Supporting information I

Direct Synthesis of Polyaryls by Consecutive Oxidative Cross-Coupling of Phenols with Arenes

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1. **General Information:**

All reagents were of reagent grade quality, purchased commercially from Sigma-Aldrich, Alfa-Aesar, or Fluka, and used without further purification. FeCl$_3$ anhydrous 98% purchased from Strem Chemicals. Purification by column chromatography was performed on Fluka chromatographic silica gel (40-63 μm). TLC analyses were performed using Merck silica gel glass plates 60 F254. NMR spectra were recorded on Bruker DPX400, or DMX500 instruments; chemical shifts are given in ppm and are relative to Me$_4$Si as an internal standard or to the residual solvent peak. IR spectra were recorded on NICOLET 380 FT-IR instrument. HR-MS data were obtained using a Thermoscientific LTQU XL Orbitrap HRMS equipped with APCI (atmospheric-pressure chemical ionization). HPLC analysis was carried out on Agilent 1260 instrument equipped with a G4212-60008 photodiode array detector, ES-MS Advion Expression unit and an Agilent reverse phase ZORBAX Eclipse plus C18 3.5 μm column (4.6 X 100 mm).
2. Experimental data:

2.1 Synthesis of starting biaryls:

2.1.1 General Suzuki coupling procedure: 

2.1.2 General procedure: A mixture of 4-bromo-2,6-dimethyl phenol (200 mg, 1 mmol), arylboronic acid (1.5 mmol), Pd(PPh₃)₄ (115 mg, 10 mol %) and NaOH (240 mg, 6 mmol) in THF/H₂O (3:1, 18 mL) were deoxygenated under vacuum and refilled with nitrogen for 3 times. The reaction was stirred at 75 °C for 16 h, cooled and ethyl acetate (15 mL) and water (10 mL) were added. The organic phase was separated and the water phase was extracted with ethyl acetate (2 x 15 mL). The combined organic phases were washed with brine, dried over Na₂SO₄ and evaporated under vacuum. The crude residue was purified by column chromatography.

2.1.3 Characterization data:

**Compound 1b**: compound 1b was prepared from 4-bromo-2,6-dimethyl phenol (200 mg, 1 mmol) and (2,4,6-trimethoxyphenylboronic acid (318 mg, 1.5 mmol) according to the general procedure. The crude residue was purified by column chromatography (hexane/ethyl acetate 9:1) to afford compound 1b (115 mg, 40% yield) as a white solid.

Characterization data of compound 1b: ¹H NMR (400 MHz, CDCl₃) δ 6.95 (s, 2H), 6.23 (s, 2H), 4.62 (s, 1H), 3.87 (s, 3H), 3.74 (s, 6H), 2.27 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 160.2, 158.6, 151.1, 131.4, 125.7, 122.5, 112.4, 90.9, 56.0, 55.5, 16.2; HRMS (ESI): m/z calcd for C₁₇H₂₁O₄ [M+H]+ 289.1434, found 289.1437.
**Compound 1ei:** A mixture of 5-bromo-2-hydroxy-3-methoxybenzaldehyde (347 mg, 1.5 mmol), (2,4,6-trimethoxyphenyl)boronic acid (477 mg, 2.25 mmol), Pd(PPh₃)₄ (173 mg, 10 mol %) and NaOH (360 mg, 9 mmol) in THF/H₂O (3:1, 27 mL) were deoxygenated under vacuum and refilled with nitrogen for 3 times. Then stirring was continued for 3 days at 85 °C. After cooling, ethyl acetate (40 mL) and water (40 mL) were added. The organic phase was separated and the water phase was extracted with ethyl acetate (3 x 30 mL). The combined organic phase were washed with brine, dried over Na₂SO₄ and evaporated under vacuum. The crude residue was purified by column chromatography; hexane/ethyl acetate 4:1 to afford compound 1ei (143 mg, 30% yield) as a yellow solid.

Characterization data of compound 1ei: ¹H NMR (400 MHz, CDCl₃) δ 9.89 (s, 1H), 7.16 (s, 1H), 7.13 (s, 1H), 6.24 (s, 2H), 3.90 (s, 3H), 3.87 (s, 3H), 3.75 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 197.0, 160.9, 158.4, 150.2, 147.5, 127.4, 125.7, 122.0, 120.5, 110.6, 90.9, 56.4, 55.9, 55.5; HRMS (ESI): m/z calcd for C₁₇H₁₉O₆ [M+H]⁺ 319.1131, found 319.1176. IR (KBr pellet): 3420 (m, broad), 1650 (s), 1580 (s), 1120 (s) cm⁻¹.

**Compound 1e:** A mixture of compound 1ei (112 mg, 0.4 mmol) and 10% Pd/C (24 mg, 40 mol %) in methanol (25 mL) was stirred under a hydrogen atmosphere at room temperature for 5 days. Then the reaction mixture was filtered through short pad of Celite and the filtrate was evaporated. The crude residue was purified by column chromatography; hexane/ethyl acetate 1:1 to afford compound 1e (40 mg, 40% yield) as a white solid.

Characterization data of compound 1e: ¹H NMR (400 MHz, CDCl₃) δ 6.73 (s, 1H), 6.72 (s, 1H), 6.25 (s, 2H), 5.70 (s, 1H), 3.88 (s, 3H), 3.87 (s, 3H), 3.75 (s, 6H), 2.29 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 160.3, 158.6, 145.7, 142.6, 123.00, 124.8, 112.7, 111.5, 91.0, 56.0 (×2), 55.5, 15.7; HRMS (ESI): m/z calcd for C₁₇H₂₁O₅ [M+H]⁺ 305.1384, found 305.1377.
**Compound 1f:** A mixture of 4-bromo-2,6-dimethoxy-phenol (247 mg, 1 mmol), (2,4,6-trimethoxy)phenylboronic acid (318 mg, 1.5 mmol), Pd(PPh₃)₄ (115 mg, 10 mol %) and NaOH (240 mg, 6 mmol) in THF/H₂O (3:1, 18 mL) were deoxygenated under vacuum and refilled with nitrogen for 3 times. Then stirring was continued for 21 h at 85 °C. After cooling, ethyl acetate (25 mL) and water (20 mL) were added. The organic phase was separated and the water phase was extracted with ethyl acetate (3 x 30 mL). The combined organic phase were washed with brine, dried over Na₂SO₄ and evaporated under vacuum. The crude residue was purified by column chromatography (hexane/ethyl acetate 7:3) to afford compound 1f (63 mg, 20% yield) as a white solid.

Characterization data of compound 1f: ¹H NMR (400 MHz, CDCl₃) δ 6.57 (s, 2H), 6.24 (s, 2H), 5.52 (s, 1H), 3.87 (overlapped, 9H), 3.74 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 160.5, 158.6, 146.6, 133.6, 124.9, 112.6, 108.1, 91.1, 56.3, 56.1, 55.5; HRMS (ESI): m/z calcd for C₁₇H₁₉O₆ [M+H]^+ 319.1131, found 319.1176.

**Compound 1g:** Compound 1g was prepared from 4-bromo-2,6-dimethylphenol (200 mg, 1 mmol) and 4-methoxyphenylboronic acid (228 mg, 1.5 mmol) according to the general conditions. The crude residue was purified by column chromatography (hexane/ethyl acetate 9:1) to afford compound 1g (157 mg, 69% yield) as a white solid.

Characterization data of compound 1g: ¹H NMR (400 MHz, CDCl₃) δ 7.47 (dd, J = 8.4 Hz, 2H), 7.18 (s, 2H), 6.95 (dd, J = 8.4 Hz, J = 2.1 Hz, 2H), 3.85 (s, 3H), 2.31 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 158.7, 151.5, 133.9, 133.2, 128.7, 127.9, 127.1, 123.4, 114.2, 55.5, 16.2; HRMS (ESI): m/z calcd for C₁₅H₁₇O₂ [M+H]^+ 229.1223, found 229.1228.
**Compound 1h**: Compound 1h was prepared from 4-bromo-2,6-dimethylphenol (200 mg, 1 mmol) and 4-tert-butylphenylboronic acid (267 mg, 1.5 mmol) according to the general procedure. The crude residue was purified by column chromatography (hexane/ethyl acetate 9:1) to afford compound 1h (182 mg, 72% yield) as a white solid.

Characterization data of compound 1h: $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.47 (dd, $J$ = 8.3 Hz, 4H), 7.24 (s, 2H), 4.66 (s, 1H), 2.33 (s, 6H), 1.38 (s, 9H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 151.8, 149.6, 138.4, 133.4, 127.4, 126.5, 125.7, 123.3, 34.6, 31.5, 16.2; HRMS (ESI): $m/z$ calcd for C$_{18}$H$_{23}$O [M+H]$^+$ 255.1743, found 255.1753.

**Compound 1i**: Compound 1i was prepared from 4-bromo-2,6-dimethylphenol (200 mg, 1 mmol) and 4-fluorophenylboronic acid (210 mg, 1.5 mmol) according to the general procedure. The crude residue was purified by column chromatography; hexane/ethyl acetate 9:1 to afford compound 1i (117 mg, 54% yield) as a white solid.

Characterization data of compound 1i: $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.48 (m, 2H), 7.17 (s, 2H), 7.08 (m, 2H), 2.31 (s, 6H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 163.1, 152.0, 137.4, 132.6, 128.4, 127.4, 123.5, 115.6, 16.2; $^{19}$F NMR (377 MHz, CDCl$_3$) $\delta$ $-117.03$; HRMS (ESI): $m/z$ calcd for C$_{14}$H$_{14}$FO [M+H]$^+$ 217.1023, found 217.1042.

### 2.2 Sequential cross-coupling products:

#### 2.2.1 General procedure:

**ortho-Directed selectivity in consecutive oxidative cross-coupling of phenols**

To a stirred solution of phenol derivative (1.0 equiv), arene (1.5-5 equiv) and FeCl$_3$ (15 mol %) in HFIP (0.5 M), di-$t$-butylperoxide (1.5-5 equiv) was added drop-wise at room temperature. Upon completion of the sequential oxidative cross-coupling reaction, as indicated by TLC and HPLC analysis, the volatiles were removed under reduced pressure. The crude residue was purified by silica-gel column chromatography affording pure polyarene products.
2.2.2 Characterization data:

**Compound 3:** To a mixture of 2,6-dimethylphenol (1a, 31 mg, 0.25 mmol), 1,3,5-trimethoxybenzene (2a, 126 mg, 0.75 mmol) and FeCl₃ (6 mg, 15 mol %) in HFIP (0.5 mL, 0.5M), di-t-butylperoxide (0.138 mL, 0.75 mmol) was added drop-wise at room temperature, stirring was continued for 2.5 h and the volatiles were removed under reduced pressure. The crude residue was purified by column chromatography; hexane/ethyl acetate 4:6 to afford compound 3 (143 mg, 58% yield) as a white solid.

**Compound 3** can also be prepared from 1b by using above procedure, in 3 h with 90% yield.

Characterization data of compound 3: ¹H NMR (400 MHz, CDCl₃) δ 5.92 (s, 4H), 5.64 (s, 2H), 3.75 (s, 6H), 3.65 (s, 3H), 3.52 (s, 12H), 3.33 (s, 6H), 2.01 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 159.8, 158.8, 158.7, 158.7, 150.9, 133.3, 122.4, 112.6, 112.5, 111.3, 89.1, 88.3, 55.3, 55.1, 54.7 54.4, 14.1; HRMS (ESI): m/z calcd for C₃₅H₄₁O₁₀ [M+H]+ 621.2694, found 621.2692.

**Compound 4:** To a mixture of 2,3-dimethylphenol (1c, 31 mg, 0.25 mmol), 1,3,5-trimethoxybenzene (2a, 210 mg, 1.25 mmol) and FeCl₃ (6 mg, 15 mol %) in HFIP (0.5 mL, 0.5M), di-t-butylperoxide (0.230 mL, 1.25 mmol) was added drop-wise at room temperature, stirring was continued for 7 h and the volatiles were removed under reduced pressure. The crude residue was purified by column chromatography; hexane/ethyl acetate 4:6 to afford compound 4 (132 mg, 85% yield) as a white solid.

Characterization data of compound 4: ¹H NMR (500 MHz, CDCl₃) δ 6.76 (s, 1H), 6.16-6.12 (m, 5H), 6.05 (s, 1H), 3.82-3.71 (overlapped, 24H), 3.62 (s, 3H), 1.84 (s, 3H), 1.44 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 203.6, 160.6, 160.4, 159.9, 159.6, 159.1, 158.6, 153.9, 146.6, 125.7, 120.6, 113.7, 112.0, 109.0, 91.6, 91.5, 91.3, 58.8, 56.4, 56.1, 55.8, 55.4, 55.3, 24.3, 17.6; HRMS (ESI): m/z calcd for C₃₅H₄₁O₁₀ [M+H]+ 621.2694, found 621.2697. IR (KBr pellet): 2930(m), 1600(s), 1580(s), 1120 (s) cm⁻¹.
Synthesis of phenolic intermediates 4a and 4b for the kinetic studies of 1c:

To a mixture of 2,3-dimethylphenol (1c, 31 mg, 0.25 mmol), 1,3,5-trimethoxybenzene (2a, 55 mg, 0.325 mmol) and FeCl₃ (6 mg, 15 mol %) in HFIP (0.5 mL, 0.5M), di-t-butylperoxide (0.069 mL, 0.375 mmol) was added drop-wise at room temperature, stirring was continued for 1 h and the volatiles were removed under reduced pressure. The crude residue was purified by column chromatography; hexane/ethyl acetate 8:2 affording compound 4a (7 mg, 10% yield) as a white solid and hexane/ethyl acetate 7:3 compound 4b (29 mg, 26% yield) as a white solid.

Characterization data of compound 4a: ¹H NMR (400 MHz, CDCl₃) δ 6.87 (d, J = 8.2 Hz, 1H), 6.67 (d, J = 8.2 Hz, 1H), 6.23 (s, 2H), 4.67 (s, 1H), 3.87 (s, 3H), 3.71 (s, 6H), 2.21 (s, 3H), 1.98 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 160.5, 158.7, 152.6, 138.0, 129.2, 126.5 (×2), 122.5, 112.4, 90.8, 56.0, 55.5, 17.1, 12.3; HRMS (ESI): m/z calcd for C₁₇H₂₁O₄ [M+H]+ 289.1434, found 289.1434.

Characterization data of compound 4b: ¹H NMR (500 MHz, CDCl₃) δ 6.83 (s, 1H), 6.24 (s, 2H), 6.21 (s, 2H), 3.85 (overlapped, 6H), 3.74 (s, 6H), 3.71 (s, 6H), 2.27 (s, 3H), 2.01 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 161.2, 160.3, 159.1, 158.8, 150.8, 137.1, 132.5, 125.2, 123.3, 117.2, 112.8, 107.3, 91.3, 90.8, 56.1, 55.9, 55.5, 55.4, 17.2, 13.0; HRMS (ESI): m/z calcd for C₂₆H₃₁O₇ [M+H]+ 455.2064, found 455.2068.
**Compound 5:** To a mixture of 2,6-dimethoxyphenol (1d, 39 mg, 0.25 mmol), 1,3,5-trimethoxybenzene (2a, 210 mg, 1.25 mmol) and FeCl₃ (6 mg, 15 mol %) in HFIP (0.5 mL, 0.5M), di-tert-butylperoxide (0.230 mL, 1.25 mmol) was added drop-wise at room temperature, stirring was continued for 3 h and the volatiles were removed under reduced pressure. The crude residue was purified by column chromatography; hexane/ethyl acetate 6:4 to afford compound 5 (83 mg, 68% yield) as a white solid.

Characterization data of compound 5: ¹H NMR (400 MHz, CDCl₃) δ 6.53 (s, 2H), 6.21 (s, 2H), 6.15 (s, 2H), 3.84 (s, 3H), 3.77 (s, 3H), 3.72 (s, 6H), 3.69 (s, 12H); ¹³C NMR (100 MHz, CDCl₃) δ 160.4, 158.5, 155.4, 152.4, 150.9, 136.5, 132.4, 128.0, 113.0, 109.8, 92.6, 91.4, 56.9, 56.7, 56.1, 55.5, 55.4; HRMS (ESI): m/z calcd for C₂₆H₃₁O₉ [M+H]⁺ 487.1963, found 487.1965. IR (KBr pellet): 2930(m), 1590 (s), 1460(s), 1220(s), 1120(s) cm⁻¹.

**Compounds 6 and 7:**

To a mixture of 1e (28 mg, 0.09 mmol), 1,3,5-trimethoxybenzene (2a, 50 mg, 0.30 mmol) and FeCl₃ (2 mg, 15 mol %) in HFIP (0.2 mL, 0.5M), di-tert-butylperoxide (0.055 mL, 0.30 mmol) was added drop-wise at room temperature, stirring was continued for 18 h and the volatiles were removed under reduced pressure. The crude residue was purified by column chromatography; hexane/ethyl acetate 1:1 to afford compound 6 (20 mg, 33% yield) as a white solid and hexane/ethyl acetate 4:6 to afford compound 7 (25 mg, 44% yield) as a white solid.

Characterization data of compound 6: ¹H NMR (400 MHz, CDCl₃) δ 6.69 (s, 1H), 6.68 (s, 1H), 6.21 (s, 2H), 6.16 (s, 2H), 6.16 (s, 2H), 3.85 (s, 3H), 3.78 (s, 3H), 3.71 (s, 6H), 3.69 (s, 6H), 3.61 (s, 3H), 2.27 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 160.3, 158.6, 155.5, 152.5, 150.4, 145.4, 132.3, 129.4, 128.3, 126.0, 114.7, 113.1, 92.7, 91.4, 56.8, 56.7, 56.1, 55.6, 55.5, 16.9; HRMS (ESI): m/z calcd for C₂₆H₃₁O₈ [M+H]⁺ 471.2013, found 471.2018.
Characterization data of compound 7: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 6.66 (s, 1H), 6.17 (s, 2H), 5.95 (overlapped, 4H), 3.77 (s, 3H), 3.75 (s, 6H), 3.69 (s, 6H), 3.60 (s, 3H), 3.51 (overlapped, 12H), 2.01 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 159.8, 159.7, 158.8, 158.5, 155.2, 152.5, 149.3, 145.5, 133.5, 130.9, 129.8, 128.3, 114.8, 113.2, 111.4, 93.7, 90.0, 89.9, 57.1, 56.6, 55.6, 55.3 (×2), 14.3; HRMS (ESI): $m/z$ calcd for C$_{35}$H$_{41}$O$_{11}$ [M+H]$^+$ 637.2643, found 637.2657.

Compound 8: To a mixture of $p$-cresol (27 mg, 0.25 mmol), 1,3,5-trimethoxybenzene (2a, 126 mg, 0.75 mmol) and FeCl$_3$ (6 mg, 15 mol %) in HFIP (0.5 mL, 0.5M), di-$t$-butylperoxide (0.138 mL, 0.75 mmol) was added drop-wise at room temperature, stirring was continued for 4 h and the volatiles were removed under reduced pressure. The crude residue was purified by column chromatography; hexane/ethyl acetate 6:4 to afford compound 8 (28 mg, 41% yield) as a white solid.

Characterization data of compound 8: $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.07 (d, $J = 7.7$ Hz, 1H), 6.99 (s, 1H), 6.92 (d, $J = 7.7$ Hz, 1H), 6.27 (s, 2H), 5.10 (s, 1H), 3.88 (s, 3H), 3.76 (s, 6H), 2.31 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 161.6, 158.9, 151.6, 132.9, 129.6, 129.2, 120.6, 115.9, 91.4, 56.2, 55.5, 20.8; HRMS (ESI): $m/z$ calcd for C$_{16}$H$_{19}$O$_4$ [M+H]$^+$ 275.1278, found 275.1283.
**Compound 9**: To a mixture of 2-tert-butyl phenol (38 mg, 0.25 mmol), 1,3,5-trimethoxybenzene (2a, 210 mg, 1.25 mmol) and FeCl₃ (6 mg, 15 mol %) in HFIP (0.5 mL, 0.5M), di-t-butylperoxide (0.230 mL, 1.25 mmol) was added drop-wise at room temperature, stirring was continued for 20 h and the volatiles were removed under reduced pressure. The crude residue was purified by column chromatography; hexane/ethyl acetate 8:2 to afford compound 9 (51 mg, 44% yield) as a white solid.

Characterization data of compound 9: ¹H NMR (400 MHz, CDCl₃) δ 7.29 (d, J = 1.9 Hz, 1H), 7.06 (d, J = 1.9 Hz, 1H), 6.26 (s, 2H), 6.23 (s, 2H), 3.86 (s, 3H), 3.85 (s, 3H), 3.74 (s, 6H), 3.73 (s, 6H), 1.45 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 161.3, 159.8, 159.2, 158.6, 151.2, 134.9, 133.2, 129.6, 123.9, 120.5, 113.4, 107.6, 91.7, 91.5, 56.2, 56.1, 55.5, 55.5, 35.0, 30.1; HRMS (ESI): m/z calcd for C₂₈H₃₅O₇ [M+H]⁺ 483.2377, found 483.2374.

**Compound 10**: To a mixture of 3,5-dimethylphenol (31 mg, 0.25 mmol), 1,3,5-trimethoxybenzene (2a, 126 mg, 0.75 mmol) and FeCl₃ (6 mg, 15 mol %) in HFIP (0.5 mL, 0.5M), di-t-butylperoxide (0.138 mL, 0.75 mmol) was added drop-wise at room temperature, stirring was continued for 4 h and the volatiles were removed under reduced pressure. The crude residue was purified by column chromatography; hexane/ethyl acetate 6:4 compound 10 (40 mg, 35% yield) as a white solid.

Characterization data of compound 10: ¹H NMR (500 MHz, CDCl₃) δ 6.78 (s, 1H), 6.26 (s, 2H), 6.24 (s, 2H), 3.87 (overlapped, 6H), 3.73 (s, 6H), 3.70 (s, 6H), 2.01 (s, 3H), 1.65 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 161.7, 160.4, 159.5, 158.6, 152.3, 138.7, 138.0, 125.9, 117.7, 113.7, 111.5, 105.3, 91.4, 91.1, 56.1, 56.0, 55.5, 55.4, 20.5, 17.6; HRMS (ESI): m/z calcd for C₂₆H₃₁O₇ [M+H]⁺ 455.2064, found 455.2059.
**Compound 11**: To a mixture of 1g (57 mg, 0.25 mmol), 1,3,5-trimethoxybenzene (2a, 126 mg, 0.75 mmol) and FeCl₃ (6 mg, 15 mol %) in HFIP (0.5 mL, 0.5M), di-t-butylperoxide (0.138 mL, 0.75 mmol) was added drop-wise at room temperature, stirring was continued for 16 h and the volatiles were removed under reduced pressure. The crude residue was purified by column chromatography; hexane/ethyl acetate 1:1 to afford compound 11 (134 mg, 96% yield) as a white solid.

Characterization data of compound 11: ¹H NMR (400 MHz, CDCl₃) δ 6.78 – 6.61 (m, 2H), 6.45 – 6.24 (m, 2H), 5.94 (s, 4H), 4.71 (s, 1H), 3.74 (s, 6H), 3.61 (s, 3H), 3.58 (s, 12H), 2.01 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 160.3, 158.1, 156.9, 150.8, 136.4, 134.9, 131.9, 130.3, 122.2, 111.5, 110.8, 90.0, 55.4, 55.3, 55.0, 13.6; HRMS (ESI): m/z calcd for C₃₃H₃₇O₈ [M+H]+ 561.2483, found 561.2479. IR (KBr pellet): 3420(m, broad), 2920(m), 1490(s), 1220(s), 1120(s) cm⁻¹.

**Compound 12**: To a mixture of 1h (64 mg, 0.25 mmol), 1,3,5-trimethoxybenzene (2a, 126 mg, 0.75 mmol) and FeCl₃ (6 mg, 15 mol %) in HFIP (0.5 mL, 0.5M), di-t-butylperoxide (0.138 mL, 0.75 mmol) was added drop-wise at room temperature, stirring was continued for 18 h and the volatiles were removed under reduced pressure. The crude residue was purified by column chromatography; hexane/ethyl acetate 7:3 to afford compound 12 (86 mg, 60% yield) as a white solid.

Characterization data of compound 12: ¹H NMR (400 MHz, CDCl₃) δ 6.77 – 6.73 (m, 2H), 6.63 – 6.60 (m, 2H), 5.92 (s, 3H), 3.72 (s, 6H), 3.55 (s, 12H), 2.04 (s, 6H), 1.11 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 160.4, 158.3, 150.8, 147.0, 139.0, 136.8, 131.7, 129.1, 122.3, 121.8, 111.6, 89.9, 55.4, 55.3, 31.4, 13.6; HRMS (ESI): m/z calcd for C₃₆H₄₃O₇ [M+H]+ 587.3003, found 587.3016.
**Compound 13:** To a mixture of 1b (20 mg, 0.069 mmol), 1,3,5-triethoxybenzene (2b, 44 mg, 0.208 mmol) and FeCl₃ (2 mg, 15 mol %) in HFIP (0.5 mL, 0.5M), di-t-butylperoxide (0.038 mL, 0.208 mmol) was added drop-wise at room temperature, stirring was continued for 1.5 h and the volatiles were removed under reduced pressure. The crude residue was purified by column chromatography; hexane/ethyl acetate 6:4 to afford compound 13 (41 mg, 85% yield) as a white solid.

Characterization data of compound 13: ¹H NMR (400 MHz, CDCl₃) δ 5.92 (s, 4H), 5.60 (s, 2H), 4.65 (s, 1H), 3.93 (q, J = 6.9 Hz, 4H), 3.78 (m, 8H), 3.63 (s, 3H), 3.26 (s, 6H), 2.04 (s, 6H), 1.36 (t, J = 6.9 Hz, 6H), 1.19 (t, J = 6.9 Hz, 12H); ¹³C NMR (100 MHz, CDCl₃) δ 167.1, 158.8, 158.7, 158.1, 150.6, 133.8, 122.1, 112.5, 112.4, 91.6, 88.3, 63.6, 63.3, 55.1, 54.0, 15.0, 14.8, 14.2; HRMS (ESI): m/z calcd for C₄₁H₅₃O₁₀ [M+H]⁺ 705.3633, found 705.3644.

**Compound 14:** To a mixture of 1h (29 mg, 0.125 mmol), 1,3,5-triethoxybenzene (2b, 79 mg, 0.375 mmol) and FeCl₃ (3 mg, 15 mol %) in HFIP (0.5 mL, 0.5M), di-t-butylperoxide (0.069 mL, 0.375 mmol) was added drop-wise at room temperature, stirring was continued for 24 h and the volatiles were removed under reduced pressure. The crude residue was purified by column chromatography; hexane/ethyl acetate 8:2 to afford compound 14 (18 mg, 21% yield) as a white solid.

Characterization data of compound 14: ¹H NMR (500 MHz, CDCl₃) δ 6.69 (s, 4H), 5.89 (s, 4H), 3.91 (q, J = 6.9 Hz, 4H), 3.84 (m, 4H), 3.64 (m, 4H), 2.01 (s, 6H), 1.33 (t, J = 6.9 Hz, 6H), 1.19 (t, J = 6.9 Hz, 12H), 1.08 (s, 9H); ¹³C NMR (125 MHz, CDCl₃) δ 159.2, 157.7, 150.3, 146.7, 139.1, 136.3, 131.9, 129.2, 121.8, 121.4, 113.0, 91.8, 63.5, 63.5, 31.4, 14.9, 13.5; HRMS (ESI): m/z calcd for C₄₂H₅₅O₇ [M+H]⁺ 671.3942, found 671.3953.
**Compound 15:** To a mixture of 1i (27 mg, 0.125 mmol), 1,3,5-triethoxybenzene (2b, 79 mg, 0.375 mmol) and FeCl$_3$ (3 mg, 15 mol %) in HFIP (0.5 mL, 0.5M), di-t-butylperoxide (0.069 mL, 0.375 mmol) was added drop-wise at room temperature, stirring was continued for 16 h and the volatiles were removed under reduced pressure. The crude residue was purified by column chromatography; hexane/ethyl acetate 8:2 to afford compound 15 (18 mg, 23% yield) as a white solid.

Characterization data of compound 15: $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 6.78 (dd, $J = 6.9$ Hz, 2H), 6.42 (t, $J = 9$ Hz, 2H), 5.91 (s, 4H), 3.92 (q, $J = 7.0$ Hz, 4H), 3.85 (m, 4H), 3.68 (m, 4H), 2.00 (s, 6H), 1.36 (t, $J = 7.0$ Hz, 6H), 1.20 (t, $J = 7.0$ Hz, 12H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 159.5, 157.5, 150.5, 138.4, 135.2, 132.0, 130.8, 130.8, 121.4, 112.1, 112.0, 91.6, 63.5, 63.4, 15.0, 13.4; $^{19}$F NMR (377 MHz, CDCl$_3$) $\delta$ -119.48; HRMS (ESI): $m/z$ calcd for C$_{38}$H$_{46}$FO$_7$ [M+H]$^+$ 633.3226, found 633.3226.

**Compound 16:** To a mixture of o-cresol (27 mg, 0.25 mmol), 1,3,5-trimethoxybenzene (2a, 42 mg, 0.25 mmol) and FeCl$_3$ (6 mg, 15 mol %) in HFIP (0.5 mL, 0.5M), di-t-butylperoxide (0.046 mL, 0.25 mmol) was added drop-wise at room temperature, stirring was continued for 23 h, while every 4 hours another portion of 2a and di-t-butylperoxide were added up to 3 equivalents in total. The volatiles were removed under reduced pressure. The crude residue was purified by column chromatography; hexane/ethyl acetate 4:6 to afford compound 16 (47 mg, 32% yield) as a white solid.

Characterization data of compound 16: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 6.97 (s, 1H), 6.25 (s, 2H), 5.98 (s, 2H), 5.95 (s, 2H), 3.86 (s, 3H), 3.78 (overlapped, 9H), 3.75 (s, 3H), 3.57 (s, 6H), 3.54 (s, 6H), 2.06 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 161.0, 159.9, 159.4, 158.9, 158.8, 158.6, 150.8, 135.0, 133.5, 126.5, 125.4, 118.4, 113.6, 111.3, 108.1, 91.5, 90.1, 89.8, 56.0, 55.5, 55.3, 55.2, 14.1; HRMS (ESI): $m/z$ calcd for C$_{34}$H$_{39}$O$_{10}$ [M+H]$^+$ 607.2538, found 607.2521.
**Compound 17:** To a mixture of 2,5-dimethylphenol (31 mg, 0.25 mmol), 1,3,5-trimethoxybenzene (2a, 126 mg, 0.75 mmol) and FeCl₃ (6 mg, 15 mol %) in TFE/HFIP (1:1, 0.5 mL, 0.5M), di-t-butylperoxide (0.138 mL, 0.75 mmol) was added drop-wise at room temperature, stirring was continued for 5 h and the volatiles were removed under reduced pressure. The crude residue was purified by column chromatography; hexane/ethyl acetate 4:6 to afford compound 17 (84 mg, 54% yield) as a white solid.

Characterization data of compound 17: ¹H NMR (500 MHz, CDCl₃) δ 6.26 (s, 2H), 5.95 (s, 2H), 5.93 (s, 2H), 5.28 (s, 1H), 3.87 (s, 3H), 3.76 (overlapped, 9H), 3.74 (s, 3H), 3.56 (s, 6H), 3.54 (s, 6H), 1.99 (s, 3H), 1.67 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 161.6, 159.8, 159.5, 159.5, 158.8, 158.5, 150.5, 136.1, 135.1, 126.8, 121.3, 118.6, 112.4, 111.5, 106.1, 91.3, 89.9, 89.6, 55.9, 55.5, 55.3, 55.3, 55.2, 53.6, 17.9, 13.7; HRMS (ESI): m/z calcd for C₃₅H₄₁O₁₀ [M+H]⁺ 621.2694, found 621.2686.

**Compound 18:** To a mixture of 2,4,6-trimethylphenol (34 mg, 0.25 mmol), anisole (2c, 81 mg, 0.75 mmol) and FeCl₃ (6 mg, 15 mol %) in HFIP (0.5 mL, 0.5M), di-t-butylperoxide (0.138 mL, 0.75 mmol) was added drop-wise at room temperature, stirring was continued for 7 h and the volatiles were removed under reduced pressure. The crude residue was purified by column chromatography; hexane/diethyl ether 19:1 to afford compound 18 (19 mg, 32% yield) as an orange liquid.

Characterization data of compound 18: ¹H NMR (400 MHz, CDCl₃) δ 7.06 – 7.04 (m, 1H), 7.04 – 7.02 (m, 1H), 6.98 – 6.96 (m, 1H), 6.96 – 6.93 (m, 1H), 6.90 (s, 1H), 4.55 (s, 1H), 3.86 (s, 3H), 2.28 (s, 3H), 1.95 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 158.4, 150.2, 140.5, 133.5, 130.5, 129.3, 128.2, 122.0, 121.7, 113.9, 55.4, 29.9, 20.3, 16.0, 13.6; HRMS (ESI): m/z calcd for C₁₆H₁₉O₂ [M+H]⁺ 243.1385, found 243.1380.
**Compound 19:** To a mixture of 2,6-dimethoxyphenol (1d, 39 mg, 0.25 mmol), 5-methoxy-1,3-benzodioxole (2d, 114 mg, 0.75 mmol) and FeCl₃ (6 mg, 15 mol %) in HFIP (0.5 mL, 0.5M), di-tert-butylperoxide (0.138 mL, 0.75 mmol) was added drop-wise at room temperature, stirring was continued for 4h and the volatiles were removed under reduced pressure. The crude residue was purified by column chromatography; hexane/ethyl acetate 4:1 to afford compound 19 (65 mg, 80% yield).

Characterization data of compound 19: 

\[ ^1H \text{NMR} (400 \text{ MHz, } \text{CDCl}_3) \delta 6.82 (s, 1H), 6.71 (s, 2H), 6.62 (s, 1H), 5.95 (s, 2H), 5.59 (s, 1H), 3.90 (s, 6H), 3.73 (s, 3H); ^13C \text{NMR} (100 \text{ MHz, } \text{CDCl}_3) \delta 151.7, 147.2, 146.7, 141.5, 133.9, 129.6, 123.4, 110.3, 106.5, 101.3, 95.6, 56.9, 56.4; \text{HRMS (ESI): } m/z \text{ calcld for C}_{16}\text{H}_{17}\text{O}_6 [M+H]^+ 305.0975, \text{ found } 305.1020. \]

**Compound 20:** To a mixture of 2,6-dimethoxyphenol (1d, 39 mg, 0.25 mmol), 5-methoxy-1,3-benzodioxole (2d, 114 mg, 0.75 mmol) and FeCl₃ (6 mg, 15 mol %) in HFIP (0.5 mL, 0.5M), di-tert-butylperoxide (0.138 mL, 0.75 mmol) was added drop-wise at room temperature, stirring was continued for 25h and the volatiles were removed under reduced pressure. The crude residue was purified by column chromatography (from hexane/ethyl acetate 17:3 to 4:1) affording a mixture of compound 20 (36 mg, 32% yield) as a brown solid and compound 19 (18 mg, 23% yield).

Characterization data of compound 20: 

\[ ^1H \text{NMR} (400 \text{ MHz, } \text{CDCl}_3) \delta 6.86 (s, 1H), 6.74 (s, 2H), 6.64 (s, 1H), 6.63 (s, 1H), 6.26 (s, 1H), 5.97 (s, 2H), 5.84 (s, 2H), 3.91 (s, 3H), 3.78 (s, 6H), 3.75 (s, 3H); ^13C \text{NMR} (100 \text{ MHz, } \text{CDCl}_3) \delta 152.9, 151.9, 147.2, 146.7, 141.5, 133.9, 129.6, 123.4, 110.4, 101.5, 101.1, 97.3, 97.1, 95.8, 57.9, 57.0, 56.4, 29.8; \text{HRMS (ESI): } m/z \text{ calcld for C}_{24}\text{H}_{23}\text{O}_9 [M+H]^+ 455.1337, \text{ found } 455.1337. \text{ IR (KBr pellet): } 2430(\text{m}), 1590(\text{s}), 1230(\text{s}), 1130 (\text{s}), 1090(\text{s}) \text{ cm}^{-1}. \]
Compound 21: To a mixture of 19 (54 mg, 0.18 mmol), 1,3,5-trimethoxybenzene (2a, 91 mg, 0.53 mmol) and FeCl₃ (43 mg, 15 mol %) in HFIP (0.4 mL, 0.5M), di-t-butylperoxide (0.100 mL, 0.53 mmol) was added drop-wise at room temperature, stirring was continued for 5 h and the volatiles were removed under reduced pressure. The crude residue was purified by column chromatography; hexane/ethyl acetate 4:1 to afford compound 21 (56 mg, 67% yield) as a yellow solid.

Characterization data of compound 21: ¹H NMR (400 MHz, CDCl₃) δ 6.83 (s, 1H), 6.69 (s, 2H), 6.60 (s, 1H), 6.14 (s, 2H), 5.93 (s, 2H), 3.76 (s, 3H), 3.72 (overlapped, 12H), 3.68 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 155.5, 152.3, 151.7, 151.1, 147.2, 141.6, 136.8, 132.4, 123.5(×2), 110.2, 108.0, 101.3, 96.1, 92.3, 56.6, 56.6, 55.5; HRMS (ESI): m/z calcd for C₂₅H₂₆O₉Na [M+Na]⁺ 493.1469, found 493.1469.

Compound 22: To a mixture of 2,6-dimethoxyphenol (1d, 39 mg, 0.25 mmol), 1,2,3-trimethoxybenzene (2e, 126 mg, 0.75 mmol) and FeCl₃ (6 mg, 15 mol %) in HFIP (0.5 mL, 0.5M), di-t-butylperoxide (0.138 mL, 0.75 mmol) was added drop-wise at room temperature, stirring was continued for 3 h and the volatiles were removed under reduced pressure. The crude residue was purified by column chromatography; hexane/ethyl acetate 4:1 to afford compound 22 (33 mg, 40% yield) as an orange liquid.

Characterization data of compound 22: ¹H NMR (400 MHz, CDCl₃) δ 7.03 (d, J = 8.6 Hz, 1H), 6.77 – 6.70 (m, 3H), 5.54 (s, 1H), 3.93 (s, 3H), 3.91 (s, 6H), 3.90 (s, 3H), 3.67 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 153.1, 151.4, 146.9, 142.7, 134.0, 129.5, 128.8, 124.7, 107.6, 106.1, 61.2, 61.0, 56.5, 56.2; HRMS (ESI): m/z calcd for C₁₇H₂₄O₆ [M+H]⁺ 321.1288, found 321.1333. IR (KBr pellet): 3390(s), 2930 (s), 1490(s), 1220(s), 1110(s) cm⁻¹.
**Compound 23:** To a mixture of 22 (22 mg, 0.07 mmol), 1,3,5-trimethoxybenzene (2a, 35 mg, 0.21 mmol) and FeCl₃ (2 mg, 15 mol %) in HFIP (0.14 mL, 0.5M), di-tert-butylperoxide (0.039 mL, 0.21 mmol) was added drop-wise at room temperature, stirring was continued for 3 h and the volatiles were removed under reduced pressure. The crude residue was purified by column chromatography; hexane/ethyl acetate 4:1 to afford compound 23 (23 mg, 71% yield) as a white solid.

Characterization data of compound 23: ¹H NMR (400 MHz, CDCl₃) δ 7.05 (d, J = 8.6 Hz, 1H), 6.73 (s, 2H), 6.71 (s, 1H), 6.14 (s, 2H), 3.92 (s, 3H), 3.88 (s, 3H), 3.77 (s, 3H), 3.73 (s, 6H), 3.72 (s, 6H), 3.61 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 155.5, 153.0, 152.3, 152.3, 151.4, 142.7, 136.9, 132.3, 128.8, 124.7, 107.5, 107.4, 92.4, 61.3, 60.9, 56.9, 56.7, 56.2, 55.6; HRMS (ESI): m/z calcd for C₁₂₆H₁₃Ο₉ [M+H]⁺ 487.1963, found 487.1942.

**Compound 24:** To a mixture of 2,6-dimethoxyphenol (1d, 39 mg, 0.25 mmol), 2,6-dimethoxynaphthalene (2f, 141 mg, 0.75 mmol) and FeCl₃ (6 mg, 15 mol %) in HFIP (0.5 mL, 0.5M), di-tert-butylperoxide (0.138 mL, 0.75 mmol) was added drop-wise at room temperature, stirring was continued for 3 h and the volatiles were removed under reduced pressure. The crude residue was purified by column chromatography; hexane/ethyl acetate 10:1 to afford compound 24 (39 mg, 44% yield) as a yellow solid.

Characterization data of compound 24: ¹H NMR (400 MHz, CDCl₃) δ 7.76 (d, J = 9.0 Hz, 1H), 7.47 (d, J = 9.3 Hz, 1H), 7.34 (d, J = 9.0 Hz, 1H), 7.14 (d, J = 2.5 Hz, 1H), 7.05 (dd, J = 9.3, 2.6 Hz, 1H), 6.59 (s, 2H), 5.62 (s, 1H), 3.92 (s, 3H), 3.88 (s, 6H), 3.84 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 156.2, 152.5, 147.0, 133.9, 130.1, 129.4, 127.6, 127.5, 127.1, 126.0, 119.3, 114.7, 107.7, 105.8, 57.2, 56.4, 55.4; HRMS (ESI): m/z calcd for C₁₂₀H₁₁₈O₅Na [M+Na]⁺ 363.1203, found 363.1189. IR (KBr pellet): 3150 (s), 2910 (m), 1590 (s), 1260 (s), 1110 (s) cm⁻¹.
**Compound 25**: To a mixture of 24 (85 mg, 0.25 mmol), 1,3,5-trimethoxybenzene (2a, 126 mg, 0.75 mmol) and FeCl₃ (6 mg, 15 mol %) in HFIP (0.5 mL, 0.5M), di-t-butylperoxide (0.138 mL, 0.75 mmol) was added drop-wise at room temperature, stirring was continued for 3 h and the volatiles were removed under reduced pressure. The crude residue was purified by column chromatography; hexane/ethyl acetate 7:3 to afford compound 25 (94 mg, 76% yield) as a yellow solid.

Characterization data of compound 25: ¹H NMR (400 MHz, CDCl₃) δ 7.74 (d, J = 9.0 Hz, 1H), 7.48 (d, J = 9.3 Hz, 1H), 7.32 (d, J = 9.0 Hz, 1H), 7.13 (d, J = 2.6 Hz, 1H), 7.04 (dd, J = 9.3, 2.6 Hz, 1H), 6.56 (s, 2H), 6.18 (s, 2H), 3.90 (s, 3H), 3.79 (s, 3H), 3.78 (overlapped, 9H), 3.71 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 156.2, 155.5, 152.5, 152.3, 151.5, 136.8, 132.3, 130.5, 130.2, 129.2, 127.6, 127.1, 126.5, 119.1, 115.4, 109.0, 105.8, 92.6, 57.5, 56.8, 56.7, 55.6, 55.4; HRMS (ESI): m/z calcd for C₂₉H₃₀O₈Na [M+Na]⁺ 529.1833, found 529.1817.

**Compound 26**: To a mixture of 2-methoxy-5-methyl phenol (35 mg, 0.25 mmol), 1,3,5-trimethoxybenzene (2a, 210 mg, 1.25 mmol) and FeCl₃ (6 mg, 15 mol %) in HFIP (0.5 mL, 0.5M), di-t-butylperoxide (0.230 mL, 1.25 mmol) was added drop-wise at room temperature, stirring was continued for 6 h and the volatiles were removed under reduced pressure. The crude residue was purified by column chromatography; hexane/ethyl acetate 4:6 to afford compound 26 (49 mg, 42% yield) as a white solid.

Characterization data of compound 26: ¹H NMR (400 MHz, CDCl₃) δ 6.69 (s, 1H), 6.27 (s, 2H), 6.24 (s, 2H), 5.39 (s, 1H), 3.87 (overlapped, 6H), 3.85 (s, 3H), 3.74 (s, 6H), 3.73 (s, 6H), 1.68 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 161.1, 160.3, 158.9, 158.7, 143.8, 142.3, 130.9, 124.3, 120.4, 113.0, 112.8, 107.1, 91.4, 91.1, 56.1, 56.0, 55.6, 55.4 (x2), 16.6; HRMS (ESI): m/z calcd for C₂₉H₃₁O₈ [M+H]⁺ 471.2013, found 471.2015.
**Compound 27:** To a mixture of 2,4-dimethoxyphenol (39 mg, 0.25 mmol), 1,3,5-trimethoxybenzene (2a, 210 mg, 1.25 mmol) and FeCl₃ (6 mg, 15 mol %) in HFIP (0.5 mL, 0.5M), di-t-butylperoxide (0.230 mL, 1.25 mmol) was added drop-wise at room temperature, stirring was continued for 3 h and the volatiles were removed under reduced pressure. The crude residue was purified by column chromatography; hexane/ethyl acetate 6:4 to afford compound 27 (58 mg, 48% yield) as a white solid.

Characterization data of compound 27: ¹H NMR (500 MHz, CDCl₃) δ 6.51 (d, J = 2.6 Hz, 1H), 6.10 (s, 1H), 5.89 (s, 2H), 5.80 (s, 2H), 3.88 (s, 3H), 3.77 (s, 3H), 3.70 (s, 3H), 3.67 (s, 3H), 3.54 (s, 6H), 3.48 (s, 6H); ¹³C NMR (125 MHz, CDCl₃) δ 160.6, 158.5, 155.1, 154.6, 152.4, 152.0, 142.0, 125.6, 108.6, 107.2, 99.2, 91.7, 89.7, 56.2, 56.1, 55.7, 55.5, 55.4; HRMS (ESI): m/z calcd for C₂₆H₃₀O₉Na [M+Na]⁺ 509.1782, found 509.1781.

**Compound 28a and 28b:** To a mixture of 2-methoxy-4-methylphenol (35 mg, 0.25 mmol), 5-methoxy-1,3-benzodioxole (2d, 114 mg, 0.75 mmol) and FeCl₃ (6 mg, 15 mol %) in HFIP (0.5 mL, 0.5M), di-t-butylperoxide (0.138 mL, 0.75 mmol) was added drop-wise at room temperature, stirring was continued for 3.5 h and the volatiles were removed under reduced pressure. The crude residue was purified by column chromatography; hexane/ethyl acetate 9:1 to afford compound 28a (44 mg, 61% yield) as a yellow liquid and hexane/ethyl acetate 17:2 compound 28b (32 mg, 29% yield) as a white solid.

Characterization data of compound 28a: ¹H NMR (400 MHz, CDCl₃) δ 6.79 (s, 1H), 6.69 (s, 1H), 6.64 (s, 2H), 5.96 (s, 2H), 5.84 (s, 1H), 3.90 (s, 3H), 3.76 (s, 3H), 2.31 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 151.6, 148.0, 147.4, 141.8, 141.0, 129.2, 125.2, 123.7, 119.4, 111.3, 111.2, 101.5, 95.6, 57.3, 56.1, 21.3; HRMS (ESI): m/z calcd for C₁₆H₁₇O₅ [M+H]⁺ 289.1026, found 289.1071.
Characterization data of compound 28b: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 6.75 (d, $J = 1.9$ Hz, 1H), 6.70 (dd, $J = 1.9$, 0.6 Hz, 1H), 6.67 (s, 1H), 6.46 (s, 1H), 6.45 (s, 1H), 6.16 (s, 1H), 5.88 (s, 2H), 5.78 (s, 2H), 3.76 (s, 3H), 3.69 (s, 3H), 3.60 (s, 3H), 2.37 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 152.2, 147.5, 143.5, 143.1, 140.9, 140.8, 140.6, 139.9, 134.7, 133.1, 127.8, 124.3, 118.9, 112.7, 111.0, 101.2, 101.0, 97.9, 97.4, 94.6, 77.2, 58.0, 56.5, 56.1, 21.6; HRMS (ESI): $m/z$ calcd for C$_{24}$H$_{22}$O$_8$Na [M+Na]$^+$ 461.1207, found 461.1195.

**Compound 29**: To a mixture of 2-methoxyphenol (31 mg, 0.25 mmol), 1,3,5-trimethoxybenzene (2a, 210 mg, 1.25 mmol) and FeCl$_3$ (6 mg, 15 mol %) in HFIP (0.5 mL, 0.5M), di-$t$-butylperoxide (0.230 mL, 1.25 mmol) was added drop-wise at room temperature, stirring was continued at 40 °C for 20 h and the volatiles were removed under reduced pressure. The crude residue was purified by column chromatography; hexane/ethyl acetate 4:6 to afford compound 29 (52 mg, 33% yield) as a white solid.

Characterization data of compound 29: $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 6.91 (d, $J = 2.1$ Hz, 1H), 6.60 (d, $J = 2.1$ Hz, 1H), 6.20 (s, 2H), 5.89 (s, 2H), 5.81 (s, 2H), 3.88 (s, 3H), 3.83 (s, 3H), 3.77 (s, 3H), 3.69 (s, 6H), 3.67 (s, 3H), 3.55 (s, 6H), 3.48 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 160.4, 160.2, 158.6, 155.1, 152.0, 151.1, 127.7, 127.4, 124.2, 114.5, 113.6, 92.0, 91.9, 89.9, 56.4, 56.2, 56.0, 55.7, 55.5; HRMS (ESI): $m/z$ calcd for C$_{34}$H$_{38}$O$_{11}$Na [M+Na]$^+$ 645.2306, found 645.2312.
3. Spectral ($^{1}H$ & $^{13}C$) data:

$^{1}H$ NMR spectrum of compound 1b (CDCl$_3$, 400 MHz)

$^{13}C$ NMR spectrum of compound 1b (CDCl$_3$, 100 MHz)
$^1$H NMR spectrum of compound 1ei (CDCl$_3$, 400 MHz)

$^{13}$C NMR spectrum of compound 1ei (CDCl$_3$, 100 MHz)
$^1$H NMR spectrum of compound 1e (CDCl$_3$, 400 MHz)

$^{13}$C NMR spectrum of compound 1e (CDCl$_3$, 100 MHz)
$^1$H NMR spectrum of compound 1f (CDCl$_3$, 400 MHz)

$^{13}$C NMR spectrum of compound 1f (CDCl$_3$, 100 MHz)
$^1$H NMR spectrum of compound 1g (CDCl$_3$, 400 MHz)

$^{13}$C NMR spectrum of compound 1g (CDCl$_3$, 100 MHz)
$^1$H NMR spectrum of compound 1h (CDCl$_3$, 500 MHz)

\[ \text{OH} \]

$^{13}$C NMR spectrum of compound 1h (CDCl$_3$, 125 MHz)

\[ \text{OH} \]
$^1$H NMR spectrum of compound 1i (CDCl$_3$, 500 MHz)

$^{13}$C NMR spectrum of compound 1i (CDCl$_3$, 125 MHz)
$^{19}$F NMR spectrum of compound 1i (CDCl$_3$, 377 MHz)
$^1$H NMR spectrum of compound 3 (CDCl$_3$, 400 MHz)

$^{13}$C NMR spectrum of compound 3 (CDCl$_3$, 100 MHz)
$^1$H NMR spectrum of compound 4 (CDCl$_3$, 500 MHz)

![$^1$H NMR spectrum of compound 4](image)

$^{13}$C NMR spectrum of compound 4 (CDCl$_3$, 125 MHz)

![$^{13}$C NMR spectrum of compound 4](image)
$^1$H NMR spectrum of compound 4a (CDCl$_3$, 400 MHz)

$^{13}$C NMR spectrum of compound 4a (CDCl$_3$, 100 MHz)
$^1$H NMR spectrum of compound 4b (CDCl$_3$, 500 MHz)

![H NMR spectrum of compound 4b](image)

$^{13}$C NMR spectrum of compound 4b (CDCl$_3$, 100 MHz)

![C NMR spectrum of compound 4b](image)
$^1$H NMR spectrum of compound 5 (CDCl$_3$, 400 MHz)

$^{13}$C NMR spectrum of compound 5 (CDCl$_3$, 100 MHz)
$^1$H NMR spectrum of compound 6 (CDCl$_3$, 400 MHz)

$^{13}$C NMR spectrum of compound 6 (CDCl$_3$, 100 MHz)
$^1$H NMR spectrum of compound 7 (CDCl$_3$, 400 MHz)

$^{13}$C NMR spectrum of compound 7 (CDCl$_3$, 100 MHz)
$^1$H NMR spectrum of compound 8 (CDCl$_3$, 500 MHz)

R = OMe

$^{13}$C NMR spectrum of compound 8 (CDCl$_3$, 125 MHz)

R = OMe
$^1$H NMR spectrum of compound 9 (CDCl$_3$, 400 MHz)

$^{13}$C NMR spectrum of compound 9 (CDCl$_3$, 100 MHz)
$^1$H NMR spectrum of compound 10 (CDCl$_3$, 500 MHz)

$^{13}$C NMR spectrum of compound 10 (CDCl$_3$, 125 MHz)
$^1$H NMR spectrum of compound 11 (CDCl$_3$, 400 MHz)

$^{13}$C NMR spectrum of compound 11 (CDCl$_3$, 100 MHz)
$^1$H NMR spectrum of compound 12 (CDCl$_3$, 400 MHz)

$^{13}$C NMR spectrum of compound 12 (CDCl$_3$, 100 MHz)
$^1$H NMR spectrum of compound 13 (CDCl$_3$, 400 MHz)

$^{13}$C NMR spectrum of compound 13 (CDCl$_3$, 100 MHz)
$^1$H NMR spectrum of compound 14 (CDCl$_3$, 500 MHz)

$^{13}$C NMR spectrum of compound 14 (CDCl$_3$, 125 MHz)
$^1$H NMR spectrum of compound 15 (CDCl$_3$, 500 MHz)

$^{13}$C NMR spectrum of compound 15 (CDCl$_3$, 125 MHz)
$^{19}$F NMR spectrum of compound 15 (CDCl$_3$, 377 MHz)

![19F NMR spectrum of compound 15 (CDCl$_3$, 377 MHz)](image_url)
$^1$H NMR spectrum of compound 16 (CDCl$_3$, 400 MHz)

$^{13}$C NMR spectrum of compound 16 (CDCl$_3$, 100 MHz)
$^1$H NMR spectrum of compound 17 (CDCl₃, 500 MHz)

$^{13}$C NMR spectrum of compound 17 (CDCl₃, 125 MHz)
$^1$H NMR spectrum of compound 18 (CDCl$_3$, 400 MHz)

$^{13}$C NMR spectrum of compound 18 (CDCl$_3$, 100 MHz)
$^1$H NMR spectrum of compound 19 (CDCl$_3$, 400 MHz)

$^{13}$C NMR spectrum of compound 19 (CDCl$_3$, 100 MHz)
$^1$H NMR spectrum of compound 20 (CDCl$_3$, 400 MHz)

$^{13}$C NMR spectrum of compound 20 (CDCl$_3$, 100 MHz)
$^1$H NMR spectrum of compound 21 (CDCl$_3$, 400 MHz)

$^{13}$C NMR spectrum of compound 21 (CDCl$_3$, 100 MHz)
$^1$H NMR spectrum of compound 22 (CDCl$_3$, 400 MHz)

$^{13}$C NMR spectrum of compound 22 (CDCl$_3$, 100 MHz)
$^1$H NMR spectrum of compound 23 (CDCl$_3$, 400 MHz)

$^{13}$C NMR spectrum of compound 23 (CDCl$_3$, 100 MHz)
$^1$H NMR spectrum of compound 24 (CDCl$_3$, 400 MHz)

$^{13}$C NMR spectrum of compound 24 (CDCl$_3$, 100 MHz)
$^1$H NMR spectrum of compound 25 (CDCl$_3$, 400 MHz)

$^{13}$C NMR spectrum of compound 25 (CDCl$_3$, 100 MHz)
$^1$H NMR spectrum of compound 26 (CDCl$_3$, 400 MHz)

$^{13}$C NMR spectrum of compound 26 (CDCl$_3$, 100 MHz)
$^1$H NMR spectrum of compound 27 (CDCl$_3$, 500 MHz)

$^{13}$C NMR spectrum of compound 27 (CDCl$_3$, 125 MHz)
$^1$H NMR spectrum of compound 28a (CDCl$_3$, 400 MHz)

$^{13}$C NMR spectrum of compound 28a (CDCl$_3$, 100 MHz)
$^1$H NMR spectrum of compound **28b** (CDCl$_3$, 400 MHz)

![1H NMR spectrum of compound 28b](image)

$^{13}$C NMR spectrum of compound **28b** (CDCl$_3$, 100 MHz)

![13C NMR spectrum of compound 28b](image)
$^1$H NMR spectrum of compound 29 (CDCl$_3$, 500 MHz)

$^{13}$C NMR spectrum of compound 29 (CDCl$_3$, 100 MHz)