Electronic Supplementary Information

Oxidative Two-way Regiocontrolled Coupling of 3-Methoxycarbonylcatechol and Indoles to Arylindoles

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1. General Information.
Unless otherwise noted, the substrates and solvents were purchased from commercial sources. Flash column chromatography was performed with Silica Gel 60 N (Kanto Chemical Co., Inc., 40-50 or 63–210 μm spherical, neutral). ¹H and ¹³C NMR spectra were recorded on a JEOL ECZ (¹H NMR: 400 MHz, ¹³C NMR: 100 MHz), ECA spectrometer (¹H NMR: 500 MHz, ¹³C NMR: 125 MHz, ²H NMR: 77 MHz), Bruker Biospin AVANCEIII (¹H NMR: 800 MHz, ¹³C NMR: 200 MHz) at room temperature in CDCl₃ and CD₃OD as a solvent (¹H NMR: δ= 7.26; ¹³C NMR: δ= 77.0 for CDCl₃, ¹H
NMR: \( \delta = 3.31 \); \(^{13}\)C NMR: \( \delta = 49.0 \) for CD\(_3\)OD). IR spectra were recorded by a Bruker FT-IR ALPHA. High-resolution mass spectra (HRMS) were measured by Shimadzu hybrid IT-TOF mass spectrometer (ESI-IT-TOF-MS) or JEOL JMS-T100TD (DART-TOF-MS). Melting points were measured by a SANSYO SMP-300 melting point apparatus. \( 1a, 2c, 2d \) and \( 2e \) were prepared as shown in Section 2. Other substrates and reagents were commercially available. 10\% Pd/C, Pt/C, and Ir/C were supplied by the N. E. Chemcat Corporation (Tokyo, Japan).

2. Preparation of substrates.

**Methyl-2,3-dihydroxybenzoate (3-methylcarbonyl catechol; \( 1a \))**

\[
\text{HO} \quad \text{OH} \quad \text{COOMe}
\]

To a solution of 2,3-dihydroxybenzoic acid (1.54 g, 10 mmol) in methanol (20 mL) was added concentrated sulfuric acid (1.0 mL, 18.3 mmol), and the reaction mixture was refluxed overnight. The solvent was concentrated in vacuo. To the residue was added water (20 mL), and the mixture was extracted with ethyl acetate (20 mL \( \times 3 \)). The organic layer was washed with water, dried over Na\(_2\)SO\(_4\), and filtered. The filtrate was concentrated in vacuo to give \( 1a \) (1.5 g, 9.1 mmol, 91\% yield).

Beige solid; \(^1\)H NMR (500 MHz, CDCl\(_3\)): \( \delta \) 10.90 (s, 1H), 7.37 (dd, \( J = 1.0, 8.0 \) Hz, 1H), 7.11 (dd, \( J = 1.0, 8.0 \) Hz, 1H), 6.80 (t, \( J = 8.0 \) Hz, 1H), 5.64 (s, 1H), 3.96 (s, 3H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \( \delta \); 170.7, 148.8, 145.0, 120.5, 119.8, 119.2, 112.3, 52.4. Spectroscopic data of \(^1\)H and \(^{13}\)C NMR of the product were identical to those reported in reference 1.

**N-Benzylindole (\( 2c \))**

\[
\text{N} \quad \text{H} \quad \text{O}
\]

To a solution of indole (590 mg, 5.04 mmol) and KOH (452 mg, 8.06 mmol) in THF (10 mL) was added benzyl chloride (0.860 mL, 7.47 mmol) at 0 \( ^\circ \)C. The reaction solution was allowed to warm to room temperature and was stirred overnight. After quenching with H\(_2\)O at 0 \( ^\circ \)C, the reaction mixture was extracted with ethyl acetate (10 mL \( \times 3 \)). The organic layer was dried over Na\(_2\)SO\(_4\), and the solvent was concentrated in vacuo. \( 2c \) (1.03 g, 4.95 mmol) was obtained in 99\% yield after purification by silica-gel column chromatography using \( n \)-hexane-ethyl acetate (30/1).

Pale red solid; \(^1\)H NMR (500 MHz, CDCl\(_3\)): \( \delta \) 7.65 (d, \( J = 8.0 \) Hz, 1H), 7.31–7.24 (m, 4H), 7.17 (t, \( J = 7.5 \) Hz, 1H), 7.14–7.10 (m, 4H), 6.56 (d, \( J = 3.0 \) Hz, 1H), 5.34 (s, 2H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \( \delta \); 137.5, 136.2, 128.7, 128.7, 128.2, 127. 6, 126.7, 121.6, 120.9, 119.5, 109.7, 101.6, 50.1. Spectroscopic data of \(^1\)H and \(^{13}\)C NMR of the product were identical to those reported in reference 2.
1-(p-Toluenesulfonyl)-IH-indole (2d)

To a stirred solution of indole (586 mg, 5.0 mmol) in THF (10 mL) cooled at 0 °C, NaH (400 mg, 10 mmol, 60% dispersed in mineral oil) was added dropwise. After stirring for 3 h, p-toluenesulfonyl chloride (1.05 g, 5.5 mmol) was added dropwise to the reaction mixture. The reaction solution was allowed to warm to room temperature and was stirred overnight. After quenching with NH₄Cl aq. at 0 °C, the reaction mixture was extracted with diethyl ether (10 mL x 3). The organic layer was dried over Na₂SO₄ and the solvent was concentrated in vacuo. 2d (1.20 g, 4.4 mmol) was obtained in 88% yield after purification by silica-gel column chromatography using n-hexane-ethyl acetate (2/1).

Pink solid; ¹H NMR (500 MHz, CDCl₃): δ 7.99 (d, J = 8.5 Hz, 1H), 7.76 (d, J = 8.0 Hz, 2H), 7.56 (d, J = 3.8 Hz, 1H), 7.52 (d, J = 8.5 Hz, 1H), 7.30 (t, J = 7.8 Hz, 1H), 7.23–7.20 (m, 3H), 6.65 (d, J = 3.8 Hz, 1H), 2.33 (s, 3H); ¹³C NMR (125 MHz, CDCl₃): δ; 144.9, 135.3, 134.8, 130.7, 129.8, 126.8, 126.3, 124.5, 123.2, 121.3, 113.5, 109.0, 21.5. Spectroscopic data of ¹H and ¹³C NMR of the product were identical to those reported in reference 3.

1-Methyl-2-phenyl-IH-indole (2n)

To a stirred solution of 2-phenylindole (773 mg, 4.0 mmol) in DMF (30 mL) cooled at 0 °C, NaH (240 mg, 6.0 mmol, 60% dispersed in mineral oil) was added dropwise. After stirring for 30 min., iodomethane (310 µL, 5.0 mmol) was added dropwise to the reaction mixture. The reaction mixture was allowed to warm to room temperature and was stirred overnight. After quenching with H₂O at 0 °C, the reaction mixture was extracted with ethyl acetate (30 mL x 3). The organic layer was dried over Na₂SO₄ and the solvent was concentrated in vacuo. 2n (605 mg, 2.9 mmol) was obtained in 73% yield after purification by silica-gel column chromatography using n-hexane-ethyl acetate (8/1).

Colorless solid; ¹H NMR (500 MHz, CDCl₃): δ 7.64 (d, J = 7.5 Hz, 1H), 7.53–7.46 (m, 4H), 7.42–7.37 (m, 2H), 7.26 (t, J = 7.5 Hz, 1H), 7.15 (t, J = 7.5 Hz, 1H), 6.57 (s, 1H), 3.76 (s, 3H); ¹³C NMR (125 MHz, CDCl₃): δ; 141.5, 138.3, 132.8, 129.4, 128.5, 127.9, 127.8, 121.6, 120.4, 119.8, 109.6, 101.6, 31.2. Spectroscopic data of ¹H and ¹³C NMR of the product were identical to those reported in reference 4.
3. Typical procedures in oxidative coupling of catechol (1) and indoles (2).

**General procedure A (with BF$_3$·Et$_2$O)**

To a suspension of catechol (1; 0.20 mmol) in CH$_2$Cl$_2$ (1.0 mL) in a dried brown test tube was added PIDA (64.4 mg, 0.2 mmol) under argon. The reaction mixture was placed on an organic reactor, Chemi Station (EYELA, Tokyo Rikakikai Co., Ltd., Tokyo, Japan), and the mixture was stirred at 25 °C for 1 h. Indole derivative (2; 3.0 eq.) as nucleophile, BF$_3$·OEt$_2$ (1.3 µL, 5 mol%), and CH$_2$Cl$_2$ (1.0 mL) were added sequentially, and the mixture was stirred at 0 °C for 1 h. After quenching with H$_2$O, the reaction mixture was extracted with CH$_2$Cl$_2$ (10 mL x 3). The organic layer was dried over Na$_2$SO$_4$ and concentrated in vacuo. Purification using flash column chromatography on silica gel (n-hexane-ethyl acetate) gave the corresponding product or mixture of regioisomers (3; 4-adduct and 4; 5-adduct). In the case to obtain the regioisomers, the product after first column chromatography was isolated by further silica-gel column chromatography eluting with CH$_2$Cl$_2$-MeOH or recrystallization.

**General procedure B (without BF$_3$·Et$_2$O)**

To a suspension of catechol (1; 0.20 mmol) in CH$_2$Cl$_2$ (1.0 mL) in a dry brown test tube was added PIDA (64.4 mg, 0.2 mmol) under argon. The reaction mixture was placed on an organic reactor, Chemi Station (EYELA, Tokyo Rikakikai Co., Ltd., Tokyo, Japan), and the mixture was stirred at 25 °C for 1 h. Indole derivative (2; 3.0 eq.) or trimethylbenzene (3.0 eq.) as nucleophile (3.0 eq.) and CH$_2$Cl$_2$ (1.0 mL) were added sequentially, and the mixture was stirred at 0 °C for 1 h. After quenching with H$_2$O, the reaction mixture was extracted with CH$_2$Cl$_2$ (10 mL x 3). The organic layer was dried over Na$_2$SO$_4$ and concentrated in vacuo. Purification using flash column chromatography on silica gel (n-hexane-ethyl acetate) gave s 4-adduct (3).
4. Spectroscopic data of the synthesized products.

(Table 1) Methyl 2,3-dihydroxy-6-(1H-indol-3-yl)benzoate (3a) and methyl 2,3-dihydroxy-5-(1H-indol-3-yl)benzoate (4a)

According to the general procedure A; Methyl-2,3-dihydroxybenzoate (1a) (33.6 mg, 0.20 mmol) was used as a substrate, and indole (2a; 70.3 mg, 0.60 mmol) was used as a nucleophile. 4a (40.8 mg, 0.144 mmol) and 3a (11.9 mg, 0.042 mmol) were obtained in 72% and 21% yield after purification using flash column chromatography on silica gel (n-hexane-ethyl acetate = 4/1). The pure product 4a was isolated by recrystallization (CHCl₃-MeOH) using a portion of generated mixture (3a and 4a).

According to the general procedure B; Methyl-2,3-dihydroxybenzoate (1a) (33.6 mg, 0.20 mmol) was used as a substrate, and indole (2a; 70.3 mg, 0.60 mmol) was used as a nucleophile. 3a (39.7 mg, 0.140 mmol) was obtained in 70% yield after purification by silica-gel column chromatography using n-hexane-ethyl acetate (4/1).

(Table 2, A; 1 g scale reaction)

According to the general procedure A; Methyl-2,3-dihydroxybenzoate (1a) (1.0 g, 6.00 mmol) was used as a substrate, and PIDA (1.93 g, 6.00 mmol), CH₂Cl₂ (each 10 mL), indole (2a; 2.11 g, 18.0 mmol) and BF₃・OEt₂ (39 µL, 5 mol%) were used for the reaction in a round flask. 4a (1.05 g, 3.42 mmol) and 3a (404 mg, 1.32 mmol) were obtained in 72% and 21% yield after purification using flash column chromatography on silica gel (n-hexane-ethyl acetate = 4/1). The pure product 4a was isolated by recrystallization (CHCl₃-MeOH) using a portion of generated mixture (3a and 4a).

According to the general procedure B; Methyl-2,3-dihydroxybenzoate (1a) (1.0 g, 6.00 mmol) was used as a substrate, and PIDA (1.93 g, 6.00 mmol), CH₂Cl₂ (each 10 mL), indole (2a; 2.11 g, 18.0 mmol) and BF₃・OEt₂ (39 µL, 5 mol%) were used for the reaction in a round flask. 3a (1.34 g, 4.38 mmol) was obtained in 70% yield after purification by silica-gel column chromatography using n-hexane-ethyl acetate (4/1).

3a; Pale yellow solid; M.p. 135.9–136.9 °C; IR (ATR) cm⁻¹: 3481, 3393, 2951, 1649, 1551, 1442, 1346, 1328, 1256, 1190, 1148, 1136, 1092, 1032, 1006; ¹H NMR (500 MHz, CDCl₃): δ 11.02 (s, 1H), 8.12 (brs, 1H), 7.46 (d, J = 8.0 Hz, 1H), 7.36 (d, J = 8.0 Hz, 1H), 7.19 (t, J = 8.0 Hz, 1H), 7.14 (d, J = 2.5 Hz, 1H), 7.12 (d, J = 8.0 Hz, 1H), 7.08 (t, J = 8.0 Hz, 1H), 6.86 (d, J = 8.0 Hz, 1H), 5.78 (s, 1H), 3.33 (s, 3H); ¹³C NMR (125 MHz, CDCl₃): δ 171.8, 148.7, 144.0, 135.6, 127.8, 127.5, 123.4, 122.0, 121.6, 120.0, 119.0, 118.9, 118.5, 112.5, 111.1, 52.0; ESI-HRMS m/z: 306.0725 ([M+Na⁺]); Calcd for
C_{16}H_{13}NO_{4}Na: 306.0737.

4a: Colorless solid; M.p. 167.3–169.4 °C; IR (ATR) cm^{-1}: 3531, 3404, 2968, 1672, 1615, 1549, 1476, 1457, 1435, 1372, 1321, 1288, 1272, 1235, 1212, 1192, 1156, 1127, 1098, 1026, 1007; \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) 10.84 (s, 1H), 8.22 (brs, 1H), 7.90 (d, \(J = 8.0\) Hz, 1H), 7.69 (d, \(J = 2.5\) Hz, 1H), 7.44–7.43 (m, 2H), 7.32 (d, \(J = 2.5\) Hz, 1H), 7.28–7.24 (m, 1H), 7.21 (t, \(J = 8.0\) Hz, 1H), 5.71 (s, 1H), 3.99 (s, 3H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta\) 170.8, 147.3, 145.2, 136.5, 127.0, 125.6, 122.5, 121.5, 120.3, 119.5, 119.2, 119.1, 117.2, 112.5, 111.4, 52.5; ESI-HRMS m/z: 306.0736 ([M+Na^+]\(^+\]); Calcd for C_{16}H_{13}NO_{4}Na: 306.0737.

(eq. 1) Methyl 3,4-dihydroxy-2',4',6'-trimethoxy-[1,1'-biphenyl]-2-carboxylate (5) and methyl 4,5-dihydroxy-2',4',6'-trimethoxy-[1,1'-biphenyl]-3-carboxylate (6)

According to the general procedure A; Methyl-2,3-dihydroxybenzoate (1a; 33.6 mg, 0.20 mmol) was used as a substrate, and 1,3,5-trimethoxybenzene (100.9 mg, 0.60 mmol) was used instead of indole nucleophile. 6 (48.1 mg, 0.144 mmol) and 5 (2.0 mg, 0.06 mmol) were obtained as mixture in 72% and 3% yield after purification using flash column chromatography on silica gel (n-hexane-ethyl acetate = 4/1). The pure product 6 was isolated by recrystallization (CHCl\(_3\)-MeOH) using a portion of generated mixture (6 and 5).

According to the general procedure B; Methyl-2,3-dihydroxybenzoate (1a) (33.6 mg, 0.20 mmol) was used as a substrate, and 1,3,5-trimethoxybenzene (100.9 mg, 0.60 mmol) was instead of indole nucleophile. 5 (44.8 mg, 0.134 mmol) was obtained in 67% yield after purification by silica-gel column chromatography using n-hexane-ethyl acetate (4/1).

5: Pale yellow solid; M.p. 149.3–150.8 °C; IR (ATR) cm^{-1}: 3392, 3004, 2952, 1655, 1605, 1584, 1512, 1456, 1430, 1369, 1336, 1270, 1228, 1205, 1190, 1155, 1115, 1083, 1052, 1033, 1005; \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 11.08 (s, 1H), 7.12 (d, \(J = 8.2\) Hz, 1H), 6.67 (d, \(J = 8.2\) Hz, 1H), 6.18 (s, 2H), 5.72 (s, 1H), 3.87 (s, 3H), 3.68 (s, 6H), 3.56 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 171.7, 160.2, 157.7, 148.5, 143.9, 126.6, 123.8, 118.2, 113.3, 112.7, 90.4, 55.9, 55.3, 52.0; ESI-HRMS m/z: 335.1102 ([M+H^+]\(^+\]); Calcd for C_{17}H_{19}O_{7}: 335.1125.
**6; Colorless solid; M.p. 191.3–194.1 °C; IR (ATR) cm⁻¹: 3450, 2945, 1659, 1603, 1581, 1470, 1452, 1437, 1412, 1359, 1312, 1296, 1224, 1199, 1153, 1118, 1069, 1047, 1029, 1009; ¹H NMR (400 MHz, CDCl₃): δ 10.87 (s, 1H), 7.35 (d, J = 1.8 Hz, 1H), 7.10 (d, J = 1.8 Hz, 1H), 6.21 (s, 2H), 5.65 (s, 1H), 3.92 (s, 3H), 3.86 (s, 3H), 3.73 (s, 6H); ¹³C NMR (100 MHz, CDCl₃): δ 170.9, 160.5, 158.3, 147.5, 144.2, 125.2, 123.2, 123.2, 111.9, 111.1, 90.7, 55.9, 55.4, 52.3; ESI-HRMS m/z: 357.0921 ([M+Na⁺]); Calcd for C₁₇H₁₈O₇Na: 357.0945.
(Table 2, A) Methyl 2,3-dihydroxy-6-(1-methyl-1H-indol-3-yl)benzoate (3b) and methyl 2,3-dihydroxy-5-(1-methyl-1H-indol-3-yl)benzoate (4b)

According to the general procedure A; Methyl-2,3-dihydroxybenzoate (1a) (33.6 mg, 0.20 mmol) was used as a substrate, and N-methylindole (2b; 75.0 μL, 0.60 mmol) was used as a nucleophile. 4b (29.7 mg, 0.100 mmol) and 3b (10.7 mg, 0.036 mmol) were obtained in 50% and 18% yield after purification using flash column chromatography on silica gel (n-hexane-ethyl acetate = 4/1). The pure product 4b was isolated by recrystallization (CH3Cl-MeOH) using a portion of generated mixture (4b and 3bc).

According to the general procedure B; Methyl-2,3-dihydroxybenzoate (1a) (33.6 mg, 0.20 mmol) was used as a substrate, and N-methylindole (2b; 75.0 μL, 0.60 mmol) was used as a nucleophile. 3b (41.0 mg, 0.138 mmol) was obtained in 69% yield after purification by silica-gel column chromatography using n-hexane-ethyl acetate (4/1).

3b; Green amorphous; IR (ATR) cm⁻¹: 3453, 2949, 1655, 1613, 1548, 1438, 1325, 1256, 1182, 1132, 1050, 1014; ¹H NMR (500 MHz, CDCl₃): δ 10.96 (s, 1H), 7.34 (d, J = 8.0 Hz, 1H), 7.32 (d, J = 8.0 Hz, 1H), 7.21 (t, J = 7.5 Hz, 1H), 7.11–7.05 (m, 2H), 7.01 (s, 1H), 6.84 (d, J = 9.0 Hz, 1H), 5.82 (s, 1H), 3.81 (s, 3H), 3.33 (s, 3H); ¹³C NMR (125 MHz, CDCl₃): δ 171.8, 148.6, 143.7, 136.5, 127.9, 127.7, 126.4, 123.4, 121.5, 119.5, 119.0, 118.6, 117.2, 112.4, 109.2, 52.0, 32.7; ESI-HRMS m/z:
320.0879 ([M+Na\(^+\)]); Calcd for C\(_{17}\)H\(_{15}\)NO\(_4\)Na: 320.0893.

**4b;** Pale green solid; M.p. 159.6–162.4 °C; IR (ATR) cm\(^{-1}\): 3492, 2953, 1675, 1616, 1544, 1483, 1468, 1443, 1416, 1390, 1336, 1282, 1252, 1220, 1193, 1152, 1220, 1193, 1152, 1134, 1051, 1022; \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 10.81 (s, 1H), 7.90 (d, \(J = 8.0\) Hz, 1H), 7.66 (d, \(J = 2.0\) Hz, 1H), 7.42 (d, \(J = 2.0\) Hz, 1H), 7.36 (d, \(J = 8.0\) Hz, 1H), 7.29 (t, \(J = 8.0\) Hz, 1H), 7.22–7.18 (m, 2H), 5.68 (s, 1H), 3.99 (s, 3H), 3.84 (s, 3H); \(^13\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 170.9, 147.0, 145.1, 137.3, 127.1, 126.3, 125.9, 122.0, 119.9, 119.6, 119.0, 118.8, 115.5, 112.5, 109.5, 52.5, 32.9; ESI-HRMS m/z: 320.0894 ([M+Na\(^+\)]); Calcd for C\(_{17}\)H\(_{15}\)NO\(_4\)Na: 320.0893.

*(Table 2, A) Methyl 6-(1-benzyl-1H-indol-3-yl)-2,3-dihydroxybenzoate (3c) and methyl 5-(1-benzyl-1H-indol-3-yl)-2,3-dihydroxybenzoate (4c)*

According to the general procedure A; Methyl-2,3-dihydroxybenzoate (1a) (33.6 mg, 0.20 mmol) was used as a substrate, and N-benzylindole (2c; 124.4 mg, 0.60 mmol) was used as a nucleophile. 4c (38.8 mg, 0.104 mmol) and 3c (16.4 mg, 0.044 mmol) were obtained in 52% and 22% yield after purification using flash column chromatography on silica gel (n-hexane-ethyl acetate = 4/1). The pure product 4c was isolated by flash column chromatography on silica gel (CH\(_2\)Cl\(_2\)) using a portion of generated mixture (4c and 3c).

According to the general procedure B; Methyl-2,3-dihydroxybenzoate (1a) (33.6 mg, 0.20 mmol) was used as a substrate, and N-Benzylindole (2c; 124.4 mg, 0.60 mmol) was used as a nucleophile. 3c (50.0 mg, 0.134 mmol) was obtained in 67% yield after purification by silica-gel column chromatography using n-hexane-ethyl acetate (4/1).

**3c;** Green amorphous; IR (ATR) cm\(^{-1}\): 3443, 3029, 1552, 1465, 1438, 1328, 1258, 1191, 1171, 1136, 1018; \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) 10.99 (s, 1H), 7.39 (d, \(J = 7.5\) Hz, 1H), 7.32–7.26 (m, 4H), 7.17 (t, \(J = 7.0\) Hz, 1H), 7.13–7.06 (m, 5H), 6.87 (d, \(J = 8.5\) Hz, 1H), 5.77 (s, 1H), 5.35 (s, 2H), 3.31 (s, 3H); \(^13\)C NMR (125 MHz, CDCl\(_3\)): \(\delta\) 171.9, 148.7, 143.9, 137.6, 136.1, 128.7, 128.1, 127.7, 127.6, 126.6, 125.8, 123.4, 121.8, 119.8, 119.2, 118.5, 117.8, 112.5, 109.7, 51.9, 49.9; ESI-HRMS m/z: 396.1205 ([M+Na\(^+\)]); Calcd for C\(_{23}\)H\(_{19}\)NO\(_4\)Na: 396.1206.
4c; Green amorphous; IR (ATR) cm⁻¹: 3449, 3031, 2952, 1672, 1620, 1549, 1466, 1440, 1383, 1333, 1295, 1279, 1228, 1192, 1176, 1152, 1131, 1019; ¹H NMR (500 MHz, CDCl₃): δ 10.83 (s, 1H), 7.91 (d, J = 7.0 Hz, 1H), 7.65 (d, J = 2.3 Hz, 1H), 7.42 (d, J = 2.3 Hz, 1H), 7.29–7.24 (m, 4H), 7.22–7.16 (m, 3H), 7.11 (d, J = 7.0 Hz, 2H), 5.80 (s, 1H), 5.26 (s, 2H), 3.93 (s, 3H); ¹³C NMR (125 MHz, CDCl₃): δ 170.8, 147.1, 145.1, 137.1, 136.9, 128.7, 127.6, 126.98, 127.0, 126.2, 125.6, 122.2, 120.1, 119.7, 119.1, 118.9, 116.1, 112.5, 110.0, 52.4, 50.0; ESI-HRMS m/z: 396.1205 ([M+Na⁺]); Calcd for C₂₃H₁₉NO₄Na: 396.1206.

(Table 2, A) Methyl 2,3-dihydroxy-6-(1-tosyl-1H-indol-3-yl)benzoate (3d)
According to the general procedure A; Methyl-2,3-dihydroxybenzoate (1a) (33.6 mg, 0.20 mmol) was used as a substrate, and N-tosylindole (2d; 162.8 mg, 0.60 mmol) was used as a nucleophile. 3d (54.2 mg, 0.124 mmol) was obtained in 62% yield after purification by silica-gel column chromatography using n-hexane-ethyl acetate (4/1).

3d; Gray solid; M.p. 73.578.4 °C; IR (ATR) cm⁻¹: 3471, 3051, 2950, 2096, 1915, 1664, 1594, 1490, 1472, 1440, 1367, 1345, 1317, 1292, 1269, 1244, 1185, 1151, 1124, 1106, 1087, 1016, 1000; ¹H NMR (500 MHz, CDCl₃): δ 11.19 (brs, 1H), 8.05 (d, J = 8.0 Hz, 1H), 7.79 (d, J = 8.0 Hz, 2H), 7.46 (s, 1H), 7.30 (t, J = 7.5 Hz, 1H), 7.23 (d, J = 8.0 Hz, 2H), 7.19–7.14 (m, 2H), 7.11 (d, J = 8.0 Hz, 1H), 6.70 (d, J = 8.0 Hz, 1H), 5.96 (brs, 1H), 3.02 (s, 3H), 2.34 (s, 3H); ¹³C NMR (125 MHz, CDCl₃): δ 171.0, 149.3, 145.1, 144.8, 135.2, 134.5, 131.4, 129.7, 126.7, 125.6, 124.9, 124.5, 123.5, 123.2, 122.8, 119.6, 118.6, 113.8, 112.2, 51.6, 21.5; ESI-HRMS m/z: 438.0993 ([M+H⁺]); Calcd for C₂₃H₂₀NO₆S: 438.1006.

(Table 2, A) Methyl 2,3-dihydroxy-6-(2-methyl-1H-indol-3-yl)benzoate (3e) and methyl 2,3-dihydroxy-5-(2-methyl-1H-indol-3-yl)benzoate (4e)
According to the general procedure A; Methyl-2,3-dihydroxybenzoate (1a) (33.6 mg, 0.20 mmol) was used as a substrate, and 2-methylindole (2e; 78.7 mg, 0.60 mmol) was used as a nucleophile. 4e (38.7 mg, 0.130 mmol) and 3e (5.9 mg, 0.020 mmol) were obtained in 65% and 10% yield after purification using flash column chromatography on silica gel (n-hexane-ethyl acetate = 4/1). The pure product 4e was isolated by recrystallization (CH₃Cl-MeOH) using a portion of generated mixture (4e and 3e).
According to the general procedure B; Methyl-2,3-dihydroxybenzoate (1a) (33.6 mg, 0.20 mmol) was used as a substrate, and 2-methylindole (2e; 78.7 mg, 0.60 mmol) was
used as a nucleophile. 3e (48.8 mg, 0.164 mmol) was obtained in 82% yield after purification by silica-gel column chromatography using n-hexane-ethyl acetate (4/1).

3e; Green amorphous, IR (ATR) cm⁻¹: 3396, 3054, 2950, 1655, 1620, 1492, 1459, 1438, 1325, 1282, 1253, 1192, 1168, 1139, 1079, 1001; ¹H NMR (500 MHz, CDCl₃): δ 11.19 (s, 1H), 7.87 (brs, 1H), 7.29 (d, J = 8.0 Hz, 1H), 7.25–7.22 (m, 1H), 7.14–7.10 (m, 2H), 7.03 (t, J = 8.0 Hz, 1H), 6.79 (dd, J = 1.0, 8.0 Hz, 1H), 5.81 (s, 1H), 3.36 (s, 3H), 2.30 (s, 3H); ¹³C NMR (125 MHz, CDCl₃): δ 171.9, 149.0, 143.8, 134.8, 130.9, 129.0, 127.8, 123.9, 121.0, 119.7, 118.5, 118.2, 114.8, 113.0, 110.0, 52.2, 12.1; DART-HRMS m/z: 298.1079 ([M+H⁺]); Calcd for C₁₇H₁₆NO₄: 298.1079.

4e; Colorless solid; M.p. 169.3173.6 °C; IR (ATR) cm⁻¹: 3435, 2946, 2015, 1657, 1616, 1479, 1459, 1446, 1369, 1303, 1273, 1240, 1225, 1192, 1169, 1149, 1054, 1015; ¹H NMR (500 MHz, CDCl₃): δ 10.87 (s, 1H), 7.94 (brs, 1H), 7.61 (d, J = 8.0 Hz, 1H), 7.51 (d, J = 1.5 Hz, 1H), 7.32 (d, J = 8.0 Hz, 1H), 7.27 (d, J = 1.5 Hz, 1H), 7.17 (td, J = 1.0, 8.0 Hz, 1H), 7.12 (td, J = 1.0, 8.0 Hz, 1H), 5.74 (s, 1H), 3.96 (s, 3H), 2.30 (s, 3H); ¹³C NMR (125 MHz, CDCl₃): δ 171.9, 147.1, 144.9, 135.0, 135.0, 131.3, 127.7, 126.7, 121.6, 121.2, 121.1, 120.0, 118.5, 113.3, 112.4, 110.3, 52.5, 12.4; DART-HRMS m/z: 298.1069 ([M+H⁺]); Calcd for C₁₇H₁₆NO₄: 298.1079.

(Table 2, A) Methyl 2,3-dihydroxy-6-(2-phenyl-1H-indol-3-yl)benzoate (3f) and methyl 2,3-dihydroxy-5-(2-phenyl-1H-indol-3-yl)benzoate (4f)

According to the general procedure A; Methyl-2,3-dihydroxybenzoate (1a) (16.8 mg, 0.10 mmol) was used as a substrate, and 2-phenylindole (2f; 57.9 mg, 0.30 mmol) was used as a nucleophile. 4f (19.8 mg, 0.055 mmol) and 3f (7.2 mg, 0.020 mmol) were obtained in 55% and 20% yield after purification using flash column chromatography on silica gel (n-hexane-ethyl acetate = 4/1). The pure product 4f was isolated by recrystallization (CH₃Cl-MeOH) using a portion of generated mixture (4f and 3f).

According to the general procedure B; Methyl-2,3-dihydroxybenzoate (1a) (16.8 mg, 0.10 mmol) was used as a substrate, and 2-Phenylindole (57.9 mg, 0.30 mmol) was used as a nucleophile. 3f (22.6 mg, 0.063 mmol) was obtained in 63% yield after isolation by silica-gel column chromatography using n-hexane-ethyl acetate (4/1).
**3f**; Green amorphous; IR (ATR) cm⁻¹: 3391, 3055, 1655, 1601, 1503, 1438, 1325, 1251, 1192, 1173, 1141, 1041; ¹H NMR (500 MHz, CDCl₃): δ 11.19 (s, 1H), 8.20 (brs, 1H), 7.41 (d, J = 8.0 Hz, 1H), 7.34–7.28 (m, 5H), 7.26–7.24 (m, 1H), 7.20 (t, J = 7.4 Hz, 1H), 7.10 (d, J = 8.8 Hz, 1H), 7.08 (t, J = 7.4 Hz, 1H), 6.80 (d, J = 8.8 Hz, 1H), 5.81 (s, 1H), 3.30 (s, 3H); ¹³C NMR (125 MHz, CDCl₃): δ 171.6, 149.2, 144.1, 135.5, 133.5, 132.5, 129.8, 128.7, 127.7, 127.5, 127.1, 124.3, 122.4, 120.2, 119.2, 118.9, 115.2, 113.0, 110.7, 52.2; ESI-HRMS m/z: 360.1216 ([M+H⁺]); Calcd for C₂₂H₁₈NO₄: 360.1230.

**4f**; Green solid; M.p. 198.4–203.4 °C; IR (ATR) cm⁻¹: 3549, 3410, 3056, 2949, 1668, 1617, 1502, 1478, 1439, 1375, 1329, 1293, 1270, 1223, 1195, 1173, 1145, 1026, 1009; ¹H NMR (500 MHz, CDCl₃): δ 10.90 (s, 1H), 8.23 (brs, 1H), 7.62 (d, J = 8.0 Hz, 1H), 7.52 (d, J = 2.3 Hz, 1H), 7.43–7.41 (m, 3H), 7.35–7.23 (m, 4H), 7.16 (t, J = 7.3 Hz, 1H), 7.13 (d, J = 2.3 Hz, 1H), 5.64 (s, 1H), 3.90 (s, 3H); ¹³C NMR (200 MHz, CDCl₃): δ 170.8, 147.5, 145.0, 135.7, 134.1, 132.4, 128.8, 128.0, 127.8, 126.4, 122.8, 122.0, 121.4, 120.4, 119.4, 113.8, 112.5, 110.9, 52.4; ESI-HRMS m/z: 360.1232 ([M+H⁺]); Calcd for C₂₂H₁₈NO₄: 360.1230.

(Table 2, A) **Methyl 3-(3,4-dihydroxy-2-(methoxycarbonyl)phenyl)-1H-indole-2-carboxylate (3g)**

According to the general procedure A; Methyl-2,3-dihydroxybenzoate (1a) (33.6 mg, 0.20 mmol) was used as a substrate, and Methyl indole-2-carboxylate (2g; 105.1 mg, 0.60 mmol) was used as a nucleophile. 3g (36.2 mg, 0.106 mmol) was obtained in 53% yield after purification by silica-gel column chromatography using n-hexane-ethyl acetate (4/1).

3g; Colorless solid; M.p. 162.5±65.3 °C; IR (ATR) cm⁻¹: 3532, 3325, 2953, 1664, 1556, 1484, 1439, 1327, 1254, 1222, 1193, 1142, 1067, 1008; ¹H NMR (500 MHz, CDCl₃): δ 11.31 (s, 1H), 9.02 (brs, 1H), 7.44–7.43 (m, 2H), 7.35 (t, J = 7.8 Hz, 1H), 7.15–7.11 (m, 2H), 6.84 (d, J = 8.5 Hz, 1H), 5.91 (s, 1H), 3.77 (s, 3H), 3.40 (s, 3H); ¹³C NMR (125 MHz, CDCl₃): δ 171.6, 162.5, 148.9, 144.6, 135.5, 128.3, 126.0, 125.6, 123.9, 123.7, 122.6, 121.4, 120. 8, 118.0, 112.9, 111.6, 52.0, 51.9; ESI-HRMS m/z: 364.0807 ([M+Na⁺]); Calcd for C₁₈H₁₅NO₆Na: 364.0792.

(Table 2, A) **Methyl 6-(2-formyl-1H-indol-3-yl)-2,3-dihydroxybenzoate (3h)**

According to the general procedure A; Methyl-2,3-dihydroxybenzoate (1a) (33.6 mg,
0.20 mmol) was used as a substrate, and Indole-2-carboxaldehyde (2h; 87.1 mg, 0.60 mmol) was used as a nucleophile. 3h (62.3 mg, 0.130 mmol) was obtained in 65% yield after purification by silica-gel column chromatography using n-hexane-ethyl acetate (4/1).

3h; Yellow solid; M.p. 98.2101.2 °C; IR (ATR) cm⁻¹: 3288, 2948, 1639, 1571, 1543, 1438, 1364, 1329, 1274, 1260, 1234, 1194, 1173, 1152, 1076, 1003; ¹H NMR (500 MHz, CDCl₃): δ 11.36 (s, 1H), 9.70 (s, 1H), 9.35 (brs, 1H), 7.48 (d, J = 8.0 Hz, 1H), 7.41–7.38 (m, 2H), 7.19 (d, J = 8.3 Hz, 1H), 7.12 (t, J = 7.8 Hz, 1H), 6.88 (d, J = 8.3 Hz, 1H), 6.05 (s, 1H), 3.33 (s, 3H); ¹³C NMR (125 MHz, CDCl₃): δ 182.4, 171.1, 149.7, 145.6, 136.6, 131.9, 130.1, 128.0, 127.4, 125.0, 123.6, 121.7, 121.2, 118.3, 112.9, 112.3, 52.3; ESI-HRMS m/z: 312.0877 ([M+H⁺]); Calcd for C₁₇H₁₄NO₅: 312.0866.

(Table 2, A) Methyl 6-(5-bromo-1H-indol-3-yl)-2,3-dihydroxybenzoate (3i)
According to the general procedure B; Methyl-2,3-dihydroxybenzoate (1a) (84.1 mg, 0.50 mmol) was used as a substrate, and 5-bromoindole (2i; 294.1 mg, 1.50 mmol) was used as a nucleophile. 3i (99.5 mg, 0.275 mmol) was obtained in 55% yield after purification by silica-gel column chromatography using n-hexane-ethyl acetate (4/1).

3i; Pale purple solid; M.p. 163.5–165.9 °C; IR (ATR) cm⁻¹: 3465, 3372, 3116, 2411, 2019, 1659, 1611, 1546, 11476, 1439, 1366, 1342, 1326, 1308, 1289, 1270, 1230, 1193, 1160, 1141, 1104, 1026; ¹H NMR (500 MHz, CDCl₃): δ 11.16 (s, 1H), 8.16 (brs, 1H), 7.48 (s, 1H), 7.28–7.26 (m, 2H), 7.14–7.12 (m, 2H), 6.82 (d, J = 8.0 Hz, 1H), 5.79 (s, 1H), 3.40 (s, 3H); ¹³C NMR (125 MHz, CDCl₃): δ 171.5, 149.1, 144.4, 134.2, 129.3, 126.9, 124.9, 123.6, 122.9, 121.8, 118.6, 118.5, 113.2, 112.6, 112.4, 52.1; ESI-HRMS m/z: 383.9838 ([M+Na⁺]); Calcd for C₁₆H₁₂NO₄NaBr: 383.9842.

(Table 2, A) Methyl 5-(5-bromo-1H-indol-3-yl)-2,3-dihydroxybenzoate (4i)
According to the general procedure A; Methyl-2,3-dihydroxybenzoate (1a) (84.1 mg, 0.50 mmol) was used as a substrate, and 5-bromoindole (2i; 294.1 mg, 1.50 mmol) was used as a nucleophile. 4i (38.0 mg, 0.105 mmol) was obtained in 21% yield after purification by silica-gel column chromatography using n-hexane-ethyl acetate (4/1).
4i; Pale yellow solid; M.p. 124.8–126.3 °C; IR (ATR) cm⁻¹: 3465, 3372, 3116, 3073, 2950, 1659, 1612, 1546, 1476, 1439, 1366, 1341, 1326, 1308, 1289, 1270, 1230, 1193, 1160, 1141, 1121, 1104, 1026; ¹H NMR (500 MHz, CDCl₃): δ 10.88 (s, 1H), 8.25 (brs, 1H), 7.98 (d, J = 1.5 Hz, 1H), 7.60 (d, J = 2.0 Hz, 1H), 7.37 (d, J = 2.0 Hz, 1H), 7.35–7.30 (m, 3H), 5.72 (s, 1H), 4.00 (s, 3H); ¹³C NMR (125 MHz, CDCl₃): δ 170.7, 147.5, 145.2, 135.1, 127.4, 126.2, 125.4, 122.6, 122.1, 119.2, 119.1, 117.1, 113.7, 112.8, 112.6, 52.6; ESI-HRMS m/z: 399.9596 ([M+K⁺]); Calcd for C₁₆H₁₂NO₄BrK : 399.9581.

(Table 2, A) Methyl 6-(5-fluoro-1H-indol-3-yl)-2,3-dihydroxybenzoate (3j) and methyl 5-(5-fluoro-1H-indol-3-yl)-2,3-dihydroxybenzoate (4j)

According to the general procedure A; Methyl-2,3-dihydroxybenzoate (1a) (33.6 mg, 0.20 mmol) was used as a substrate, and 5-fluoroindole (2j; 81.1 mg, 0.60 mmol) was used as a nucleophile. 4j (30.1 mg, 0.100 mmol) and 3j (16.3 mg, 0.054 mmol) were obtained in 50% and 27% yield after purification using flash column chromatography on silica gel (n-hexane-ethyl acetate = 4/1). The pure product 4j was isolated by recrystallization (CHCl₃-MeOH) using a portion of generated mixture (4j and 3j).

According to the general procedure B; Methyl-2,3-dihydroxybenzoate (1a) (33.6 mg, 0.20 mmol) was used as a substrate, and 5-fluoroindole (2j; 81.1 mg, 0.60 mmol) was used as a nucleophile. 3j (41.0 mg, 0.136 mmol) was obtained in 68% yield after purification by silica-gel column chromatography using n-hexane-ethyl acetate (4/1).

3j; Colorless solid; M.p. 153.9-155.0 °C; IR (ATR) cm⁻¹: 3475, 3411, 2922, 2150, 2028, 1660, 1625, 1577, 1482, 1440, 1346, 1283, 1265, 1192, 1172, 1145, 1092, 1026; ¹H NMR (500 MHz, CDCl₃): δ 11.10 (s, 1H), 8.15 (brs, 1H), 7.31 (dd, J = 3.0, 8.5 Hz, 1H), 7.18 (d, J = 2.0 Hz, 1H), 7.12 (d, J = 8.0 Hz, 1H), 7.00 (dd, J = 2.5, 9.3 Hz, 1H), 6.94 (ddd, J = 3.0, 9.3, 9.3 Hz, 1H), 6.83 (d, J = 8.0 Hz, 1H), 5.81 (s, 1H), 3.39 (s, 3H); ¹³C NMR (200 MHz, CDCl₃): δ 171.6, 158.7 (d, J = 234.0 Hz), 149.0, 144.3, 132.1, 128.1 (d, J = 10.0 Hz), 127.2, 123.5, 123.4, 119.2 (d, J = 6.0 Hz), 118.5, 112.4, 111.7 (d, J = 8.0 Hz), 110.4 (d, J = 28.0 Hz), 104.0 (d, J = 22.0 Hz, 1H), 52.0; ¹⁹F NMR (470 MHz, CDCl₃): δ -124.1—-124.2 (m); DART-HRMS m/z: 302.0828 ([M+H⁺]); Calcd for C₁₆H₁₃FNO₄: 302.0829.
4j; Gray solid; M.p. 183.0–187.5 °C; IR (ATR) cm⁻¹: 3475, 3410, 2921, 2047, 1659, 1625, 1577, 1482, 1440, 1346, 1265, 1192, 1172, 1145, 1107, 1092, 1026; ¹H NMR (500 MHz, CDCl₃): δ 10.86 (s, 1H), 8.24 (brs, 1H), 7.63 (d, J = 2.5 Hz, 1H), 7.55 (dd, J = 2.5, 9.5 Hz, 1H), 7.37–7.33 (m, 3H), 7.01 (td, J = 2.5, 9.5 Hz, 1H), 5.73 (s, 1H), 4.00 (s, 3H); ¹³C NMR (125 MHz, CDCl₃): δ 170.8, 158.4 (d, J = 233.6 Hz), 147.4, 145.3, 133.0, 126.5, 125.9 (d, J = 9.5 Hz), 123.2, 119.0, 118.8, 117.5 (d, J = 3.6 Hz), 112.6, 112.1 (d, J = 10.6 Hz), 110.9 (d, J = 27.5 Hz), 104.6 (d, J = 23.9 Hz), 52.6; ¹⁹F NMR (470 MHz, CDCl₃): δ -123.6–-123.6 (m); ESI-HRMS m/z: 340.0399 ([M+K⁺]); Calcd for C₁₆H₁₂NO₄FK: 340.0382.

(Table 2, A) Methyl 3-(3,4-dihydroxy-2-(methoxycarbonyl)phenyl)-1H-indole-5-carboxylate (3k) and methyl 3-(3,4-dihydroxy-5-(methoxycarbonyl)phenyl)-1H-indole-5-carboxylate (4k)

According to the general procedure A; Methyl-2,3-dihydroxybenzoate (1a) (33.6 mg, 0.20 mmol) was used as a substrate, and methyl indole-5-carboxylate (2k; 105.1 mg, 0.60 mmol) was used as a nucleophile. 4k (25.3 mg, 0.074 mmol) and 3k (17.1 mg, 0.050 mmol) were obtained in 37% and 25% yield after purification using flash column chromatography on silica gel (n-hexane-ethyl acetate = 4/1). The pure product 4k was isolated by recrystallization (CHCl₃-MeOH) using a portion of generated mixture (4k and 3k).

According to the general procedure B; Methyl-2,3-dihydroxybenzoate (1a) (33.6 mg, 0.20 mmol) was used as a substrate, and methyl indole-5-carboxylate (2k; 105.1 mg, 0.60 mmol) was used as a nucleophile. 3k (28.7 mg, 0.084 mmol) was obtained in 42% yield after purification by silica-gel column chromatography using n-hexane-ethyl acetate (4/1).

3k; Brown solid; M.p. 160.3–162.3 °C; IR (ATR) cm⁻¹: 3340, 2952, 1676, 1647, 1610, 1436, 1341, 1257, 1194, 1153, 1131, 1088, 1028, 1003; ¹H NMR (500 MHz, CDCl₃): δ 11.20 (s, 1H), 8.43 (brs, 1H), 8.10 (s, 1H), 7.92 (d, J = 1.5, 8.5 Hz, 1H), 7.42 (d, J = 8.5 Hz, 1H), 7.19 (d, J = 1.5 Hz, 1H), 7.13 (d, J = 8.5 Hz, 1H), 6.84 (d, J = 8.5 Hz, 1H), 5.86 (s, 1H), 3.90 (s, 1H), 3.33 (s, 3H); ¹³C NMR (125 MHz, CDCl₃): δ 171.5, 168.1, 149.1, 144.5, 138.2, 127.4, 126.8, 123.7, 123.4, 122.9, 122.1, 122.0, 120.2, 118.5, 112.5, 110.9, 52.0, 51.9; ESI-HRMS m/z: 364.0783 ([M+Na⁺]); Calcd for C₁₈H₁₅NO₆Na: 364.0792.
4k; Brown solid; M.p. 220.9–221.8 °C; IR (ATR) cm⁻¹: 3339, 2952, 1696, 1662, 1616, 1548, 1477, 1437, 1372, 1355, 1322, 1281, 1249, 1189, 1154, 1110, 1088, 1028, 1011; ¹H NMR (400 MHz, CDCl₃): δ 10.90 (s, 1H), 8.61 (s, 1H), 8.42 (brs, 1H), 7.97 (dd, J = 1.4, 8.4 Hz, 1H), 7.65 (d, J = 2.4 Hz, 1H), 7.45–7.43 (m, 2H), 7.37 (d, J = 2.4 Hz, 1H), 5.75 (s, 1H), 3.99 (s, 3H), 3.95 (s, 3H); ¹³C NMR (125 MHz, CDCl₃): δ 170.8, 168.1, 147.6, 145.2, 139.0, 126.1, 125.4, 124.3, 123.9, 122.7, 122.6, 119.4, 118.7, 112.6, 111.1, 52.6, 51.9; ESI-HRMS m/z: 364.0790 ([M+Na⁺]); Calcd for C₁₈H₁₅NO₆Na: 364.0792.

(Table 2, A) Methyl 2,3-dihydroxy-6-(5-methoxy-1H-indol-3-yl)benzoate (3l) and methyl 2,3-dihydroxy-5-(5-methoxy-1H-indol-3-yl)benzoate (4l)

According to the general procedure A; Methyl-2,3-dihydroxybenzoate (1a) (33.6 mg, 0.20 mmol) was used as a substrate, and 5-methoxyindole (2l; 88.3 mg, 0.60 mmol) was used as a nucleophile. 4l (27.6 mg, 0.088 mmol) and 3l (21.9 mg, 0.070 mmol) were obtained in 44% and 35% yield after purification using flash column chromatography on silica gel (n-hexane-ethyl acetate = 4/1). The pure product 4l was isolated by recrystallization (CHCl₃-MeOH) using a portion of generated mixture (4l and 3l).

According to the general procedure B; Methyl-2,3-dihydroxybenzoate (1a) (33.6 mg, 0.20 mmol) was used as a substrate, and 5-methoxyindole (2l; 88.3 mg, 0.60 mmol) was used as a nucleophile. 3l (44.5 mg, 0.142 mmol) was obtained in 71% yield after purification by silica-gel column chromatography using n-hexane-ethyl acetate (4/1).

3l; Brown amorphous; IR (ATR) cm⁻¹: 3406, 2591, 1675, 1625, 1582, 1438, 1261, 1208, 1193, 1174, 1145, 1116, 1037, 1000; ¹H NMR (500 MHz, CDCl₃): δ 10.93 (s, 1H), 8.10 (brs, 1H), 7.26 (d, J = 8.3 Hz, 1H), 7.12 (d, J = 8.3 Hz, 1H), 7.10 (d, J = 2.0 Hz, 1H), 6.86–6.84 (m, 2H), 6.80 (d, J = 2.0 Hz, 1H), 5.88 (s, 1H), 3.77 (s, 3H), 3.36 (s, 3H); ¹³C NMR (125 MHz, CDCl₃): δ 171.8, 154.4, 148.6, 143.9, 130.7, 127.8, 127.8, 123.3, 122.4, 118.6, 118.5, 112.6, 112.4, 111.9, 100.3, 55.8, 52.1; ESI-HRMS m/z: 313.0848 ([M+Na⁺]); Calcd for C₁₇H₁₅NO₅Na: 336.0842.

4l; Brown solid; M.p. 220.9–221.8 °C; IR (ATR) cm⁻¹: 3339, 2952, 1696, 1662, 1616, 1548, 1477, 1437, 1372, 1322, 1281, 1249, 1189, 1154, 1110, 1088, 1028, 1011; ¹H NMR (400 MHz, CDCl₃): δ 10.90 (s, 1H), 8.61 (s, 1H), 8.42 (brs, 1H), 7.97 (dd, J = 1.4, 8.4 Hz, 1H), 7.65 (d, J = 2.4 Hz, 1H), 7.45–7.43 (m, 2H), 7.37 (d, J = 2.4 Hz, 1H), 5.75 (s, 1H), 3.99 (s, 3H), 3.95 (s, 3H); ¹³C NMR (125 MHz, CDCl₃): δ 170.8, 168.1, 147.6, 145.2, 139.0, 126.1, 125.4, 124.3, 123.9, 122.7, 122.6, 119.4, 118.7, 112.6, 111.1, 52.6, 51.9; ESI-HRMS m/z: 364.0790 ([M+Na⁺]); Calcd for C₁₈H₁₅NO₆Na: 364.0792.
7.29 (d, J = 2.0 Hz, 1H), 6.92 (dd, J = 2.0, 9.0 Hz, 1H), 5.70 (s, 1H), 3.98 (s, 3H), 3.87 (s, 3H); 13C NMR (125 MHz, CDCl3): δ 170.8, 154.7, 147.2, 145.2, 131.7, 127.1, 126.1, 122.3, 119.2, 119.1, 117.1, 112.6, 112.5, 112.1, 101.5, 56.0, 52.5; ESI-HRMS m/z: 314.1013 ([M+H+]); Calcd for C17H16NO5: 314.1023.

(Table 2, A) Methyl 2,3-dihydroxy-6-(5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1H-indol-3-yl)benzoate (3m) and methyl 2,3-dihydroxy-5-(5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1H-indol-3-yl)benzoate (4m)

According to the general procedure A; Methyl-2,3-dihydroxybenzoate (1a) (33.6 mg, 0.20 mmol) was used as a substrate, and 5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1H-indole (2m; 145.9 mg, 0.60 mmol) was used as a nucleophile. 4m (29.5 mg, 0.072 mmol) and 3m (18.0 mg, 0.044 mmol) were obtained in 36% and 22% yield after purification using flash column chromatography on silica gel (n-hexane-ethyl acetate = 4/1). The pure product 3o was isolated by flash column chromatography on silica gel (CH2Cl2-MeOH = 20/1) using a portion of generated mixture (4m and 3m).

According to the general procedure B; Methyl-2,3-dihydroxybenzoate (1a) (16.8 mg, 0.10 mmol) was used as a substrate, and 5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1H-indole (2m; 76.0 mg, 0.30 mmol) was used as a nucleophile. 3m (38.4 mg, 0.136 mmol) was obtained in 68% yield after purification by silica-gel column chromatography using n-hexane-ethyl acetate (4/1).

3m: Brown amorphous; IR (ATR) cm⁻¹: 3367, 2976, 1658, 1613, 1440, 1354, 1259, 1193, 1139, 1073, 1033, 1000; ¹H NMR (500 MHz, CDCl3): δ 11.16 (s, 1H), 8.26 (brs, 1H), 7.88 (s, 1H), 7.67 (d, J = 8.0 Hz, 1H), 7.38 (d, J = 8.0 Hz, 1H), 7.10 (d, J = 8.0 Hz, 1H), 7.08 (d, J = 2.5 Hz, 1H), 6.84 (d, J = 8.0 Hz, 1H), 5.88 (s, 1H), 3.32 (s, 3H), 1.34 (s, 12H); 13C NMR (125 MHz, CDCl3): δ 171.7, 148.9, 144.2, 137.6, 128.1, 127.7, 127.4, 127.0, 123.7, 121.8, 119.3, 118.4, 112.7, 110.5, 83.4, 51.9, 24.8; ESI-HRMS m/z: 432.1598 ([M+Na⁺]); Calcd for C₂₂H₂₄NO₆BNa: 432.1593.

Carbon bearing the boron substituent could not be observed in ¹³C NMR of 3m.⁵

4m: Brown amorphous; IR (ATR) cm⁻¹: 3393, 2978, 2016, 1673, 1613, 1478, 1441, 1353, 1298, 1233, 1193, 1140, 1105, 1012; ¹H NMR (500 MHz, CDCl3): δ 10.84 (s, 1H), 8.43 (brs, 1H), 8.39 (s, 1H), 7.70 (d, J = 8.3 Hz, 1H), 7.62 (d, J = 1.5 Hz, 1H), 7.46 (d, J = 1.5 Hz, 1H), 7.37 (d, J = 8.3 Hz, 1H), 7.22 (d, J = 3.0 Hz, 1H), 5.90 (s, 1H), 3.96 (s, 3H), 1.38 (s, 12H); ¹³C NMR (125
MHz, CDCl₃): δ 170.8, 147.3, 145.0, 138.5, 128.5, 127.2, 126.8, 125.4, 121.6, 119.6, 119.5, 117.7, 112.4, 110.8, 83.6, 52.4, 24.8; ESI-HRMS m/z: 410.1784 ([M+H⁺]); Caled for C₂₂H₂₅NO₆B: 410.1773.

Carbon bearing the boron substituent could not be observed in ¹³C NMR of 4m.⁵

(Table 2, A) Methyl 2,3-dihydroxy-6-(1-methyl-2-phenyl-IH-indol-3-yl)benzoate (3n) and methyl 2,3-dihydroxy-5-(1-methyl-2-phenyl-IH-indol-3-yl)benzoate (4n)

According to the general procedure A; Methyl-2,3-dihydroxybenzoate (1a) (33.6 mg, 0.20 mmol) was used as a substrate, and N-methyl-2-phenyl-IH-indole (2n; 124.4 mg, 0.60 mmol) was used as a nucleophile. 4n (57.5 mg, 0.154 mmol) and 3n (9.0 mg, 0.024 mmol) were obtained in 77% and 12% yield after purification using flash column chromatography on silica gel (n-hexane-ethyl acetate = 4/1). The pure product 4n was isolated by recrystallization (CHCl₃-MeOH) using a portion of generated mixture (4n and 3n).

According to the general procedure B; Methyl-2,3-dihydroxybenzoate (1a) (33.6 mg, 0.20 mmol) was used as a substrate, and N-methyl-2-phenyl-IH-indole (2n; 124.4 mg, 0.60 mmol) was used as a nucleophile. 3n (60.5 mg, 0.162 mmol) was obtained in 81% yield after purification by silica-gel column chromatography using n-hexane-ethyl acetate (4/1).

3n; Pale green solid; M.p. 90.9–95.2 °C; IR (ATR) cm⁻¹: 3507, 3054, 2950, 1658, 1604, 1466, 1439, 1358, 1324, 1256, 1193, 1151, 1137, 1016, 1000; ¹H NMR (500 MHz, CDCl₃): δ 10.93 (s, 1H), 7.39 (t, J = 7.5 Hz, 2H), 7.35–7.31 (m, 3H), 7.28–7.25 (m, 1H), 7.21 (d, J = 7.5 Hz, 2H), 7.12 (t, J = 7.5 Hz, 1H), 6.69 (d, J = 8.0 Hz, 1H), 5.68 (s, 1H), 3.73 (s, 1H), 3.36 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 171.6, 148.6, 143.5, 137.2, 137.2, 131.6, 130.5, 128.2, 128.1, 127.9, 127.7, 124.6, 121.8, 119.9, 119.0, 118.4, 115.5, 113.1, 109.3, 52.2, 31.2; ESI-HRMS m/z: 396.1194 ([M+Na⁺]); Caled for C₂₃H₁₉NO₄Na: 396.1206.

4n; Colorless solid; M.p. 158.2–158.8 °C; IR (ATR) cm⁻¹: 3467, 3055, 2952, 1672, 1619, 1550, 1499, 1467, 1440, 1372, 1328, 1296, 1275, 1242, 1229, 1193, 1154, 1129, 1090, 1053, 1018; ¹H NMR (500 MHz, CDCl₃): δ 10.77 (s, 1H), 7.74 (d, J = 8.0 Hz, 1H), 7.42–7.37 (m, 5H), 7.33–7.30 (m, 3H), 7.20 (t, J = 8.0 Hz, 1H), 6.97 (d, J = 1.5 Hz, 1H), 5.51 (s, 1H), 3.89 (s, 3H), 3.68 (s, 3H); ¹³C NMR (125 MHz, CDCl₃): δ 170.8, 146.9, 144.6, 137.7, 137.1, 131.5, 131.0, 128.5, 128.2, 126.9, 126.6, 122.2, 121.7,
121.6, 120.2, 119.3, 113.8, 112.2, 109.6, 52.4, 30.9; ESI-HRMS m/z: 396.1208 ([M+Na^+]); Calcd for C_{23}H_{19}NO_4Na: 396.1206.

(Table 2, A) Methyl 2,3-dihydroxy-6-(6-methyl-1H-indol-3-yl)benzoate (3o) and methyl 2,3-dihydroxy-5-(6-methyl-1H-indol-3-yl)benzoate (4o)

According to the general procedure A; Methyl-2,3-dihydroxybenzoate (1a) (16.8 mg, 0.10 mmol) was used as a substrate, and 6-methylindole (2o; 39.4 mg, 0.30 mmol) was used as a nucleophile. 4o (6.5 mg, 0.022 mmol) and 3o (1.8 mg, 0.006 mmol) were obtained in 22% and 6% yield after purification using flash column chromatography on silica gel (n-hexane-ethyl acetate = 4/1). The pure product 4o was isolated by recrystallization (CHCl_3-MeOH) using a portion of generated mixture (4o and 3o).

According to the general procedure B; Methyl-2,3-dihydroxybenzoate (1a) (16.8 mg, 0.10 mmol) was used as a substrate, and 6-methylindole (2o; 39.4 mg, 0.30 mmol) was used as a nucleophile. 3o (9.8 mg, 0.033 mmol) was obtained in 33% yield after purification by silica-gel column chromatography using n-hexane-ethyl acetate (4/1).

3o; Colorless solid; M.p. 142.8–144.4 °C; IR (ATR) cm\(^{-1}\): 3426, 3388, 3052, 2958, 1678, 1618, 1545, 1478, 1434, 1368, 1342, 1281, 1246, 1188, 1138, 1074, 1055, 1015; \(^1\)H NMR (500 MHz, CDCl_3): \(\delta\) 10.98 (s, 1H), 7.98 (brs, 1H), 7.24 (d, \(J = 8.0\) Hz, 1H), 7.18 (s, 1H), 7.11 (d, \(J = 8.3\) Hz, 1H), 7.07 (d, \(J = 2.0\) Hz, 1H), 6.92 (d, \(J = 8.0\) Hz, 1H), 6.86 (d, \(J = 8.3\) Hz, 1H), 5.76 (s, 1H), 3.36 (s, 3H), 2.46 (s, 3H); \(^{13}\)C NMR (125 MHz, CDCl_3): \(\delta\) 171.8, 148.6, 143.9, 136.1, 131.8, 128.0, 125.3, 123.4, 121.8, 121.0, 118.7, 118.6, 118.5, 112.5, 111.0, 52.0, 21.6; ESI-HRMS m/z: 298.1048 ([M+H^+]); Calcd for C_{17}H_{16}NO_4: 298.1074.

4o; Gray solid; M.p. 95.3–100.2 °C; IR (ATR) cm\(^{-1}\): 3481, 3423, 2948, 1663, 1545, 1439, 1381, 1330, 1286, 1265, 1192, 1166, 1142, 1094, 1032, 1005; \(^1\)H NMR (500 MHz, CDCl_3): \(\delta\) 10.82 (s, 1H), 8.08 (brs, 1H), 7.77 (d, \(J = 8.5\) Hz, 1H), 7.67 (d, \(J = 2.5\) Hz, 1H), 7.43 (d, \(J = 2.5\) Hz, 1H), 7.24 (d, \(J = 2.5\) Hz, 1H), 7.04 (d, \(J = 8.5\) Hz, 1H), 5.71 (s, 1H), 3.98 (s, 3H), 2.49 (s, 3H); \(^{13}\)C NMR (125 MHz, CDCl_3): \(\delta\) 170.9, 147.2, 145.1, 137.0, 132.3, 127.2, 123.4, 122.1, 120.8, 119.2, 119.1, 118.9, 117.0, 112.5, 111.3, 52.5, 21.6; ESI-HRMS m/z: 320.0895 ([M+Na^+]); Calcd for C_{17}H_{15}NO_4Na: 320.0893.

(Table 2, A) Methyl 2,3-dihydroxy-6-(7-methyl-1H-indol-3-yl)benzoate (3p) and
**methyl 2,3-dihydroxy-5-(7-methyl-1H-indol-3-yl)benzoate (4p)**

According to the general procedure A; Methyl-2,3-dihydroxybenzoate (1a) (16.8 mg, 0.10 mmol) was used as a substrate, and 7-methylindole (2p; 39.4 mg, 0.30 mmol) was used as a nucleophile. 4p (18.7 mg, 0.063 mmol) and 3p (3.3 mg, 0.011 mmol) were obtained in 63% and 11% yield after purification using flash column chromatography on silica gel (n-hexane-ethyl acetate = 4/1). The pure product 4p was isolated by flash column chromatography on silica gel (CH2Cl2-MeOH = 20/1) using a portion of generated mixture (4p and 3p).

According to the general procedure B; Methyl-2,3-dihydroxybenzoate (1a) (16.8 mg, 0.10 mmol) was used as a substrate, and 7-methylindole (2p; 39.4 mg, 0.30 mmol) was used as a nucleophile. 3p (19.6 mg, 0.066 mmol) was obtained in 66% yield after purification by silica-gel column chromatography using n-hexane-ethyl acetate (4/1).

![Chemical Structure of 4p]

**3p**; Brown amorphous; IR (ATR) cm⁻¹: 3405, 3050, 2950, 1614, 1552, 1483, 1429, 1313, 1258, 1245, 1191, 1139, 1105, 1058, 1005; ¹H NMR (500 MHz, CDCl₃): δ 11.00 (s, 1H), 8.06 (brs, 1H), 7.22 (d, J = 7.0 Hz, 1H), 7.17 (d, J = 2.0 Hz, 1H), 7.12 (d, J = 8.0 Hz, 1H), 7.04–7.00 (m, 2H), 6.87 (d, J = 8.0 Hz, 1H), 5.76 (s, 1H), 3.36 (s, 3H), 2.54 (s, 3H); ¹³C NMR (125 MHz, CDCl₃): δ 171.8, 148.7, 143.9, 135.2, 131.8, 128.0, 127.0, 123.4, 122.5, 121.3, 120.2, 119.4, 118.5, 116.8, 112.5, 52.1, 16.6; ESI-HRMS m/z: 336.0646 ([M+K⁺]); Calcd for C₁₇H₁₅NO₄K: 336.0633.

**4p**; Green amorphous; IR (ATR) cm⁻¹: 3426, 3388, 3052, 2958, 1678, 1618, 1545, 1478, 1434, 1368, 1342, 1281, 1246, 1188, 1138, 1074, 1055, 1015; ¹H NMR (500 MHz, CDCl₃): δ 10.85 (s, 1H), 8.15 (brs, 1H), 7.75 (d, J = 7.8 Hz, 1H), 7.68 (s, 1H), 7.44 (s, 1H), 7.32 (s, 1H), 7.14 (t, J = 7.8 Hz, 1H), 7.07 (d, J = 7.8 Hz, 1H), 3.99 (s, 3H), 2.53 (s, 3H); ¹³C NMR (125 MHz, CDCl₃): δ 170.9, 147.2, 145.1, 136.1, 127.2, 125.1, 123.0, 121.2, 120.5 (2C), 119.2, 119.1, 117.7, 117.3, 112.5, 52.5, 16.6; DART-HRMS m/z: 298.1078 ([M+H⁺]); Calcd for C₁₇H₁₆NO₄: 298.1079.

(***Table 2, B***) Methyl 5-(bromo-1H-indol-3-yl)benzo[a][1,3]dioxole-4-carboxylate (7)

To a solution of 3i (178.0 mg, 0.50 mmol) in DMSO (2.0 mL) were added CH₂Cl₂ (0.07 mL, 1.0 mmol) and CsCO₃ (325.8 mg, 1.0 mmol) under argon. The reaction mixture was stirred at 80 °C for 24 h. After quenching with H₂O, the reaction mixture was extracted with AcOEt (10 mL x 3). The organic layer was dried over Na₂SO₄ and
concentrated in vacuo. Purification using flash column chromatography on silica gel (n-hexane-ethyl acetate = 2/1) gave 3 (95.4 mg, 0.25 mmol) in 51% yield.

7; Purple amorphous; IR (ATR) cm⁻¹: 3368, 2949, 2895, 1710, 1626, 1549, 1499, 1448, 1348, 1269, 1231, 1192, 1173, 1132, 1100, 1046, 1017; ¹H NMR (500 MHz, CDCl₃): δ 8.32 (brs, 1H), 7.66 (s, 1H), 7.26 (d, J = 8.0 Hz, 1H), 7.20 (d, J = 8.0 Hz, 1H), 7.14 (d, J = 2.5 Hz, 1H), 6.97–6.94 (m, 2H), 6.11 (s, 2H), 3.68 (s, 3H); ¹³C NMR (125 MHz, CDCl₃): δ 166.4, 147.0, 146.9, 134.5, 128.5, 126.9, 125.1, 124.2, 123.6, 121.7, 115.8, 114.7, 113.4, 112.8, 110.4, 102.0, 52.4; DART-HRMS m/z: 374.0000 ([M+H⁺]); Calcd for C₁₇H₁₃BrNO₄: 374.0028.

(Table 2, B) Methyl 5-(5-(3,5-dimethoxyphenyl)-1H-indol-3-yl)benzo[a][1,3]dioxole-4-carboxylate (8)

To a solution of 7 (37.4 mg, 0.10 mmol) and 3,5-methoxyphenylboronic acid (79.2 mg, 0.3 mmol) in EtOH/toluene (1/1; 1.0 mL) was added aq. Na₂CO₃ (1M, 0.25 mL) under argon. Then, Pd(PPh₃)₄ (4.6 mg, 0.008 mmol) was added. Reaction mixture was stirred at 100 °C for 5 h. After filtration, the reaction mixture was extracted with AcOEt (10 mL x 3). The organic layer was dried over Na₂SO₄ and concentrated in vacuo. Purification using flash column chromatography on silica gel (n-hexane-ethyl acetate = 3/1) gave 8 (20.2 mg, 0.047 mmol) in 47% yield.

8; Pale green solid; M.p. 62.2–66.4 °C; IR (ATR) cm⁻¹: 3358, 2949, 2169, 2141, 1711, 1590, 1457, 1416, 1330, 1267, 1233, 1202, 1152, 1049, 1016; ¹H NMR (500 MHz, CDCl₃): δ 8.23 (brs, 1H), 7.76 (s, 1H), 7.48–7.43 (m, 2H), 7.26–7.25 (m, 1H), 7.04 (d, J = 8.0 Hz, 1H), 6.96 (d, J = 8.0 Hz, 1H), 6.78 (d, J = 2.0 Hz, 1H), 6.43 (dd, J = 2.0, 2.0 Hz, 1H), 6.11 (s, 2H), 3.86 (s, 6H), 3.57 (s, 3H); ¹³C NMR (125 MHz, CDCl₃): δ 116.6, 160.9, 147.0, 146.7, 144.6, 135.6, 133.6, 127.4, 127.2, 124.1, 122.1, 117.6, 116.7, 114.8, 111.4, 110.4, 105.6, 105.9, 98.5, 55.4, 52.2; DART-HRMS m/z: 432.1474 ([M+H⁺]); Calcd for C₂₅H₂₂NO₆: 432.1447.

(Table 2, C) 2,3-Dihydroxy-6-(1H-indol-3-yl)benzaldehyde (9)

According to the general procedure A; 2,3-dihydroxybenzaldehyde (1b) (27.6 mg, 0.20 mmol) was used as a substrate, and indole (2a; 70.3 mg, 0.60 mmol) was used as a nucleophile. 9 (18.2 mg, 0.072 mmol) was obtained in 36% yield after purification by silica-gel column chromatography using n-hexane-ethyl acetate (5/1). According to the general procedure B; 2,3-dihydroxybenzaldehyde (1b) (27.6 mg, 0.20
mmol) was used as a substrate, and indole (2a; 70.3 mg, 0.60 mmol) was used as a nucleophile. 9 (20.3 mg, 0.080 mmol) was obtained in 40% yield after purification by silica-gel column chromatography using n-hexane-ethyl acetate (4/1).

9; Orange solid; M.p. 169.4–172.6 °C IR (ATR) cm⁻¹: 3347, 3221, 3051, 1624, 1531, 1494, 1476, 1441, 1421, 1394, 1346, 1327, 1284, 1258, 1221, 1186, 1135, 1124, 1089, 1052, 1042, 1014; ¹H NMR (500 MHz, CDCl₃): δ 12.07 (s, 1H), 9.49 (s, 1H), 8.20 (brs, 1H), 7.57 (d, J = 8.0 Hz, 1H), 7.51 (d, J = 8.0 Hz, 1H), 7.26 (t, J = 7.8 Hz, 1H), 6.97 (d, J = 8.0 Hz, 1H), 5.78 (s, 1H); ¹³C NMR (125 MHz, CDCl₃): δ 198.1, 149.5, 143.6, 135.9, 131.0, 127.7, 124.3, 123.0, 122.2, 121.4, 120.9, 119.2, 118.4, 113.4, 111.4; DART-HRMS m/z: 254.0827 ([M+H⁺]); Calcd for C₁₇H₁₅N₂O₅: 254.0817.

(Table 2, C) 3-(hydroxymethyl)-4-(1H-indol-3-yl)benzene-1,2-diol (10)
To a solution of 9 (50.7 mg, 0.20 mmol) in MeOH (2.0 mL) was added NaBH₄ (11.3 mg, 0.30 mmol) at 0 °C. After stirring at room temperature for 0.5 h, reaction mixture was quenched with H₂O. The reaction mixture was extracted with AcOEt (10 mL x 3). The organic layer was dried over Na₂SO₄ and concentrated in vacuo. Purification using flash column chromatography on silica gel (n-hexane-ethyl acetate = 2/1) gave 10 (40.1 mg, 0.12 mmol) in 60% yield.

Brown solid; M.p. 157.2–160.1 °C; IR (ATR) cm⁻¹: 3417, 3046, 2542, 2224, 1702, 1614, 1587, 1546, 1489, 1449, 1373, 1342, 1305, 1281, 1270, 1250, 1229, 1209, 1141, 1118, 1070, 1004; ¹H NMR (500 MHz, CD₃OD): δ 7.45 (d, J = 7.8 Hz, 1H), 7.39 (d, J = 7.8 Hz, 1H), 7.27 (s, 1H), 7.11 (t, J = 7.3 Hz, 1H), 7.00 (t, J = 7.3 Hz, 1H), 6.84–6.81 (m, 2H), 4.70 (s, 2H); ¹³C NMR (125 MHz, CD₃OD): δ 146.9, 145.6, 138.6, 129.7, 129.1, 127.3, 125.4, 123.8, 123.2, 121.0, 121.0, 117.3, 116.3, 113.1, 60.6; DART-HRMS m/z: 336.1102 ([M+H⁺]); Calcd for C₁₇H₁₀O₇: 335.1125.)
5. Optimization using 3-methoxycarbonyl catechol (1a) and trimethoxybenzene (TMB).

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1) Limitation of arene nucleophiles

**Scheme S1**

2) Limitation of substrates in the reaction using indole.

**Scheme S2**
7. DFT calculation

All calculations were conducted with M06-2X+GD3 level of density functional theory calculation, in which Grimme’s D3 version of empirical dispersion correction was included. The 6-311+G(d) basis set was adopted for the calculations. The CH2Cl2 solvent effects were included by the IEFPCM method. The normal mode analyses were performed to characterize the optimized structures and to calculate the Gibbs free energies at $T = 298.15$ K.

Figure S1. 1) Optimized structures of proton-activated ortho-benzoquinones (A) and their Gibbs free energies (kcal/mol) relative to that of the most stable intermediate (d), and 2) natural population analysis charges and LUMO of the most stable intermediate (d).

First, we calculated proton-activated ortho-benzoquinones (A) to determine the most favourable proton-activation site (Figure S1-1). In the most stable conformer, the proton attached to the carbonyl oxygen next to the methoxycarbonyl group and formed intramolecular hydrogen bond with the methoxy carbonyl group (Figure S1-1(d)). The natural population analysis (NPA) charge density and the lowest unoccupied molecular orbital (LUMO) are shown in Figure S1-2. The C4 position is positively charged, and the LUMO distributed mainly on the C4 position. These results indicates that the nucleophilic attack of indole at C4 position is more prefered than the nucleophilic attack at C5 position for the proton-activated ortho-benzoquinone.
Figure S2. 1) Optimized structures of BF$_3$-activated ortho-benzoquinones (A) and their Gibbs free energies (kcal/mol) relative to that of the most stable intermediate (g), and 2) top and side views, and energy change upon planarization of (g), and 3) top and side views of (a). *Electronic energy relative to that of (g).

Next, we investigate the most favourable BF$_3$-activation site of ortho-benzoquinone (A). The optimized structures and the Gibbs free energies relative to the
most stable intermediate (g) are shown in Figure S3-1. The magnitude of O-C-C-C dihedral angle in (g) is 37.4°, whereas that in the second most stable conformer (a) is 20.3°. Since the planarization was required to proceed the reaction from (g), as shown below, we also investigated the reaction from the second most stable intermediate (a).

To find out the plausible pathway, each reaction path was analyzed according to the following procedures. First, we optimized the structure of Int-2 intermediates by DFT calculation, followed by the calculation of the potential energy curve (PEC) for the rotation around C(benzoquinone)-C(indole) axis. We could obtain local minimum structures (Int’s) by conducting geometry optimization from the minima of the rotational PEC. Then the corresponding TS, Int-1, and product could be calculated by the general procedures. We focused on only the most stable Int-2 in each reaction path in this study.

Figures S2 and S3 show the reaction energy profiles of the indole addition. The ΔG value of TS in the indole addition to (a) (Path I and Path II) is lower than that in the indole addition to (g) (Path III and Path IV), thus, the addition to (a) to give 4a is preferred to the addition to (g) to give 3a. The most favoured path is Path I to give 4a, which is consistent with the experimental results. Thus, the BF3 activation was likely to occur on the carbonyl oxygen at C1 position resulting in 4a. As shown in Figure S4, planarization of the benzoquinone was required to proceed the reaction from (g) unlike the reaction from (a). One can consider that such planarization made the reaction from (g) unfavorable.
Figure S3. Reaction energy profiles of indole addition to the second most stable BF$_3$-activated ortho-benzoquinone A (a) to give 4a.
Figure S4. Reaction energy profiles of indole addition to the most stable BF$_3$-activated ortho-benzoquinone A (g) to give 3a.
Figure S5. Top and side views of the TSs of Path I and Path II.
Figure S6. Reaction energy profiles of indole addition to the less stable BF3-activated ortho-benzoquinone A (d) to give 3a.

When BF3 activates the carbonyl moiety at C1 or C2 position of A, the energy differences from each intermediate to the corresponding transition state are similar in comparison.
with Figure S3 and S6. However, the original energy of the coordination (a) between BF$_3$ and the C1 carbonyl moiety of A is lower than that of the coordination (d) between BF$_3$ and the C2 carbonyl moiety of A as shown in Figure S2. Therefore, 4a, obtained via the path shown in Figure S3, was selectively obtained.

Figure S7. The DFT calculation of Ts-indole

BF$_3$•Et$_2$O-catalyzed reactions using 2d, 2g, and 2h gave only the 4-adducts (3d, 3g, and 3h) as the main products in Table 2. BF$_3$ can coordinate both the intermediate A and 2d, 2g, and 2h as indoles having Ts, CO$_2$Me and CHO moieties. DFT calculation indicates that nucleophilicity of N-Ts-indole decreases by the coordination of BF$_3$ in comparison with HOMO levels shown in Figure S7. Therefore, this is not reason to facilitate the reaction.

Alternatively, B(OH)$_3$ or HF, resulted by the decomposition of BF$_3$ with the contaminated H$_2$O, was proposed to facilitate the reaction. However, the use of B(OH)$_3$ or HF instead of BF$_3$ resulted no reaction.

The reason is still unclear, and the further detailed investigation is needed to elucidate this phenomenon.
8. Deuteration of indole and the reactions using deuterated indole

**General procedure C;** Indole (0.3 mmol), 10% Pd/C, Pt/C or Ir/C (10 wt%), (cyclohexane (0.5 mL)) and D₂O (1.5 mL) were added to a test tube. The reaction mixture was stirred at 80 °C for 24 h under hydrogen gas (balloon), then the reaction mixture was cooled down to room temperature and passed through celite pad to remove the catalyst. The combined filtrates were extracted with AcOEt (20 mL × 3), and the organic layers were dried over Na₂SO₄, and concentrated in vacuo. The residue was purified by silica-gel column chromatography using n-hexane-ethyl acetate (6/1).

**Table S4**

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**Table S5**

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<td>cyclohexane (0.5)</td>
<td>95 93 96 96 96</td>
<td>73</td>
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</table>
Scheme S3; scale up

**Procedure;** Indole (3.0 mmol), 10% Pt/C (35.1 mg, 10 wt%), cyclohexane (5 mL) and D$_2$O (15 mL) were added to a 50 mL flask. The reaction mixture was stirred at 80 °C for 24 h under hydrogen gas (balloon), then the reaction mixture was cooled down to room temperature and passed through celite pad to remove the catalyst. The combined filtrates were extracted with AcOEt (20 mL x 3), and the organic layers were dried over Na$_2$SO$_4$, and concentrated in vacuo. The residue was purified by silica-gel column chromatography using n-hexane-ethyl acetate (6/1), and indole-$d_6$ (257 mg, 2.1 mmol) was obtained in 69% yield.

**The reaction of eq. 2 without BF$_3$•Et$_2$O;** To a suspension of catechol (1; 0.20 mmol) in CH$_2$Cl$_2$ (1.0 mL) in a dry brown test tube was added PIDA (64.4 mg, 0.2 mmol) under argon. The reaction mixture was placed on an organic reactor, Chemi Station (EYELA, Tokyo Rikakikai Co., Ltd., Tokyo, Japan), and the mixture was stirred at 25 °C for 1 h. Indole-$d_6$ (3.0 eq.) as nucleophile and CH$_2$Cl$_2$ (1.0 mL) were added sequentially, and the mixture was stirred at 0 °C for 1 h. After quenching with H$_2$O, the reaction mixture was extracted with CH$_2$Cl$_2$ (10 mL x 3). The organic layer was dried over Na$_2$SO$_4$ and concentrated in vacuo. The residue was purified by silica-gel column chromatography using n-hexane-ethyl acetate (4/1), and 4-adduct ($3-d_6$) (27.8 mg, 0.096 mmol) was obtained in 48% yield.
The reaction of eq. 2 with BF$_3$•Et$_2$O; To a suspension of catechol (1; 0.20 mmol) in CH$_2$Cl$_2$ (1.0 mL) in a dried brown test tube was added PIDA (64.4 mg, 0.2 mmol) under argon. The reaction mixture was placed on an organic reactor, Chemi Station (EYELA, Tokyo Rikakikai Co., Ltd., Tokyo, Japan), and the mixture was stirred at 25 °C for 1 h. Indole-$d_6$ (2; 3.0 eq.) as nucleophile, BF$_3$•OEt$_2$ (1.3 µL, 5 mol%), and CH$_2$Cl$_2$ (1.0 mL) were added sequentially, and the mixture was stirred at 0 °C for 1 h. After quenching with H$_2$O, the reaction mixture was extracted with CH$_2$Cl$_2$ (10 mL x 3). The organic layer was dried over Na$_2$SO$_4$ and concentrated in vacuo. The residue was purified by silica-gel column chromatography using n-hexane-ethyl acetate (4/1), and the regioisomers (4-$d_6$ and 3-$d_6$) were obtained. The pure 5-adduct (4-$d_6$) was isolated by recrystallization (CHCl$_3$/n-hexane).
9. References.


10. $^1$H and $^{13}$C NMR spectra of the newly synthesized substrates and products.

$^1$H NMR of methyl-2,3-dihydroxybenzoate (1a)

$^{13}$C NMR of methyl-2,3-dihydroxybenzoate (1a)
$^1$H NMR of N-benzylindole (2c)

$^{13}$C NMR of N-benzylindole (2c)
$^1$H NMR of 1-(p-toluenesulfonyl)-$^1$H-indole (2d)

$^{13}$C NMR of 1-(p-toluenesulfonyl)-$^1$H-indole (2d)
$^1$H NMR of 1-methyl-2-phenyl-$IH$-indole (2n)

$^{13}$C NMR of 1-methyl-2-phenyl-$IH$-indole (2n)
$^1$H NMR of methyl 2,3-dihydroxy-6-(1H-indol-3-yl)benzoate (3a)

$^{13}$C NMR of methyl 2,3-dihydroxy-6-(1H-indol-3-yl)benzoate (3a)
$^1$H NMR of methyl 2,3-dihydroxy-5-(1H-indol-3-yl)benzoate (4a)

$^{13}$C NMR of methyl 2,3-dihydroxy-5-(1H-indol-3-yl)benzoate (4a)
$^1$H NMR of methyl 3,4-dihydroxy-2',4',6'-trimethoxy-[1,1'-biphenyl]-2-carboxylate (5)

$^{13}$C NMR of methyl 3,4-dihydroxy-2',4',6'-trimethoxy-[1,1'-biphenyl]-2-carboxylate (5)
HMBC of methyl 3,4-dihydroxy-2’,4’,6’-trimethoxy-[1,1’-biphenyl]-2-carboxylate (5)
HMOC of methyl 3,4-dihydroxy-2’,4’,6’-trimethoxy-[1,1’-biphenyl]-2-carboxylate (5)
$^1$H NMR of methyl 4,5-dihydroxy-2',4',6'-trimethoxy-[1,1'-biphenyl]-3-carboxylate (6)

$^{13}$C NMR of methyl 4,5-dihydroxy-2',4',6'-trimethoxy-[1,1'-biphenyl]-3-carboxylate (6)
HMBC of methyl 4,5-dihydroxy-2‘,4’,6’-trimethoxy-[1,1’-biphenyl]-3-carboxylate (6)
HMQC of methyl 4,5-dihydroxy-2',4',6'-trimethoxy-[1,1'-biphenyl]-3-carboxylate (6)
$^1$H NMR of methyl 2,3-dihydroxy-6-(1-methyl-$IH$-indol-3-yl)benzoate (3b)

$^{13}$C NMR of methyl 2,3-dihydroxy-6-(1-methyl-$IH$-indol-3-yl)benzoate (3b)
$^1$H NMR of methyl 2,3-dihydroxy-5-(1-methyl-$^1$H-indol-3-yl)benzoate ($4b$)

$^{13}$C NMR of methyl 2,3-dihydroxy-5-(1-methyl-$^1$H-indol-3-yl)benzoate ($4b$)
$^1$H NMR of methyl 6-(1-benzyl-$1H$-indol-3-yl)-2,3-dihydroxybenzoate (3c)

$^{13}$C NMR of methyl 6-(1-benzyl-$1H$-indol-3-yl)-2,3-dihydroxybenzoate (3c)
\(^1\)H NMR of methyl 5-(1-benzyl-\(1\)H-indol-3-yl)-2,3-dihydroxybenzoate (4c)

\(^{13}\)C NMR of methyl 5-(1-benzyl-\(1\)H-indol-3-yl)-2,3-dihydroxybenzoate (4c)
$^1$H NMR of methyl 2,3-dihydroxy-6-(1-tosyl-1H-indol-3-yl)benzoate (3d)

$^{13}$C NMR of methyl 2,3-dihydroxy-6-(1-tosyl-1H-indol-3-yl)benzoate (3d)
$^1$H NMR of methyl 2,3-dihydroxy-6-(2-methyl-$^1$H-indol-3-yl)benzoate (3e)

$^{13}$C NMR of methyl 2,3-dihydroxy-6-(2-methyl-$^1$H-indol-3-yl)benzoate (3e)
$^1$H NMR of methyl 2,3-dihydroxy-5-(2-methyl-$^1$H-indol-3-yl)benzoate (4e)

![$^1$H NMR spectrum](image1)

$^{13}$C NMR of methyl 2,3-dihydroxy-5-(2-methyl-$^1$H-indol-3-yl)benzoate (4e)

![$^{13}$C NMR spectrum](image2)
$^1$H NMR of methyl 2,3-dihydroxy-6-(2-phenyl-$1H$-indol-3-yl)benzoate (3f)

$^{13}$C NMR of methyl 2,3-dihydroxy-6-(2-phenyl-$1H$-indol-3-yl)benzoate (3f)
$^1$H NMR of methyl 2,3-dihydroxy-5-(2-phenyl-$^1$H-indol-3-yl)benzoate (4f)

$^{13}$C NMR of methyl 2,3-dihydroxy-5-(2-phenyl-$^1$H-indol-3-yl)benzoate (4f)
$^1$H NMR of methyl 3-(3,4-dihydroxy-2-(methoxycarbonyl)phenyl)-1H-indole-2-carboxylate (3g)

13C NMR of methyl 3-(3,4-dihydroxy-2-(methoxycarbonyl)phenyl)-1H-indole-2-carboxylate (3g)
$^1$H NMR of methyl 6-(2-formyl-$1^H$-indol-3-yl)-2,3-dihydroxybenzoate (3h)

$^{13}$C NMR of methyl 6-(2-formyl-$1^H$-indol-3-yl)-2,3-dihydroxybenzoate (3h)
$^1$H NMR of methyl 6-(5-bromo-$^1$H-indol-3-yl)-2,3-dihydroxybenzoate (3i)

$^{13}$C NMR of methyl 6-(5-bromo-$^1$H-indol-3-yl)-2,3-dihydroxybenzoate (3i)
$^1$H NMR of methyl 5-(5-bromo-$^1$H-indol-3-yl)-2,3-dihydroxybenzoate (4i)

\[
\text{HO} \quad \text{OH} \quad \text{COOMe} \\
\text{Br} \quad \text{NH} \\
(500 \text{MHz, CDCl}_3)
\]

$^{13}$C NMR of methyl 5-(5-bromo-$^1$H-indol-3-yl)-2,3-dihydroxybenzoate (4i)

\[
\text{HO} \quad \text{OH} \quad \text{COOMe} \\
\text{Br} \quad \text{NH} \\
(125 \text{MHz, CDCl}_3)
\]
$^1$H NMR of methyl 6-(5-fluoro-$H$-indol-3-yl)-2,3-dihydroxybenzoate (3j)

![NMR spectrum of methyl 6-(5-fluoro-$H$-indol-3-yl)-2,3-dihydroxybenzoate (3j)]

$^{13}$C NMR of methyl 6-(5-fluoro-$H$-indol-3-yl)-2,3-dihydroxybenzoate (3j)

![NMR spectrum of methyl 6-(5-fluoro-$H$-indol-3-yl)-2,3-dihydroxybenzoate (3j)]
$^{19}$F NMR of methyl 6-(5-fluoro-$^1$H-indol-3-yl)-2,3-dihydroxybenzoate (3j)
$^1$H NMR of methyl 5-(5-fluoro-$^1$H-indol-3-yl)-2,3-dihydroxybenzoate (4j)

$^{13}$C NMR of methyl 5-(5-fluoro-$^1$H-indol-3-yl)-2,3-dihydroxybenzoate (4j)
$^{19}\text{F NMR of methyl 5-}(\text{5-fluoro-1H-indol-3-yl})\text{-2,3-dihydroxybenzoate (4j)}$
$^1$H NMR of methyl 3-(3,4-dihydroxy-2-(methoxycarbonyl)phenyl)-$^{1}H$-indole-5-carboxylate (3k)

![NMR spectrum](image1)

$^{13}$C NMR of methyl 3-(3,4-dihydroxy-2-(methoxycarbonyl)phenyl)-$^{1}H$-indole-5-carboxylate (3k)

![NMR spectrum](image2)
\(^1\)H NMR of methyl 3-(3,4-dihydroxy-5-(methoxycarbonyl)phenyl)-1\(H\)-indole-5-carboxylate (4k)

\(^{13}\)C NMR of methyl 3-(3,4-dihydroxy-5-(methoxycarbonyl)phenyl)-1\(H\)-indole-5-carboxylate (4k)
$^1$H NMR of methyl 2,3-dihydroxy-6-(5-methoxy-$^1$H-indol-3-yl)benzoate (3l)

$^{13}$C NMR of methyl 2,3-dihydroxy-6-(5-methoxy-$^1$H-indol-3-yl)benzoate (3l)
1H NMR of methyl 2,3-dihydroxy-5-(5-methoxy-1H-indol-3-yl)benzoate (4I)

13C NMR of methyl 2,3-dihydroxy-5-(5-methoxy-1H-indol-3-yl)benzoate (4I)
$^{1}$H NMR of methyl 2,3-dihydroxy-6-(5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1H-indol-3-yl)benzoate (3m)

$^{13}$C NMR of methyl 2,3-dihydroxy-6-(5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1H-indol-3-yl)benzoate (3m)
$^1$H NMR of methyl 2,3-dihydroxy-5-(5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1H-indol-3-yl)benzoate (4m)

$^{13}$C NMR of methyl 2,3-dihydroxy-5-(5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1H-indol-3-yl)benzoate (4m)
$^1$H NMR of methyl 2,3-dihydroxy-6-(1-methyl-2-phenyl-$IH$-indol-3-yl)benzoate (3n)

$^{13}$C NMR of methyl 2,3-dihydroxy-6-(1-methyl-2-phenyl-$IH$-indol-3-yl)benzoate (3n)
$^1$H NMR of methyl 2,3-dihydroxy-5-(1-methyl-2-phenyl-$^1$H-indol-3-yl)benzoate ($4n$)

$^{13}$C NMR of methyl 2,3-dihydroxy-5-(1-methyl-2-phenyl-$^1$H-indol-3-yl)benzoate ($4n$)
$^1$H NMR of methyl 2,3-dihydroxy-6-(methyl-$^{1}H$-indol-3-yl)benzoate (3o)

$^{13}$C NMR of methyl 2,3-dihydroxy-6-(methyl-$^{1}H$-indol-3-yl)benzoate (3o)
$^1$H NMR of methyl 2,3-dihydroxy-5-(6-methyl-$^1$H-indol-3-yl)benzoate (4o)

$^{13}$C NMR of methyl 2,3-dihydroxy-5-(6-methyl-$^1$H-indol-3-yl)benzoate (4o)
$^1$H NMR of methyl 2,3-dihydroxy-6-(7-methyl-$^1$H-indol-3-yl)benzoate (3p)

$^{13}$C NMR of methyl 2,3-dihydroxy-6-(7-methyl-$^1$H-indol-3-yl)benzoate (3p)
$^1$H NMR of methyl 2,3-dihydroxy-5-(7-methyl-$^{1}H$-indol-3-yl)benzoate (4p)

$^{13}$C NMR of methyl 2,3-dihydroxy-5-(7-methyl-$^{1}H$-indol-3-yl)benzoate (4p)
H NMR of methyl 5-(bromo-1H-indol-3-yl)benzo[α][1,3]dioxole-4-carboxylate (7)

13C NMR of methyl 5-(bromo-1H-indol-3-yl)benzo[α][1,3]dioxole-4-carboxylate (7)
$^1$H NMR of methyl 5-(5-(3,5-dimethoxyphenyl)-1H-indol-3-yl)benzo[α][1,3]dioxole-4-carboxylate (8)

$^{13}$C NMR of methyl 5-(5-(3,5-dimethoxyphenyl)-1H-indol-3-yl)benzo[α][1,3]dioxole-4-carboxylate (8)
$^1$H NMR of 2,3-dihydroxy-6-($1H$-indol-3-yl)benzaldehyde (9)

$^{13}$C NMR of 2,3-dihydroxy-6-($1H$-indol-3-yl)benzaldehyde (9)
$^1$H NMR of 3-(hydroxymethyl)-4-(1$H$-indol-3-yl)benzene-1,2-diol (10)

$^{13}$C NMR of 3-(hydroxymethyl)-4-(1$H$-indol-3-yl)benzene-1,2-diol (10)