Supporting Information

Selective Monoarylation of Aromatic Ketones and Esters
via Cleavage of Aromatic Carbon–Heteroatom Bonds
by Trialkylphosphine Ruthenium Catalysts

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I. General Information

$^1$H and $^{13}$C{1H} spectra were recorded on a JEOL ECX-400, AL-400, or ALPHA-400 spectrometer. IR spectra were recorded on a JASCO FT/IR-410 infrared spectrometer. ESI-MS was performed on a JEOL JMS-T100LCS. GC analysis was performed using a Shimazu GC-2014 equipped with a CBP-10 capillary column (25 m x 0.22 mm, film thickness 0.25 μm). The temperature for GC analysis was programmed from 70 to 250 °C at 10 °C/min ramp with a final hold time of 30 min (injection temperature, 250 °C; detector temperature, 250 °C). Flash chromatography was carried out with aluminium oxide 90 active basic (Merck Millipore) or silica gel 60N (Kanto Chemical Co., Inc.). Melting points were determined on a Stanford Research Systems MPA 100 instrument.

II. Solvent and Materials

Unless otherwise noted, all reactions were carried out under nitrogen and all commercial reagents were used without further purification. RuH$_2$(CO)(PPh$_3$)$_3$ (5),$^1$ RuH(OAc)(CO)(PPh$_3$)$_2$,$^2$ RuH(OAc)(CO)(PCy$_3$)$_2$,$^3$ RuHCl(CO)(PCy$_3$)$_2$,$^4$ RuHCl(CO)(P$i$Pr$_3$)$_2$ (6),$^5$ aromatic ketone 8a,$^6$ 8b,$^7$ 8d,$^8$ 8e$^8$ and 2,4-dimethoxytoluene$^9$ were prepared by according to the literature procedure. 2',6'-Dimethoxyacetophenone (1) was recrystallized from hexane. Anhydrous toluene and CH$_2$Cl$_2$ were purchased from Kanto Chemical Co. Inc and passed through solvent purification columns (Glass Counter Solvent purification system). 98% HCO$_2$H, AgNO$_3$, DMF, and hexane solution of $^n$BuLi were purchased from Kanto Chemical Co. Inc and used as received. Anhydrous MeOH, MeCN, and benzoyl chloride were purchased from Wako Pure Chemical Industries, Ltd. and used as received. Styrene and 4-methoxy-4-methyl-2-pentanone were dried from CaH$_2$ and distilled under nitrogen. CsF, $i$PrOH, $t$BuOH, 2',4',6'-trimethoxybenzoic acid, and K$_2$S$_2$O$_8$ were purchased from Nacalai Tesque, Inc and used as received. Tert-butyl 2,2,2-trichloroacetimidate and 2,6-dimethoxybenzoyl chloride were purchased from Sigma-Aldrich Co. LLC. and used as received. Arylboronates were prepared from arylboronic acids and 2,2-dimethyl-1,3-propanediol in Et$_2$O.

III. Preparation of RuH(OAc)(CO)(P$i$Pr$_3$)$_2$

The synthesis of RuH(OAc)(CO)(P$i$Pr$_3$)$_2$ was performed using a similar procedure to the one reported by Werner and coworkers.$^5$

\[
\text{RuHCl(CO)(P$i$Pr$_3$)$_2$ (0.37 mmol)} + \text{MeOH (12.5 mL), rt, 3 h} \rightarrow \frac{0.64 \text{ mmol KOAc}}{\text{RuH(OAc)(CO)(P$i$Pr$_3$)$_2$}} \quad (58\%)
\]

To a solution of 179 mg of RuHCl(CO)(P$i$Pr$_3$)$_2$ (0.369 mmol) in 12.5 mL of MeOH was added 43.6 mg
of KOAc (0.644 mmol). The mixture was stirred for 3 h at room temperature. The solvent was evaporated in vacuo, the residue was extracted twice with 5 mL of benzene. The combined extracts were concentrated to ca. 0.25 mL in vacuo, and addition of MeOH gave a black precipitate. The precipitate was removed by filtration, and the filtrates were evaporated to dryness in vacuo to afford RuH(OAc)(CO)(P\textsubscript{3}Pr\textsubscript{3})\textsubscript{2} (110 mg, 58%) as a cream powder. The analytical data for this complex are in good agreement with those reported in literature.\textsuperscript{5}

IV. Preparation of Arylboronate 2o

\[
\begin{align*}
\text{HO-B} \quad \text{HO} \quad \text{HO} \\
\text{O} \quad \text{H} \quad \text{O} \\
\text{Bn} \quad \text{Bn} \quad \text{Bn}
\end{align*}
\]

A 200 mL round-bottom flask was charged with 1.4 g of arylboronic acid (4.2 mmol), 0.55 g of 2,2-dimethyl-1,3-propanediol (5.3 mmol) and 40 mL of Et\textsubscript{2}O. The mixture was stirred for 14 h at room temperature under air. After the reaction, 1.6 g of CaCl\textsubscript{2} (15 mmol) was introduced to the mixture, which was then stirred for 1 h, filtered through Celite, and concentrated. Purification of the crude material by silica gel column chromatography (hexane:AcOEt = 5:1) afforded 1.7 g (quant) of arylbornate 2o as a white solid: Mp 113-115 °C; \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \delta 1.01 (s, 6H), 3.74 (s, 4H), 5.17 (s, 2H), 5.18 (s, 2H), 6.94 (d, J = 8.4 Hz, 1H), 7.28-7.39 (m, 7H), 7.43-7.45 (m, 3H), 7.48 (d, J = 7.2 Hz, 2H);\textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): \delta 21.9, 31.9, 70.8, 71.1, 72.2, 113.9, 119.7, 127.2, 127.4, 127.6, 127.7, 128.0, 128.35, 128.40, 137.3, 137.5, 148.4, 151.2 (The signal corresponding to the carbon atom adjacent to the boron atom was not observed probably due to the significant broadening caused by the coupling with the boron nuclei); IR (KBr): 3065 w, 3026 m, 2961 m, 2927 m, 1598 s, 1515 s, 1478 s, 1454 m, 1422 s, 1376 m, 1318 s, 1272 s, 1145 s, 1126 s, 1021 s, 910 m, 879 m, 852 m, 830 m, 812 m, 789 m, 739 s, 697 s, 681 s, 652 m, 563 w, 490 w, 480 w cm\textsuperscript{-1}; Anal. calcd for C\textsubscript{25}H\textsubscript{27}BO\textsubscript{4}: C, 74.64; H, 6.77. Found: C, 74.67; H: 6.65.

V. General Procedure for Monoarylation of 2’,6’-Dimethoxyacetophenone (1)

\[
\begin{align*}
\text{MeO} \quad \text{OMe} \quad \text{B} \quad \text{Ar} \\
\text{O} \quad \text{H} \quad \text{O} \\
\text{MeO} \quad \text{Ar}
\end{align*}
\]
**General Procedure A:** In a glove box, 2',6'-dimethoxyacetophenone (1) (0.5 mmol), arylboronate 2 (0.6 mmol), RuHCl(CO)(PPr$_3$)$_2$ (6) (0.01 mmol), CsF (0.02 mmol), styrene (0.5 mmol), and 0.5 mL of toluene were placed in an oven-dried sealed tube containing a magnetic stirring bar. The mixture was heated at 80 °C for 15 min. After the reaction, volatile materials were removed by rotary evaporation. The crude material was passed through a basic aluminium oxide column to remove the remaining arylboronate. Further purification of the product was performed by silica gel column chromatography or gel permeation chromatography (GPC).

**General Procedure B:** In a glove box, 2',6'-dimethoxyacetophenone (1) (0.5 mmol), arylboronate 2 (0.6 mmol), RuHCl(CO)(PPr$_3$)$_2$ (6) (0.02 mmol), CsF (0.04 mmol), styrene (1.0 mmol), and 0.5 mL of toluene were placed in an oven-dried sealed tube containing a magnetic stirring bar. The mixture was heated at 80 °C for 1 h. After the reaction, volatile materials were removed by rotary evaporation. The crude material was passed through a basic aluminium oxide column to remove the remaining arylboronate. Further purification of the product was performed by silica gel column chromatography.

**General Procedure C:** In a glove box, 2',6'-dimethoxyacetophenone (1) (0.5 mmol), arylboronate 2 (0.6 mmol), RuHCl(CO)(PPr$_3$)$_2$ (6) (0.05 mmol), CsF (0.1 mmol), styrene (2.5 mmol), and 0.5 mL of toluene were placed in an oven-dried sealed tube containing a magnetic stirring bar. The mixture was heated at 60 °C for 24 h. After the reaction, volatile materials were removed by rotary evaporation. The crude material was passed through a basic aluminium oxide column to remove the remaining arylboronate. Further purification of the product was performed by silica gel column chromatography.

**Arylation product 3a**
Following the General Procedure A, 93.6 mg (83% yield) of arylation product 3a was obtained as a white solid after silica gel column chromatography (hexane:AcOEt = 20:1). Mp 62-64 °C; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 2.15 (s, 3H), 3.86 (s, 3H), 6.94 (d, $J$ = 8.4 Hz, 1H), 6.97 (d, $J$ = 8.4 Hz, 1H), 7.33-7.40 (m, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 32.4, 55.8, 109.8, 122.2, 127.6, 128.4, 128.8, 129.8, 131.1, 139.7, 139.9, 155.4, 204.9; IR (KBr): 3086 w, 3059 w, 3008 m, 2970 m, 2940 m, 2836 m, 1695 s, 1591 s, 1570 s, 1495 m, 1462 s, 1427 s, 1350 m, 1279 s, 1252 s, 1240 s, 1173 m, 1121 s, 1034 m, 1016 s, 802 s, 762s, 706 s, 595 m, 536 m cm$^{-1}$; HRMS (ESI-TOF) m/z: [M+Na]$^+$ Calcd for C$_{15}$H$_{14}$NaO$_2$ 249.08915; Found 249.08918.
**Arylation product 3b**

Following the General Procedure A except that the reaction was conducted for 2 h, 99.6 mg (74% yield) of arylation product 3b was obtained as a white solid after silica gel column chromatography (hexane:AcOEt = 5:1) and GPC. Mp 102-104 °C; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 2.14 (s, 3H), 2.98 (s, 6H), 3.84 (s, 3H), 6.74 (d, $J$ = 8.0 Hz, 2H), 6.87 (d, $J$ = 8.4 Hz, 1H), 6.96 (d, $J$ = 7.6 Hz, 1H), 7.23 (d, $J$ = 8.4 Hz, 2H), 7.34 (dd, $J$ = 8.0, 8.0 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 32.3, 40.4, 55.8, 108.9, 112.3, 122.1, 127.5, 129.6, 129.7, 130.8, 140.1, 149.8, 155.4, 205.5; IR (KBr): 3087 m, 3001 m, 2965 m, 2935 m, 2805 m, 1698 s, 1610 s, 1572 s, 1523 s, 1462 s, 1354 s, 1250 s, 1195 m, 1170 m, 1120 s, 1030 s, 948 s, 822 s, 797 s, 751 s, 586 m, 544 m cm$^{-1}$; HRMS (ESI-TOF) m/z: [M+Na]$^+$ Calcd for C$_{17}$H$_{19}$NNaO$_2$ 292.13135; Found 292.13138.

**Arylation product 3c**

Following the General Procedure A, 104 mg (81% yield) of arylation product 3c was obtained as a white solid after silica gel column chromatography (hexane:AcOEt = 5:1). Mp 123-124 °C; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 2.14 (s, 3H), 3.83 (s, 3H), 3.85 (s, 3H), 6.90-6.96 (m, 4H), 7.27 (d, $J$ = 8.8 Hz, 2H), 7.36 (dd, $J$ = 8.0, 7.6 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 32.4, 55.2, 55.8, 109.4, 113.9, 122.2, 129.8, 130.0, 131.1, 132.0, 139.6, 155.4, 159.2, 205.2; IR (KBr): 3086 w, 3011 w, 2999 w, 2972 w, 2839, 2958 m, 1689 s, 1608 m, 1567 s, 1515 s, 1464 s, 1437 m, 1292 m, 1257 s, 1183 m, 1124 s, 1021 s, 835 s, 799 s, 752 m, 545 m cm$^{-1}$; HRMS (ESI-TOF) m/z: [M+Na]$^+$ Calcd for C$_{16}$H$_{16}$NaO$_3$ 279.09971; Found 279.09968.

**Arylation product 3d**

Following the General Procedure A, 95.7 mg (80% yield) of arylation product 3d was obtained as a colorless oil after silica gel column chromatography (hexane:AcOEt = 20:1). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 2.16 (s, 3H), 2.37 (s, 3H), 3.84 (s, 3H), 6.91 (d, $J$ = 8.4 Hz, 1H), 6.95 (d, $J$ = 8.0 Hz, 1H), 7.17-7.24 (m, 4H), 7.35 (dd, $J$ = 8.4, 7.6 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 21.1, 32.4, 55.8, 109.6, 122.2, 128.7, 129.1, 129.8, 131.1, 136.8, 137.4, 139.9, 155.4, 205.0; IR (NaCl): 3021 w, 2961 w, 2940 w, 2838 w, 1703 s, 1579 m, 1516 m, 1465 s, 1435 m, 1349 m, 1255 s, 1125 s, 1031 m, 1017 m, 823 m, 792 s, 747 m, 584 w cm$^{-1}$; HRMS (ESI-TOF) m/z: [M+Na]$^+$ Calcd for C$_{16}$H$_{16}$NaO$_2$ 263.1048; Found 263.1043.
Arylation product 3e
Following the General Procedure A except that the reaction was conducted for 1 h, 114 mg (78% yield) of arylation product 3e was obtained as a white solid after silica gel column chromatography (hexane:AcOEt = 20:1). Mp 90-92 °C; 1H NMR (400 MHz, CDCl3): δ 2.24 (s, 3H), 3.87 (s, 3H), 6.94 (dd, J = 6.8, 0.9 Hz, 1H), 6.99 (d, J = 8.0 Hz, 1H), 7.40 (dd, J = 8.4, 8.0 Hz, 1H), 7.45 (d, J = 8.4 Hz, 2H), 7.63 (d, J = 7.6 Hz, 2H); 13C NMR (100 MHz, CDCl3): δ 32.5, 55.8, 110.5, 122.1, 124.1 (q, J = 271.8 Hz), 125.2 (q, J = 3.7 Hz), 129.2, 129.6 (q, J = 32.2 Hz), 130.1, 131.1, 138.5, 143.4, 155.8, 204.3; IR (KBr): 3092 w, 3014 w, 2977 w, 2946 w, 2846 w, 1697 s, 1617 m, 1569 m, 1468 m, 1437 m, 1326 s, 1255 s, 1166 s, 1121 s, 1069 s, 1013 s, 855 m, 797 w, 751 s, 612 w, 588 w cm⁻¹; HRMS (ESI-TOF) m/z: [M+Na]⁺ Calcd for C16H13F3NaO2 317.0765; Found 317.0771.

Arylation product 3f
Following the General Procedure A, 97.7 mg (80% yield) of arylation product 3f was obtained as a white solid after silica gel column chromatography (hexane:AcOEt = 20:1). Mp 93-95 °C; 1H NMR (400 MHz, CDCl3): δ 2.17 (s, 3H), 3.86 (s, 3H), 6.93 (d, J = 7.6 Hz, 1H), 6.94 (d, J = 8.4 Hz, 1H), 7.06-7.09 (m, 2H), 7.29-7.32 (m, 2H), 7.38 (dd, J = 8.0, 7.6 Hz, 1H); 13C NMR (100 MHz, CDCl3): δ 32.4, 55.7, 109.9, 115.3 (d, J = 21.4 Hz), 122.1, 129.8, 130.5 (d, J = 8.2 Hz), 131.1, 135.6 (d, J = 3.3 Hz), 138.7, 155.5, 162.3 (d, J = 246.9 Hz), 204.8; IR (KBr): 3095 w, 3020 w, 2971 w, 2941 w, 2843 w, 1696 s, 1598 s, 1575 s, 1511 s, 1465 s, 1438 s, 1353 m, 1306 s, 1254 s, 1159 s, 1124 s, 1026 s, 842 s, 671 s, 751 m, 593 m, 538 s cm⁻¹; HRMS (ESI-TOF) m/z: [M+Na]⁺ Calcd for C15H13FNaO2 267.0797; Found 267.0789.

Arylation product 3g
Following the General Procedure A, 95.2 mg (73% yield) of arylation product 3g was obtained as a white solid after silica gel column chromatography (hexane:AcOEt = 20:1). Mp 93-94 °C; 1H NMR (400 MHz, CDCl3): δ 2.20 (s, 3H), 3.86 (s, 3H), 6.92 (d, J = 8.0 Hz, 1H), 6.95 (d, J = 8.4 Hz, 1H), 7.25-7.28 (m, 2H), 7.34-7.39 (m, 3H); 13C NMR (100 MHz, CDCl3): δ 32.5, 55.8, 110.1, 122.1, 128.6, 130.0, 130.2, 131.0, 133.8, 138.1, 138.6, 155.6, 204.7; IR (KBr): 3089 w, 3013 w, 2966 w, 2939 w, 2841 w, 1695 s, 1591 s, 1579 s, 1562 m, 1496 m, 1463 s, 1437 s, 1351 m, 1304 m, 1273 s, 1240 s, 1179 m, 1126 m, 1090 s, 1026 s, 1010 s, 840 s, 795 s, 748 m, 593 m, 534 m cm⁻¹; HRMS (ESI-TOF) m/z: [M+Na]⁺ Calcd for C15H13ClNaO2 283.0502; Found 283.0493.
Arylation product 3h
Following the General Procedure B, 125 mg (81% yield) of arylation product 3h was obtained as a white solid after silica gel column chromatography (hexane:AcOEt = 20:1). Mp 93-94 °C; ¹H NMR (400 MHz, CDCl₃): δ 2.20 (s, 3H), 3.85 (s, 3H), 6.92 (d, J = 7.2 Hz, 1H), 6.95 (d, J = 8.0 Hz, 1H), 7.20 (d, J = 8.0 Hz, 2H), 7.37 (dd, J = 8.4, 8.0 Hz, 1H), 7.50 (d, J = 8.8 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 32.5, 55.9, 110.2, 122.05, 122.06, 130.0, 130.5, 131.1, 131.5, 138.6, 138.7, 155.7, 204.7; IR (KBr): 3086 m, 307 m, 2967 m, 2941 m, 2839 m, 1695 s, 1589 s, 1577 s, 1559 s, 1462 s, 1434 s, 1351 s, 1303 s, 1271 s, 1250 s, 1175 m, 1122 s, 1076 s, 1022 s, 1007 s, 970 m, 842 s, 827 s, 795 s, 749 s, 595 m, 537 s cm⁻¹; HRMS (ESI-TOF) m/z: [M+Na]⁺ Calcd for C₁₅H₁₃BrNaO₂ 326.9997; Found 327.0003.

Arylation product 3i
Following the General Procedure C, 138 mg (78% yield) of arylation product 3i was obtained as a white solid after silica gel column chromatography (hexane:AcOEt = 15:1). Mp 107-110 °C; ¹H NMR (400 MHz, CDCl₃): δ 2.20 (s, 3H), 3.86 (s, 3H), 6.92 (d, J = 7.8 Hz, 1H), 6.95 (d, J = 8.2 Hz, 1H), 7.07 (d, J = 7.8 Hz, 2H), 7.38 (dd, J = 7.8, 7.4 Hz, 1H), 7.71 (d, J = 8.2 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 32.5, 55.8, 93.7, 110.1, 121.9, 130.0, 130.7, 130.9, 137.4, 138.7, 139.2, 155.6, 204.5; IR (KBr): 3065 m, 3008 m, 2966 m, 2939 m, 2838 m, 1698 s, 1575 s, 1551 s, 1495 s, 1462 s, 1432 s, 1348 s, 1312 s, 1303 s, 1267 s, 1234 s, 1176 s, 1122 s, 1064 s, 1023s, 1006 s, 975 s, 846 s, 828 s, 794 s, 750 s, 634 m, 592 s, 535 s, 522 s, 414 m cm⁻¹; HRMS (ESI-TOF) m/z: [M+Na]⁺ Calcd for C₁₅H₁₃InaO₂ 374.9858; Found 374.9866.

Arylation product 3j
Following the General Procedure B except that the reaction was conducted for 3 h, 96.5 mg (76% yield) of arylation product 3j was obtained as a colorless oil after silica gel column chromatography (hexane:AcOEt = 15:1). ¹H NMR (400 MHz, CDCl₃): δ 2.17 (s, 3H), 3.84 (s, 3H), 5.27 (d, J = 11.2 Hz, 1H), 5.77 (d, J = 17.6 Hz, 1H), 6.72 (dd, J = 17.6, 11.2 Hz, 1H), 6.92 (d, J = 8.4 Hz, 1H), 6.96 (d, J = 7.6 Hz, 1H), 7.30 (d, J = 8.4 Hz, 2H), 7.36 (dd, J = 8.0, 8.0 Hz, 1H), 7.42 (d, J = 8.4 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 32.4, 55.8, 109.8, 114.2, 122.0, 126.2, 129.0, 129.8, 131.0, 136.2, 136.8, 139.1, 139.5, 155.5, 204.8; IR (NaCl): 3009 m, 2939 m, 2839 w, 1696 s, 1577 s, 1465 s, 1435 m, 1350 m, 1309 m, 1256 s, 1126 m, 1033 m, 1014 m, 844 m, 794 m, 748 m, 667 w, 583 w cm⁻¹; HRMS (ESI-TOF) m/z: [M+Na]⁺ Calcd for C₁₇H₁₆NaO₂ 275.1048; Found 275.1063.
Arylation product 3k

Following the General Procedure A, 102 mg (80% yield) of arylation product 3k was obtained as a colorless oil after silica gel column chromatography (toluene:hexane:AcOEt = 10:10:1). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 2.17 (s, 3H), 3.81 (s, 3H), 3.85 (s, 3H), 6.88-6.95 (m, 4H), 6.98 (d, $J = 7.6$ Hz, 1H), 7.29 (d, $J = 8.0$ Hz, 1H), 7.37 (dd, $J = 8.4$, 7.6 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 32.4, 55.2, 55.8, 109.9, 113.4, 114.3, 121.3, 122.0, 129.4, 129.8, 131.0, 139.8, 141.0, 155.4, 159.4, 204.8; IR (NaCl): 3068 w, 3002 w, 2940 w, 2837 w, 1700 s, 1593 s, 1572 s, 1493m, 1572 s, 1436 m, 1419 m, 1351 m, 1259 s, 1181 m, 1124 m, 1047 m, 1028 s, 784 m, 748 m, 703 m cm$^{-1}$; HRMS (ESI-TOF) m/z: [M+Na]$^+$ Calcd for C$_{16}$H$_{16}$NaO$_3$ 279.0997; Found 279.1000.

Arylation product 3l

Following the General Procedure A, 95.7 mg (80% yield) of arylation product 3l was obtained as a colorless oil after silica gel column chromatography (hexane:AcOEt = 20:1). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 2.16 (s, 3H), 2.36 (s, 3H), 3.84 (s, 3H), 6.92 (d, $J = 8.4$ Hz, 1H), 6.95 (d, $J = 6.8$ Hz, 1H), 7.11-7.15 (m, 3H), 7.23-7.27 (m, 1H), 7.35 (dd, $J = 8.0$, 7.6 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 21.3, 32.4, 55.8, 109.7, 122.2, 125.9, 128.2, 128.3, 129.5, 129.7, 131.0, 138.0, 139.6, 140.1, 155.4, 204.8; IR (NaCl): 3007 m, 2939 m, 2838 m, 1702 s, 1574 s, 1466 m, 1435 m, 1350 m, 1311 m, 1258 s, 1241 s, 1123 s, 1040 s, 1007 m, 782 s, 747 m, 707 m, 670 m cm$^{-1}$; HRMS (ESI-TOF) m/z: [M+Na]$^+$ Calcd for C$_{16}$H$_{16}$NaO$_2$ 263.1048; Found 263.1042.

Arylation product 3m

Following the General Procedure B, 111 mg (73% yield) of arylation product 3m was obtained as a colorless oil after silica gel column chromatography (hexane:AcOEt = 20:1). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 2.23 (s, 3H), 3.86 (s, 3H), 6.92 (d, $J = 8.0$ Hz, 1H), 6.95 (d, $J = 8.4$ Hz, 1H), 7.22-7.26 (m, 2H), 7.38 (dd, $J = 8.4$, 7.6 Hz, 1H), 7.46-7.50 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 32.5, 55.8, 110.3, 122.1, 122.4, 127.6, 129.8, 130.0, 130.6, 131.1, 131.7, 138.3, 141.8, 155.6, 204.4; IR (NaCl): 3065 w, 3005 m, 2963 m, 2939 m, 2838 m, 1699 s, 1591 s, 1577 s, 1558 s, 1463 s, 1436 s, 1403m, 1351 s, 1309 m, 1262 s, 1177 m, 1127 s, 1074 m, 1030 s, 964 w, 868 m, 783 s, 767 m, 745 m, 698 s, 599 m cm$^{-1}$; HRMS (ESI-TOF) m/z: [M+Na]$^+$ Calcd for C$_{15}$H$_{15}$BrNaO$_2$ 326.9997; Found 327.0004.
**Arylation product 3n**

Following the General Procedure A except that the reaction was conducted for 1 h, 112 mg (81% yield) of arylation product 3n was obtained as a white solid after silica gel column chromatography (hexane:AcOEt = 20:1). Mp 107-110 °C; 1H NMR (400 MHz, CDCl3): δ 2.14 (s, 3H), 3.85 (s, 3H), 6.94 (d, J = 8.6 Hz, 1H), 7.05 (d, J = 7.4 Hz, 1H), 7.39 (dd, J = 8.6, 7.4 Hz, 1H), 7.45-7.50 (m, 3H), 7.80-7.85 (m , 4H); 13C NMR (100 MHz, CDCl3): δ 32.5, 55.8, 109.9, 122.5, 126.2, 126.3, 126.9, 127.6, 127.9, 128.0, 128.2, 129.9, 131.3, 132.5, 133.1, 137.1, 139.8, 155.5, 204.8; IR (KBr): 3052 w, 2956 w, 2836 w, 1692 s, 1578 m, 1460 m, 1354 m, 1302 m, 1270 s, 1255 s, 1239 s, 1112 s, 1029 s, 866 m, 831 s, 795 s, 756 m, 746 m, 592 m, 537 w, 477 m cm⁻¹; HRMS (ESI-TOF) m/z: [M+Na]+ Calcd for C19H16NaO2 299.1048; Found 299.1050.

**Arylation product 3o**

Following the General Procedure B, 166 mg (76% yield) of arylation product 3o was obtained as a yellow oil after silica gel column chromatography (hexane:AcOEt = 30:1). 1H NMR (400 MHz, CDCl3): δ 2.06 (s, 3H), 3.83 (s, 3H), 5.16 (s, 2H), 5.17 (s, 2H), 6.84 (dd, J = 8.4, 2.0 Hz, 1H), 6.88 (d, J = 8.4 Hz, 2H), 6.93 (d, J = 7.6 Hz, 2H), 7.24-7.45 (m, 11H); 13C NMR (100 MHz, CDCl3): δ 32.3, 55.8, 71.1, 71.2, 109.6, 114.7, 115.7, 122.02, 122.05, 127.25, 127.33, 127.7, 127.8, 128.4, 128.5, 129.7, 131.0, 133.0, 137.0, 137.1, 139.5, 148.5, 148.6, 155.4, 205.1; IR (NaCl): 3063 w, 3032 w, 2938 w, 1696 s, 1569 m, 1512 s, 1465 s, 1435 m, 1411 m, 1382 m, 1350 m, 1258 s, 1207 m, 1140 m, 1120 s, 1009 m, 794 m, 737 m, 697 m, 597 w cm⁻¹; HRMS (ESI-TOF) m/z: [M+Na]+ Calcd for C29H26NaO4 461.1729; Found 461.1730.

**Arylation product 3p**

Following the General Procedure B, 90.4 mg (70% yield) of arylation product 3p was obtained as a yellow oil after silica gel column chromatography (hexane:AcOEt = 10:1). 1H NMR (400 MHz, CDCl3): δ 2.33 (s, 3H), 3.74 (s, 3H), 3.86 (s, 3H), 6.88-6.94 (m, 3H), 6.99 (dd, J = 7.8, 7.6 Hz, 1H), 7.20 (d, J = 6.4 Hz, 1H), 7.31 (dd, J = 7.6, 7.2 Hz, 1H), 7.37 (dd, J = 8.4, 7.6 Hz, 1H); 13C NMR (100 MHz, CDCl3): δ 31.3, 55.0, 55.7, 110.0, 110.4, 120.7, 123.3, 128.9, 129.1, 130.0, 131.1, 131.4, 137.2, 155.5, 155.8, 203.3; IR (KBr): 3050 w, 2972 w, 2945 w, 2843 w, 1690 s, 1589 m, 1571 m, 1496 m, 1469 m, 1430 m, 1351 m, 1308 m, 1279 s, 1261 s, 1246 m, 1187 w, 1132 m, 1106 m, 1094 m, 1051 m, 1016 s, 858 w, 793 m, 760 s, 746 s, 665 w, 596 w cm⁻¹; HRMS (ESI-TOF) m/z: [M+Na]+ Calcd for C16H16NaO3 279.0997; Found 279.0996.
Arylation product 3q

Following the General Procedure B, 97.4 mg (90% yield) of arylation product 3q was obtained as a colorless oil after silica gel column chromatography (hexane:AcOEt = 20:1). 1H NMR (400 MHz, CDCl₃): δ 2.48 (s, 3H), 3.83 (s, 3H), 6.43 (dd, J = 3.3, 1.8 Hz, 1H), 6.56 (d, J = 3.1 Hz, 1H), 6.85 (d, J = 8.2 Hz, 1H), 7.24 (dd, J = 7.8, 0.8 Hz, 1H), 7.33 (dd, J = 8.2, 7.8 Hz, 1H), 7.44 (d, J = 1.6 Hz, 1H); 13C NMR (100 MHz, CDCl₃): δ 31.9, 55.8, 108.2, 109.9, 111.6, 118.6, 127.7, 128.6, 129.8, 142.7, 151.5, 155.7, 205.2; IR (NaCl): 3391 w, 3146 m, 3119 m, 3003 s, 2967 s, 2942 s, 2840 m, 1770 m, 1699 s, 1568 s, 1458 s, 1435 s, 1351 s, 1260 s, 1124 s, 1037 s, 918 m, 886 m, 826 s, 792 s, 744 s, 595 s, 420 m cm⁻¹; HRMS (ESI-TOF) m/z: [M+Na]⁺ Calcd for C₁₃H₁₂NaO₃ 239.0684; Found 239.0679.

Arylation product 3r

Following the General Procedure B, 94.3 mg (81% yield) of arylation product 3r was obtained as a colorless oil after silica gel column chromatography (hexane:AcOEt = 20:1). 1H NMR (400 MHz, CDCl₃): δ 2.27 (s, 3H), 3.83 (s, 3H), 6.91 (d, J = 8.0 Hz, 1H), 7.01-7.03 (m, 2H), 7.08 (dd, J = 8.0, 1.2 Hz, 1H), 7.31-7.35 (m, 2H); 13C NMR (100 MHz, CDCl₃): δ 32.1, 55.8, 110.2, 122.3, 126.2, 127.3, 127.7, 129.3, 130.8, 131.7, 140.5, 155.5, 205.0; IR (NaCl): 3386 w, 3105 m, 3073 m, 3003 s, 2964 m, 2940 m, 2838 m, 2083 w, 1925 w, 1699 s, 1575 s, 1467 s, 1435 s, 1351 s, 1296 s, 1267 s, 1115 s, 1051 s, 1010 s, 989 m, 963 m, 856 s, 814 s, 791 s, 744 s, 705 s, 596 m, 582 m, 533 m, 500 m, 402 m cm⁻¹; HRMS (ESI-TOF) m/z: [M+Na]⁺ Calcd for C₁₃H₁₂NaO₂S 255.0456; Found 255.0466.

Arylation product 3s

Following the General Procedure B, 93.3 mg (86% yield) of arylation product 3s was obtained as a colorless oil after silica gel column chromatography (hexane:AcOEt = 15:1). 1H NMR (400 MHz, CDCl₃): δ 2.33 (s, 3H), 3.84 (s, 3H), 6.51 (d, J = 8.4 Hz, 1H), 7.00 (d, J = 8.0 Hz, 1H), 7.33 (dd, J = 8.0, 8.0 Hz, 1H), 7.43 (s, 1H), 7.48 (s, 1H); 13C NMR (100 MHz, CDCl₃): δ 32.1, 55.7, 109.6, 110.9, 121.3, 123.6, 129.80, 129.84, 130.5, 140.4, 143.1, 155.5, 205.8; IR (NaCl): 3386 w, 3148 w, 3003 m, 2942 m, 2840 m, 1771 m, 1698 s, 1574 s, 1507 s, 1464 s, 1435 s, 1352 s, 1316 s, 1261 s, 1164 s, 1046 s, 1006 s, 948 s, 875 s, 822 s, 786 s, 744 s, 600 s, 533 m cm⁻¹; HRMS (ESI-TOF) m/z: [M+Na]⁺ Calcd for C₁₃H₁₂NaO₃ 239.0684; Found 239.0690.
**Arylation product 3t**

Following the General Procedure B except that the reaction was conducted for 2 h, 74.0 mg (64% yield) of arylation product 3t was obtained as a colorless oil after silica gel column chromatography (hexane:AcOEt = 15:1). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 2.20 (s, 3H), 3.84 (s, 3H), 6.90 (d, $J = 8.0$ Hz, 1H), 7.02 (d, $J = 8.0$ Hz, 1H), 7.13 (dd, $J = 4.8$, 1.6 Hz, 1H), 7.25 (dd, $J = 2.8$, 0.8 Hz, 1H), 7.33-7.37 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 32.2, 55.8, 109.8, 121.7, 123.6, 125.8, 128.3, 129.8, 130.8, 134.0, 139.7, 155.4, 205.4; IR (NaCl): 3385 w, 3105 m, 3003 m, 2963 m, 2940 m, 2838 m, 1699 s, 1594 s, 1577 s, 1468 s, 1435 s, 1350 s, 1295 s, 1260 s, 1120 s, 1098 s, 1035 s, 1006 m, 964 m, 921 m, 869 m, 841 s, 782 s, 745 s, 663 s, 601 m, 533 m cm$^{-1}$; HRMS (ESI-TOF) m/z: [M+Na]$^+$ Calcd for C$_{13}$H$_{12}$NaO$_2$S 255.0456; Found 255.0450.

**VI. Competition Experiment of 1 with Arylboronate 2c and 2e**

In a glove box, 2',6'-dimethoxyacetophenone (1) (0.5 mmol), arylboronate 2c (1 mmol), 2e (1 mmol), RuHCl(CO)(P$_3$Pr$_3$)$_2$ (6) (0.01 mmol), CsF (0.02 mmol), styrene (0.5 mmol), and 0.5 mL of toluene were placed in an oven-dried sealed tube containing a magnetic stirring bar. The mixture was heated at 80 °C for 10 min. After the reaction, volatile materials were removed by rotary evaporation, and $\alpha$-xylylene oxide was added to the crude materials as an internal standard. $^1$H NMR analysis of the resulting mixture revealed that 3c and 3e were obtained in 15% and 32% yields, respectively.
VII. Sequential Ortho C–O Arylation of Acetophenone Derivative 3a

In a glove box, 2′-methoxy-6′-phenylacetophenone (3a) (0.3 mmol), arylboronate 2 (0.45 mmol), RuH2(CO)(PPh3)3 (5) (0.024 mmol) and 0.3 mL of toluene were placed in an oven-dried sealed tube containing a magnetic stirring bar. The mixture was heated at 120 °C for 4 h. After the reaction, the crude material was passed through a basic aluminium oxide column to remove the remaining arylboronate. Further purification of the product was performed by silica gel column chromatography.

Arylation product 7c

Silica gel column chromatography (hexane:AcOEt = 15:1) afforded 89.6 mg (99% yield) of arylation product 7c as a white solid: Mp 90-92 °C; 1H NMR (400 MHz, CDCl3): δ 1.88 (s, 3H), 3.84 (s, 3H), 6.93 (d, J = 8.8 Hz, 2H), 7.29 (d, J = 8.4 Hz, 2H), 7.31-7.39 (m, 7H), 7.46 (dd, J = 8.0, 7.2, 1H); 13C NMR (100 MHz, CDCl3): δ 32.9, 55.2, 113.8, 127.5, 128.3, 128.6, 128.9, 129.1, 129.2, 130.2, 132.6, 138.5, 138.9, 140.4, 141.3, 159.1, 206.5; IR (KBr): 3007 w, 2961 w, 2932 w, 2836 w, 1690 s, 1609 s, 1690 m, 1513 s, 1454 s, 1349 m, 1248 s, 1177 s, 1108 m, 1029 s, 842 s, 809 s, 765 s, 706 s, 600 m, 581 m, 520 m cm−1; HRMS (ESI-TOF) m/z: [M+Na]+ Calcd for C21H18NaO2 325.1205; Found 325.1202.

Arylation product 7e

Silica gel column chromatography (hexane:AcOEt = 20:1) afforded 99.8 mg (97% yield) of arylation product 7e as a white solid: Mp 148-151 °C; 1H NMR (400 MHz, CDCl3): δ 1.86 (s, 3H), 7.32-7.53 (m, 10H), 7.66 (d, J = 8.4 Hz, 2H); 13C NMR (100 MHz, CDCl3): δ 32.9, 124.1 (q, J = 271 Hz), 125.3 (q, J = 3.7 Hz), 127.8, 128.5, 128.9, 129.0, 129.1, 129.5, 129.7 (q, J = 32.5 Hz), 129.8, 137.6, 139.2, 139.9, 141.2, 144.0, 205.8; IR (KBr): 3057 w, 1697 s, 1618 s, 1494 w, 1448 m, 1428 m, 1403 m, 1354 s, 1324 s, 1246 s, 1158 s, 1129 s, 1108 s, 1068 s, 1019 s, 851 s, 810 s, 768 s, 709 s, 681 m, 596 m, 510 m cm−1; HRMS (ESI-TOF) m/z: [M+Na]+ Calcd for C21H15F3NaO 363.0973; Found 363.0963.
VIII. Preparation of Acetophenone Derivative 8c

A 100 mL round-bottom flask was charged with 1.53 g of 2',6'-dihydroxyacetophenone (10 mmol), 3.33 g of K₂CO₃ (24 mmol), 1.8 mL of bromoethane (24 mmol), and 10 mL of DMF. The mixture was stirred under air at 60 °C for 16 h. After the reaction, the mixture was extracted three times with Et₂O. Combined organic portions were washed with H₂O and brine, quickly dried over Na₂SO₄, filtered and concentrated. Purification of the crude material by silica gel column chromatography (hexane:AcOEt = 10:1) afforded acetophenone derivative 8c in 1.79 g (85% yield) as a white solid: Mp 82-84 °C; ¹H NMR (400 MHz, CDCl₃): δ 1.36 (t, J = 6.8 Hz, 6H), 2.49 (s, 3H), 4.03 (q, J = 6.8 Hz, 4H), 6.52 (d, J = 8.8 Hz, 2H), 7.21 (t, J = 8.4 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 14.7, 32.2, 64.2, 104.8, 121.2, 130.3, 156.0, 202.8; IR (KBr): 2985 m, 2935 m, 2892 m, 1710 s, 1593 s, 1458 s, 1394 s, 1350 m, 1288 s, 1253 s, 1117 s, 1092 s, 1055 m, 873 s, 781 s, 637 s, 596 m, 471 m cm⁻¹; HRMS (ESI-TOF) m/z: [M+Na]⁺ Calcd for C₁₂H₁₆NaO₃ 231.0997; Found 231.0994.

IX. Procedures for Monoarylation of Various Aromatic Ketones 8

Monoarylation of 8a

In a glove box, 2',4',6'-trimethoxyacetophenone (8a) (0.5 mmol), phenylboronate 2a (0.6 mmol), RuHCl(CO)(PᵢPr₃)₂ (6) (0.01 mmol), CsF (0.02 mmol), styrene (0.5 mmol), and 0.5 mL of toluene were placed in an oven-dried sealed tube containing a magnetic stirring bar. The mixture was heated at 80 °C for 15 min. After the reaction, volatile materials were removed by rotary evaporation. The crude material was passed through a basic aluminium oxide column to remove the remaining arylboronate. Further purification by silica gel column chromatography (hexane:AcOEt = 5:1) afforded 95.8 mg (74% yield) of arylation product 9a as a colorless oil: ¹H NMR (400 MHz, CDCl₃): δ 2.13 (s, 3H), 6.47 (d, J = 2.4 Hz, 1H), 6.49 (d, J = 2.4 Hz, 1H), 7.32-7.38 (m, 5H); ¹³C NMR (100...
MHz, CDCl3): δ 32.7, 55.5, 55.8, 97.6, 106.3, 124.4, 127.7, 128.4, 128.7, 140.2, 141.7, 157.3, 160.8, 204.3; IR (NaCl): 3058 m, 3003 s, 2939 s, 2840 s, 1697 s, 1597 s, 1455 s, 1413 s, 1349 s, 1234 s, 1205 s, 1146 s, 1080 s, 1040 s, 1023 s, 966 m, 936 m, 836 s, 774 s, 703 s, 638 m, 565 s cm⁻¹; HRMS (ESI-TOF) m/z: [M+Na]⁺ Calcd for C₁₆H₁₆NaO₃ 279.0997; Found 279.1007.

**Monoarylation of 8b**

![Diagram](image)

In a glove box, benzophenone derivative 8b (0.5 mmol), phenylboronate 2a (0.6 mmol), RuHCl(CO)(P*i*Pr)₂ (6) (0.01 mmol), CsF (0.02 mmol), styrene (0.5 mmol), and 0.5 mL of toluene were placed in an oven-dried sealed tube containing a magnetic stirring bar. The mixture was heated at 120 °C for 30 min. After the reaction, volatile materials were removed by rotary evaporation. The crude material was passed through a basic aluminium oxide column to remove the remaining arylboronate. Further purification by silica gel column chromatography (hexane:AcOEt = 10:1) afforded 109 mg (69% yield) of arylation product 9c as a white solid: Mp 96-98 °C; 'H NMR (400 MHz, CDCl₃): δ 3.72 (s, 3H), 3.88 (s, 3H), 6.55 (s, 2H), 7.15-7.19 (m, 3H), 7.24-7.30 (m, 4H), 7.41 (t, J = 7.4 Hz, 1H), 7.67 (dd, J = 8.4, 1.6 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 55.5, 55.8, 97.5, 106.3, 121.4, 127.4, 128.0, 128.1, 128.8, 129.3, 132.7, 138.3, 139.9, 142.7, 158.3, 161.1, 197.0; IR (KBr): 3083 w, 3056 w, 3009 w, 2963 m, 2932 m, 2838 m, 2836 s, 1596 s, 1456 s, 1411 s, 1351 s, 1291 s, 1255 s, 1239 s, 1207 s, 1169 s, 1131 s, 1054 m, 1024 s, 943 s, 836 s, 774 s, 760 s, 722 s, 702 s, 599 s cm⁻¹; HRMS (ESI-TOF) m/z: [M+Na]⁺ Calcd for C₂₁H₁₈NaO₃ 341.1154; Found 341.1145.
Monoarylation of 8c

In a glove box, 2',6'-diethoxyacetophenone (8c) (0.5 mmol), phenylboronate 2a (0.6 mmol), RuHCl(CO)(PPr3)2 (6) (0.02 mmol), CsF (0.04 mmol), styrene (1.0 mmol), and 0.5 mL of toluene were placed in an oven-dried sealed tube containing a magnetic stirring bar. The mixture was heated at 80 °C for 1 h. After the reaction, volatile materials were removed by rotary evaporation. The crude material was passed through a basic aluminium oxide column to remove the remaining arylboronate. Further purification by silica gel column chromatography (hexane:AcOEt = 20:1) afforded 95.4 mg (80% yield) of arylation product 9c as a white solid: Mp 67-68 °C; 1H NMR (400 MHz, CDCl3): δ 1.40 (t, J = 7.1 Hz, 3H), 2.21 (s, 3H), 4.09 (q, J = 7.1 Hz, 2H), 6.91 (d, J = 8.2 Hz, 1H), 6.94 (d, J = 7.4 Hz, 1H), 7.33-7.36 (m, 6H); 13C NMR (100 MHz, CDCl3): δ 14.7, 32.5, 64.2, 110.8, 122.2, 127.5, 128.3, 128.8, 129.8, 131.5, 139.9, 140.0, 155.0, 204.8; IR (KBr): 3091 w, 2979 m, 2932 w, 2882 w, 1701 s, 1571 s, 1497 m, 1455 s, 1392 m, 1351 m, 1245 s, 1181 w, 1126 s, 1047 s, 1025 m, 941 m, 803 m, 768 s, 706 s, 593 m, 535 m cm⁻¹; HRMS (ESI-TOF) m/z: [M+Na]+ Calcd for C16H16NaO2 263.10480; Found 263.10478.

Monoarylation of 8d

In a glove box, acetophenone derivative (8d) (0.5 mmol), phenylboronate 2a (0.6 mmol), RuHCl(CO)(PPr3)2 (6) (0.05 mmol), CsF (0.1 mmol), styrene (1 mmol), and 0.5 mL of toluene were placed in an oven-dried sealed tube containing a magnetic stirring bar. The mixture was heated at 120 °C for 1 h. After the reaction, volatile materials were removed by rotary evaporation. The crude material was passed through a basic aluminium oxide column to remove the remaining arylboronate. Further purification by silica gel column chromatography (hexane:AcOEt = 20:1) afforded 112 mg of C–OMe bond cleavage product 9d (77% yield) as a colorless oil and 10.0 mg of C–OPh bond cleavage product...
3a (9% yield) as a white solid, respectively.

**Arylation product 9d**

\[
\text{δ} \ 2.21 \text{ (s, 3H)}, 6.90 \text{ (d, } J = 8.2 \text{ Hz, 1H)}, 7.05 \text{ (d, } J = 8.2 \text{ Hz, 2H)}, 7.11-7.15 \text{ (m, 2H)}, 7.33-7.41 \text{ (m, 8H)}; \ \text{13C NMR (100 MHz, CDCl}_3\text{): } \delta 32.4, 117.5, 119.0, 123.7, 124.9, 127.8, 128.5, 128.9, 129.8, 129.9, 133.7, 139.4, 140.7, 153.3, 156.9, 203.7; \ \text{IR (NaCl): } 3387 \text{ m, 1703 s, 1594 s, 1566 s, 1490 s, 1455 s, 1431 s, 1351 s, 1300 s, 1237 s, 1210 s, 1162 s, 1105 m, 1089 m, 1073 m, 1051 m, 1023 m, 1000 w, 964 m, 908 s, 823 m, 793 m, 761 s, 702 s, 600 m cm}^-1; \ \text{HRMS (ESI-TOF) m/z: } [\text{M+Na}]^+ \ \text{Calcd for C}_{20}\text{H}_{16}\text{NaO}_2 \text{ 311.1048; Found 311.1044.}
\]

**Monoarylation of 8e**

In a glove box, acetophenone derivative (8e) (0.5 mmol), phenylboronate 2a (0.5 mmol), RuHCl(CO)(P\text{Pr}_3)_2 (6) (0.02 mmol), CsF (0.04 mmol), styrene (1 mmol), and 0.5 mL of toluene were placed in an oven-dried sealed tube containing a magnetic stirring bar. The mixture was heated at 80 °C for 1 h. After the reaction, volatile materials were removed by rotary evaporation. The crude material was passed through a basic aluminium oxide column to remove the remaining arylboronate. Further purification of the product was performed by silica gel column chromatography (hexane:AcOEt = 15:1) afforded 101 mg of C–NMe\text{2} bond cleavage product 3a (89% yield).
X. Procedures for Preparation of Aromatic Esters 10

Preparation of Aromatic Ester 10a

The esterification was performed using a similar procedure to the one for the synthesis of aromatic esters reported by Tamaddon and coworkers.10

A 50 mL round-bottom flask was charged with 2.2 g of 2′,6′-dihydroxybenzoic acid (11 mmol), 81 mg of ZnO (1 mmol), and 4 mL of iPrOH. This solution was stirred under air at 40 °C for 6 h. After the reaction, the mixture was extracted three times with AcOEt. Combined organic portions were washed with Sat. NaHCO3 aq, H2O, and brine, quickly dried over Na2SO4, filtered and concentrated. Purification of the crude material by reprecipitation with acetone/hexane afforded aromatic ester 10a in 2.0 g (83% yield) as a white solid: Mp 66-68 °C; 1H NMR (400 MHz, CDCl3): δ 1.35 (d, J = 6.4 Hz, 6H), 3.81 (s, 6H), 5.31 (sept, J = 6.4 Hz, 1H), 6.55 (d, J = 8.0 Hz, 2H), 7.26 (d, J = 8.4 Hz, 1H); 13C NMR (100 MHz, CDCl3): δ 21.8, 56.0, 68.6, 104.0, 113.7, 130.7, 157.2, 166.1; IR (KBr): 3016 m, 2984 m, 2842 w, 1723 s, 1597 s, 1476 s, 1435 s, 1374 m, 1293 s, 1255 s, 1177 m, 1111 s, 1073 s, 1027 m, 914 m, 855 m, 786 m, 762 m, 740 m, 630 m, 505 w, 425 w cm⁻¹; HRMS (ESI-TOF) m/z: [M+Na]+ Calcd for C12H16NaO4 247.0946; Found 247.0940.

Preparation of Aromatic Ester 10b

A 30 mL two-necked flask was charged with 2.2 g of 2′,6′-dihydroxybenzoic acid (11 mmol) and 81 mg of ZnO (1 mmol). The flask was evacuated and back-filled under N2 flow for 3 times. Then, 1 mL of pyridine, 10 mL of toluene and 4 mL of tBuOH were added to the flask. The resulting solution was stirred at 100 °C for 14 h. After the reaction, the mixture was extracted three times with AcOEt. Combined organic portions were washed with Sat. NaHCO3 aq, H2O, and brine, quickly dried over Na2SO4, filtered and concentrated. Purification of the crude material by silica gel column chromatography (hexane:AcOEt =
10:1) afforded aromatic ester 10b in 1.39 g (53% yield) as a white solid: Mp 89-92 °C; 1H NMR (400 MHz, CDCl₃): δ 1.58 (s, 9H), 3.81 (s, 6H), 6.53 (d, J = 8.2 Hz, 2H), 7.23 (t, J = 8.2 Hz, 1H); 13C NMR (100 MHz, CDCl₃): δ 28.2, 56.0, 81.7, 104.0, 115.0, 130.3, 157.0, 165.8; IR (KBr): 3103 w, 3010 m, 2973 m, 2949 m, 2840 m, 1725 s, 1597 s, 1475 s, 1434 m, 1369 m, 1295 s, 1255 s, 1171 m, 1112 s, 1076 s, 1028 m, 849 m, 796 m, 768 m, 740 w, 712 w, 629 m, 503 w, 459 w cm⁻¹; HRMS (ESI-TOF) m/z: [M+Na]⁺ Calcd for C₁₃H₁₈NaO₄ 261.1103; Found 261.1100.

XI. Procedures for Arylation of Aromatic Esters 10

Arylation of Aromatic Ester 10a

In a glove box, aromatic ester 10a (0.5 mmol), arylboronate 2a (0.6 mmol), RuHCl(CO)(PPr₃)₂ (6) (0.02 mmol), CsF (0.04 mmol), styrene (1.0 mmol), and 0.5 mL of toluene were placed in an oven-dried sealed tube containing a magnetic stirring bar. The mixture was stirred at 100 °C for 12 h. After the reaction, volatile materials were removed by rotary evaporation. The crude material was passed through a basic aluminum oxide column to remove the remaining arylboronate. Further purification by silica gel column chromatography (hexane:AcOEt = 15:1) afforded 72.6 mg (54% yield) of arylation product 11a as a colorless oil: 1H NMR (400 MHz, CDCl₃): δ 1.01 (d, J = 6.4 Hz, 6H), 3.87 (s, 3H), 5.03 (sept, J = 6.4 Hz, 1H), 6.93 (d, J = 8.0 Hz, 1H), 6.96 (dd, J = 8.0, 1.0 Hz, 1H), 7.32-7.40 (m, 6H); 13C NMR (100 MHz, CDCl₃): δ 21.3, 56.0, 68.5, 109.9, 121.9, 123.7, 127.4, 128.1, 128.5, 130.2, 140.1, 141.1, 156.3, 167.3; IR (NaCl): 3061 s, 2979 s, 2938 m, 2839 m, 1726 s, 1572 s, 1499 m, 1468 s, 1433 s, 1374 s, 1311 s, 1260 s, 1180 m, 1099 s, 1067 s, 1039 s, 1019 s, 917 m, 866 m, 852 m, 796 m, 761 s, 701 s, 643 m cm⁻¹; HRMS (ESI-TOF) m/z: [M+Na]⁺ Calcd for C₁₇H₁₈NaO₃ 293.1154; Found 293.1154.
Arylation of Aromatic Ester 10b

In a glove box, aromatic ester 10b (0.5 mmol), arylboronate 2a (0.6 mmol), RuHCl(CO)(P\text{Pr}_3)_2 (6) (0.05 mmol), CsF (0.1 mmol), styrene (1.0 mmol), and 0.5 mL of toluene were placed in an oven-dried sealed tube containing a magnetic stirring bar. The mixture was stirred at 100 °C for 12 h. After the reaction, volatile materials were removed by rotary evaporation. The crude material was passed through a basic aluminium oxide column to remove the remaining arylboronate. Further purification by silica gel column chromatography (hexane:AcOEt = 20:1) afforded 65.7 mg (47% yield) of arylation product 11b as a colorless oil: 1H NMR (400 MHz, CDCl3): δ 1.29 (s, 9H), 3.87 (s, 3H), 6.92 (t, J = 7.6 Hz, 2H), 7.33-7.42 (m, 6H); 13C NMR (100 MHz, CDCl3): δ 27.7, 56.0, 81.5, 109.9, 121.8, 124.8, 127.3, 128.0, 128.7, 129.7, 140.1, 140.8, 156.2, 166.6; IR (NaCl): 3061 w, 2977 m, 2933 m, 2838 w, 1724 s, 1572 m, 1499 m, 1467 s, 1432 m, 1392 m, 1368 m, 1328 s, 1286 s, 1258 s, 1172 s, 1130 s, 1108 s, 1069 m, 1039 m, 1020 m, 849 m, 804 m, 761 s, 701 m, 645 w cm\(^{-1}\); HRMS (ESI-TOF) m/z: [M+Na\(^+\)] Caled for C\(_{18}\)H\(_{20}\)NaO\(_3\) 307.1310; Found 307.1297.

XII. Formal Synthesis of Altertenuol

Preparation of Aromatic Ester 12

To a solution of 0.42 g of 2',4',6'-trimethoxybenzoic acid (2 mmol) and 4 mL of dry CH\(_2\)Cl\(_2\) was added 0.87 g of tert-butyl 2,2,2-trichloroacetimidate (4 mmol). The mixture was stirred at room temperature for 18 h under air, which was then quenched by addition of NaHCO\(_3\). The resulting mixture was filtered through a short plug of silica gel and concentrated. Purification of the crude material by silica gel column chromatography (hexane:AcOEt = 5:1) afforded aromatic ester 12 in 0.487 g (91% yield) as a white solid: Mp 103-105 °C; 1H NMR (400 MHz, CDCl3): δ 1.55 (s, 9H), 3.796 (s, 6H), 3.804 (s, 3H), 6.08 (s, 2H); 13C NMR (100 MHz, CDCl3): δ 28.2, 55.3, 55.9, 81.3, 90.6, 108.1, 158.2, 161.9, 165.7; IR (KBr): 3006
Monoarylation of Aromatic Ester 12 with Arylboronate 2o

In a glove box, aromatic ester 12 (0.5 mmol), arylboronate 2o (0.6 mmol), RuHCl(CO)(PPr₃)₂ (6) (0.05 mmol), CsF (0.1 mmol), styrene (1 mmol), and 0.5 mL of toluene were placed in an oven-dried sealed tube containing a magnetic stirring bar. The mixture was stirred at 100 °C for 12 h. After the reaction, volatile materials were removed by rotary evaporation. The crude material was passed through a basic aluminium oxide column to remove the remaining arylboronate. Purification of the crude material by silica gel column chromatography (toluene:AcOEt = 30:1) afforded aromatic ester 13 in 151 mg (57% yield) as a colorless oil: ¹H NMR (400 MHz, CDCl₃):  δ 1.24 (s, 9H), 3.79 (s, 3H), 3.84 (s, 3H), 5.16 (s, 2H), 5.19 (s, 2H), 6.33 (d,  J = 2.4 Hz, 1H), 6.43 (d,  J = 2.0 Hz, 1H), 6.92 (s, 2H), 7.03 (s, 1H), 7.30 (d,  J = 7.6 Hz, 2H), 7.36 (t,  J = 8.0 Hz, 4H), 7.44-7.47 (m, 4H); ¹³C NMR (100 MHz, CDCl₃):  δ 27.7, 55.3, 55.9, 71.0, 71.2, 81.0, 97.4, 105.7, 114.7, 115.3, 117.9, 121.5, 127.2, 127.3, 127.65, 127.67, 128.3, 128.4, 134.1, 137.07, 137.13, 141.6, 148.2, 148.4, 157.7, 160.6, 166.7; IR (NaCl): 3064 w, 3032 w, 2975 m, 2937 m, 2840 w, 1720 s, 1601 s, 1572 s, 1455 m, 1418 m, 1391 m, 1368 m, 1258 s, 1212 m, 1158 s, 1104 m, 1035 m, 911 m, 848 m, 813 m, 735 m, 697 m, 665 w cm⁻¹; HRMS (ESI-TOF) m/z: [M+Na]+ Calcd for C₃₃H₃₄NaO₆ 549.2253; Found 549.2243.
Removal of *tert*-Butyl Group of Aromatic Ester 13

The deprotection of *tert*-butyl group was performed using a similar procedure to the one reported by Gagné and coworkers.\textsuperscript{11}

A 20 mL round-bottom flask was charged with 118 mg of aromatic ester 13 (0.22 mmol), 0.5 mL of 98\% HCO\textsubscript{2}H and 0.5 mL of CH\textsubscript{2}Cl\textsubscript{2}. This solution was stirred under air at room temperature for 3 h. After the reaction, the mixture was extracted three times with Et\textsubscript{2}O. Combined organic portions were washed with H\textsubscript{2}O and brine, quickly dried over Na\textsubscript{2}SO\textsubscript{4}, filtered and concentrated. Purification of the crude material by silica gel column chromatography (hexane:AcOEt = 2:1 to 0:1) afforded carboxylic acid 14 in 98.1 mg (93\% yield) as a cream solid: Mp 136-138 °C; \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): δ 3.80 (s, 6H), 5.15 (s, 4H), 6.38 (d, \textit{J} = 2.8 Hz, 1H), 6.42 (d, \textit{J} = 2.0 Hz, 1H), 6.93 (s, 2H), 7.01 (s, 1H), 7.25-7.37 (m, 6H), 7.42-7.45 (m, 4H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): δ 55.4, 56.0, 71.0, 71.1, 97.3, 106.4, 114.60, 114.64, 114.9, 121.1, 127.3, 127.6, 127.7, 128.37, 128.41, 133.6, 137.20, 137.24, 142.7, 148.5, 148.6, 155.6, 158.2, 161.4, 172.2; IR (KBr): 3030 s, 2935 s, 1698 s, 1601 s, 1514 s, 1454 s, 1402 m, 1383 m, 1260 s, 1212 s, 1162 s, 1132 s, 1016 s, 933 m, 912 w, 838 m, 812 m, 734 s, 696 s, 606 m, cm\textsuperscript{-1}; HRMS (ESI-TOF) m/z: [M+Na]\textsuperscript{+} Calcd for C\textsubscript{29}H\textsubscript{26}NaO\textsubscript{6} 493.16271; Found 493.16265.
Oxidative Cyclization of Carboxylic Acid 14

The oxidative cyclization was performed using a similar procedure to the one reported by Gevorgyan and coworkers.\textsuperscript{12}

\[
\begin{array}{c}
\text{MeO} \\
\text{MeO} \\
\text{O} \\
\text{Bn} \\
\text{MeO} \\
\text{MeO} \\
\text{O} \\
\text{Bn} \\
\end{array}
\stackrel{0.04 \text{ mmol AgNO}_3, 0.6 \text{ mmol K}_2\text{S}_2\text{O}_8}{\text{MeCN 1 mL, H}_2\text{O 1 mL}} \stackrel{50 \degree \text{C}, 18 \text{ h}}{\text{1 mL}}
\begin{array}{c}
\text{MeO} \\
\text{MeO} \\
\text{O} \\
\text{Bn} \\
\text{MeO} \\
\text{MeO} \\
\text{O} \\
\text{Bn} \\
\end{array}
\]

A sealed tube was charged with 94 mg of carboxylic acid 14 (0.2 mmol), 162 mg of K$_2$S$_2$O$_8$ (0.6 mmol), 6.8 mg of AgNO$_3$ (0.04 mmol), 1 mL of MeCN and 1 mL of H$_2$O. This solution was stirred under air at 50 °C for 18 h. After the reaction, the mixture was extracted three times with CH$_2$Cl$_2$. Combined organic portions were quickly dried over Na$_2$SO$_4$, filtered and concentrated. Purification of the crude material by silica gel column chromatography (hexane:AcOEt:CH$_2$Cl$_2$ = 1:1:3) afforded lactone 15 in 68 mg (72% yield) as a white solid. The analytical data for 15 are in good agreement with those reported in literature.\textsuperscript{13}

XIII. Preparation of 2,6-Dimethoxy-3-Methylbenzophenone

To a stirred solution of 0.38 g of 2,4-dimethoxytoluene (2.5 mmol) in 1.25 mL of THF at 0 °C was added dropwise 1.95 mL of $^\text{t}$BuLi in hexane (1.54 M, 3.0 mmol). After stirred for 2 h, the resulting mixture was added dropwise via a cannula to a solution of 0.35 g of benzoyl chloride (2.5 mmol) in 2.5 mL of THF at −78°C. The mixture was stirred for 2 h, and an aqueous solution of 2 M HCl was introduced to the reaction mixture. The solution was then extracted three times with Et$_2$O. Combined organic portions were washed with H$_2$O and brine, quickly dried over MgSO$_4$, filtered, and concentrated. Purification of the crude material by silica gel column chromatography (hexane:AcOEt = 15:1) afforded 2,6-dimethoxy-3-methylbenzophenone in 83% yield (0.53 g) as a white solid: Mp 123-125 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 2.26 (s, 3H), 3.64 (s, 3H), 3.69 (s, 3H), 6.67 (d, $J = 8.5$ Hz, 1H), 7.21 (d, $J = 8.5$ Hz, 1H), 7.43 (t, $J = 7.6$ Hz, 1H).
Hz, 2H), 7.55 (t, J = 7.4 Hz, 1H), 7.84 (d, J = 7.4 Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 15.3, 55.8, 61.7, 106.7, 123.1, 123.4, 128.4, 132.1, 133.3, 137.6, 155.6, 156.0, 195.6; IR (KBr) 2938 s, 2840 m, 1673 s, 1593 s, 1475 s, 1206 m, 1161 m, 1013 s, 966 m, 909 m, 839 m, 806 m, 697 s, 608 w, 559 w, 456 w cm$^{-1}$; HRMS (ESI-TOF) m/z: [M+Na]$^+$ Calcd for C$_{16}$H$_{16}$NaO$_3$ 279.0997; Found 279.0994.

XIV. References

XV. NMR spectra

\(^1\)H NMR (CDCl\(_3\))
$^{13}\text{C}$$^1\text{H}$ NMR (CDCl$_3$)
$^{13}\text{C}^{1\text{H}}$ NMR (CDCl$_3$)
$^1$H NMR (CDCl$_3$)
$^{13}\text{C}^{1\text{H}}$ NMR (CDCl$_3$)
$^{1}H$ NMR (CDCl$_3$)
$^1$H NMR (CDCl$_3$)
$^{13}\text{C}^{1\text{H}}$ NMR (CDCl$_3$)
$^1$H NMR (CDCl$_3$)
$^1$H NMR (CDCl$_3$)
$^{13}$C$\{^1$H$\}$ NMR (CDCl$_3$)
$^1$H NMR (CDCl$_3$)
$^{13}\text{C}^{1}\text{H}$ NMR (CDCl$_3$)
$^1$H NMR (CDCl$_3$)
$^{13}\text{C}^{1}\text{H}\}$ NMR (CDCl$_3$)
$^1$H NMR (CDCl$_3$)
$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl$_3$)
$^1$H NMR (CDCl$_3$)
$^{13}\text{C}^{1}\text{H} \text{ NMR (CDCl}_3\text{)}$
$^{1}\text{H NMR (CDCl}_3\text{)}$

The diagram shows a spectrum with peaks at various ppm values. The peaks are labeled with their chemical shifts, for example, around 7.39, 7.37, 3.85, 3.80, and 2.17 ppm. The structure of the compound is also shown on the right side of the diagram.
$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl$_3$)
$^1$H NMR (CDCl$_3$)
$^{13}\text{C}^{1\text{H}} \text{ NMR (CDCl}_3\text{)}$
$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl$_3$)
$^1$H NMR (CDCl$_3$)
$^{13}\text{C}$$\text{H}_2$ NMR (CDCl$_3$)
$^1$H NMR (CDCl$_3$)
$^{13}$C\{\textsuperscript{1}H\} NMR (CDCl\textsubscript{3})
$^1$H NMR (CDCl$_3$)
$^{13}\text{C} \{^1\text{H}\} \text{ NMR (CDCl}_3\text{)
$^1$H NMR (CDCl$_3$)
$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl$_3$)
\(^1\)H NMR (CDCl\(_3\))
$^{13}$C\{$^1$H\} NMR (CDCl$_3$)
$^1\text{H NMR (CDCl}_3\text{)}$
$^{13}\text{C}^{1\text{H}}$ NMR (CDCl$_3$)
$^1$H NMR (CDCl$_3$)
$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl$_3$)
$^1$H NMR (CDCl$_3$)
$^{13}$C{$^1$H} NMR (CDCl$_3$)
$^1$H NMR (CDCl$_3$)
$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl$_3$)
$^1$H NMR (CDCl$_3$)
$^{13}\text{C}^{1\text{H}}\text{ NMR (CDCl}_3\text{)}$
$^1$H NMR (CDCl$_3$)
$^{13}$C$^{1H}$ NMR (CDCl$_3$)
$^1$H NMR (CDCl$_3$)
$^{13}$C\textsuperscript{1}H\textsuperscript{-}NMR (CDCl\textsubscript{3})
$^{13}$C$^{1}$H NMR (CDCl$_3$)
$^1$H NMR (CDCl$_3$)
$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl$_3$)
$^1$H NMR (CDCl$_3$)
$^{13}\text{C}^{1\text{H}}$ NMR (CDCl$_3$)
^1H NMR (CDCl₃)
$^{13}\text{C}^{1}\text{H}}$ NMR (CDCl$_3$)
$^1$H NMR (CDCl$_3$)

MeO
O'Pr

11a

PPM

6.009
1.000
3.067
6.052
7.401
7.386
7.383
7.362
7.344
7.339
7.322
7.253
6.973
6.971
6.954
6.951
6.940
6.920
5.072
5.056
5.040
5.026
5.010
4.994
4.978
3.873
1.615
1.015
0.999
0.000

S84
$^{13}\text{C}\left\{^1\text{H}\right\}$ NMR (CDCl$_3$)
$^1$H NMR (CDCl$_3$)
$^{13}\text{C}^{1\text{H}}$ NMR (CDCl$_3$)
$^1$H NMR (CDCl$_3$)
$^{13}\text{C}^{1\text{H}} \text{ NMR (CDCl}_3\text{)}$
$^1$H NMR (CDCl$_3$)
$^1$H NMR (CDCl$_3$)

PPM

7.494, 7.477, 7.461, 7.443, 7.401, 7.396, 7.383, 7.378, 7.363, 7.337, 7.325, 7.315, 7.250, 6.823, 6.739, 6.734, 6.441, 5.206, 4.007, 3.931, 3.903, 3.535, 3.021, 2.980, 2.000, 1.000, 0.000

S94
$^{13}$C{$^1$H} NMR (CDCl$_3$)

![NMR Spectrum](image_url)
$^1\text{H NMR (CDCl}_3\text{)}$
$^{13}\text{C}^{1}\text{H}} \text{ NMR (CDCl}_3\text{)}$