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Base-Mediated Aerobic Oxidation of Hagemann's Ester: Competitive Hydroxylation at C-1 and C-3 Positions

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The Hagemann's ester (Fig. 1) has been extensively used for the synthesis of various complex compounds.[1,2] The reason might be due to its highly-functionalized nature and ready availability.[1,2] The reaction of Hagemann's ester and an electrophile can occur theoretically at C-1, C-3, C-5, and C-2' positions (Fig. 1). As an example, however, it has been generally accepted that the site preference for alkylation was C-3, the resulting C-3-alkyl derivatives often being accompanied by small amounts of the C-1-alkyl products.[1a] Although the Hagemann's ester could be air-oxidized to poly-substituted phenol or catechol derivatives, a small piece of work has been reported,[3] to the best of our knowledge. Irie and co-workers examined an aerobic oxidation under the influence of KF/DMSO/O_2 at 60 °C to obtain C-1 oxidation product (62%) along with a trace amount of C-3 oxidation product (1%).[3a] Stoodley and co-workers obtained a C-1 oxidation product only under the influence of excess amounts of activated charcoal (3 days, reflux, 50%).[3b]

Recently, we have synthesized many interesting compounds using an aerobic oxidation under the influence of a base such as DBU and K_2CO_3.[4] Meantime we decided to examine the aerobic oxidation of Hagemann's ester under basic conditions. We imagined that C-1 oxidation would produce either **3a** or **4a**, while **2a** could be produced by C-3 oxidation, as shown in Scheme 1. Thus we prepared compound **1a** from benzaldehyde and methyl acetoacetate according to the reported procedure as a *cis*/*trans* mixture (*ca.* 1:8),[1b,1e,2c,2h] and examined an aerobic oxidation. Initial experiment of **1a** with K_2CO_3/DMF under O_2 balloon atmosphere produced **2a** (25%) and **3a** (35%) in moderate yields. We could not obtain a phenol derivative **4a** at all. Aerobic oxidation of **1a**, most likely *via* the carbanion intermediate **I**, would produce **II** and **3a**. The intermediate **II** was converted to a catechol derivative **2a** by tautomerization and concomitant aerobic oxidation.

The ratio of **2a**/**3a** as well as the combined yields could be improved by modifying the reaction conditions, thus we examined various aerobic oxidation conditions, as shown in Table 1. However, the use of K_2CO_3, DBU, and TBAF (entries 1-3) afforded similar yields of products (60-67%), while the use of imidazole and pyridine was not effective (entries 4 and 5). Solvent effect was also negligible (entries 6-8), unfortunately. Although the difference is small we chose the conditions in entry 7 as the optimum one based on the combined yields.

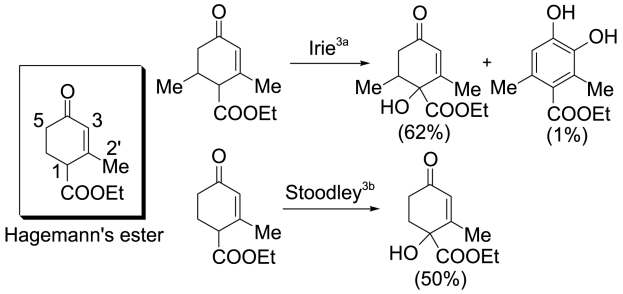
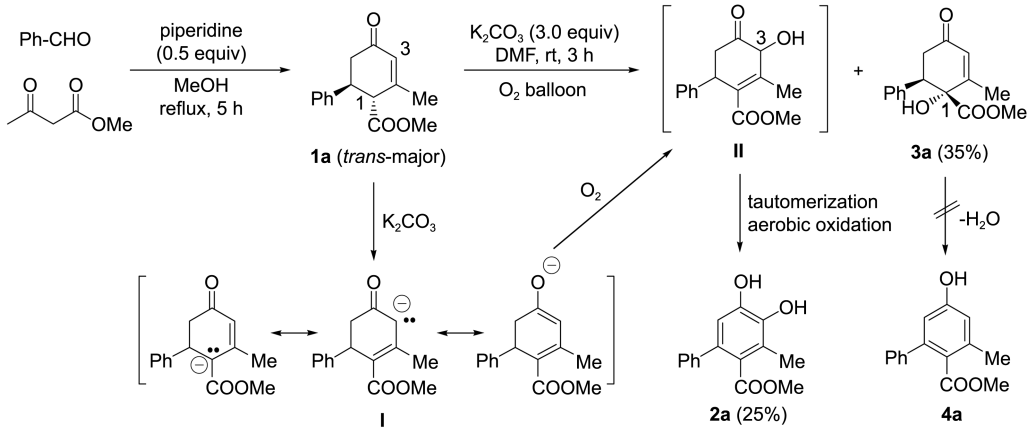


Figure 1. Typical Hagemann's ester and precedent oxidation results.



Scheme 1

Table 1. Oxidation of **1a** under various conditions

Entry	Conditions[a]	**2a** (%)[b] / **3a** (%)[b]
1	K_2CO_3 (3.0 equiv), DMF, rt, 3 h	25 / 35
2	DBU (3.0 equiv), DMF, rt, 3 h	29 / 38
3	TBAF (3.0 equiv), THF, rt, 3 h	24 / 40
4	Imidazole (3.0 equiv), DMF, rt, 24 h	trace / trace
5	pyridine, 100 °C 12 h	0 / 0
6	DBU (3.0 equiv), CH_3CN, rt, 3 h	20 / 31
7	DBU (2.0 equiv), CH_2Cl_2, rt, 5 h	27 / 48
8	DBU (0.5 equiv), DMF, rt, 5 h	23 / 40

[a]Carried out under O_2 balloon. [b]Isolated yield.

In order to check the generality, starting materials **1b-h** were prepared[1,2] and examined an aerobic oxidation under the optimum conditions. The results are summarized in Table 2. In the reactions of 6-aryl derivatives (entries 1-5), the yields of catechol derivatives **2a-e** were low (19-27%), while the yields of C-1 oxidation products **3a-e** were moderate (45-52%). The reaction of 6-pentyl derivative **1f** produced **3f** (59%) as a major product (entry 6). Trace amount of **2f** was observed on TLC; however, we could not obtain **2f** in appreciable amounts. The reaction of 6-methyl derivative **1g** also afforded **3g** (61%) as a major product (entry 7), and this result is similar to that of Irie.[3a] Quite surprisingly, the reaction of **1h** produced catechol **2h** as a major product in moderate yield (47%, entry 8). The different reactivity of **1h** is not clear at this stage.[5]

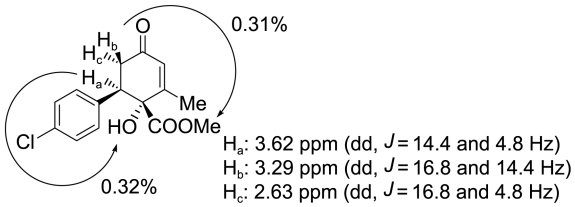


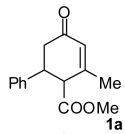
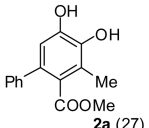
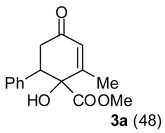
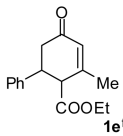
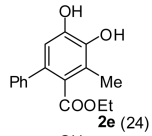
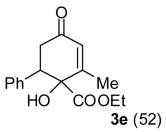
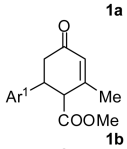
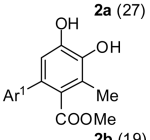
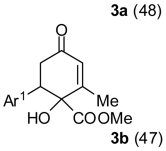
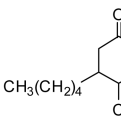
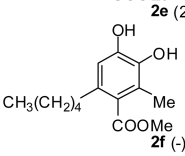
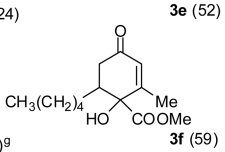
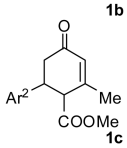
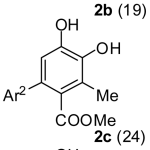
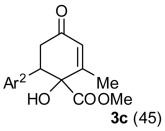
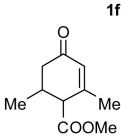
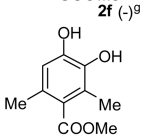
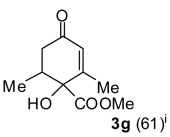
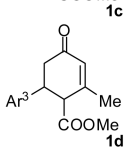
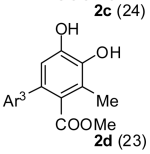
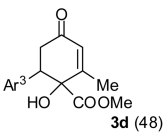
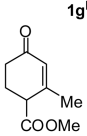
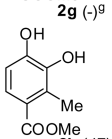
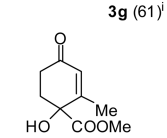
Figure 2. NOE results of compound **3d**.

It is interesting to note that compounds **3a-f** were obtained as single diastereomers although we used *cis*/*trans* mixtures of **1a-f**.[3a] The only exception was 6-methyl derivative **3g** (entry 7). A trace amount of the other diastereomer was contaminated (*ca.* 10%). The stereochemistry of **3a-f** is thought to be as that shown in Figure 2, tentatively.[6] NOE experimental results with **3d** stated that the substituent at C-6 and an ester moiety are positioned in a *cis*-relationship.

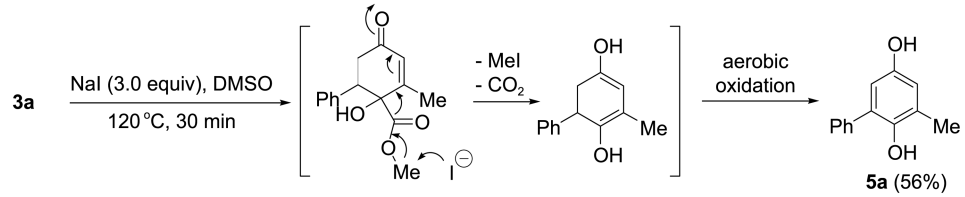
A useful synthetic application of C-1 oxidation products was demonstrated in Scheme 2, with **3a** as a representative example.[7] Treatment of **3a** with NaI in DMSO (120 °C, 30 min) produced **5a** *via* NaI/O_2-assisted concomitant dealkoxycarbonylation/aerobic oxidation.[8]

In summary, we examined an aerobic oxidation of various Hagemann's ester under the influence of DBU in CH_2Cl_2. Hydroxylation at C-1 position is favored to produce 1-

Table 2. DBU-mediated aerobic oxidation of Hagemann's ester

Entry	Substrate[a]	Product (%)[b]		Entry	Substrate[a]	Product (%)[b]	
1	 **1a**	 **2a** (27)	 **3a** (48)	5	 **1e**[f]	 **2e** (24)	 **3e** (52)
2[c]	 **1b**	 **2b** (19)	 **3b** (47)	6	 **1f**	 **2f** (-)[g]	 **3f** (59)
3[d]	 **1c**	 **2c** (24)	 **3c** (45)	7	 **1g**[h]	 **2g** (-)[g]	 **3g** (61)[i]
4[e]	 **1d**	 **2d** (23)	 **3d** (48)	8	 **1h**	 **2h** (47)	 **3h** (-)[g]

[a]Conditions: aldehyde (2.0 mmol), methyl acetoacetate (2.5 equiv), piperidine (0.5 equiv), MeOH, reflux, 5 h. [b]Conditions: DBU (2.0 equiv), CH_2Cl_2, rt, 5 h, O_2 balloon. [c]Ar^1 is 4-MePh. [d]Ar^2 is 4-MeOPh. [e]Ar^3 is 4-ClPh. [f]Ethyl acetoacetate was used. [g]Failed to isolate. [h]Conditions: rt, 2 days. [i]Trace amount (*ca.* 10%) of the other stereoisomer was mixed.



Scheme 2

hydroxycyclohexenone derivatives in moderate yields, while hydroxylation at C-3 position occurred as a minor pathway.

Experimental Section

Typical Procedure for the Preparation of 1a. A stirred solution of benzaldehyde (212 mg, 2.0 mmol), methyl acetoacetate (580 mg, 5.0 mmol), and piperidine (85 mg, 1.0 mmol) in MeOH (6 mL) was heated to reflux for 5 h. After aqueous extractive workup and column chromatographic purification process (hexanes/EtOAc, 6:1) compound **1a** was isolated a white solid, 342 mg (70%).[1b,1e,2c,2h] Other Hagemann's esters (**1b-d**, **1e**,[2d-g] **1f**,[2j] **1g**,[2c] **1h**[2d-g]) were prepared similarly, and the spectroscopic data of unknown compounds, **1b-d** are as follows.

Compound 1b: 60%; white solid, mp 101-102 ºC; IR (KBr) 1737, 1674, 1632, 1435 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.96 (s, 3H), 2.32 (s, 3H), 2.57-2.74 (m, 2H), 3.55-3.68 (m, 2H), 3.61 (s, 3H), 6.05 (s, 1H), 7.09 (d, J = 8.7 Hz, 2H), 7.12 (d, J = 8.7 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.00, 22.42, 42.67, 43.42, 52.15, 54.34, 126.90, 128.37, 129.43, 137.02, 137.83, 155.97, 171.85, 197.39; ESIMS *m/z* 259 (M^++H).

Compound 1c: 61%; white solid, mp 74-75 ºC; IR (KBr) 1736, 1672, 1612, 1514, 1436, 1254 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.96 (s, 3H), 2.56-2.73 (m, 2H), 3.53-3.66 (m, 2H), 3.60 (s, 3H), 3.79 (s, 3H), 6.05 (s, 1H), 6.85 (d, J = 8.4 Hz, 2H), 7.13 (d, J = 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 22.36, 42.84, 43.12, 52.13, 54.54, 55.16, 114.06, 128.07, 128.36, 132.88, 156.03, 158.68, 171.88, 197.39; ESIMS *m/z* 275 (M^++H).

Compound 1d: 59%; white solid, mp 106-107 ºC; IR (KBr) 1735, 1669, 1631, 1492, 1435 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.97 (s, 3H), 2.55-2.74 (m, 2H), 3.54-3.70 (m, 2H), 3.62 (s, 3H), 6.06 (s, 1H), 7.16 (d, J = 8.4 Hz, 2H), 7.29 (d, J = 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 22.35, 42.38, 43.17, 52.22, 53.99, 128.37, 128.44, 128.92, 133.13, 139.31, 155.72, 171.52, 196.67; ESIMS *m/z* 279 (M^++H), 281 (M^++2+H).

Typical Procedure for the Synthesis of 2a and 3a. To a stirred solution of **1a** (244 mg, 1.0 mmol) in CH_2Cl_2 (2 mL) was added DBU (304 mg, 2.0 mmol), and the reaction mixture was stirred at room temperature for 5 h under O_2 balloon atmosphere. After aqueous extractive workup and column chromatographic purification process (hexanes/EtOAc, 4:1) compounds **2a** (70 mg, 27%) and **3a** (126 mg, 48%) were isolated. Other entries were carried out similarly, and the spectroscopic data of unknown compounds, **2a-e**, **2h** and **3a-g** are as follows.

Compound 2a: 27%; pale yellow oil; IR (film) 3397, 1697, 1611, 1489 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.26 (s, 3H), 3.55 (s, 3H), 5.49 (br s, 1H), 6.08 (br s, 1H), 6.68 (s, 1H), 7.25-7.36 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 12.76, 52.06, 114.03, 122.75, 126.07, 127.01, 128.04, 128.20, 133.09, 140.70, 141.67, 144.14, 171.04; ESIMS *m/z* 259 (M^++H). Anal. Calcd for $C_{15}H_{14}O_4$: C, 69.76; H, 5.46. Found: C, 69.99; H, 5.62.

Compound 3a: 48%; white solid, mp 117-118 ºC; IR (KBr) 3495, 1736, 1670, 1437, 1234 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.94 (s, 3H), 2.65 (dd, J = 16.8 and 4.5 Hz, 1H), 3.35 (dd, J = 16.8 and 14.7 Hz, 1H), 3.64 (dd, J = 14.7 and 4.5 Hz, 1H), 3.77 (s, 3H), 3.82 (s, 1H), 6.10 (s, 1H), 7.18-7.21 (m, 2H), 7.29-7.33 (m, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 18.86, 39.79, 50.15, 53.55, 78.89, 128.03, 128.26, 128.47, 129.29, 136.92, 158.60, 172.23, 197.79; ESIMS *m/z* 261 (M^++H). Anal. Calcd for $C_{15}H_{16}O_4$: C, 69.22; H, 6.20. Found: C, 69.51; H, 6.07.

Compound 2b: 19%; white solid, mp 164-166 ºC; IR (KBr) 3131, 1719, 1604, 1501, 1299 cm^{-1}; ^1H NMR ($CDCl_3$ + DMSO-d_6, 300 MHz) δ 2.26 (s, 3H), 2.35 (s, 3H), 3.56 (s, 3H), 6.60 (br s, 1H), 6.75 (s, 1H), 7.13 (d, J = 8.4 Hz, 2H), 7.19 (d, J = 8.4 Hz, 2H), 8.70 (br s, 1H); ^{13}C NMR ($CDCl_3$ + DMSO-d_6, 75 MHz) δ 12.79, 20.97, 51.58, 114.03, 122.59, 125.49, 127.82, 128.74, 132.23, 136.20, 138.18, 141.99, 144.76, 170.46; ESIMS *m/z* 273 (M^++H). Anal. Calcd for $C_{16}H_{16}O_4$: C, 70.57; H, 5.92. Found: C, 70.34; H, 6.05.

Compound 3b: 47%; white solid, mp 110-111 ºC; IR (KBr) 3367, 1736, 1666, 1434, 1235 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.93 (s, 3H), 2.33 (s, 3H), 2.62 (dd, J = 16.8 and 4.5 Hz, 1H), 3.32 (dd, J = 16.8 and 14.7 Hz, 1H), 3.59 (dd, J = 14.7 and 4.5 Hz, 1H), 3.68 (s, 1H), 3.77 (s, 3H), 6.08 (s, 1H), 7.07 (d, J = 8.1 Hz, 2H), 7.13 (d, J = 8.1 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 18.86, 20.99, 39.89, 49.80, 53.49, 78.91, 128.07, 129.15, 129.25, 133.84, 137.67, 158.63, 172.29, 197.93; ESIMS *m/z* 275 (M^++H). Anal. Calcd for $C_{16}H_{18}O_4$: C, 70.06; H, 6.61. Found: C, 70.17; H, 6.93.

Compound 2c: 24%; pale yellow oil; IR (film) 3398, 1699, 1610, 1499, 1293 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.22 (s, 3H), 3.59 (s, 3H), 3.79 (s, 3H), 5.76 (br s, 1H), 6.59 (s, 1H), 6.81 (br s, 1H), 6.83 (d, J = 8.7 Hz, 2H), 7.13 (d, J = 8.7 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 12.74, 52.09, 55.22, 113.65, 113.93, 122.56, 125.93, 129.12, 132.48, 133.20, 141.47, 144.18, 158.60, 171.27; ESIMS *m/z* 289 (M^++H). Anal. Calcd for $C_{16}H_{16}O_5$: C, 66.66; H, 5.59. Found: C, 66.43; H, 5.72.

Compound 3c: 45%; white solid, mp 113-114 ºC; IR (KBr) 3490, 1735, 1672, 1612, 1513, 1438, 1257 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.93 (s, 3H), 2.61 (dd, J = 16.8 and 4.5 Hz, 1H), 3.30 (dd, J = 16.8 and 14.7 Hz, 1H), 3.57 (dd, J = 14.7 and 4.5 Hz, 1H), 3.72 (s, 1H), 3.77 (s, 3H), 3.78 (s, 3H), 6.08 (s, 1H), 6.85 (d, J = 8.7 Hz, 2H), 7.12 (d, J = 8.7 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 18.83, 39.98, 49.33, 53.45, 55.08, 78.95, 113.75, 128.84, 129.21 (2C), 158.61, 159.15, 172.23, 197.89; ESIMS *m/z* 291 (M^++H). Anal. Calcd for $C_{16}H_{18}O_5$: C, 66.19; H, 6.25. Found: C, 66.45; H, 6.51.

Compound 2d: 23%; pale yellow solid, mp 156-158 ºC; IR (KBr) 3384, 1718, 1603, 1486, 1304 cm^{-1}; ^1H NMR ($CDCl_3$ + DMSO-d_6, 300 MHz) δ 2.25 (s, 3H), 3.59 (s, 3H), 5.46 (br s, 1H), 5.95 (br s, 1H), 6.63 (s, 1H), 7.17 (d, J = 8.4 Hz, 2H), 7.30 (d, J = 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$ + DMSO-d_6, 75 MHz) δ 12.70, 51.51, 113.81, 122.84, 125.22, 127.99, 129.21, 130.72, 132.42, 139.61, 142.38, 144.88, 169.97; ESIMS *m/z* 293 (M^++H), 295 (M^++2+H). Anal. Calcd for $C_{15}H_{13}ClO_4$: C, 61.55; H, 4.48. Found: C, 61.49; H, 4.41.

Compound 3d: 48%; white solid, mp 98-99 ºC; IR (KBr) 3497, 1735, 1670, 1492, 1246 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.93 (s, 3H), 2.63 (dd, J = 16.8 and 4.8 Hz, 1H), 3.29 (dd, J = 16.8 and 14.4 Hz, 1H), 3.62 (dd, J = 14.4 and 4.8 Hz, 1H), 3.70 (s, 1H), 3.78 (s, 3H), 6.09 (s, 1H), 7.14 (d, J = 8.4 Hz, 2H), 7.30 (d, J = 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$,

75 MHz) δ 18.84, 39.67, 49.35, 53.74, 78.73, 128.65, 129.29, 129.64, 133.93, 135.46, 158.51, 172.19, 197.29; ESIMS *m/z* 295 (M^++H), 297 (M^++2+H). Anal. Calcd for $C_{15}H_{15}ClO_4$: C, 61.13; H, 5.13. Found: C, 61.47; H, 5.44.

Compound 2e: 24%; pale yellow oil; IR (film) 3386, 1690, 1608, 1488, 1300 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.94 (t, *J* = 7.2 Hz, 3H), 2.24 (s, 3H), 4.03 (q, *J* = 7.2 Hz, 2H), 5.74 (br s, 1H), 6.58 (s, 1H), 6.69 (br s, 1H), 7.18-7.32 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 12.70, 13.50, 61.46, 114.02, 122.70, 125.94, 126.94, 128.09, 128.16, 133.11, 140.73, 141.70, 144.18, 171.01; ESIMS *m/z* 273 (M^++H).

Compound 3e: 52%; pale yellow oil; IR (film) 3495, 1731, 1672, 1453, 1234 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.27 (t, *J* = 7.2 Hz, 3H), 1.94 (s, 3H), 2.65 (dd, *J* = 16.5 and 4.2 Hz, 1H), 3.37 (dd, *J* = 16.5 and 14.7 Hz, 1H), 3.64 (dd, *J* = 14.7 and 4.2 Hz, 1H), 3.73 (s, 1H), 4.21 (q, *J* = 7.2 Hz, 2H), 6.10 (s, 1H), 7.21-7.35 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 14.00, 18.78, 39.78, 49.93, 63.20, 78.63, 127.92, 128.34, 128.36, 129.11, 136.88, 158.93, 171.63, 197.93; ESIMS *m/z* 275 (M^++H).

Compound 3f: 59%; pale yellow oil; IR (film) 3500, 1732, 1670, 1437, 1229 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.88 (t, *J* = 6.9 Hz, 3H), 1.17-1.42 (m, 7H), 1.68-1.79 (m, 1H), 1.90 (s, 3H), 2.23-2.34 (m, 1H), 2.46 (dd, *J* = 16.8 and 13.5 Hz, 1H), 2.63 (dd, *J* = 16.8 and 5.1 Hz, 1H), 3.84 (s, 3H), 4.02 (s, 1H), 6.00 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 13.90, 18.66, 22.39, 26.37, 29.62, 31.54, 39.46, 43.83, 53.63, 78.05, 129.28, 159.49, 173.52, 197.97; ESIMS *m/z* 255 (M^++H). Anal. Calcd for $C_{14}H_{22}O_4$: C, 66.12; H, 8.72. Found: C, 66.44; H, 8.56.

Compound 3g: 61%; white solid, mp 89-90 °C; IR (KBr) 3389, 1739, 1657, 1434, 1237 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.00 (d, *J* = 6.0 Hz, 3H), 1.91 (s, 3H), 2.42-2.65 (m, 3H), 3.86 (s, 3H), 4.06 (s, 1H), 6.00 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 15.42, 18.65, 39.03, 42.14, 53.63, 78.45, 129.39, 159.31, 173.29, 197.87; ESIMS *m/z* 199 (M^++H). Anal. Calcd for $C_{10}H_{14}O_4$: C, 60.59; H, 7.12. Found: C, 60.42; H, 7.34.

Compound 2h: 47%; pale yellow solid, mp 160-161 °C; IR (KBr) 3119, 1710, 1611, 1585, 1435, 1298 cm^{-1}; ^1H NMR ($CDCl_3$ + DMSO-d_6, 300 MHz) d 2.50 (s, 3H), 3.83 (s, 3H), 6.70 (br s, 1H), 6.73 (d, *J* = 8.4 Hz, 1H), 7.41 (d, *J* = 8.4 Hz, 1H), 8.90 (br s, 1H); ^{13}C NMR ($CDCl_3$ + DMSO-d_6, 75 MHz) d 12.94, 51.38, 111.58, 121.82, 123.23, 127.23, 142.98, 147.49, 168.08; ESIMS *m/z* 183 (M^++H). Anal. Calcd for $C_9H_{10}O_4$: C, 59.34; H, 5.53. Found: C, 59.56; H, 5.78.

Synthesis of Compound 5a. To a stirred solution of **3a** (104 mg, 0.4 mmol) in DMSO (1 mL) was added NaI (180 mg, 1.2 mmol), and the reaction mixture was heated to 120 °C for 30 min. After aqueous extractive workup and column chromatographic purification process (hexanes/EtOAc, 4:1) compounds **5a** was isolated, 45 mg (56%).

Compound 5a: yellow oil; IR (film) 3444, 1711, 1602, 1468, 1430 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.25 (s, 3H), 4.75 (br s, 1H), 4.91 (br s, 1H), 6.56 (d, *J* = 2.7 Hz, 1H), 6.64 (d, *J* = 2.7 Hz, 1H), 7.38-7.50 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 16.37, 113.94, 117.28, 125.94, 127.90, 128.23, 128.99, 129.27, 137.15, 144.51, 148.56; ESIMS *m/z* 201 (M^++H). Anal. Calcd for $C_{13}H_{12}O_2$: C, 77.98; H, 6.04. Found: C, 77.71; H, 6.37.

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References and Notes

1. For the synthesis of Hagemann's ester and related compounds, see: (a) Pollini, G. P.; Benetti, S.; De Risi, C.; Zanirato, V. *Tetrahedron* **2010**, *66*, 2775-2802 and further references cited therein. (b) Kingsbury, C. A.; Egan, R. S.; Perun, T. J. *J. Org. Chem*. **1970**, *35*, 2913-2918. (c) Gassama, A.; d'Angelo, J.; Cave, C.; Mahuteau, J.; Riche, C. *Eur. J. Org. Chem*. **2000**, 3165-3169. (d) Nour, M.; Tan, K.; Jankowski, R.; Cave, C. *Tetrahedron: Asymmetry* **2001**, *12*, 765-769. (e) Nitta, H.; Takimoto, K.; Ueda, I. *Chem. Pharm. Bull*. **1992**, *40*, 858-863. (f) Yang, Y.-Q.; Chai, Z.; Wang, H.-F.; Chen, X.-K.; Cui, H.-F.; Zheng, C.-W.; Xiao, H.; Li, P.; Zhao, G. *Chem. Eur. J*. **2009**, *13*, 13295-13298.
2. For the synthetic applications of Hagemann's ester, see: (a) Srikrishna, A.; Ramachary, D. B. *Tetrahedron Lett*. **2000**, *41*, 2231-2233. (b) Banerjee, M.; Mukhopadhyay, R.; Achari, B.; Banerjee, A. K. *Synthesis* **2006**, 1263-1272. (c) Majetich, G.; Allen, S. *ARKIVOC* **2010**, *iv*, 104-124. (d) Ramachary, D. B.; Ramakumar, K.; Narayana, V. V. *J. Org. Chem*. **2007**, *72*, 1458-1463. (e) Ramachary, D. B.; Ramakumar, K.; Narayana, V. V. *Chem. Eur. J*. **2008**, *14*, 9143-9147. (f) Ramachary, D. B.; Narayana, V. V.; Ramakumar, K. *Eur. J. Org. Chem*. **2008**, 3907-3911. (g) Ramachary, D. B.; Narayana, V. V.; Prasad, M. S.; Ramakumar, K. *Org. Biomol. Chem*. **2009**, *7*, 3372-3378. (h) Niwas, S.; Bhaduri, A. P. *Synthesis* **1983**, 110-111. (i) Kotnis, A. S. *Tetrahedron Lett*. **1990**, *31*, 481-484. (j) Trost, B. M.; Fortunak, J. M. *J. Am. Chem. Soc*. **1980**, *102*, 2841-2843.
3. For the oxidation of Hagemann's ester, see: (a) Irie, H.; Katakawa, J.; Tomita, M.; Mizuno, Y. *Chem. Lett*. **1981**, 637-640. (b) Sriyani Ananda, G. D.; Cremins, P. J.; Stoodley, R. J. *J. Chem. Soc., Chem. Commun*. **1987**, 882-883.
4. For our recent results on aerobic oxidation, see: (a) Kim, K. H.; Lee, H. S.; Kim, S. H.; Lee, K. Y.; Lee, J.-E.; Kim, J. N. *Bull. Korean Chem. Soc*. **2009**, *30*, 1012-1020. (b) Kim, J. M.; Lee, S.; Kim, S. H.; Lee, H. S.; Kim, J. N. *Bull. Korean Chem. Soc*. **2008**, *29*, 2215-2220. (c) Lee, H. S.; Kim, J. M.; Kim, J. N. *Tetrahedron Lett*. **2007**, *48*, 4119-4122. (d) Kim, S. C.; Lee, K. Y.; Lee, H. S.; Kim, J. N. *Tetrahedron* **2008**, *64*, 103-109. (e) Park, D. Y.; Lee, K. Y.; Gowrisankar, S.; Kim, J. N. *Bull. Korean Chem. Soc*. **2008**, *29*, 701-704. For recent examples of aerobic oxidation by other groups, see: (f) Huang, Y.; Gan, H.; Li, S.; Xu, J.; Wu, X.; Yao, H. *Tetrahedron Lett*. **2010**, *51*, 1751-1753.
5. When we repeated the reaction of Stoodley (activated charcoal, EtOAc, reflux, 24 h), C-1-oxidation product was formed as the major one, as reported.[3b]
6. Trials for obtaining a crystal for X-ray diffraction failed.[3a]
7. For the synthesis and synthetic applications of 1-substituted Hagemann's ester derivatives, see: (a) Cui, H.-F.; Yang, Y.-Q.; Chai, Z.; Li, P.; Zheng, C.-W.; Zhu, S.-Z.; Zhao, G. *J. Org. Chem*. **2010**, *75*, 117-122. (b) Jung, M. E.; Novack, A. R. *Tetrahedron Lett*. **2005**, *46*, 8237-8240. (c) Jung, M. E.; Nishimura, N.; Novack, A. R. *J. Am. Chem. Soc*. **2005**, *127*, 11206-11207. (d) Shapland, P. D. P.; Thomas, E. J. *Tetrahedron* **2009**, *65*, 4201-4211.
8. For NaI/O_2-assisted concomitant dealkoxycarbonylation/aerobic oxidation, see: (a) Lee, H. S.; Kim, S. H.; Kim, Y. M.; Kim, J. N. *Tetrahedron Lett*. **2010**, *51*, 5071-5075. (b) Im, Y. J.; Lee, K. Y.; Kim, T. H.; Kim, J. N. *Tetrahedron Lett*. **2002**, *43*, 4675-4678. (c) Santi, R.; Bergamini, F.; Citterio, A.; Sebastiano, R.; Nicolini, M. *J. Org. Chem*. **1992**, *57*, 4250-4255.