J* = 6.7), 3.97 (q, 1, *J* = 6.1), 2.67 (dd, 1, *J* = 14.7, 9.8), 2.22 (br s, 1, NH), 2.14 (dd, 1, *J* = 14.7, 5.0), 1.78 (d, 3, *J* = 6.7), 1.19 (d, 1, *J* = 6.1); ^{13}C NMR 170.4, 169.9, 162.2, 151.2, 147.0, 139.0, 136.0, 135.4, 129.8, 127.8, 127.8, 126.9, 135.6, 124.4, 119.8, 115.0, 85.9, 80.8, 59.0, 53.3, 49.2, 38.0, 18.0, 16.9; IR (KBr) 3338 (br), 1690 (br), 1606. The spectral data are identical to those previously reported.[4]

Aniline Precursor to 28. To a solution of **21b** (200 mg, 0.32 mmol) in acetic acid (3.0 mL) was added zinc dust (600 mg). The mixture was stirred at rt for 30 min. The zinc dust was filtered off and the filtrate was concentrated. The residue was dissolved in EtOAc (10 mL), which was washed with saturated $NaHCO_3$ (3 × 10 mL), brine (10 mL), dried (Na_2SO_4) and evaporated under reduced pressure to give crude amine**.**

To a mixture of crude amine and EDAC (150 mg, 0.76 mmol) in MeCN (2 mL) was added anthranilic acid (102 mg, 0.74 mmol) in several portions over 60 min at rt with stirring. The reaction mixture was stirred for an additional 20 min, and concentrated under reduced pressure. The residue was dissolved in CH_2Cl_2 (10 mL), which was washed with water (5 mL) and saturated $NaHCO_3$ (3 × 10 mL), dried (Na_2SO_4) and concentrated. Flash chromatography on silica gel (50:1 CH_2Cl_2/EtOAc) gave the aniline (154 mg, 85%) as a white solid: mp 191-194 ºC; $[\alpha]_D$ +176.6 (*c* 0.24 in $CHCl_3$); ^{1}H NMR (5:1 mixture of rotamers) 8.00 (d, 1, *J* = 7.9), 7.49 (d, 1, *J* = 8.0), 7.45-7.36 (m, 5), 7.37 (td, 1, *J* = 8.0, 1.0), 7.29 (d, 1, *J* = 8.0), 7.25 (t, 1, *J* = 8.0), 7.17 (t, *J* = 8.0), 6.74 (d, 1, *J* = 6.7, NH), 6.66-6.56 (m, 2), 5.95 (br, 1), 5.57 (br, 2, NH), 5.27 (d, 1 *J* = 12.2), 5.18 (d, 1, *J* = 12.2), 4.48-4.00 (m, 1), 4.16 (m, 1), 2.74 (dd, 1, *J* = 14.0, 10.4), 2.29 (dd, 1, *J* = 14.0, 9.1), 2.01-1.73 (m, 3), 0.93 (br d, 3, *J* = 6.7), 0.85 (br d, 3, *J* = 6.7); ^{1}H NMR (minor rotamer, partial) 7.91 (d, 1, *J* = 8.0), 7.45 (d, 1, *J* = 8.0), 6.78 (d, 1, *J* = 6.7, NH), 6.63-6.52 (m, 2), 5.93 (s, 1), 5.35 (d, 1, *J* = 12.2), 5.07 (d, 1, *J* = 12.2), 4.39 (m, 1), 3.98 (m, 1), 2.83 (dd, 1, *J* = 13.4, 9.8), 2.50-2.40 (m, 1), 2.14-1.96 (m, 3), 0.98 (d, 3, *J* = 6.7); ^{13}C NMR (major rotamer) 174.6, 168.95, 168.90, 154.1, 149.2, 136.0, 135.6, 132.9, 130.6, 129.5, 128.70 (2 C), 128.68 (2 C), 128.5, 127.4, 127.2, 126.1, 117.4, 116. 5, 116.1, 113.8, 89.7, 83.7, 68.3, 62.2, 51.3, 39.9, 35.1, 24.1, 23.5, 22.0; ^{13}C NMR (minor rotamer, partial) 174.1, 165.9,

128.9, 125.7, 113.8, 90.1, 64.0, 51.0, 37.9, 35.6, 24.2, 22.3; IR (KBr) 3460 (br, NH), 3358 (br, NH), 2959, 1788, 1702, 1642, 1610, 1585, 1522;

Diamide 28. To a solution of the aniline (125 mg, 0.22 mmol) and EDAC (93 mg, 0.48 mmol) in MeCN (2 mL) was added *N*-Fmoc-L-alanine (150 mg, 0.48 mmol). The resulting mixture was stirred at rt for 1.5 h and concentrated. The residue was dissolved in CH_2Cl_2 (10 mL), which was washed with water (5 mL) and saturated $NaHCO_3$ (3 × 10 mL), dried (Na_2SO_4), and concentrated. Flash chromatography on silica gel (20:1 CH_2Cl_2/EtOAc) gave **28** (165 mg, 87%) as a white solid: mp 141-143 ºC; $[\alpha]_D$ +145.3 (*c* 0.22 in $CHCl_3$); ^{1}H NMR (10:1 mixture of rotamers, major rotamer) 11.25 (br s, 1, NH), 8.38 (br d, 1, *J* = 7.9), 8.01 (d, 1, *J* = 8.0), 7.72 (d, 2, *J* = 8.0), 7.70-7.61 (m, 2), 7.53-7.53 (m, 3), 7.42-7.30 (m, 8), 7.30-7.17 (m, 3), 7.03 (t, 1, *J* = 8.0), 5.91 (br s, 1), 5.79 (br d, 1, *J* = 7.1, NH), 5.23 (d, 1, *J* = 12.2), 5.17 (d, 1, *J* = 12.2), 4.46 (m, 1), 4.43-4.26 (m, 4), 4.18 (dd, 1, *J* = 11.7, 9.4), 2.73 (dd, 1, *J* = 13.8, 11.7), 2.25 (dd, 1, *J* = 13.8, 9.4), 1.95-1.72 (m, 3), 1.51 (br d, 3, *J* = 6.7), 0.91 (br d, 3, *J* = 6.7), 0.83 (br d, 3, *J* = 6.7); ^{1}H NMR (minor rotamer, partial) 11.07 (br s, 1, NH), 8.42 (br d, 1, *J* = 7.9), 7.89 (d, 1, *J* = 8.0), 5.84 (br s, 1), 5.74 (br d, 1, *J* = 7.1, NH), 5.35 (d, 1, *J* = 12.2), 4.99 (d, 1, *J* = 12.2),4.09 (m, 3), 4.02 (m, 1), 2.87 (m, 1), 2.03 (m, 1), 1.37 (br, 3), 0.95 (br d, 3, *J* = 6.7), 0.81 (br d, 3, *J* = 6.7); ^{13}C NMR (major rotamer) 175.0, 171.0, 168.85, 168.79, 155.9, 154.2, 144.0, 143.6 (2 C), 141.2 (2 C), 139.0, 136.1, 135.7, 135.4, 133.2, 130.9, 128.8 (2 C), 128.6 (3 C), 127.6 (2 C), 127.0 (2 C), 126.8, 125.9, 125.3, 125.1 (2 C), 123.3, 121.7, 119.9 (2 C), 116.2, 90.2, 83.6, 68.3, 67.1, 62.2, 51.7 (2 C), 47.0, 40.0, 34.7, 24.1, 23.5, 22.0, 19.0; ^{13}C NMR (minor rotamer, partial) 171.2, 139.3, 135.0, 133.4, 131.2, 129.5, 119.2, 91.7, 84.2, 24.5; IR (KBr) 3347 (br), 2958, 1794, 1707, 1647, 1602, 1522. Anal. Calcd for $C_{50}H_{47}N_5O_9$: C, 69.67; H, 5.50; N, 8.12. Found: C, 69.44; H, 5.41, N, 7.92.

Iminobenzoxazine from 28. To a solution of Ph_3P (78 mg, 0.3 mmol, 2.0 eq) in dry CH_2Cl_2 (5 mL) was added a Br_2 solution in CH_2Cl_2 (1.0 M, 0.29 mmol, 1.95 eq) under N_2. The resulting solution was stirred at rt for 15 min, and Et_3N (0.10 mL, 3 eq) and **28** (130 mg, 0.15 mmol) were added. The resulting mixture was stirred at rt for 15 min and concentrated. The

residue was shaken with anhydrous benzene (5 mL) and the triethylamine hydrobromide was filtered off. The filtrate was concentrated to give a light brown residue. Flash chromatography on silica gel (30:1 CH_2Cl_2/EtOAc) gave the iminobenzoxazine (98 mg, 77%) as a light-yellow solid: mp 129-131 ºC; $[\alpha]_D$ +86.9 (*c* 0.17 in $CHCl_3$); ^{1}H NMR (3:1 mixture of rotamers, major rotamer) 8.13 (d, 1, *J* = 8.0), 7.78-7.72 (m, 2), 7.68-7.56 (m, 3), 7.56-7.48 (m, 2), 7.48-7.23 (m, 13), 6.03 (s, 1), 5.76 (d, 1, *J* = 8.5, NH), 5.40 (br d, 1, *J* = 12.2), 5.21 (d, 1, *J* = 12.2), 5.02 (dd, 1, *J* = 9.2, 7.9), 4.66-4.53 (m, 2), 4.44-4.31 (m, 2), 4.27-4.16 (m, 1), 2.99 (dd, 1, *J* = 13.8, 9.2), 2.22 (dd, 1, *J* = 13.8, 7.9), 2.16-1.75 (m, 3) 1.62 (br d, 3, *J* = 6.7), 0.93 (br d, 3, *J* = 6.7), 0.83 (br, d, 3, *J* = 6.7); ^{1}H NMR (minor rotamer, partial) 7.93 (d, 1, *J* = 8.0), 7.78 (d, 2, *J* = 8.0), 5.98 (s, 1), 5.86 (d, 1, *J* = 8.5, NH), 5.45 (d, 1, *J* = 12.2), 5.30 (m, 1), 4.50 (m, 1), 4.19 (m, 1), 2.90 (m, 1), 2.12 (m, 1), 2.16-1.75 (m, 3) 1.58 (br d, 3, *J* = 6.7), 0.98 (br d, 3, *J* = 6.7), 0.85 (br, d, 3, *J* = 6.7); ^{13}C NMR (major rotamer) 174.4, 169.0, 159.4, 155.7, 154.2, 149.7, 143.8 (2 C), 141.3 (2 C), 136.1, 135.2, 133.8, 130.7, 129.2, 128.8, 128.5 (2 C), 128.5 (2 C), 127.9, 127.7 (2 C), 127.1, 127.0 (2 C), 126.4, 126.2, 125.9, 125.4, 125.2 (2 C), 124.9, 119.9 (2 C), 119.0, 116.2, 90.2, 83.6, 68.2, 67.0, 55.4, 49.1, 47.1, 40.0, 38.0, 24.1, 23.5, 22.0, 19.4; ^{13}C NMR (minor rotamer, partial),144.0, 143.2, 141.2 (2 C), 134.0, 120.0 (2 C), 119.0, 118.4, 115.0, 89.9, 83.1, 72.2, 68.0, 62.9, 54.8, 49.4, 46.7, 37.5, 22.3, 19.2; IR (KBr) 3413 (br), 2957, 1793, 1725, 1717, 1676, 1654, 1607, 1522, 1507.

***N*-19-Cbz-Fumiquinazoline I (29).** To a solution of the iminobenzoxazine (84 mg, 0.10 mmol) in dry EtOAc (0.5 mL) was added dry piperidine (0.1 mL, 10 eq). The resulting mixture was stirred at rt for 10 min, and concentrated under reduced pressure to the give crude amidine, which was dissolved in dry MeCN (4 mL). The solution was refluxed for 2 h, cooled down, and concentrated to give a light red residue. Flash chromatography on silica gel (5:1 CH_2Cl_2/EtOAc) gave **29** (43 mg, 70%) as a white solid: mp 161-162 ºC; $[\alpha]_D$ -21.8 (*c* 0.25 in $CHCl_3$); ^{1}H NMR (3:1 mixture of rotamers, major rotamer) 8.20 (d, 1, *J* = 7.9), 7.75 (t, 2, *J* = 7.9), 7.69 (d, 1, *J* = 7.9), 7.48 (d, 1, *J* = 7.9), 7.47 (d, 1, *J* = 7.9), 7.43-7.32 (m, 6), 7.03 (t, 1, *J* = 7.9), 6.71 (s, 1, NH), 5.74 (s, 1), 5.59 (dd, 1, *J* = 7.7, 5.5), 5.24 (s, 2), 4.59 (q, 1, *J* = 6.7), 4.53 (m, 1), 4.30 (s,

OH), 2.29 (dd, 1, *J* = 14.6, 7.7), 2.20 (dd, 1, *J* = 14.6, 5.5), 2.16-2.05 (m, 1), 2.00-1.79 (m, 2), 1.68 (br d, 3, *J* = 6.7), 0.93 (d, 3, *J* = 6.7), 0.85 (d, 3, *J* = 6.7); ^{1}H NMR (minor rotamer, partial) 8.26 (d, 1, *J* = 7.9), 7.82 (t, 1, *J* = 7.9), 7.74 (t, 1, *J* = 7.9), 7.18 (t, 1, *J* = 7.9), 7.14 (t, 1, *J* = 7.9), 6.65 (s, 1, NH), 5.85 (s, 1), 5.22 (d, 1, *J* = 12.2), 5.09 (d, 1, *J* = 12.2), 4.64 (br, 1), 4.35 (s, OH), 1.70 (br d, 3, *J* = 6.7), 1.02 (d, 3, *J* = 6.7), 0.90 (d, 3, *J* = 6.7); ^{13} NMR (major rotamer) 169.2, 167.3, 160.8, 154.9, 151.2, 146.7, 136.5, 135.5, 135.2, 134.6, 129.8, 128.7 (2 C), 128.6 (3 C), 127.32, 127.26, 127.1, 126.2, 125.4, 120.4, 116.5, 86.7, 81.0, 68.3, 62.9, 52.3, 49.4, 39.9, 35.5, 24.2, 23.6, 22.1, 17.9; ^{13} NMR (minor rotamer, partial) 168.8, 168.2, 161.3, 152.5, 150.5, 146.8, 137.1, 135.0, 130.1, 128.7, 128.5, 127.9, 127.8, 127.6, 127.5, 126.4, 120.1, 116.7, 86.4, 81.2, 68.0, 63.0, 52.3, 49.1, 38.3, 37.1, 22.3, 17.2 IR (KBr) 3460 (br), 3285 (br), 2957, 1701, 1686, 1654, 1607, 1578, 1568, 1507. Anal. Calcd for $C_{35}H_{35}N_5O_6 \bullet H_2O$: 65.72; H, 5.79; N, 10.95. Found: C, 65.48; H, 5.52, N, 10.71.

Fumiquinazoline I (30). To a solution of **29** (29 mg, 0.047 mmol) in MeOH (2 mL) was added 5% Pd/C (15 mg). The suspension was stirred at rt under H_2 for 30 min. The catalyst was filtered off and the filtrate was evaporated to give crude **30**. Flash chromatography on silica gel (2.5:1 CH_2Cl_2/EtOAc) gave pure fumiquinazoline I (**30**) (22 mg, 96%) as a light yellow solid: mp 169-171 ºC (lit^{20} 116-120 ºC); $[\alpha]_D$ -222.4 (*c* 0.10 in $CHCl_3$, lit.^{20} -138); λ_{max} (MeOH) nm 208 (log ε 4.90), 224 (4.80), 230 (4.78), 255 (4.47), 266 (4.39), 277 (4.28), 304 (3.79), 318 (3.47); ^{1}H NMR 8.32 (dd, 1, *J* = 7.9, 1.2), 7.83 (td, 1, *J* = 7.9, 1.2), 7.74 (d, 1, *J* = 7.9), 7.56 (td, 1, *J* = 7.9, 1.2), 7.55 (d, 1, *J* = 7.3), 7.45 (d, 1, *J* = 7.3), 7.30 (td, 1, *J* = 7.9, 1.2), 7.19 (br s, 1 NH), 7.18 (t, 1, *J* = 7.9, 1.2), 5.82 (dd, 1, 9.8, 3.7), 5.64 (s, 1, OH), 5.44 (d, 1, *J* = 6.4), 4.76 (q, 1, *J* = 6.7), 3.59 (br, 1), 2.59 (dd, 1, *J* = 14.6, 9.8), 2.14 (dd, 1, *J* = 14.6, 3.6), 1.77 (d, 3, *J* = 6.7), 1.58 (br, 1, NH), 1.57-1.48 (m, 1), 1.42-1.33 (m, 1), 1.03-0.85 (m, 1), 0.75 (d, 3, *J* = 6.7), 0.71 (d, 3, *J* = 6.7); ^{1}H NMR (*d*$_6$-acetone) 8.23 (dd, 1, *J* = 7.9, 1.2), 7.87 (td, 1, *J* = 7.9, 1.2), 7.77 (s, 1, NH), 7.73 (d, 1, *J* = 7.9), 7.56 (t, 1, *J* = 7.9), 7.55 (d, 1, *J* = 7.3), 7.36 (d, 1, *J* = 7.3), 7.28 (td, 1, *J* = 7.6, 1.2), 7.15 (td, 1, *J* = 7.3, 1.2), 5.74 (dd, 1, 9.8, 4.4), 5.69 (s, 1, OH), 5.39 (d, 1, *J* = 7.3), 5.11 (q, 1, *J* = 6.7), 3.59 (br m,1), 2.73 (dd, 1, *J* = 14.7, 9.8), 2.63 (br, 1,

NH), 2.13 (dd, 1, J = 14.7, 4.4), 1.74 (d, 3, J = 6.7), 1.48-1.35 (m, 2), 1.25-1.13 (m, 1), 0.78 (d, 3, J = 6.7), 0.77 (d, 3, J = 6.7); ^{13}C NMR (d_6-acetone) 174.1, 170.0, 163.0, 153.6, 148.2, 140.3, 138.5, 135.5, 129.9, 128.3, 127.9, 127.5, 125.9, 125.5, 121.2, 115.9, 88.8, 81.8, 63.0, 54.2, 49.7, 42.3, 38.5, 25.6, 23.5, 21.6, 16.9; IR (KBr) 3347 (br), 2956, 1696 (br), 1607, 1651, 1570. The spectral data are identical to those previously reported.[18]