**Supporting Information**

**Methyl *N*-Boc-(1-acetyl-6-bromoindol-3-yl)glycine (10a)**

A solution of indolin-3-one **6a** (500 mg, 1.76 mmol) and ylide **7a** (1.18 g 3.52 mmol) in benzene (6 ml) was heated under refluxing for 3 h. The reaction mixture was concentrated under reduced pressure. The residue was purified by silica-gel column chromatography with AcOEt-hexane (1 : 5) to give 3-alkylidenindoline **8a** (589 mg, 96 % *E* : *Z* = 1:7). To a suspension of this product (100 mg, 0.29 mmol), TMS-$N_3$ (0.39 ml, d = 0.86, 2.9 mmol), and MS-4A (100 mg) in methylene chloride (3 ml), $MeSO_3H$ (0.19 ml, d = 1.48, 2.9 mmol) was added with stirring at 0 °C. After 2 h, MS-4A was filtered off from the reaction mixture. After concentration of the filtrate, the residue was chromatographed on silica-gel column with AcOEt-hexane (1 : 3) to give azide **9a** (mp 142 °C, 99.2 mg, 96 %). A solution of **9a** (7.4 mg, 0.021 mmol) and triphenylphosphine (11 g, 0.042 mmol) in THF (0.2 ml)-$H_2O$ (0.008 ml) was stirred at room temperature till the disappearance of **9a** was observed by t.l.c. After concentration of the reaction mixture, the residue was chromatographed on silica-gel column with AcOEt-hexane (1 : 2) to give **10a** (mp 164 °C, 8.3 mg, 93 %).

IR ($CHCl_3$) ν $cm^{-1}$ : 3430, 1748, 1715.

$^1$H-NMR ($CDCl_3$, 270MHz) _ : 1.44 (9H, s, t-Bu), 2.62 (3H, s, NCOMe), 3.76 (3H, s, $CO_2Me$), 5.56 (1H, brs, CHN), 7.42 (1H, s, C2-H), 7.43 (1H, dd, *J* = 8.6, 2.0 Hz, C5-H), 7.51 (1H, d, *J* = 8.6 Hz, C4-H), 8.66 (1H, d, *J* = 2.0 Hz, C7-H).

MS m/s (%) : 426 (M+2, 17), 424 ($M^+$, 18), 370 (91), 368 (93), 338 (92), 336 (91), 311 (78), 309 (80), 269 (64), 267 (100), 225 (54), 223 (68), 117 (21), 57 (72), 43 (22).

**Allyl *N*-Boc-*N*-methyl-(1-acetyl-6-bromoindol-3-yl)glycine ester (16)**

A solution of indolin-3-one **6a** (1.24 g, 4.37 mmol) and ylide **7b** (3.14 g 8.72 mmol) in benzene (47 ml) was heated under refluxing for 3.5 h. The reaction mixture was concentrated under reduced pressure to give a residue, which was dissolved in 33 ml of methylene chloride, TMS-$N_3$ (9.25 ml, d = 0.86, 69.6 mmol) and MS-4A (1.32 g) were added to this solution. To this suspension, $MeSO_3H$ (5.07 ml, d = 1.48, 78.0 mmol) was added with stirring at 0 °C. After 15 min. at room temperature, MS-4A was filtered off from the reaction mixture. After concentration of the filtrate, the obtained residue containing **9g** (IR: 2110, 1744, 1721 $cm^{-1}$) was dissolved with THF (44 ml)-$H_2O$ (6.7 ml). To the solution, triphenylphosphine (1.36 g, 5.2 mmol) was added, and the mixture was stirred at room temperature till the disappearance of **9g** was observed by t.l.c. After removal of the solvent, the residue was dissolved with methylene chloride (44.5 ml). To this solution, DMAP (126 mg, 1.03 mmol) and $Ac_2O$ (0.44 ml, 4.78 mmol) was added, and the mixture was stand at room temperature. After concentration of the reaction mixture, the obtained residue was purified by silica-gel column chromatography with AcOEt-hexane (1 : 2) to give allyl *N*-acetyl(1-acetyl-6-bromoindol-3-yl)glycine ester (0.98 g, 57 % overall yield form **6a**, mp163°C, IR: 1740, 1716, 1678 $cm^{-1}$) as white crystals. A solution of this *N*-acetyl derivative (0.825 mg, 2.09 mmol), 2, 6-di(*t*-butyl)-4-methylpyridine (9.06 g, 44.28 mmol), and MeOTf (2.47 ml, d = 1.45, 21.8 mmol) in methylene chloride (49.5 ml) was heated under reflux for 2 h. After cooling to room temperature, acetic acid (70% , 49.4 ml) was added to the reaction mixture. After 1 h, the reaction mixture was made basic with sat. $NaHCO_3$, and extracted with methylene chloride. The extract was dried over $MgSO_4$. $Boc_2O$ (8.47 ml, d = 0.95, 36.93 mmol) was added to the solution, which was stand at room temperature overnight. After concentration of the reaction mixture, the obtained residue

was purified by silica-gel column chromatography with AcOEt-hexane (1 : 1) to give **16** (0.934 g, 96 %) as a viscous oil.
IR ($CHCl_3$) ν $cm^{-1}$ : 1743, 1710, 1682.
$^1$H-NMR ($CDCl_3$, 300MHz) _ : 1.32 (9H, s, t-Bu), 2.62 (3H, s, NCOMe), 2.69 (3H, s, NMe), 4.72 (1H, dd, *J* = 13.2, 5.7 Hz, C**H**HCH=C), 4.76 (1H, dd, *J* = 13.2, 5.7 Hz, CH**H**CH=C), 5.28 (1H, d, *J* = 10.1 Hz, CH=CH**H**), 5.37 (1H, dd, *J* = 17.1, 1.4 Hz, CH=C**H**H), 5.94 (1H, ddt, *J* = 17.1, 10.1, 5.7 Hz, C**H**=$CH_2$), 6.32 (1H, brs, C**H**NMe), 7.36 (1H, d, *J* = 8.3 Hz, C4-H), 7.41 (1H, dd, *J* = 8.3, 1.5 Hz, C5-H), 7.49 (1H, d, *J* = 0.9 Hz, C2-H), 8.66 (1H, s, C7-H).
MS m/s (%) : 466 (M+2, 6), 464 ($M^+$, 6), 410 (62), 408 (62), 352 (82), 350 (83), 325 (95), 323 (100), 283 (36), 281 (68), 279 (45), 239 (35), 237 (46), 57 (71), 41 (25).

***N*-Boc-*N*-methyl-(1-acetyl-6-bromoindol-3-yl)glycine (4)**

A solution of **16** (777 mg, 1.67 mmol) and $RuCl(PPh_3)_3$ (172 mg, 0.18 mmol) in EtOH-$H_2O$ (9 : 1, 10 ml) was heated at 70 °C for 20 h. After concentration of the reaction mixture, the residue was purified by column chromatography on silica-gel with $CH_2Cl_2$-MeOH (5 : 1) to give **4** (542mg, 76 %) as a viscous oil.
IR ($CHCl_3$) ν $cm^{-1}$ : 1716, 1684.
$^1$H-NMR ($CDCl_3$, 300MHz) _: 1.42 (9H, s, t-Bu), 2.52 (3H, s, NCOMe), 2.57 (3H, s, NMe), 6.10 (1H, brs, C**H**NMe), 7.23 (1H, d, *J* = 8.1 Hz, C5-H), 7.27 (1H, d, *J* = 7.9, C4-H), 7.49 (1H, s, C2-H), 8.53 (1H, s, C7-H).

**Methyl *N*-Boc-*N*-methyl-(1-acetyl-6-bromoindol-3-yl)glycine-(1-acetyl-6-bromo-indol-3-yl)glycine ester (17)**

To a solution of **4** (56 mg, 0.13 mmol) and methyl indolylglycine ester **3a** (116 mg, 0.27 mmol) in dry THF (4 ml), a solution of BOP (70 mg, 0.16 mmol) and DIEA(28 _l, 0.16 mmol) was added at 0 °C, and then the mixture was stirred at 0 °C for 30 min. After standing at room temperature for 4 h, the reaction mixture was extracted with AcOEt. The extract was washed with 1*N* HCl and with brine, dried over $MgSO_4$, and concentrated. The residue was purified by column chromatography on silica-gel with AcOEt-hexane (1 : 1) to give **17** (67 mg, 67 %) and **18** (21 mg, 21 %).
**17**: mp 210 °C
IR ($CHCl_3$) ν $cm^{-1}$ : 1748, 1717, 1686.
$^1$H-NMR ($CDCl_3$, 300MHz) _: 1.45 (9H, s, t-Bu), 2.38 (3H, s, NCOMe**,** N'-1), 2.56 (3H, s, NCOMe**,** N''-1), 2.62 (3H, s, NMe), 3.71 (3H, s, $CO_2$Me), 5.76 (1H, d, *J* = 7.2 Hz, NHC**H**), 6.04 (1H, brs, NMeC**H**), 7.16 (1H, d, *J* = 8.3 Hz, C'4-H), 7.19 (1H, s, C'2-H), 7.30 (1H, dd, *J* = 8.6, 1.7 Hz, C''5-H), 7.39 (1H, dd, *J* = 8.3, 1.7 Hz, C'5-H), 7.46 (1H, d, *J* = 8.6 Hz, C''4-H), 7.48 (1H, s, C''2-H), 8.58 (1H, d, *J* = 1.7 Hz, C7''-H), 8.60 (1H, d, *J* = 1.7 Hz, C7'-H)
MS m/s (%) : 734 (M+4, 1) 732 (M+2, 1), 730 ($M^+$, 1), 325 (18), 323 (20), 295 (31), 293 (31), 282 (12), 281 (77), 280 (13), 279 (74), 278 (20), 277 (48), 253 (11), 251 (13), 239, (30), 237, (36), 224 (11), 223 (12), 222 (11), 201 (18), 73 (14), 57 (20), 56 (61), 55 (23), 44 (91), 43 (27), 42 (14), 41 (100), 39 (32)

**3, 6-Di(3-indolyl)-1-methylpiperazine-2, 5-dione (2)**

A solution of **17** (43 mg, 0.058 mg) in $HCO_2H$ (10 ml) was kept at room temperature for 1 h. After removal of $HCO_2H$, amine (mp 178–181 °C, 37 mg, 99.7 %) as white crystals were obtained. To a solution of this amine (8 mg, 0.012 mmol) in MeOH (4 ml), 28% $NH_4OH$ was added at 0°C. After 1 h and 4,5 h, further $NH_4OH$ (each 1 ml) was added. The reaction mixture was concentrated to give residue, which was purified

by silica-gel column chromatography with $CH_2Cl_2$-MeOH (7 : 1) to give **2** (mp 229–232 °C, 4.6 mg, 70 %) as white crystals.
IR (KBr) ν $cm^{-1}$ : 1662.
$^1$H-NMR (acetone-$d_6$, 300MHz) _: 2.97 (3H, s, NMe), 5.47 (1H, s, NHC**H**), 5.55 (1H, s, NMeC**H**), 7.16 (1H, dd, *J* = 8.4, 1.8 Hz, C'4-H), 7.22 (1H, dd, *J* = 8.6, 1.8 Hz, C''4-H), 7.446 (1H, d, *J* = 0.9 Hz, C'2-H), 7.447 (1H, s, NHCO), 7.45 (1H, d, *J* = 0.9 Hz, C''2-H), 7.57 (1H, d, *J* = 8.4 Hz, C'5-H), 7.62 (1H, dd, *J* = 1.8, 0.6 Hz, C'7-H), 7.66 (1H, dd, *J* = 1.8, 0.6 Hz, C''7-H), 7.76 (1H, d, *J* = 8.6 Hz, C''5-H), 10.39 (1H, s, N'1-H), 10.58 (1H, s, N''2-H).
MS m/s (%) : 518 (M+4, 18) 516 (M+2, 37), 514 ($M^+$, 24), 321 (99), 319 (100), 239 (25), 237 (49), 235 (28), 225 (30), 223 (37), 71 (20).

**Dragmacidin A (1b)**

$BH_3$-THF (1.0 M, 0.88 ml, 0.88 mmol) was added to a solution of **2** (35.3mg , 0.068 mmol) in THF (0.6 ml) at 0 °C, and the mixture was stirred at room temperature. After 5 days, since intermediates still remained, furthermore $BH_3$-THF (1.0 M, 0.5 ml, 0.5 mmol) was added to the mixture. The reaction mixture was stirred at the same temperature for a day, and 1*N* HCl (0.31 ml) was added at 0 °C. The reaction mixture was stirred for 2 h, condensed, and neutralized with $NaHCO_3$, and extracted with AcOEt. The extract was dried over $MgSO_4$ and concentrated. The residue was purified by silica-gel column chromatography with AcOEt-MeOH (9 : 1) to give **1b** (14.8 mg, 45 %) as a viscous oil.
IR (KBr) ν $cm^{-1}$ : 3422, 3290, 2945, 2840, 2795, 1616, 1545.
$^1$H-NMR (acetone-$d_6$, 400MHz) _: 2.08 (3H, s, NMe), 2.36 (1H, t, *J* = 10.8 Hz, C**H**$_2$NMe, ax), 3.06 (1H, dd, *J* = 11.6, 3.2 Hz, C**H**$_2$NH, eq), 3.17 (1H, dd, *J* = 10.8, 2.6 Hz, C**H**$_2$NMe, eq), 3.29 (1H, dd, *J* = 11.6, 10.4 Hz, C**H**$_2$NH, ax), 3.39 (1H, dd, *J* = 10.4, 3.2 Hz, C**H**NMe), 4.41 (1H, dd, *J* = 10.4, 2.6 Hz, C**H**NH), 7.168 (1H, dd, *J* = 8.4, 1.2 Hz, C'5-H), 7.172 (1H, dd, *J* = 8.4, 1.2 Hz, C''5-H), 7.35 (1H, d, *J* = 2.4 Hz, C''2-H), 7.38 (1H, d, *J* = 1.9, Hz, C'2-H), 7.60 (1H, d, *J* = 1.2 Hz, C''7-H), 7.61 (1H, d, *J* = 1.2 Hz, C'7-H), 7.81 (1H, d, *J* = 8.4 Hz, C'4-H), 7.91 (1H, d, *J* = 8.4 Hz, C''4-H), 10.27 (1H, bs, N'1-H), 10.27 (1H, bs, N''1-H),
MS m/s (%) : 490 (M+4, 1) 488 (M+2, 2), 480 ($M^+$, 1), 293 (17), 291 (19), 253 (96), 251 (100), 223 (75), 221 (58), 210 (19), 208 (9), 197 (65), 195 (70)
$^{13}$C-NMR (acetone-$d_6$, 100MHz) _: 44.0, 54.2, 54.4, 63.0, 64.2, 114.85, 114.81, 115.01, 115.7, 116.7, 118.1, 121.8, 122.1, 122.2, 122.3, 123.5, 124.7, 126.3, 126.4, 138.3, 138.4.

**Natural Dragmacidin A**

lit.[2], IR (film) ν $cm^{-1}$ : 3413, 3284, 2947, 2837, 2790, 1615, 1546.
$^1$H-NMR (acetone-$d_6$, 400MHz) _: 2.09 (3H, s, NMe), 2.38 (1H, dd, *J* = 11.0, 10.4 Hz, C**H**$_2$NMe, ax), 3.07 (1H, dd, *J* = 11.0, 3.0 Hz, C**H**$_2$NH, eq), 3.18 (1H, dd, *J* = 11.0, 2.6 Hz, C**H**$_2$NMe, eq), 3.29 (1H, dd, *J* = 11.0, 10.5 Hz, C**H**$_2$NH, ax), 3.41 (1H, dd, *J* = 10.5, 3.0 Hz, C**H**NMe), 4.43 (1H, dd, *J* = 10.4, 2.6 Hz, C**H**NH), 7.17 (1H, dd, *J* = 8.5, 1.2 Hz, C'5-H), 7.18 (1H, dd, *J* = 8.5, 1.4 Hz, C''5-H), 7.35 (1H, d, *J* = 2.3 Hz, C''2-H), 7.39 (1H, d, *J* = 1.8, Hz, C'2-H), 7.61 (1H, d, *J* = 1.4 Hz, C''7-H), 7.61 (1H, d, *J* = 1.2 Hz, C'7-H), 7.81 (1H, d, *J* = 8.5 Hz, C'4-H), 7.91 (1H, d, *J* = 8.5 Hz, C''4-H), 10.28 (1H, bs, N'1-H), 10.28 (1H, bs, N''1-H),
MS m/s (%) : 490 (M+4, 1) 488 (M+2, 2), 480 ($M^+$, 1), 293 (11), 291 (11), 253 (80), 251 (80), 223 (60), 221 (60), 210 (12), 208 (12), 197 (100), 195 (100)
$^{13}$C-NMR (acetone-$d_6$, 100MHz) _: 44.2, 54.1, 54.3, 63.3, 64.2, 115.0, 115.0, 115.1,

115.2, 117.5, 118.8, 122.1, 122.4, 122.4, 122.6, 123.9, 124.9, 125.0, 126.6, 138.7, 138.8.