JOC The Journal of Organic Chemistry
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A Direct and Mild Formylation Method for Substituted Benzenes Utilizing Dichloromethyl Methyl Ether–Silver Trifluoromethanesulfonate

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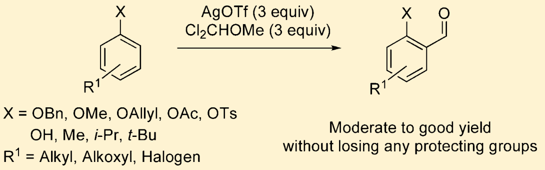
Ⓢ *Supporting Information*

ABSTRACT: A silver trifluoromethanesulfonate (AgOTf)-promoted direct and mild formylation of benzenes has been developed. The reaction utilizing dichloromethyl methyl ether (Cl_2CHOMe) and AgOTf powerfully formylated various substituted benzenes under temperature conditions as low as −78 °C without losing the protecting groups on the phenolic hydroxyl group.



Many formylation reactions of aromatic compounds have been reported over the last decades.[1] Reimer and Tiemann first reported the direct formylation reaction of benzenes known as the Reimer–Tiemann reaction, which utilized dichlorocarbene generated from chloroform under strongly basic conditions. This formylation reaction has been applied to the synthesis of vanillin on an industrial scale.[2] Similar to the Reimer–Tiemann reaction, a Friedel–Crafts electrophilic aromatic substitution, such as Gatterman reaction, is useful to introduce a formyl group onto a benzene ring.[3] In particular, the Vilsmeier–Haack reaction has been widely utilized in current organic syntheses because of facile in situ preparation of the reactive species generated from $POCl_3$ and DMF.[4] Related concise reaction conditions, such as the Duff reaction, have been found.[5] A reaction utilizing dichloromethyl methyl ether (Cl_2CHOMe) as a formylating reagent for benzenes[6] is also well-known and has been applied to the natural product syntheses.[7] Dichloromethyl methyl ether can act as a formyl chloride equivalent for the formylation, and the active species can be readily generated in situ in the presence of a Friedel–Crafts catalyst such as strong Lewis acids, i.e., $TiCl_4$, $SnCl_4$, and $AlCl_3$. The formylations via electrophilic aromatic substitution of phenol derivatives **2** are facile and efficient methods to obtain the corresponding benzaldehyde derivatives **1**. However, partial removal of the protecting group of the phenols **2** was often observed because formylation proceeds under harsh conditions such as highly acidic conditions (Figure 1).[8] Therefore, a formylation method for alkoxybenzenes without losing the protecting groups would be an attractive and useful method in organic syntheses. Herein, we report the direct formylation method for alkyl- or alkoxybenzenes utilizing the highly reactive formylating reagent, Cl_2CHOMe–silver trifluoromethanesulfonate (AgOTf).

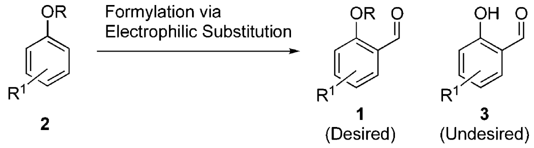


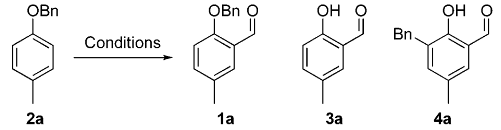
Figure 1. Problematic formylation in protected salicylaldehyde.

The formylation of *p*-benzyloxytoluene **2a** was initially investigated (Table 1). The formylations of **2a** by treatment with phosphorus oxychloride in DMF[4] at 80 °C or *N*-methylformanilide (NMFA) at 100 °C did not proceed, and the substrate was completely recovered (entries 1 and 2). The reaction with hexamethylenetetramine (HMTA)[5] in TFA gave the undesired phenol **4a**. The benzyloxy group at the *ortho*-position of the formyl group in **1a** was easily deprotected under acidic conditions,[9] and a capture of the benzyl cation in Friedel–Crafts fashion concomitantly occurred to provide the undesired phenol **4a** (entry 3).[10] Although it has been reported that Cl_2CHOMe is a highly reactive formylating reagent,[6] the reaction with Cl_2CHOMe–$TiCl_4$ gave a complex mixture because of strong Lewis acid (entry 4). While the formylation with milder Lewis acids $SnCl_4$ and $AlCl_3$ provided an inseparable mixture of the desired **1a** and the debenzylated product **3a** (entries 5 and 6), the reaction of **2a** utilizing AgOTf smoothly proceeded at −78 °C to afford the desired **1a** in 76% yield without formation of the debenzylated product **3a** (entry 7). On the other hand, other Ag salts such as $AgClO_4$, $AgNTf_2$, AgCl, and AgI did not promote the desired formylation of **2a** (entries 8–11); therefore, it should be noted that AgOTf specifically promoted the formylation of *p*-benzyloxytoluene **2a** without loss of a benzyl group.

Under optimal reaction conditions, the scope of the substrate in AgOTf-promoted formylation of substituted benzenes **2** was investigated, and the results are summarized in Table 2. The substrates, *p*-allyloxy- and *p*-methoxytoluenes **2b** and **2c**, were smoothly converted into the corresponding aldehydes **1b** and **1c** without loss of the ethereal protecting groups (entries 1 and 2). On the other hand, acetoxy- and tosyloxytoluenes **2d** and **2e** were not formylated because of the electron-withdrawing

Received: January 24, 2013
Published: March 11, 2013

Table 1. Investigation of the Reaction Conditions for Formylation of 2a



entry	reagent (equiv)	solvent	temp (°C)	time	ratio of **1a**:**3a**[a]	product (yield, %)[b]
1	$POCl_3$ (5)	DMF	80	12 h		no reaction
2	$POCl_3$ (5)	NMFA	100	24 h		no reaction
3	HMTA (1.1)	TFA	reflux	1 h		**4a** (28)
4	Cl_2CHOMe (3)−$TiCl_4$ (3)	CH_2Cl_2	−78	10 min		complex mixture
5	Cl_2CHOMe (3)−$SnCl_4$ (3)	CH_2Cl_2	−78	10 min	4:1	**1a**, **3a**[c]
6	Cl_2CHOMe (3)−$AlCl_3$ (3)	CH_2Cl_2	−78	10 min	1.8:1	**1a**, **3a**[c]
7	Cl_2CHOMe (3)−AgOTf (3)	CH_2Cl_2	−78	10 min	>95:5	**1a** (76)
8	Cl_2CHOMe (3)−$AgClO_4$ (3)	CH_2Cl_2	−78	1 h		complex mixture
9	Cl_2CHOMe (3)−$AgNTf_2$ (3)	CH_2Cl_2	−78	15 min		complex mixture
10	Cl_2CHOMe (3)−AgCl (3)	CH_2Cl_2	rt	1 h		no reaction
11	Cl_2CHOMe (3)−AgI (3)	CH_2Cl_2	rt	1 h		no reaction

[a] The ratio of **1a** and **3a** was determined by crude ^{1}H NMR. [b] Isolated yield. [c] Inseparable mixture of **1a** and **3a**.

protecting group on the phenols (entries 3 and 4). The formylation of anisole **2f** was complete within 5 min at −78 °C, and the product **1f** was concurrently obtained with the regioisomer **1f′** in the ratio of 1:1.5 (entry 5). The formylation of 1,3-dimethoxybenzene **2g** was also smoothly performed at −78 °C to provide **1g** in 58% yield (entry 6). In contrast to the formylation of **2g**, 1,3,5-trimethoxybenzene **2h** was intact at −78 °C but was consumed at 0 °C leading to **1h** in 65% yield and double formylated **1h′** (4%) (entry 7). The anisole derivatives containing electron-withdrawing groups **2i**−**k** were smoothly consumed at −78 °C to regioselectively provide aldehydes **1i**−**k** in moderate yields (entries 8−10). Among the 3,5-dimethylphenol derivatives, methyl ether **2l** smoothly underwent formylation at −78 °C leading to the desired **1l** (51%) and its regioisomer **1l′** (18%) (entry 11). The formylation of phenol **2m** at 0 °C provided the desired **1m** (40%) and **1m′** (15%), although the alkylation of the phenolic hydroxyl group in **2m** was initially faster than the formylation of the benzene ring at −78 °C; therefore, a higher temperature would be required to provide the desired **1m** via a rearrangement of the formyl equivalent onto the benzene ring (entry 12). The formylation of acetate **2n** was also investigated. The substrate **2n** was completely consumed at 0 °C; however, an inseparable mixture of **1n** and its regioisomer **1n′** was obtained in a ratio of 1.2:1 (entry 13).[11] Pentasubstituted benzene **2o** was smoothly formylated to provide the desired **1o** in 70% yield without performing demethylation of the methyl ethers (entry 14). In AgOTf-promoted formylation of alkylbenezene derivatives, the electron-rich 1,3,5-trialkylbenzenes **2p** and **2q** were readily formylated at −78 °C to give **1p** and **1q** in moderate yields, respectively (entries 15 and 16). The formylation of the substrate **2r**, however, did not proceed because of steric hindrance from the *t*-Bu groups (entry 17). Pentamethylbenzene **2s**, known as a radical scavenger, smoothly reacted at −78 °C to give **1s** in 77% yield (entry 18). The formylation of the *mono*-bromobenzene derivative **2t** proceeded at 0 °C to afford **1t** and its regioisomer **1t′** in a ratio of 3:1 (entry 19). Due to the electron-withdrawing effect of a bromine atom, the electrophilic substitution of dibromo substituted **2u** hardly proceeded, thereby a trace amount of **1u** and **1u′** was provided (entry 20). The polycyclic aromatic compound such as **2v** was also tolerated in this condition and the corresponding formylated product **1v** was provided in good yield (entry 21). In addition, the reaction conditions we developed powerfully formylated the electron-deficient heteroaromatics **2w**, 3-formyl indole derivative **1w** was obtained in moderate yield (entry 22).[12]

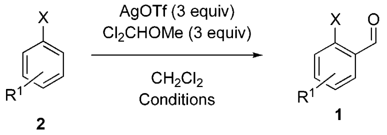
This proposed formylation would proceed via the reaction pathway illustrated in Figure 2. Activation of Cl_2CHOMe by AgOTf may initially occur, leading to a highly active species **5**. Nucleophilic addition of benzenes to **5** preferentially at the *ortho*-position of an electron-rich substituent, such as OR, in a Friedel−Crafts fashion, followed by hydrolysis would provide the corresponding aldehyde **1**. Although highly acidic trifluoromethanesulfonic acid is generated under the reaction conditions, the protecting groups of phenols would be tolerant under a low reaction temperature.

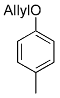
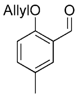
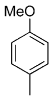
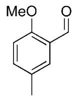
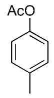
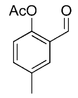
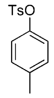
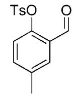
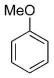
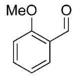
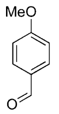
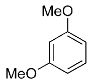
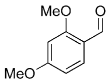
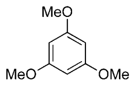
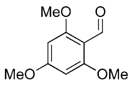
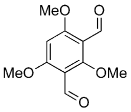
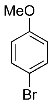
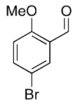
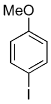
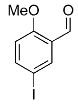
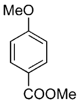
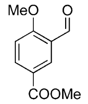
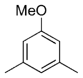
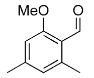
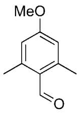
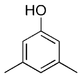
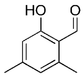
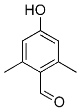
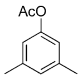
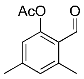
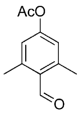
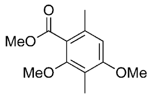
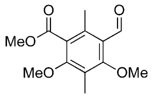
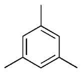
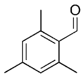
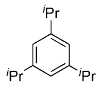
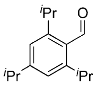
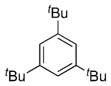
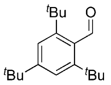
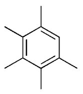
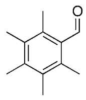
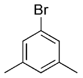
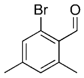
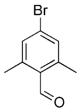
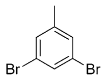
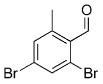
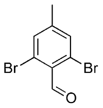
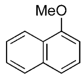
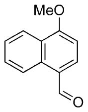
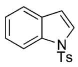
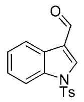
In conclusion, we have demonstrated the formylation of substituted benzenes under mild conditions. A formylating species generated from Cl_2CHOMe−AgOTf is highly reactive, and the formylation of benzenes smoothly proceeded at low temperature (−78−0 °C) to provide the corresponding aldehydes in moderate yields. The protecting groups of phenol such as benzyl, allyl, and methyl ether are tolerant under such reaction conditions; therefore, the reaction should be useful in the synthesis of highly functionalized aromatic compounds.

■ EXPERIMENTAL SECTION

General Techniques. Chemicals and solvents were all purchased from commercial suppliers and used without further purification. All reactions in solution phase were monitored by thin-layer chromatography carried out on glass-packed silica gel plates (60F-254) with UV light and visualized by *p*-anisaldehyde H_2SO_4−ethanol solution or phosphomolybdic acid ethanol solution. Flash column chromatography was carried out with silica gel (40−100 μm) with the indicated solvent system. ^{1}H NMR spectra (400 MHz) and ^{13}C NMR spectra (100 MHz) were recorded in the indicated solvent. Chemical shifts (δ) are reported in units parts per million (ppm) relative to the signal for internal tetramethylsilane (0.00 ppm for ^{1}H) for solutions in chloroform-*d*. NMR spectral data are reported as follows: chloroform-*d* (77.0 ppm for ^{13}C), methanol-d_3 (3.30 ppm for ^{1}H), dimethyl sulfoxide-d_4 (2.49 ppm for ^{1}H and 39.5 ppm for ^{13}C) when internal standard is not indicated. Multiplicities are reported by the following abbreviations: s (singlet), d (doublet), t (triplet), m (multiplet), dd (double doublet), dt (double triplet), dq (double quartet), ddd

Table 2. Scope and Limitation of the Formylation Utilizing $Cl_2CHOMe-AgOTf$



Entry	Substrate	Conditions	Product (Yield %)[a]
1	 **2b**	−78 °C 10 min	 **1b** (76)
2	 **2c**	−78 °C 10 min	 **1c** (69)
3	 **2d**	0 °C 12 h	 **1d** (0)
4	 **2e**	0 °C 12 h	 **1e** (0)
5	 **2f**	−78 °C 10 min	 **1f** (28)  **1f′** (43)
6	 **2g**	−78 °C 5 min	 **1g** (58)
7	 **2h**	0 °C 15 min	 **1h** (65)  **1h′** (4)
8	 **2i**	−78 °C 10 min	 **1i** (61)
9	 **2j**	−78 °C 10 min	 **1j** (51)
10	 **2k**	−78 °C 10 min ;0 °C 20 min	 **1k** (66)
11	 **2l**	−78 °C 10 min	 **1l** (51)  **1l′** (18)
12	 **2m**	0 °C 30 min	 **1m** (40)  **1m′** (15)
13[b]	 **2n**	0 °C 30 min	 **1n**  **1n′**
14	 **2o**	−78 °C 10 min ;0 °C 25 min	 **1o** (70)
15	 **2p**	−78 °C 20 min	 **1p** (69)
16	 **2q**	−78 °C 20 min	 **1q** (72)
17	 **2r**	0 °C 12 h	 **1r** (0)
18	 **2s**	−78 °C 10 min	 **1s** (77)
19	 **2t**	0 °C 10 min	 **1t** (62)  **1t′** (19)
20	 **2u**	rt 1.5 h	 **1u** (3)  **1u′** (2)
21	 **2v**	−78 °C 10 min ;0 °C 10 min	 **1v** (83)
22	 **2w**	−78 °C 10 min ;0 °C 30 min	 **1w** (66)

[a] Isolated yield. [b] Inseparable mixture of **1n** and **1n′** was obtained in 49% yield after column chromatography. The ratio of **1n** and **1n′** was determined to be 1.2:1 by ^{1}H NMR.

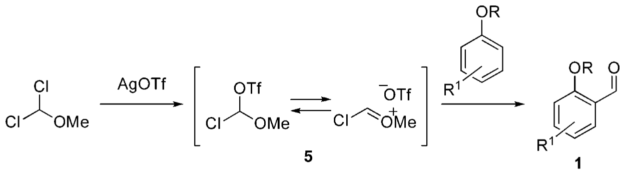


Figure 2. Plausible reaction mechanism of the AgOTf-promoted formylation.

(double double doublet), ddt (double double triplet), *J* (coupling constants in hertz). High-resolution mass spectra were measured on TOF-MS with EI probe. Infrared spectra are reported in reciprocal centimeters (cm^{-1}). Melting points were measured on a melting point apparatus and are not corrected.

1-Benzyloxy-4-methylbenzene (2a).[13] To a solution of 4-methylphenol (541 mg, 5.00 mmol) in DMF (10 mL) were added K_2CO_3 (2.07 g, 15.0 mmol, 3.0 equiv) and benzyl bromide (891 μL, 7.50 mmol, 1.5 equiv) at room temperature under an argon atmosphere. After being stirred at room temperature for 5.5 h, the reaction mixture was filtered through a pad of Celite. The filtrate was diluted with EtOAc and acidified with 3 M HCl. The organic layer was separated, and the aqueous layer was extracted twice with EtOAc. The combined organic layers were washed with brine twice, saturated aq $NaHCO_3$,and brine, dried with $MgSO_4$, and filtered. The filtrate was concentrated in vacuo, and the resulting residue was purified by flash column chromatography on silica gel (eluted with hexane/EtOAc = 20:1) to afford benzyl ether **2a** (906 mg, 4.57 mmol, 91%) as a white solid: mp 37−38 °C (lit.[14] mp 41−42 °C); ^1H NMR (400 MHz, $CDCl_3$) δ 7.31−7.44 (5H, m), 7.08 (2H, d, *J* = 8.4 Hz), 6.88 (2H, d, *J* = 8.4 Hz), 5.04 (2H, s), 2.29 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.7, 137.3, 130.1, 129.9, 128.5, 127.8, 127.4, 115.8, 114.7, 70.0, 20.5; IR (neat) 3031, 2922, 1615, 1585, 1511, 1455, 1239, 1026, 734, 696 cm^{-1}; HREIMS calcd for $C_{14}H_{14}O$ 198.1045, found 198.1036.

1-Allyloxy-4-methylbenzene (2b).[15] To a solution of 4-methylphenol (541 mg, 5.00 mmol) in DMF (10 mL) were added K_2CO_3 (2.07 g, 15.0 mmol, 3.0 equiv) and allyl bromide (648 μL, 7.50 mmol, 1.5 equiv) at room temperature under an argon atmosphere. After being stirred at room temperature for 3.5 h, the reaction mixture was filtered through a pad of Celite. The filtrate was diluted with EtOAc and acidified with 3 M HCl. The organic layer was separated, and the aqueous layer was extracted twice with EtOAc. The combined organic layers were washed with brine twice, saturated aq $NaHCO_3$, and brine, dried with $MgSO_4$, and filtered. The filtrate was concentrated in vacuo, and the resulting residue was purified by flash column chromatography on silica gel (eluted with hexane/EtOAc = 20:1) to afford allyl ether **2b** (622 mg, 4.20 mmol, 84%) as a colorless oil: ^1H NMR (400 MHz, $CDCl_3$) δ 7.07 (2H, d, *J* = 8.8 Hz), 6.82 (2H, d, *J* = 8.8 Hz), 6.01 (1H, ddt, *J* = 17.2, 10.2, 5.2 Hz), 5.40 (1H, dq, *J* = 17.2, 1.4 Hz), 5.27 (1H, dq, *J* = 10.2, 1.4 Hz), 4.51 (2H, dt, *J* = 5.2, 1.4 Hz), 2.28 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.4, 133.5, 129.84, 129.77, 117.2, 114.5, 68.7, 20.3; IR (neat) 3029, 2922, 1613, 1585, 1510, 1291, 1241, 1029, 818 cm^{-1}; HREIMS calcd for $C_{10}H_{12}O$ 148.0888, found 148.0887.

4-Methylphenyl Acetate (2d).[16] To a solution of 4-methylphenol (300 mg, 2.77 mmol) in dry CH_2Cl_2 (5.0 mL) were added triethylamine (965 μL, 6.93 mmol, 2.5 equiv), acetic anhydride (315 μL, 3.33 mmol, 1.2 equiv), and DMAP (16.9 mg, 0.139 mmol, 0.05 equiv) at room temperature under an argon atmosphere. After being stirred at room temperature for 12 h, the reaction mixture was quenched with 3 M HCl. The organic layer was separated, and the aqueous layer was extracted twice with EtOAc. The combined organic layers were washed with saturated aq $NaHCO_3$ and brine, dried with $MgSO_4$, and filtered. The filtrate was concentrated in vacuo, and the resulting residue was purified by flash column chromatography on silica gel (eluted with hexane/EtOAc = 9:1) to afford acetate **2d** (382 mg, 2.54 mmol, 92%) as a colorless oil: ^1H NMR (400 MHz, $CDCl_3$) δ 7.17 (2H, d, *J* = 8.4 Hz), 6.96 (2H, d, *J* = 8.4 Hz), 2.34 (3H, s), 2.28 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.5, 148.5, 135.3, 129.8, 121.2, 20.9, 20.7; IR (neat) 3035, 2925, 1760, 1506, 1369, 1217, 1197, 1166, 909 cm^{-1}; HREIMS calcd for $C_9H_{10}O_2$ 150.0681, found 150.0684.

4-Methylphenyl Tosylate (2e).[17] To a solution of 4-methylphenol (300 mg, 2.77 mmol) in dry CH_2Cl_2 (5.0 mL) were added triethylamine (965 μL, 6. 93 mmol, 2.5 equiv), *p*-toluenesulfonyl chloride (635 mg, 3.33 mmol, 1.2 equiv), and DMAP (16.9 mg, 0.139 mmol, 0.05 equiv) at room temperature under an argon atmosphere. After being stirred at room temperature for 12 h, the reaction mixture was quenched with 3 M HCl. The organic layer was separated, and the aqueous layer was extracted twice with EtOAc. The combined organic layers were washed with saturated aq $NaHCO_3$ and brine, dried with $MgSO_4$, and filtered. The filtrate was concentrated in vacuo, and the resulting residue was purified by flash column chromatography on silica gel (eluted with hexane/EtOAc = 9:1) to afford tosylate **2e** (629 mg, 2.40 mmol, 87%) as a white solid: mp 68−69 °C (lit.[18] mp 68−69 °C); ^1H NMR (400 MHz, $CDCl_3$) δ 7.70 (2H, d, *J* = 8.6 Hz), 7.30 (2H, d, *J* = 8.6 Hz), 7.06 (2H, d, *J* = 8.6 Hz), 6.85 (2H, d, *J* = 8.5 Hz), 2.44 (3H, s), 2.30 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.5, 145.2, 136.7, 132.5, 130.0, 129.7, 128.5, 122.0, 21.7, 20.8; IR (neat) 3041, 1597, 1376, 1198, 1175, 1158, 829, 654 cm^{-1}; HREIMS calcd for $C_{14}H_{14}O_3S$ 262.0664, found 262.0664.

3,5-Dimethylphenyl Acetate (2n).[19] To a solution of 3,5-dimethylphenol (1.00 g, 8.19 mmol) in dry CH_2Cl_2 (10 mL) were added triethylamine (3.41 mL, 24.6 mmol, 3.0 equiv), acetic anhydride (1.08 mL, 11.5 mmol, 1.4 equiv), and DMAP (20.0 mg, 0.164 mmol, 0.02 equiv) at room temperature under an argon atmosphere. After being stirred at room temperature for 2 h, the reaction mixture was quenched with 3 M HCl. The organic layer was separated, and the aqueous layer was extracted twice with EtOAc. The combined organic layers were washed with saturated aq $NaHCO_3$ and brine, dried with $MgSO_4$, and filtered. The filtrate was concentrated in vacuo, and the resulting residue was purified by flash column chromatography on silica gel (eluted with hexane/EtOAc = 9:1) to afford acetate **2n** (1.30 g, 7.92 mmol, 97%) as a colorless oil: ^1H NMR (400 MHz, $CDCl_3$) δ 6.86 (1H, s), 6.70 (2H, s), 2.31 (3H, s), 2.28 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.4, 150.4, 139.0, 127.3, 119.0, 21.0, 20.8; IR (neat) 2921, 1761, 1618, 1591, 1369, 1210, 1137, 1032, 677 cm^{-1}; HREIMS calcd for $C_{10}H_{12}O_2$ 164.0837, found 164.0823.

Methyl 2,4-Dimethoxy-3,6-dimethylbenzoate (2o). To a solution of methyl 2,4-dihydroxy-3,6-dimethylbenzoate[20] (1.00 g, 5.10 mmol) in DMF (10 mL) were added K_2CO_3 (5.64 g, 40.8 mmol, 8.0 equiv) and methyl iodide (925 μL, 20.4 mmol, 4.0 equiv) at room temperature under an argon atmosphere. After being stirred at 50 °C for 9 h, the reaction mixture was filtered through a pad of Celite. The filtrate was diluted with EtOAc and acidified with 3 M HCl. The organic layer was separated, and the aqueous layer was extracted twice with EtOAc. The combined organic layers were washed with brine twice, saturated aq $NaHCO_3$, and brine, dried with $MgSO_4$, and filtered. The filtrate was concentrated in vacuo, and the resulting residue was purified by flash column chromatography on silica gel (eluted with hexane/EtOAc = 9:1) to afford methyl ether **2o** (1.12 g, 5.01 mmol, 98%) as a colorless oil. **2o**: ^1H NMR (400 MHz, $CDCl_3$) δ 6.46 (1H, S), 3.90 (3H, s), 3.82 (3H, s), 3.75 (3H, s), 2.30 (3H, s), 2.10 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.8, 159.2, 156.5, 134.5, 120.6, 117.0, 107.6, 61.6, 55.4, 51.8, 19.6, 8.5; IR (neat) 2949, 1733, 1605, 1579, 1464, 1322, 1277, 1154, 1121 cm^{-1}; HREIMS calcd for $C_{12}H_{16}O_4$ 224.1049, found 224.1052.

General Procedure for the Formylation of the Benzenes 2 Utilizing Cl_2CHOMe−AgOTf. To a suspension of substrate **2** (1.00 mmol) and AgOTf (3.00 mmol, 3.0 equiv) in dry CH_2Cl_2 (1.5 mL/mmol) was added a solution of Cl_2CHOMe (3.00 mmol, 3.0 equiv) in dry CH_2Cl_2 (0.5 mL/mmol) at −78 °C under an argon atomosphere. After being stirred at the optimal temperature (see, Table 2), the reaction mixture was quenched with saturated aqueous $NaHCO_3$. After being stirred at room temperature for 30 min, the reaction mixture was filtered through a pad of Celite. The organic layer was separated and the aqueous layer was extracted twice with EtOAc. The combined organic layers were washed with brine, dried with $MgSO_4$, and filtered. The filtrate was concentrated in vacuo, and the resulting residue was purified by flash column chromatography on silica gel (eluted with hexane/EtOAc = 50/1−1/4) to afford the desired benzaldehyde derivative **1**.

*2-Benzyloxy-4-methylbenzaldehyde (**1a**):*[21] yield 76% (172 mg, 0.760 mmol); white solid; mp 56−57 °C (lit.[22] mp 58.5−59 °C); R_f 0.52 (hexane/EtOAc = 4:1); ^{1}H NMR (400 MHz, CDCl$_3$) δ 10.5 (1H, s), 7.65 (1H, d, J = 2.0 Hz), 7.31−7.44 (6H, m), 6.94 (1H, d, J = 8.4 Hz), 5.15 (2H, s), 2.30 (3H, s); ^{13}C NMR (100 MHz, CDCl$_3$) δ 189.8, 159.1, 136.5, 136.2, 130.4, 128.6, 128.4, 128.2, 127.2, 124.8, 113.0, 70.5, 20.2; IR (neat) 3033, 2923, 2861, 1685, 1612, 1583, 1500, 1286, 1246, 1220, 1160, 1025, 725, 696 cm^{-1}; HREIMS calcd for C$_{15}$H$_{14}$O$_2$ 226.0994, found 226.0978.

*2-Allyloxy-4-methylbenzaldehyde (**1b**):*[23] yield 69% (122 mg, 0.691 mmol); yellowish oil; R_f 0.53 (hexane/EtOAc = 4:1); ^{1}H NMR (400 MHz, CDCl$_3$) δ 10.5 (1H, s), 7.64 (1H, d, J = 2.4 Hz), 7.33 (1H, dd, J = 8.2, 2.4 Hz), 6.88 (1H, d, J = 8.2 Hz), 6.07 (1H, ddt, J = 17.2, 10.6, 5.0 Hz), 5.44 (1H, dq, J = 17.2, 1.4 Hz), 5.33 (1H, dq, J = 10.6, 1.4 Hz), 4.63 (1H, dt, J = 5.0, 1.4 Hz), 2.31 (3H, s); ^{13}C NMR (100 MHz, CDCl$_3$) δ 189.8, 159.0, 136.4, 132.5, 130.2, 128.3, 124.7, 117.8, 112.8, 69.2, 20.2; IR (neat) 2860, 1685, 1612, 1496, 1284, 1247, 1224, 1161, 995 cm^{-1}; HREIMS calcd for C$_{11}$H$_{12}$O$_2$ 176.0837, found 176.0823.

*2-Methoxy-4-methylbenzaldehyde (**1c**):*[24] yield 60% (89.4 mg, 0.595 mmol); yellowish oil; R_f 0.53 (hexane/EtOAc = 4:1); ^{1}H NMR (400 MHz, CDCl$_3$) δ 10.4 (1H, s), 7.63 (1H, d, J = 2.4 Hz), 7.36 (1H, dd, J = 8.4, 2.4 Hz), 6.89 (1H, d, J = 8.4 Hz), 3.91 (3H, s), 2.32 (3H, s); ^{13}C NMR (100 MHz, CDCl$_3$) δ 189.9, 159.9, 136.5, 129.9, 128.4, 124.4, 111.5, 55.6, 20.1; IR (neat) 2946, 2863, 1680, 1611, 1583, 1497, 1394, 1285, 1254, 1157, 1029 cm^{-1}; HREIMS calcd for C$_9$H$_{10}$O$_2$ 150.0681, found 150.0670.

*2-Methoxybenzaldehyde (**1f**):*[25] yield 28% (38.6 mg, 0.284 mmol), an orange oil; R_f 0.27 (hexane/EtOAc = 9:1); ^{1}H NMR (400 MHz, CDCl$_3$) δ 10.5 (1H, s), 7.83 (1H, dd, J = 7.6, 1.6 Hz), 7.56 (1H, ddd, J = 8.4, 7.6, 1.6 Hz), 7.03 (1H, t, J = 7.6 Hz), 6.89 (1H, d, J = 8.4 Hz), 3.93 (3H, s); ^{13}C NMR (100 MHz, CDCl$_3$) δ 189.8, 161.8, 135.9, 128.5, 124.8, 120.6, 111.6, 55.6; IR (neat) 2945, 2845, 1688, 1600, 1484, 1287, 1246, 758 cm^{-1}; HREIMS calcd for C$_8$H$_8$O$_2$ 136.0524, found 136.0518.

*4-Methoxybenzaldehyde (**1f′**):*[26] yield 43% (59.1 mg, 0.434 mmol); yellowish oil; R_f 0.19 (hexane/EtOAc = 9:1); ^{1}H NMR (400 MHz, CDCl$_3$) δ 9.89 (1H, s), 7.85 (2H, d, J = 8.8 Hz), 7.01 (2H, d, J = 8.8 Hz), 3.90 (3H, s); ^{13}C NMR (100 MHz, CDCl$_3$) δ 190.8, 164.5, 131.9, 129.9, 114.2, 55.5; IR (neat) 2841, 1684, 1600, 1577, 1511, 1260, 1160, 834 cm^{-1}; HREIMS calcd for C$_8$H$_8$O$_2$ 136.0524, found 136.0518.

*2,4-Dimethoxybenzaldehyde (**1g**):*[27] yield 58% (96.4 mg, 0.580 mmol); white solid; mp 66−67 °C (lit.[28] mp 69−71 °C); R_f 0.09 (hexane/EtOAc = 9:1); ^{1}H NMR (400 MHz, CDCl$_3$) δ 10.3 (1H, s), 7.82 (1H, d, J = 8.4 Hz), 6.56 (1H, d, J = 8.4 Hz), 6.45 (1H, s), 3.91 (3H, s), 3.88 (3H, s); ^{13}C NMR (100 MHz, CDCl$_3$) δ 188.3, 166.2, 163.6, 130.8, 119.1, 105.7, 97.9, 55.61, 55.59; IR (neat) 2977, 2863, 2781, 1673, 1600, 1580, 1456, 1335, 1285, 1268, 1216, 1028, 829 cm^{-1}; HREIMS calcd for C$_9$H$_{10}$O$_3$ 166.0630, found 166.0616.

*2,4,6-Trimethoxybenzaldehyde (**1h**):*[29] yield 65% (127 mg, 0.647 mmol); white solid; mp 132−133 °C (lit.[29] mp 115−116 °C); R_f 0.18 (hexane/EtOAc = 9:1); ^{1}H NMR (400 MHz, CDCl$_3$) δ 10.4 (1H, s), 6.08 (2H, s), 3.89 (6H, s), 3.88 (3H, s); ^{13}C NMR (100 MHz, CDCl$_3$) δ 187.7, 166.2, 164.1, 108.8, 90.2, 56.0, 55.5; IR (neat) 2975, 2881, 2843, 2796, 1671, 1606, 1578, 1475, 1334, 1230, 1217, 1129, 809 cm^{-1}; HREIMS calcd for C$_{10}$H$_{12}$O$_4$ 196.0736, found 196.0729.

*2,4-Diformyl-1,3,5-trimethoxybenzene (**1h′**):*[30] yield 4% (7.9 mg, 0.0352 mmol); white solid; mp 169−170 °C (lit.[29] mp 70 °C); R_f 0.30 (hexane/EtOAc = 1:4); ^{1}H NMR (400 MHz, CDCl$_3$) δ 10.3 (1H, s), 6.28 (1H, s), 4.01 (6H, s), 3.96 (3H, s); ^{13}C NMR (100 MHz, CDCl$_3$) δ 187.1, 167.9, 167.2, 112.7, 90.9, 64.9, 56.3; IR (neat) 2953, 2859, 1679, 1589, 1559, 1236, 1149, 1106 cm^{-1}; HREIMS calcd for C$_{11}$H$_{12}$O$_5$ 224.0685, found 224.0674.

*5-Bromo-2-methoxybenzaldehyde (**1i**):*[31] yield 61% (132 mg, 0.612 mmol); white solid; mp 116−117 °C (lit.[31] mp 116−119 °C); R_f 0.30 (hexane/EtOAc = 1:4); ^{1}H NMR (400 MHz, CDCl$_3$) δ 10.4 (1H, s), 7.93 (1H, d, J = 2.6 Hz), 7.64 (1H, dd, J = 8.8, 2.6 Hz), 6.90 (1H, d, J = 8.8 Hz), 3.93 (3H, s); ^{13}C NMR (100 MHz, CDCl$_3$) δ 188.3, 160.7, 138.3, 131.0, 126.1, 113.7, 113.5, 56.0; IR (neat) 3103, 2967, 2844, 1674, 1590, 1477, 1389, 1266, 1243, 1178, 1019, 823, 756 cm^{-1}; HREIMS calcd for C$_8$H$_7$BrO$_2$ 213.9629, found 213.9597.

*5-Iodo-2-methoxybenzaldehyde (**1j**):*[32] yield 51% (133 mg, 0.506 mmol); white solid; mp 144−145 °C (lit.[32] mp 142−143 °C); R_f 0.32 (hexane/EtOAc = 9:1); ^{1}H NMR (400 MHz, CDCl$_3$) δ 10.3 (1H, s), 8.10 (1H, d, J = 2.4 Hz), 7.81 (1H, dd, J = 8.8, 2.4 Hz), 6.79 (1H, d, J = 8.8 Hz), 3.92 (3H, s); ^{13}C NMR (100 MHz, CDCl$_3$) δ 188.2, 161.4, 144.1, 137.0, 126.5, 114.1, 83.0, 55.8; IR (neat) 2963, 1671, 1584, 1472, 1389, 1268, 1244, 1176, 1020, 819 cm^{-1}; HREIMS calcd for C$_8$H$_7$IO$_2$ 261.9491, found 261.9498.

*Methyl 3-formyl-4-methoxybenzoate (**1k**):* yield 66% (128 mg, 0.657 mmol); white solid; mp 101−102 °C; R_f 0.17 (hexane/EtOAc = 4:1); ^{1}H NMR (400 MHz, CDCl$_3$) δ 10.5 (1H, s), 8.51 (1H, d, J = 2.2 Hz), 8.25 (1H, dd, J = 9.0, 2.2 Hz), 7.05 (1H, d, J = 9.0 Hz), 4.01 (3H, s), 3.91 (3H, s); ^{13}C NMR (100 MHz, CDCl$_3$) δ 188.8, 165.9, 164.7, 137.1, 130.6, 124.4, 122.9, 111.5, 56.0, 52.1; IR (neat) 2952, 1714, 1685, 1606, 1267, 1125, 761 cm^{-1}; HREIMS calcd for C$_{10}$H$_{10}$O$_4$ 194.0579, found 194.0572.

*4,6-Dimethyl-2-methoxybenzaldehyde (**1l**):* yield 51% (84.0 mg, 0.512 mmol); white solid; mp 48−49 °C; R_f 0.30 (hexane/EtOAc = 9:1); ^{1}H NMR (400 MHz, CDCl$_3$) δ 10.6 (1H, s), 6.64 (1H, s), 6.63 (1H, s), 3.88 (3H, s), 2.55 (3H, s), 2.35 (3H, s); ^{13}C NMR (100 MHz, CDCl$_3$) δ 191.7, 163.3, 145.6, 142.0, 125.0, 121.0, 109.7, 55.7, 22.1, 21.4; IR (neat) 2965, 2926, 1678, 1599, 1319, 1148 cm^{-1}; HREIMS calcd for C$_{10}$H$_{12}$O$_2$ 164.0837, found 164.0829.

*2,6-Dimethyl-4-methoxybenzaldehyde (**1l′**):*[33] yield 18% (28.8 mg, 0.175 mmol); white solid; mp 42−43 °C (lit.[34] 40−41 °C); R_f 0.26 (hexane/EtOAc = 9:1); ^{1}H NMR (400 MHz, CDCl$_3$) δ 10.5 (1H, s), 6.59 (2H, s), 3.84 (3H, s), 2.61 (6H, s); ^{13}C NMR (100 MHz, CDCl$_3$) δ 191.6, 162.7, 144.5, 125.9, 114.8, 55.2, 21.0; IR (neat) 2961, 2923, 1678, 1609, 1462, 1304, 1202, 1097, 832 cm^{-1}; HREIMS calcd for C$_{10}$H$_{12}$O$_2$ 164.0837, found 164.0824.

*4,6-Dimethyl-2-hydroxybenzaldehyde (**1m**):*[35] yield 40% (60.1 mg, 0.402 mmol); white solid (mp 49−50 °C (lit.[6] mp 49 °C); R_f 0.43 (hexane/EtOAc = 4:1); ^{1}H NMR (400 MHz, CDCl$_3$) δ 12.0 (1H, s), 10.2 (1H, s), 6.63 (1H, s), 6.54 (1H, s), 2.56 (3H, s), 2.31 (3H, s); ^{13}C NMR (100 MHz, CDCl$_3$) δ 194.5, 163.4, 149.2, 141.8, 123.1, 116.5, 116.1, 22.1, 17.9; IR (neat) 3412, 2928, 2884, 1641, 1572, 1443, 1311, 1238, 1193, 1038, 804, 757 cm^{-1}; HREIMS calcd for C$_9$H$_{10}$O$_2$ 150.0681, found 150.0668.

*2,6-Dimethyl-4-hydroxybenzaldehyde (**1m′**):*[36] yield 15% (22.6 mg, 0.150 mmol); white solid; mp 194−195 °C (lit.[37] 190−191 °C); R_f 0.21 (hexane/EtOAc = 4:1); ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.3 (1H, s), 6.52 (2H, s), 3.34 (6H, s); ^{13}C NMR (100 MHz, DMSO-d_6) δ 191.4, 161.4, 144.1, 124.3, 116.3, 20.5; IR (neat) 3132, 2961, 2931, 1652, 1603, 1560, 1315, 1272, 1157, 641 cm^{-1}; HREIMS calcd for C$_9$H$_{10}$O$_2$ 150.0681, found 150.0689.

*2-Acetoxy-4,6-dimethylbenzylaldehyde (**1n**) and 4-Acetoxy-2,6-dimethylbenzaldehyde (**1n′**):* yield 49% (determined by ^{1}H NMR, **1n**:**1n′** = 1.2:1). **1n**:[11] colorless oil; R_f 0.20 (hexane/EtOAc = 9:1); ^{1}H NMR (400 MHz, CDCl$_3$) δ 10.3 (1H, s), 6.95 (1H, s), 6.80 (1H, s), 2.60 (3H, s), 2.36 (3H, s), 2.35 (3H, s); ^{13}C NMR (100 MHz, CDCl$_3$) δ 189.3, 169.5, 152.7, 145.7, 142.3, 130.4, 123.6, 121.7, 21.6, 20.8, 20.2; IR (neat) 2926, 1773, 1691, 1618, 1369, 1202, 1140, 1050 cm^{-1}; HREIMS calcd for C$_{11}$H$_{12}$O$_3$ 192.0786, found 192.0782. **1n′**:[11] a colorless oil; R_f 0.20 (hexane/EtOAc = 9:1); ^{1}H NMR (400 MHz, CDCl$_3$) δ 10.6 (1H, s), 6.85 (2H, s), 2.61 (6H, s), 2.31 (3H, s); ^{13}C NMR (100 MHz, CDCl$_3$) δ 192.2, 168.9, 153.5, 143.5, 130.2, 122.6, 21.1, 20.7; IR (neat) 2927, 1771, 1683, 1596, 1199, 1134 cm^{-1}; HREIMS calcd for C$_{11}$H$_{12}$O$_3$ 192.0786, found 192.0768.

*Methyl 4,6-dimethoxy-2,5-dimethyl-3-formylbenzoate (**1o**):*[38] yield 70% (177 mg, 0.703 mmol); yellowish oil; R_f 0.26 (hexane/EtOAc = 4:1); ^{1}H NMR (400 MHz, CDCl$_3$) δ 10.4 (1H, s), 3.94 (3H, s), 3.84 (3H, s), 3.82 (3H, s), 2.47 (3H, s), 2.23 (3H, s); ^{13}C NMR (100 MHz, CDCl$_3$) δ 191.5, 168.1, 165.1, 160.3, 137.1, 127.2, 124.2, 123.1, 63.1, 61.7, 52.4, 17.2, 8.9; IR (neat) 2950, 1735, 1685, 1570, 1310, 1206, 1106 cm^{-1}; HREIMS calcd for $C_{13}H_{16}O_5$ 252.0998, found 252.0991.

*2,4,6-Trimethylbenzaldehyde (**1p**):*[39] yield 69% (102.3 mg, 0.690 mmol); yellowish oil; R_f 0.35 (hexane/EtOAc = 9:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.6 (1H, s), 6.89 (2H, s), 2.57 (6H, s), 2.31 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.9, 143.8, 141.4, 130.5, 129.9, 21.4, 20.4; IR (neat) 2963, 2922, 2863, 1683, 1609, 1436, 1208, 1148, 852, 782 cm^{-1}; HREIMS calcd for $C_{10}H_{12}O$ 148.0888, found 148.0873.

*2,4,6-Triisopropylbenzaldehyde (**1q**):*[40] yield 72% (168.0 mg, 0.723 mmol); yellowish oil; R_f 0.53 (hexane/EtOAc = 9:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.7 (1H, s), 7.11 (2H, s), 3.60 (2H, septet, J = 6.8 Hz), 3.60 (1H, septet, J = 6.8 Hz), 1.274 (6H, d, J = 6.8 Hz), 1.266 (3H, d, J = 6.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.0, 153.6, 150.4, 121.6, 34.7, 28.7, 24.2, 23.7; IR (neat) 2964, 1691, 1604, 1459, 878 cm^{-1}; HREIMS calcd for $C_{16}H_{24}O$ 232.1827, found 232.1823.

*Pentamethylbenzaldehyde (**1s**):* yield 77% (136 mg, 0.773 mmol); white solid; mp 150−151 °C (lit.[41] 143−148.5 °C); R_f 0.41 (hexane/EtOAc = 9:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.6 (1H, s), 2.42 (6H, s), 2.29 (3H, s), 2.24 (6H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.5, 140.0, 134.5, 133.6, 133.0, 17.6, 16.1; IR (neat) 2921, 2868, 1688, 1566, 1287, 755 cm^{-1}; HREIMS calcd for $C_{12}H_{16}O$ 176.1201, found 176.1181.

*2-Bromo-4,6-dimethylbenzaldehyde (**1t**):* yield 62% (133 mg, 0.621 mmol); white solid; mp 39−40 °C; R_f 0.40 (hexane/EtOAc = 9:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.5 (1H, s), 7.35 (1H, s), 7.01 (1H, s), 2.56 (3H, s), 2.35 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.2, 144.9, 142.6, 132.3, 132.2, 129.1, 128.7, 21.24, 21.16; IR (neat) 2970, 2927, 2858, 2761, 1691, 1601, 1376, 1131, 848 cm^{-1}; HREIMS calcd for C_9H_9BrO 211.9837, found 211.9822.

*4-Bromo-2,6-dimethylbenzaldehyde (**1t′**):*[42] yield 19% (39 mg, 0.186 mmol); white solid; mp 66−67 °C; R_f 0.36 (hexane/EtOAc = 9:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.6 (1H, s), 7.27 (2H, s), 2.59 (6H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.5, 143.0, 132.5, 131.1, 127.7, 20.3; IR (neat) 2964, 2925, 1690, 1577, 1417, 1256, 852 cm^{-1}; HREIMS calcd for C_9H_9BrO 211.9837, found 211.9824.

*2,4-Dibromo-6-methylbenzaldehyde (**1u**):* yield 3% (7.7 mg, 0.0277 mmol); white solid; mp 58−59 °C; R_f 0.41 (hexane/EtOAc = 9:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.5 (1H, s), 7.70 (1H, d, J = 1.6 Hz), 7.39 (1H, d, J = 1.6 Hz), 2.57 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.6, 144.0, 134.4, 134.1, 130.5, 128.7, 127.7, 21.1; IR (neat) 2927, 2869, 1699, 1573, 1537, 1379, 1170, 892, 856, 791 cm^{-1}; HREIMS calcd for $C_8H_6Br_2O$ 275.8785, found 275.8776.

*2,6-Dibromo-4-methylbenzaldehyde (**1u′**):*[43] yield 2% (5.1 mg, 0.0184 mmol); white solid; mp 100−101 °C (lit.[43] mp 95−97 °C); R_f 0.37 (hexane/EtOAc = 9:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.2 (1H, s), 7.48 (2H, s), 2.37 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.9, 145.6, 134.4, 129.6, 125.1, 20.9; IR (neat) 2924, 2865, 2761, 1706, 1587, 1058, 858, 733 cm^{-1}; HREIMS calcd for $C_8H_6Br_2O$ 275.8785, found 275.8795.

*4-Methoxynaphthalene-1-carbaldehyde (**1v**):*[44] yield 77% (143 mg, 0.766 mmol); yellowish oil; R_f 0.16 (hexane/EtOAc = 9:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.2 (1H, s), 9.31 (1H, d, J = 8.4 Hz), 8.34 (1H, d, J = 8.7 Hz), 7.93 (1H, d, J = 8.0 Hz), 7.70 (1H, ddd, J = 8.4, 7.0, 1.2 Hz), 7.58 (1H, ddd, J = 8.7, 7.0, 1.2 Hz), 6.93 (1H, d, J = 8.0 Hz), 4.11 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.2, 160.7, 139.6, 131.8, 129.4, 126.3, 125.4, 124.9, 124.8, 122.3, 102.8, 55.9; IR (neat) 2940, 2846, 1677, 1619, 1513, 1429, 1251, 1220, 1092, 1059, 765 cm^{-1}; HREIMS calcd for $C_{12}H_{10}O_2$ 186.0681, found 186.0669.

*1-[(4-Methylphenyl)sulfonyl]-1H-indole-3-carbaldehyde (**1w**):*[45] yield 66% (198 mg, 0.661 mmol); yellowish solid; mp 146−147 °C (lit.[45] mp 147−149 °C); R_f 0.15 (hexane/EtOAc = 4:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.1 (1H, s), 8.26 (1H, d, J = 7.8 Hz), 8.23 (1H, s), 7.95 (1H, dd, J = 7.8, 1.1 Hz), 7.86 (2H, d, J = 8.4 Hz), 7.41 (1H, dt, J = 7.8, 1.3 Hz), 7.36 (1H, dt, J = 7.8, 1.1 Hz), 7.30 (2H, d, J = 8.4 Hz), 2.38 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.3, 146.1, 136.2, 135.2, 134.4, 130.3, 127.2, 126.3, 125.0, 122.6, 122.4, 113.2, 21.6; IR (neat) 3127, 2824, 1679, 1596, 1541, 1379, 1177, 1100, 970, 748, 661 cm^{-1}; HREIMS calcd for $C_{16}H_{12}NO_3S$ 299.0616, found 299.0615.

*3-Benzyl-2-hydroxy-5-methylbenzaldehyde (**4a**):* yield 28% (63 mg, 0.28 mmol); yellowish powder; mp 74−75 °C; R_f 0.42 (hexane/EtOAc = 9:1); ^{1}H NMR (400 MHz, CD_3OD) δ 9.86 (1H, s), 7.13−7.28 (5H, m), 7.24 (2H, s), 3.95 (2H, s), 2.27 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.6, 157.4, 140.1, 138.6, 131.6, 129.6, 128.9, 128.8, 128.4, 126.1, 120.1, 34.7, 20.3; IR (neat) 3026, 2923, 2851, 1651, 1603, 1452, 1260, 696 cm^{-1}; HREIMS calcd for $C_{15}H_{14}O_2$ 226.0994, found 226.1005.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Copies of ^{1}H and ^{13}C NMR spectra for **1a−1w**, **2o**, and **4a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by Platform for Drug Discovery, Informatics and Structural Life Science from the Ministry of Education, Culture, Sports, Science and Technology, Japan. We also thank to CAMPUS Asia Support for the Formation of a Core Center under the MEXT for financial support (K.O.).

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