Supporting Information for
New Synthetic Method for Indole-2-carboxylate and Its Application
to Total Synthesis of Duocarmycin SA

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2-Benzyloxy-4-nitroaniline (9). K_2CO_3 (18.0 g, 130.2 mmol) and benzyl bromide (11.3 g, 66.1 mmol) were successively added to a solution of **8** (10.0 g, 64.9 mmol) in acetone (500 ml) and the mixture was refluxed for 8 h. After being cooled, the inorganic precipitate was filtered through a Celite pad and the filtrate was concentrated *in vacuo*. The resulting solid was recrystallized from AcOEt to afford **9** (14.8 g, 93%) as yellow needles; mp 151-153°C, lit.^{s1} mp 144-145°C; IR (film, cm^{-1}) 3483, 3363, 1626, 1481, 1229; $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 4.57 (2H, br s), 5.15 (2H, s), 6.65 (1H, d, $J = 8.8$ Hz), 7.37-7.45 (5H, m), 7.77 (1H, d, $J = 2.4$ Hz), 7.82 (1H, dd, $J = 8.8, 2.4$ Hz); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ 70.8, 107.2, 111.9, 119.3, 127.8, 128.4, 128.7, 135.6, 138.4, 143.4, 144.4; MS m/z 244 (M^+ , 13.1%), 91 (100%); HRMS Calcd $\text{C}_{13}\text{H}_{12}\text{N}_2\text{O}_3$: 244.0848. Found: 244.0818; *Anal.* Calcd $\text{C}_{13}\text{H}_{12}\text{N}_2\text{O}_3$: C, 63.93; H, 4.95; N, 11.47. Found: C, 64.02; H, 5.12; N, 11.42.

2-Benzyloxy-6-iodo-4-nitroaniline (10). ICl (16.6 g, 102.2 mmol) was added to a solution of **9** (5.0 g, 20.5 mmol) in THF (400 ml) at room temperature and the mixture was refluxed for 3 h. Saturated aqueous $\text{Na}_2\text{S}_2\text{O}_3$ (200 ml) was added to the mixture and the aqueous phase was extracted with AcOEt. The organic solution was washed with saturated aqueous NaCl solution, dried over anhydrous MgSO_4 , and concentrated. The residue was chromatographed on silica gel [AcOEt-hexane (1:4)] to afford **10** (6.9 g, 91%) as a yellow solid; mp 105-106°C (yellow needles from AcOEt-hexane); IR (film, cm^{-1}) 3481, 3375, 1499, 1323, 1221; $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 5.02 (2H, s), 5.15 (2H, br s), 7.73-7.38 (5H, m), 7.72 (1H, d, $J = 2.3$ Hz), 8.28 (1H, d, $J = 2.3$ Hz); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ 71.2, 78.3, 106.4, 127.8, 128.0, 128.6, 128.7, 135.0, 138.4, 142.9, 143.8; MS m/z : 370 (M^+ , 55%), 91 (100%); HRMS Calcd

C₁₃H₁₁IN₂O₃: 369.9814. Found: 369.9808; *Anal.* Calcd for C₁₃H₁₁IN₂O₃: C, 42.18; H, 3.00; N, 7.57. Found: C, 42.15; H, 3.03; N, 7.48.

N-Methanesulfonyl-2-benzyloxy-6-iodo-4-nitroaniline (7). A solution of **10** (1.00 g, 2.70 mmol) in anhydrous THF (17 ml) was added to a suspension of NaH [60% in oil, 0.324 g, 8.10 mmol, washed with anhydrous hexane (50 ml)] in anhydrous THF (10 ml) at 0°C. After being stirred at the same temperature for 30 min, MsCl (0.89 g, 7.77 mmol) was added to the mixture and the stirring was continued for 12 h at room temperature. H₂O was added to the mixture and the aqueous phase was extracted with AcOEt. The organic solution was washed with saturated aqueous NaCl solution, dried over anhydrous MgSO₄, and the solvent was evaporated to afford **11**, which was used to the next reaction without further purification.

TBAF (1.0 M solution in THF, 13 ml, 13.0 mmol) was added to a solution of **11** in THF (27 ml) at room temperature and stirred for 2 days. H₂O was added to the mixture and the aqueous phase was extracted with AcOEt. The combined organic solution was washed with saturated aqueous NaCl solution, dried over anhydrous MgSO₄, and concentrated. The residue was purified by silica gel column chromatography [AcOEt-hexane (1:3)] to provide **7** [0.91 g, 75% (2 steps)] as a yellow solid and **10** (0.25 g, 25%) was recovered from the later fraction. **7**; mp 203-204°C (colorless plates from AcOEt-hexane); IR (film, cm⁻¹) 3254, 1524, 1323, 1148; ¹H-NMR (400 MHz, CDCl₃) δ 3.02 (3H, s), 5.20 (2H, s), 6.39 (1H, br s), 7.41-7.48 (5H, m), 7.90 (1H, d, *J* = 2.4 Hz), 8.36 (1H, d, *J* = 2.4 Hz); ¹³C-NMR (100 MHz, CDCl₃) δ 43.5, 72.3, 97.2, 108.1, 126.5, 128.7, 128.9, 129.2, 133.8, 134.3, 146.3, 152.4; MS *m/z* 448 (M⁺, 11.6%), 367 (16.3%), 91 (100%); HRMS Calcd C₁₄H₁₃IN₂O₅S: 447.9590. Found: 447.9611; *Anal.* Calcd C₁₄H₁₃IN₂O₅S: C, 37.51; H, 2.92; N, 6.25. Found: C, 37.53; H, 2.95; N, 6.33.

Methyl 7-Benzyloxy-1-methanesulfonyl-5-nitroindole-2-carboxylate (5). $i\text{Pr}_2\text{NEt}$ (0.14 ml, 0.80 mmol), **7** (57 mg, 0.13 mmol), methyl propiolate (31.7 μl , 0.36 mmol), and $\text{Pd}(\text{PPh}_3)_4$ (14.7 mg, 0.01 mmol) were added successively to a solution of ZnBr_2 (85.8 mg, 0.38 mmol) in THF (1.3 ml) at room temperature and the mixture was refluxed for 11 h. Saturated aqueous NH_4Cl was added to the mixture and the aqueous solution was extracted with AcOEt. The organic solution was washed with saturated aqueous NaCl solution, dried over anhydrous MgSO_4 , and the solvent was evaporated. The residue was chromatographed on silica gel [AcOEt-hexane (1:4)] to afford **5** (29 mg, 56%) as a colorless solid; mp 201-202°C (colorless needles from AcOEt-hexane); IR (film, cm^{-1}) 1730, 1524, 1339, 1175; ^1H -NMR (400 MHz, CDCl_3) δ 3.42 (3H, s), 3.93 (3H, s), 5.29 (2H, s), 7.26 (1H, s), 7.38 - 7.50 (3H, m), 7.58 (2H, dd, $J = 7.7, 1.6$ Hz), 7.91 (1H, d, $J = 1.7$ Hz), 8.18 (1H, d, $J = 1.7$ Hz); ^{13}C -NMR (100 MHz, CDCl_3) δ 42.9, 52.9, 72.2, 104.9, 111.7, 117.5, 128.7 (two peaks are overlapped), 129.0, 130.2, 132.7, 134.4, 136.2, 145.6, 147.5, 160.5; MS m/z 404 (M^+ , 1.8%), 91 (100%); HRMS Calcd $\text{C}_{18}\text{H}_{16}\text{N}_2\text{O}_7\text{S}$: 404.0678. Found: 404.0671; *Anal.* Calcd $\text{C}_{18}\text{H}_{16}\text{N}_2\text{O}_7\text{S}$: C, 53.46; H, 3.99; N, 6.93. Found: C, 53.24; H, 3.99; N, 6.64.

Methyl 7-Benzyloxy-4-iodo-1-methanesulfonyl-5-(N-methoxycarbonylamino)indole-2-carboxylate (18). PtO_2 (27 mg, 0.12 mmol) was added to a solution of **5** (241 mg, 0.60 mmol) in AcOEt (12 ml) and stirred under hydrogen atmosphere for 12 h. PtO_2 was filtered off and the filtrate was concentrated in vacuo to afford **16**, which was used to the next reaction without further purification. NIS (142 mg, 0.63 mmol) was added to a solution of **16** in anhydrous THF (6 ml) at 0°C and the

mixture was stirred for 5 min. Saturated aqueous Na₂SO₃ solution was added to the mixture and extracted with AcOEt. The combined organic solution was washed with saturated aqueous NaCl solution, dried over anhydrous MgSO₄, and the solvent was evaporated to afford **17**, which was used to the next reaction without further purification.

DMAP (16 mg, 0.13 mmol) and ClCO₂Me (92 μ l, 1.19 mmol) were added to a solution of **17** in pyridine (6 ml) at 0°C and the mixture was stirred for 2.5 h. Saturated aqueous CuSO₄ solution was added to the mixture and the aqueous phase was extracted with AcOEt. The combined organic solution was washed with saturated aqueous NaCl solution and dried over anhydrous MgSO₄. The solvent was evaporated and the residue was chromatographed on silica gel [AcOEt-hexane (1:2)] to afford **18** [247mg, 74% (from **5**)] as a colorless solid; mp 187-188°C (colorless needles from AcOEt-hexane); IR (film, cm⁻¹) 1730, 1358, 1225, 1173; ¹H-NMR (400 MHz, CDCl₃) δ 3.37 (3H, s), 3.83 (3H, s), 3.91 (3H, s), 5.21 (2H, s), 7.03 (1H, s), 7.09 (1H, s), 7.40-7.42 (3H, m), 7.56 (2H, d, *J* = 6.6 Hz), 8.01 (1H, br s); MS *m/z* 558 (M⁺, 5.2%), 431 (5.2%), 352 (12.4%), 121 (18.8%), 91 (100%); HRMS Calcd C₂₀H₁₉IN₂O₇S: 557.9958. Found: 557.9974; *Anal.* Calcd for C₂₀H₁₉IN₂O₇S: C, 43.02; H, 3.43; N, 5.02. Found: C, 42.72; H, 3.48; N, 4.79.

Methyl 7-Benzyloxy-1-methanesulfonyl-5-(*N*-methoxycarbonylamino)-4-(1-propyn-3-ol)indole-2-carboxylate (19**).** CuI (7.2 mg, 0.038 mmol), propargyl alcohol (0.45 ml, 7.73 mmol), and PdCl₂(PPh₃)₂ (8.0 mg, 0.011 mmol) were added to a solution of **18** (212 mg, 0.38 mmol) in Et₃N (1.3 ml) and DMF (3.8 ml) and the mixture was stirred at 50°C for 2 h. H₂O was added to the mixture and extracted with AcOEt. The combined organic solution was washed with saturated aqueous NaCl solution and dried over anhydrous MgSO₄. The solvent was evaporated to provide a yellow solid, which was recrystallized from chloroform-methanol to afford **19** (154 mg, 83%) as yellow prisms; mp

172-174°C; IR (film, cm^{-1}) 3395, 1730, 1360, 1219, 1171; ^1H -NMR (400 MHz, CDCl_3) δ 2.04 (1H, t, J = 6.0 Hz), 3.37 (3H, s), 3.81 (3H, s), 3.90 (3H, s), 4.61 (2H, d, J = 6.0 Hz), 5.22 (2H, s), 7.23 (1H, s), 7.40-7.42 (4H, m), 7.57 (2H, d, J = 6.4 Hz), 8.07 (1H, br s, NH); ^{13}C -NMR (100 MHz, CDCl_3) δ 42.8, 51.6, 52.56, 52.64, 71.6, 77.7, 96.4, 97.2, 101.6, 117.3, 124.8, 128.5, 128.7, 129.0, 132.1, 134.4, 135.1, 138.1, 148.1, 153.8, 160.9; MS m/z 486 (M^+ , 40.8%), 407 (39.3%), 121 (52.1%), 91 (100%); HRMS Calcd $\text{C}_{23}\text{H}_{22}\text{N}_2\text{O}_8\text{S}$: 486.1097. Found: 486.1136.

Methyl 4-(Benzyloxy)-6,7-dihydro-6-(methoxycarbonyl)-3H-pyrrolo[3,2-f]quinoline-2-carboxylate (22). Pd-C (92mg) and quinoline (20 μl) were added to a solution of **19** (500 mg, 1.03 mmol) in THF (8.8 ml) and MeOH (4.4 ml). After being stirred for 8 h under H_2 atmosphere, the mixture was filtered through a Celite pad and the filtrate was concentrated to afford **20**, which was used to the next reaction without further purification.

Diethyl azodicarboxylate (40% toluene solution, 0.9 ml, 2.07 mmol) was added to a solution of **20** and PPh_3 (540 mg, 2.06 mmol) in THF (10 ml) at 0°C and stirred for 2 h at room temperature. MeOH (5 ml) and K_2CO_3 (414 mg, 3.00 mmol) were added to the mixture and stirred for another 12 h. The mixture was filtered through a Celite pad and the filtrate was extracted with AcOEt. The combined organic solution was washed with saturated aqueous NaCl solution, dried over anhydrous MgSO_4 , and concentrated. The residue was chromatographed on silica gel [AcOEt-hexane (1:3)] to provide **22**^{S2} [400 mg, 99% (from **19**)] as a light yellow solid; mp 171-173°C (light yellow plates from AcOEt-hexane); IR (film, cm^{-1}) 1699, 1251; ^1H -NMR (400 MHz, CDCl_3) δ 3.73 (3H, s), 3.93 (3H, s), 4.42 (2H, m), 5.22 (2H, s), 6.01 (1H, m), 6.81 (1H, d, J = 9.7 Hz), 7.23 (1H, d, J = 2.4 Hz), 7.25 (1H, s), 7.37-7.49 (5H, m), 9.04 (1H, br s, NH); ^{13}C -NMR (100 MHz, CDCl_3) δ 43.6, 51.9, 52.9, 70.4, 106.6,

114.8, 123.0, 124.8, 125.1, 125.7, 127.3, 127.6, 128.1, 128.1, 128.05, 128.11, 136.3, 143.7, 154.9, 161.7; MS m/z 392 (M^+ , 100%), 301 (82.7%), 225 (79.5%), 91 (40.0%); HRMS Calcd $C_{22}H_{20}N_2O_5$: 392.1372. Found: 392.1391; *Anal.* Calcd for $C_{22}H_{20}N_2O_5$: C, 67.32; H, 5.14; N, 7.14. Found: C, 67.28; H, 5.17; N, 7.07.

Methyl 4-(Benzyloxy)-3,7,8,9-tetrahydro-8-hydroxy-6-(methoxycarbonyl)-6H-pyrrolo[3,2-f]quinoline-2-carboxylate (4). MCPBA (69% purity 59.0 mg, 0.236 mmol) was added to a solution of **22** (46.0 mg, 0.117 mmol) in anhydrous CH_2Cl_2 (1.2 ml) at $0^\circ C$. After being stirred for 5 min, Et_3SiH (89 μ l, 0.557 mmol) and $BF_3\cdot OEt_2$ (110 μ l, 0.868 mmol) were added and the stirring was continued for another 10 min at the same temperature. H_2O was added to the mixture and the aqueous phase was extracted with $CHCl_3$. The organic solution was washed with saturated aqueous NaCl solution, dried over anhydrous $MgSO_4$, and the solvent was evaporated. The residue was purified by silica gel column chromatography [AcOEt-hexane (1:1)] to afford **4** (20.1 mg, 42%) as colorless prisms; IR (film, cm^{-1}) 3294, 1697, 1441, 1346, 1250; 1H -NMR (400 MHz, $CDCl_3$) δ 2.89 (1H, dd, $J = 17.3, 4.9$ Hz), 3.23 (1H, dd, $J = 17.3, 5.9$ Hz), 3.75 (3H, s), 3.75-3.92 (2H, m), 3.92 (3H, s), 4.36 (1H, m), 5.18 (2H, s), 7.11 (1H, s), 7.17 (1H, br s), 7.36-7.48 (5H, m), 9.18 (1H, br s, NH); ^{13}C -NMR (100 MHz, $CDCl_3$) δ 32.9, 50.5, 52.0, 53.1, 64.9, 70.4, 104.0, 106.9, 112.1, 125.5, 126.8, 127.2, 127.8, 128.2, 128.6, 130.9, 136.4, 143.2, 156.1, 161.9; MS m/z 410 (M^+ , 100%), 319 (28.4%), 225 (16.8%), 91 (38.0%); HRMS Calcd $C_{22}H_{22}N_2O_6$: 410.1478. Found: 410.1488.

The spectral data of **4** was identified with that of the published data.^{S2,3}

Methyl 4-(Benzyloxy)-3,7,8,9-tetrahydro-8-methanesulfonyloxy-6-(methoxycarbonyl)-6H-pyrrolo[3,2-*f*]quinoline-2-carboxylate (24). MsCl (2.2 μ l, 0.028 mmol) was added to a solution of **4** (5.9 mg, 0.014 mmol) and Et₃N (6 μ l, 0.043 mmol) in anhydrous CH₂Cl₂ (1 ml) and stirred for 1 h at room temperature. H₂O was added to the mixture and extracted with AcOEt. The organic solution was washed with saturated aqueous NaCl solution, dried over anhydrous MgSO₄, and concentrated. The residue was chromatographed on silica gel [AcOEt-hexane (1:2)] to afford **24** (5.3 mg, 75%) as colorless amorphous; IR (film, cm⁻¹) 1703, 1339, 1252; ¹H-NMR (400 MHz, CDCl₃) δ 3.06 (3H,s), 3.21 (1H, dd, *J* = 17.8, 4.0 Hz), 3.39 (1H, dd, *J* = 17.8, 6.2 Hz), 3.77 (3H,s), 3.84 (1H, dd, *J* = 13.6, 2.5 Hz), 3.92 (3H, s), 4.28 (1H, dd, *J* = 13.6, 5.9 Hz), 5.19 (2H, s), 5.31 (1H, m), 7.10 (1H, d, *J* = 2.5 Hz), 7.37-7.48 (6H, m), 9.17 (1H, br s, NH); ¹³C-NMR (100 MHz, CDCl₃) δ 30.8, 38.8, 48.1, 52.1, 53.2, 70.5, 73.5, 103.8, 106.6, 110.4, 125.6, 126.8, 127.1, 127.8, 128.3, 128.6, 130.8, 136.2, 143.6, 155.6, 161.7; MS *m/z* 488 (M⁺, 89.6%), 379 (30.2%), 301 (100%), 269 (32.8%), 225 (38.6%), 91 (84.9%); HRMS Calcd C₂₃H₂₄N₂O₈S: 488.1253. Found: 488.1268.

Methyl 1,2,4,5,8,8a-Hexahydro-4-oxocyclopropa[*c*]pyrrolo[3,2-*e*]indole-6-carboxylate (2). Pd(OH)₂ (3 mg, 0.021 mmol) was added to a solution of **24** (5.3 mg, 0.011 mmol) in MeOH (1 ml) and the mixture was stirred under H₂ atmosphere for 1h. The mixture was filtered through a Celite pad and the filtrate was concentrated. MeOH (1 ml) and K₂CO₃ (4.5 mg, 0.033 mmol) were added to the residue and stirred for 1.5 h at room temperature. Saturated aqueous NH₄Cl solution was added to the

mixture and extracted with CHCl₃-MeOH (9:1) solution. The organic solution was washed with saturated aqueous NaCl solution and dried over anhydrous MgSO₄. The solvent was evaporated and the residue was purified by preparative TLC [CHCl₃-MeOH (9:1 v/v)] to afford **2** (2.2 mg, 83%) as a colorless solid; IR (film, cm⁻¹) 1701, 1597, 1524, 1306, 1223; ¹H-NMR (400 MHz, CDCl₃) δ 1.33 (1H, t, *J* = 4.0 Hz), 1.58 (1H, dd, *J* = 7.7, 4.0 Hz), 2.77 (1H, m), 3.63 (1H, d, *J* = 10.4 Hz), 3.82 (1H, m), 3.86 (3H, s), 5.16 (1H, br s, NH), 5.61 (1H, s), 6.52 (1H, s), 9.88 (1H, br s, NH); ¹³C-NMR (100 MHz, CDCl₃) δ 26.0, 27.5, 31.3, 51.2, 51.9, 96.8, 107.5, 124.9, 127.5, 132.5, 161.1, 171.7, 177.1; MS *m/z* 244 (M⁺, 100%), 212 (61.3%), 155 (77.5%). HRMS Calcd C₁₃H₁₂N₂O₃: 244.0848. Found: 244.0863. The spectral data of **2** was identified with that of the published data.^{S2,3}

Duocarmycin SA (1). K₂CO₃ (19.6 mg, 0.142 mmol) and **3**^{S2,4} (6.4 mg, 21.3 μmol) were added to a solution of **2** (3.5 mg, 14.2 μmol) in DMF (0.5 ml) at room temperature and stirring was continued for 3 h at same temperature. The reaction mixture was diluted with CH₂Cl₂ (2 ml), then citric acid monohydrate (33 mg, 0.16 mmol) and H₂O (2 ml) were added. After being stirred for 2 min, the mixture was extracted with CH₂Cl₂-MeOH (9:1) and the organic solution was washed with saturated aqueous NaHCO₃ solution. The organic phase was dried over anhydrous MgSO₄ and concentrated in vacuo. The residue was purified by preparative TLC [CH₂Cl₂-MeOH (9:1 v/v)] to afford duocarmycin SA (**1**) (3.6 mg, 53%) as yellow powder; IR (film, cm⁻¹) 3244 (br), 2937, 2837, 1717, 1618, 1650, 1520, 1491, 1466, 1429, 1387, 1304, 1265, 1207, 1140, 1109, 1047, 999, 752; ¹H-NMR (400 MHz, CDCl₃) δ 1.57-1.58 (1H, m), 1.75 (1H, dd, *J* = 7.2, 4.8 Hz), 2.75-2.83 (1H, m), 3.89 (3H, s), 3.91 (3H, s), 3.94 (3H, s), 4.07 (3H, s), 4.38 (1H, d, *J* = 10.2 Hz), 4.46 (1H, dd, *J* = 10.2, 4.9 Hz), 6.60

(1H, s), 6.78 (1H, s), 6.94 (1H, s), 7.02 (1H, s), 9.24 (1H, br s, NH), 9.80 (1H, br s, NH); ¹³C-NMR (100 MHz, CDCl₃) δ 23.6, 26.1, 31.4, 52.2, 54.9, 56.3, 61.2, 61.5, 97.5, 107.5, 107.7, 112.4, 123.1, 126.1, 126.5, 128.2, 129.6, 131.4, 138.7, 140.8, 150.3, 160.7, 160.8, 161.2, 177.5; FAB-MS *m/z* 477 (M⁺).

The spectral data of **1** was identified with that of the published data.^{S2,5}

General Procedure for Table 1. ⁱPr₂NEt, 2-iodoaniline derivatives (**12a-e**), methyl propiolate, and Pd(PPh₃)₄ were successively added to a solution ZnBr₂ in THF at rt and refluxed for 17 h. Saturated aqueous NH₄Cl solution was added to the reaction mixture and extracted with AcOEt (three times). The combined organic solution was washed with saturated aqueous NaCl solution, dried over anhydrous MgSO₄, and concentrated at the reduced pressure.

N-[2-(Carbomethoxyethynyl)phenyl]methanesulfonamide (13a**) and Methyl 1-Methylsulfonylindole-2-carboxylate (**14a**) (entry 1).** ZnBr₂ (182 mg, 0.81 mmol), ⁱPr₂NEt (0.28 ml, 1.61 mmol), **12a** (80 mg, 0.27 mmol), methyl propiolate (0.048 ml, 0.054 mmol), and Pd(PPh₃)₄ (9.3 mg, 0.0081 mmol) in THF (3 ml) were reacted according to the general procedure. The residue was chromatographed on silica gel [AcOEt-hexane (1:3)] to afford **13a**^{S6} (38%), **14a**^{S6} (10%), and **12a** (22%) as an inseparable mixture. The yields of the each compound were determined by ¹H-NMR spectrum. The analytical sample was obtained by repeating the chromatography.

13a: mp 123°C (colorless needles from AcOEt-hexane); IR (film, cm⁻¹) 3294, 3015, 2226, 1713, 1491, 1400, 1342, 1159; ¹H-NMR (400 MHz, CDCl₃) δ 3.08 (3H, s), 3.87 (3H, s), 7.02 (1H, s), 7.19 (1H, t, *J* =

7.6 Hz), 7.49 (1H, t, $J = 8.0$ Hz), 7.59 (1H, d, $J = 7.6$ Hz), 7.64 (1H, d, $J = 8.0$ Hz); ^{13}C -NMR (100 MHz, CDCl_3) δ 40.1, 53.1, 80.9, 86.9, 110.6, 120.3, 124.9, 132.5, 134.0, 139.3, 153.5; MS m/z : 253 (M^+ , 60.1%), 221 (100%). HRMS Calcd $\text{C}_{11}\text{H}_{11}\text{NO}_4\text{S}$: 253.0409. Found: 253.0397.

14a: mp 88-90°C (colorless pole from AcOEt-hexane); IR (film, cm^{-1}) 1730, 1367, 1350, 1267, 1205, 1170; ^1H -NMR (400 MHz, CDCl_3) δ 3.71 (3H, s), 3.95 (3H, s), 7.27-7.32 (2H, m), 7.44 (1H, t, $J = 7.3$ Hz), 7.63 (1H, d, $J = 8.3$ Hz), 8.04 (1H, d, $J = 8.3$ Hz); ^{13}C -NMR (100 MHz, CDCl_3) δ 43.5, 52.7, 115.0, 117.3, 122.7, 123.8, 127.17, 127.24, 130.4, 138.5, 161.3; MS m/z : 253 (M^+ , 65.0%), 175 (100%), 143 (81.5%); HRMS Calcd $\text{C}_{11}\text{H}_{11}\text{NO}_4\text{S}$: 253.0409. Found: 253.0400.

N-[2-(Carbomethoxyethynyl)-4-methylphenyl]methanesulfonamide (13b) (entry 2). ZnBr_2 (134 mg, 0.60 mmol), $i\text{Pr}_2\text{NEt}$ (0.21 ml, 1.2 mmol), **12b** (62 mg, 0.20 mmol), methyl propiolate (0.036 ml, 0.4 mmol), and $\text{Pd}(\text{PPh}_3)_4$ (6.9 mg, 0.0060 mmol) in THF (2 ml) were reacted according to the general procedure. The residue was chromatographed on silica gel [AcOEt-hexane (1:3) to afford **13b** (31.4 mg, 59%) and **14b** (1 mg, 2%); **13b**: mp 98°C (colorless needles from AcOEt-hexane); IR (film, cm^{-1}) 3265, 2216, 1713, 1499, 1337, 1308, 1229, 1155; ^1H -NMR (400 MHz, CDCl_3) δ 2.33 (3H, s), 3.03 (3H, s), 3.13 (3H, s), 6.87 (1H, s), 7.29 (1H, dd, $J = 8.5, 2.0$ Hz), 7.39 (1H, d, $J = 2.0$ Hz), 7.52 (1H, d, $J = 8.5$ Hz); ^{13}C -NMR (100 MHz, CDCl_3) δ 20.6, 39.9, 53.1, 81.3, 86.4, 111.2, 121.5, 133.3, 134.1, 135.3, 136.8, 153.6; MS m/z : 267 (M^+ , 79.7%), 235 (100%). HRMS Calcd $\text{C}_{12}\text{H}_{13}\text{NO}_4\text{S}$: 267.0565. Found: 267.0562.

N-[2-(Carbomethoxyethynyl)-5-methoxyphenyl]methanesulfonamide (13c) (entry 3). ZnBr₂ (82.4 mg, 0.37 mmol), *i*Pr₂NEt (0.13 ml, 0.746 mmol), **12c** (40 mg, 0.122 mmol), methyl propiolate (0.023 ml, 0.259 mmol), and Pd(PPh₃)₄ (4.2 mg, 0.0036 mmol) in THF (2 ml)) were reacted according to the general procedure. The residue was chromatographed on silica gel [AcOEt-hexane (1:3)] to afford **13c** (7 mg, 20%); mp 157°C (colorless needles from AcOEt-hexane); IR (film, cm⁻¹) 3283, 2214, 1707, 1612, 1568, 1510, 1396, 1301, 1155; ¹H-NMR (400 MHz, CDCl₃) δ 3.07 (3H, s), 3.85 (3H, s), 3.86 (3H, s), 6.71 (1H, dd, *J* = 8.8, 2.4 Hz), 6.99 (1H, s), 7.19 (1H, d, *J* = 2.4 Hz), 7.50 (1H, d, *J* = 8.8 Hz); ¹³C-NMR (100 MHz, CDCl₃) δ 40.0, 53.0, 55.8, 81.9, 86.6, 102.2, 105.5, 111.4, 135.4, 141.3, 153.9, 162.9; MS *m/z*: 283 (M⁺, 100%), 251 (74.1%). HRMS Calcd C₁₂H₁₃NO₅S: 283.0514. Found: 283.0518.

Methyl 6-Chloro-1-methylsulfonylindole-2-carboxylate (14d) (entry 4). ZnBr₂ (202 mg, 0.90 mmol), *i*Pr₂NEt (0.31 ml, 1.78 mmol), **12d** (100 mg, 0.30 mmol), methyl propiolate (0.054 ml, 0.61 mmol), and Pd(PPh₃)₄ (10 mg, 0.0087 mmol) in THF (3 ml) were reacted according to the general procedure. The residue was chromatographed on silica gel [AcOEt-hexane (1:2)] to afford **14d** (75%, determined by ¹H-NMR spectrum). The analytical sample was afforded by repeating the chromatography; mp 157°C (colorless pole from AcOEt-hexane); IR (film, cm⁻¹) 1728, 1607, 1539, 1367, 1352, 1201, 1169; ¹H-NMR (600 MHz, CDCl₃) δ 3.73 (3H, s), 3.95 (3H, s), 7.26 (1H, d, *J* = 0.7 Hz), 7.28 (1H, dd, *J* = 8.2, 1.9 Hz), 7.55 (1H, d, *J* = 8.2 Hz), 8.08 (1H, d, *J* = 1.9 Hz); ¹³C-NMR (100 MHz, CDCl₃) δ 43.7, 52.8, 153.9, 162.9.

115.2, 116.8, 123.4, 124.6, 125.6, 130.9, 133.3, 138.6, 161.0; MS m/z : 287 (M^+ , 67.1%), 256 (12.1%), 209 (100%). HRMS Calcd $C_{11}H_{10}^{35}ClNO_4S$: 287.0019. Found: 287.0002, $C_{11}H_{10}^{37}ClNO_4S$: 288.9990. Found: 288.9969.

Methyl 5-Cyano-1-methylsulfonylindole-2-carboxylate (14e) (entry 5). $ZnBr_2$ (74 mg, 0.33 mmol), iPr_2NEt (0.11 ml, 0.63 mmol), **12e** (35.6 mg, 0.11 mmol), methyl propiolate (0.020 ml, 0.22 mmol), and $Pd(PPh_3)_4$ (3.8 mg, 0.0033 mmol) in THF (1.1 ml) were reacted according to the general procedure. The residue was chromatographed on silica gel [AcOEt-hexane (1:3)] to afford **14e** (21 mg, 69%); mp 152°C (colorless powder from AcOEt-hexane); IR (film, cm^{-1}) 2934, 2228, 1732, 1604, 1437, 1371, 1350, 1277, 1209, 1175, 1150; 1H -NMR (400 MHz, $CDCl_3$) δ 3.78 (3H, s), 3.98 (3H, s), 7.31 (1H, s), 7.66 (1H, dd, J = 8.8, 1.6 Hz), 7.99 (1H, d, J = 1.6 Hz), 8.16 (1H, d, J = 8.8 Hz); ^{13}C -NMR (100 MHz, $CDCl_3$) δ 43.9, 53.1, 107.6, 115.9, 116.1, 118.7, 127.2, 127.6, 129.5, 132.5, 139.8, 160.6; MS m/z : 278 (M^+ , 46.5%), 247 (11.2%), 200 (100%), 168 (85.9%), 140 (31.9%); HRMS Calcd $C_{12}H_{10}N_2O_4S$: 278.0361. Found: 278.0336.

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