A Convenient Method for Converting Hydroxyacetophenones into Their Ethylene or Trimethylene Acetals

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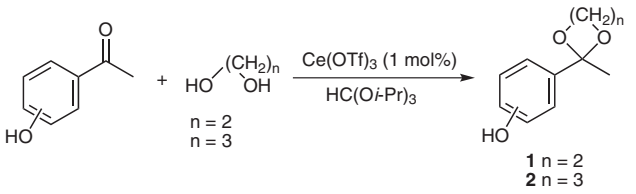
Abstract: Various types of hydroxyacetophenones are efficiently converted into the corresponding ethylene acetals in the presence of ethane-1,2-diol, triisopropyl orthoformate, and a catalytic amount of cerium(III) trifluoromethanesulfonate under mild reaction conditions. The homologous trimethylene acetals can be also prepared in the same way.

Key words: acetal, cerium(III) trifluoromethanesulfonate, hydroxyacetophenone, Lewis acid, protecting group



Scheme 1

Cyclic acetals (ethylene or trimethylene acetals) are one of the most widely used and versatile protecting groups for ketones in organic synthesis because of their stability under basic or slightly acidic conditions.[1] Although the cyclic acetalization of acetophenone usually presents few problems,[2] hydroxyacetophenones cannot undergo acetalization under acid-catalyzed conditions in satisfactory yields. For example, the *p*-toluenesulfonic acid catalyzed condensation of 4-hydroxy-2-methylacetophenone with ethane-1,2-diol is reported to afford only 3-methylphenol, a deacetylation product, in 83% yield.[3] Thus, they are usually prepared by first protecting the phenolic group, then acetalization, followed by removing the protecting group, which generates the desired phenolic acetal.[4] Although Venanzi et al.[5] reported the preparation of hydroxyacetophenone cyclic acetals from the parent ketones and ethane-1,2-diol or propane-1,3-diol using $[Ru(MeCN)_3(triphos)](OTf)_2$ as a Lewis acid catalyst in refluxing benzene, this involves some annoying problems: (1) longer reaction times; (2) failure to afford the desired product in the trimethylene acetalization of 4-hydroxyacetophenone; (3) the use of an expensive Lewis acid catalyst, etc. Thus, the development of more convenient and efficient methods for the preparation of phenolic cyclic acetals are still being pursued.[6] Herein we report an efficient and versatile procedure for the cyclic acetalization of various hydroxyacetophenones using ethane-1,2-diol or propane-1,3-diol and triisopropyl orthoformate in the presence of a catalytic amount of cerium(III) trifluoromethanesulfonate[7] (1 mol%) (Scheme 1).

Initially, we examined the reaction of 2-hydroxyacetophenone as a model substrate with ethane-1,2-diol (1.5 equiv) and triisopropyl orthoformate (1.5 equiv) in the presence of cerium(III) trifluoromethanesulfonate (1 mol%) in hexane at 40 °C (Table 1, entry 1). After 18 hours, the usual workup of the reaction mixture gave the desired 2-(2-hydroxyphenyl)-2-methyl-1,3-dioxolane (**1a**) in 95% isolated yield as the sole product.[8] When this reaction was attempted in the absence of cerium(III) trifluoromethanesulfonate or triisopropyl orthoformate, ethylene acetalization did not proceed at all (entries 2 and 3). A screening of orthoformates revealed that triisopropyl orthoformate gave the best result (entries 1, 4, and 5). The effect of other solvents such as toluene, tetrahydrofuran, ethyl acetate, acetonitrile, and nitromethane were also studied, but in comparison with hexane the yields were found to be considerably lower, probably because the cerium active site is occupied by solvent molecules (entries 6–10). Among metal triflates tested, cerium(III) trifluoromethanesulfonate was the most effective in this acetalization (entries 1 and 11–16). In addition, traditional Brønsted acids and Lewis acids were less active or inert (entries 17–23).

Next, we investigated substrate generality in the cerium(III) trifluoromethanesulfonate catalyzed ethylene acetalization of hydroxyacetophenones with ethane-1,2-diol (1.5 equiv) and triisopropyl orthoformate (1.5 equiv) in hexane (Table 2). The reactions proceeded not only for *o*-hydroxyacetophenone, but also *m*- and *p*-isomers to give the corresponding acetals **1a–c** in high to excellent yields (entries 1–3).[9] It is worthy to note that 4-hydroxy-2-methylacetophenone can be acetalized to give **1d** in quantitative yield under the described reaction conditions without formation of 3-methylphenol (entry 4), which was obtained in substantial amounts when the acetalization was carried out by the conventional *p*-toluenesulfonic acid/ethane-1,2-diol method.[3] In addition, the properties of the substituent groups in the aromatic ring, whether electron-donating group (entry 5) or electron-withdrawing group (entry 6), had no obvious effect on the acetalization under these conditions. The homologous derivatives **2a–f** (trimethylene acetals) could also be made using our protocol, by substituting propane-1,3-diol for ethane-1,2-diol, in

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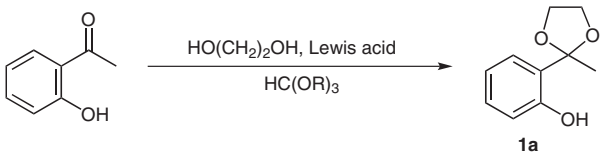
Table 1 Ethylene Acetalization of 2-Hydroxyacetophenone in the Presence of Various Lewis Acids[a]

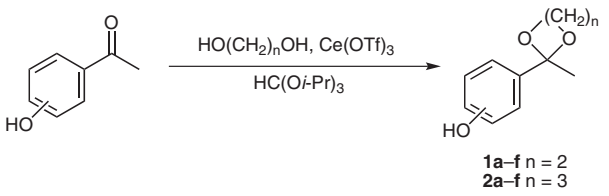


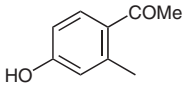
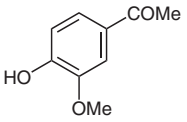
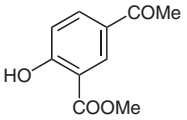
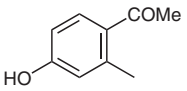
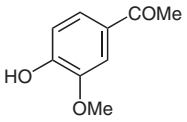
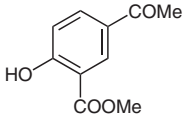
Entry	Lewis acid	Solvent	$HC(OR)_3$	Yield[b] (%)
1	$Ce(OTf)_3$	hexane	$HC(Oi\text{-}Pr)_3$	98 (95)
2[c]	–	hexane	$HC(Oi\text{-}Pr)_3$	0
3[d]	$Ce(OTf)_3$	hexane	–	0
4	$Ce(OTf)_3$	hexane	$HC(OMe)_3$	80
5	$Ce(OTf)_3$	hexane	$HC(OEt)_3$	80
6	$Ce(OTf)_3$	toluene	$HC(Oi\text{-}Pr)_3$	65
7	$Ce(OTf)_3$	THF	$HC(Oi\text{-}Pr)_3$	37
8	$Ce(OTf)_3$	EtOAc	$HC(Oi\text{-}Pr)_3$	46
9	$Ce(OTf)_3$	MeCN	$HC(Oi\text{-}Pr)_3$	0
10	$Ce(OTf)_3$	$MeNO_2$	$HC(Oi\text{-}Pr)_3$	12
11	TMSOTf	hexane	$HC(Oi\text{-}Pr)_3$	68
12	$Sc(OTf)_3$	hexane	$HC(Oi\text{-}Pr)_3$	17
13	$In(OTf)_3$	hexane	$HC(Oi\text{-}Pr)_3$	24
14	$La(OTf)_3$	hexane	$HC(Oi\text{-}Pr)_3$	0
15	$Gd(OTf)_3$	hexane	$HC(Oi\text{-}Pr)_3$	0
16	$Yb(OTf)_3 \cdot 2H_2O$	hexane	$HC(Oi\text{-}Pr)_3$	2
17	p-TsOH·H_2O	hexane	$HC(Oi\text{-}Pr)_3$	5
18	TfOH	hexane	$HC(Oi\text{-}Pr)_3$	79
19	$BF_3 \cdot OEt_2$	hexane	$HC(Oi\text{-}Pr)_3$	3
20	$AlCl_3$	hexane	$HC(Oi\text{-}Pr)_3$	0
21	$Ce(NO_3)_3 \cdot 6H_2O$	hexane	$HC(Oi\text{-}Pr)_3$	0
22	$CeCl_3 \cdot 7H_2O$	hexane	$HC(Oi\text{-}Pr)_3$	0
23	$CeI_3 \cdot 9H_2O$	hexane	$HC(Oi\text{-}Pr)_3$	0

[a] Conditions: o-HOC_6H_4COMe (2.0 mmol), $HO(CH_2)_2OH$ (3.0 mmol), $HC(OR)_3$ (3.0 mmol), Lewis acid (0.02 mmol), solvent (4 mL), 40 °C, 18 h, unless otherwise noted.
[b] The yield was determined by ^1H NMR analysis of the crude products. Isolated yields are given in parentheses.
[c] In the absence of $Ce(OTf)_3$.
[d] In the absence of $HC(Oi\text{-}Pr)_3$.

high to excellent yields (entries 7–12). In particular, it should be noted that 4-hydroxyacetophenone, which undergoes trimethylene acetalization with difficulty by Venanzi's method,[5] could be easily converted into the corresponding trimethylene acetal **2c** in 88% yield (entry 9).

Table 2 Ethylene or Trimethylene Acetalization of Hydroxyacetophenones Using Cerium(III) Trifluoromethanesulfonate[a]



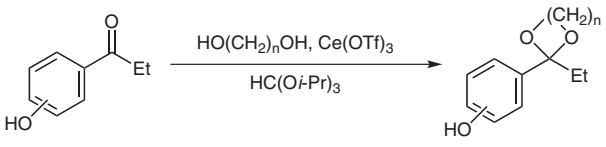
Entry	Substrate	n	Temp, time	Product	Yield[b] (%)
1	o-HOC_6H_4COMe	2	40 °C, 18 h	**1a**	95
2	m-HOC_6H_4COMe	2	25 °C, 1 h	**1b**	99
3	p-HOC_6H_4COMe	2	25 °C, 2 h	**1c**	97
4		2	25 °C, 4 h	**1d**	100
5		2	25 °C, 1 h	**1e**	91
6		2	25 °C, 2 h	**1f**	99
7	o-HOC_6H_4COMe	3	40 °C, 20 h	**2a**	90
8	m-HOC_6H_4COMe	3	25 °C, 1 h	**2b**	98
9	p-HOC_6H_4COMe	3	25 °C, 1.5 h	**2c**	88
10		3	25 °C, 4 h	**2d**	95
11		3	25 °C, 3 h	**2e**	98[c]
12		3	25 °C, 2 h	**2f**	98

[a] Conditions: substrate (2.0 mmol), diol (3.0 mmol), $HC(Oi\text{-}Pr)_3$ (3.0 mmol), $Ce(OTf)_3$ (0.02 mmol), hexane (4 mL).
[b] Isolated yield.
[c] Isolated as the acetate after acetylation (Ac_2O/pyridine) because deacetalization was observed during purification.

Finally, in order to extend the scope of our methodology further, the ethylene or trimethylene acetalization of hydroxypropiophenones was investigated. As shown in Table 3, the reactions proceeded smoothly to give the desired cyclic acetals **3** and **4** in excellent yields without any other side products.

Our protocol is superior to Venanzi's method,[5] which has been claimed to be the best of the previously available procedures for the conversion of hydroxyacetophenones

Table 3 Ethylene or Trimethylene Acetalization of Hydroxypropiophenones Using Cerium(III) Trifluoromethanesulfonate[a]



3a,**b** n = 2
4a,**b** n = 3

Entry	Substrate	n	Temp, time	Product	Yield[b] (%)
1	*o*-HOC_6H_4COEt	2	40 °C, 48 h	**3a**	95
2	*p*-HOC_6H_4COEt	2	25 °C, 2.5 h	**3b**	98
3	*o*-HOC_6H_4COEt	3	40 °C, 48 h	**4a**	94
4	*p*-HOC_6H_4COEt	3	25 °C, 6 h	**4b**	94

[a] Conditions: substrate (2.0 mmol), diol (3.0 mmol), $HC(Oi\text{-}Pr)_3$ (3.0 mmol), $Ce(OTf)_3$ (0.02 mmol), hexane (4 mL).
[b] Isolated yield.

into their respective cyclic acetals. Comparative data are summarized in Table 4.

In conclusion, we have demonstrated an efficient and versatile method for the ethylene or trimethylene acetalization of hydroxyacetophenones using ethane-1,2-diol or propane-1,3-diol and triisopropyl orthoformate catalyzed by cerium(III) trifluoromethanesulfonate. This new method has the following advantages: (1) cerium(III) trifluoromethanesulfonate is commercially available, (2) highly catalytic activity, (3) wide applicability, (4) operational simplicity, (5) mild reaction conditions, (6) high yields.

Melting points were determined on a Büchi 535 melting point apparatus and are uncorrected. The NMR spectra were recorded on a Jeol JNM-LA 500 instrument. Chemical shifts are given as δ values with reference to TMS as an internal standard. Mass spectra were obtained on a Jeol JMS-70 employing EI. Column chromatography was performed on Merck silica gel 60 (70–230 mesh). Et_3N (0.1%) was always used as a mobile-phase additive to prevent deacetalization. All chemicals were purchased from commercial suppliers and used without purification prior to use; $Ce(OTf)_3$ was purchased from Alfa Aesar.

2-(4-Hydroxyphenyl)-2-methyl-1,3-dioxolane (1c); Typical Procedure

To a mixture of 4-hydroxyacetophenone (273 mg, 2.0 mmol), ethane-1,2-diol (187 mg, 3.0 mmol), and $Ce(OTf)_3$ (11.8 mg, 0.02 mmol) in hexane (4 mL) was added $HC(Oi\text{-}Pr)_3$ (571 mg, 3.0 mmol) at 25 °C. The mixture was stirred for 2 h and the mixture was quenched with Et_3N (101 mg, 1.0 mmol) and sat. $NaHCO_3$. The organic materials were extracted with Et_2O containing 0.1% Et_3N, washed with sat. NaCl, dried (Na_2SO_4), and evaporated. Column chromatography of the residue (silica gel, 7% EtOAc–hexane containing 0.1% Et_3N) afforded **1c** (350 mg, 97%); mp 73.9–76.1 °C (Lit.[5] 80–82 °C).

^1H NMR (500 MHz, $CDCl_3$): δ = 1.65 (s, 3 H), 3.75–3.83 (m, 2 H), 4.00–4.07 (m, 2 H), 6.79 (d, *J* = 8.6 Hz, 2 H), 7.35 (d, *J* = 8.6 Hz, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 27.4, 64.2, 109.1, 115.0, 126.7, 134.7, 155.6.

MS (EI, 70 eV): *m*/*z* = 180 $[M]^+$.

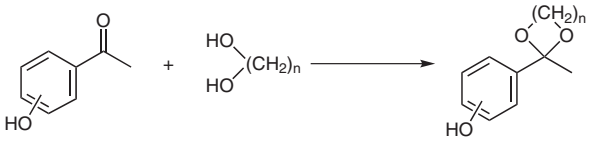
2-(2-Hydroxyphenyl)-2-methyl-1,3-dioxolane (1a)

Mp 61.6–63.2 °C (Lit.[5] 61.5–63.5 °C).

^1H NMR (500 MHz, $CDCl_3$): δ = 1.69 (s, 3 H), 3.83–3.91 (m, 2 H), 4.06–4.13 (m, 2 H), 6.86 (t, *J* = 8.0 Hz, 2 H), 7.19 (t, *J* = 8.0 Hz, 1 H), 7.29 (d, *J* = 8.0 Hz, 1 H), 8.19 (s, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 26.5, 64.3, 109.9, 117.1, 120.0, 126.1, 126.4, 129.9, 154.4.

Table 4 Comparison of Protocols for the Ethylene or Trimethylene Acetalization of Hydroxyacetophenones



1a–c n = 2
2a–c n = 3

Entry	Substrate	n	Product	This work[a]		Venanzi's work[b]	
				Temp, time	Yield (%)	Temp, time	Yield (%)
1	*o*-HOC_6H_4COMe	2	**1a**	40 °C, 18 h	95	reflux, 136 h	93
2	*o*-HOC_6H_4COMe	3	**2a**	40 °C, 20 h	90	reflux, 144 h	95
3	*m*-HOC_6H_4COMe	2	**1b**	25 °C, 1 h	99	reflux, 168 h	94[c]
4	*m*-HOC_6H_4COMe	3	**2b**	25 °C, 1 h	98	reflux, 23 h	99
5	*p*-HOC_6H_4COMe	2	**1c**	25 °C, 2 h	97	reflux, 19 h	95
6	*p*-HOC_6H_4COMe	3	**2c**	25 °C, 1.5 h	88	n.r.[d]	0

[a] Molar ratio: substrate/diol/$HC(Oi\text{-}Pr)_3$/$Ce(OTf)_3$ (1:1.5:1.5:0.01), hexane.
[b] Molar ratio: substrate/diol/$[Ru(MeCN)_3(triphos)](OTf)_2$ (1:5.0:0.0005), benzene, unless otherwise noted.
[c] Molar ratio: substrate/$[Ru(MeCN)_3(triphos)](OTf)_2$ (1:0.001).
[d] No reaction.

MS (EI, 70 eV): *m*/*z* = 180 [M]$^+$.

2-(3-Hydroxyphenyl)-2-methyl-1,3-dioxolane (1b)
Mp 89.1–90.9 °C (Lit.[5] 88–90 °C).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.65 (s, 3 H), 3.76–3.84 (m, 2 H), 4.01–4.08 (m, 2 H), 5.30 (s, 1 H), 6.77 (d, *J* = 7.6 Hz, 1 H), 6.99 (s, 1 H), 7.05 (d, *J* = 7.6 Hz, 1 H), 7.22 (t, *J* = 7.6 Hz, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 27.4, 64.4, 108.9, 112.3, 114.9, 117.4, 129.6, 144.8, 155.8.

MS (EI, 70 eV): *m*/*z* = 180 [M]$^+$.

2-(4-Hydroxy-2-methylphenyl)-2-methyl-1,3-dioxolane (1d)
Mp 97.0–100.2 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.66 (s, 3 H), 2.44 (s, 3 H), 3.69–3.77 (m, 2 H), 3.98–4.05 (m, 2 H), 4.91 (br, 1 H), 6.61 (dd, *J* = 2.8, 8.6 Hz, 1 H), 6.63 (d, *J* = 2.8 Hz, 1 H), 7.40 (d, *J* = 8.6 Hz, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 20.6, 26.4, 63.8, 109.5, 112.1, 118.5, 127.7, 132.7, 137.5, 155.2.

MS (EI, 70 eV): *m*/*z* = 179 [M – CH_3]$^+$.

HRMS (EI): *m*/*z* [M – CH_3]$^+$ calcd for $C_{10}H_{11}O_3$: 179.0708; found: 179.0715.

2-(4-Hydroxy-3-methoxyphenyl)-2-methyl-1,3-dioxolane (1e)
Mp 104.4–108.7 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.65 (s, 3 H), 3.78–3.82 (m, 2 H), 3.90 (s, 3 H), 4.01–4.05 (m, 2 H), 5.61 (s, 1 H), 6.87 (d, *J* = 8.9 Hz, 1 H), 6.97–7.03 (m, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 27.7, 55.9, 64.3, 108.0, 108.8, 114.0, 118.2, 136.3, 145.2, 146.2.

MS (EI, 70 eV): *m*/*z* = 210 [M]$^+$.

HRMS (EI): *m*/*z* [M]$^+$ calcd for $C_{11}H_{14}O_4$: 210.0892; found: 210.0884.

2-[4-Hydroxy-3-(methoxycarbonyl)phenyl]-2-methyl-1,3-dioxolane (1f)
Mp 51.5–53.3 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.63 (s, 3 H), 3.76–3.79 (m, 2 H), 3.95 (s, 3 H), 4.02–4.05 (m, 2 H), 6.95 (d, *J* = 8.6 Hz, 1 H), 7.57 (dd, *J* = 2.5, 8.6 Hz, 1 H), 7.95 (d, *J* = 2.5 Hz, 1 H), 10.75 (s, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 27.4, 52.2, 64.4, 108.3, 111.7, 117.4, 126.6, 132.8, 134.3, 161.2, 170.4.

MS (EI, 70 eV): *m*/*z* = 238 [M]$^+$.

HRMS (EI): *m*/*z* [M]$^+$ calcd for $C_{12}H_{14}O_5$: 238.0841; found: 238.0838.

2-(2-Hydroxyphenyl)-2-methyl-1,3-dioxane (2a)
Mp 61.8–63.6 °C (Lit.[5] 62.5–64.5 °C).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.35 (d-like, *J* = 13.4 Hz, 1 H), 1.57 (s, 3 H), 2.13–2.24 (m, 1 H), 3.87–3.99 (m, 4 H), 6.92 (t-like, *J* = 8.6 Hz, 2 H), 7.22–7.29 (m, 2 H), 8.16 (s, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 24.9, 29.9, 61.6, 101.6, 117.1, 120.1, 123.3, 128.0, 129.9, 154.9.

MS (EI, 70 eV): *m*/*z* = 194 [M]$^+$.

2-(3-Hydroxyphenyl)-2-methyl-1,3-dioxane (2b)
Mp 143.4–144.9 °C (Lit.[5] 143–145 °C).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.27 (d-like, *J* = 13.1 Hz, 1 H), 1.52 (s, 3 H), 2.07–2.19 (m, 1 H), 3.82–3.91 (m, 4 H), 5.63 (br, 1 H), 6.81 (d, *J* = 7.7 Hz, 1 H), 6.98 (s, 1 H), 7.01 (d, *J* = 7.7 Hz, 1 H), 7.28 (t, *J* = 7.7 Hz, 1 H).

^{13}C NMR (125 Hz, $CDCl_3$): δ = 25.3, 32.2, 61.3, 100.9, 113.5, 114.8, 118.8, 130.2, 142.6, 156.6.

MS (EI, 70 eV): *m*/*z* = 194 [M]$^+$.

2-(4-Hydroxyphenyl)-2-methyl-1,3-dioxane (2c)
Mp 143.0–145.6 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.26 (d-like, *J* = 11.3 Hz, 1 H), 1.50 (s, 3 H), 2.05–2.17 (m, 1 H), 3.78–3.89 (m, 4 H), 5.30 (br, 1 H), 6.87 (d, *J* = 8.6 Hz, 2 H), 7.30 (d, *J* = 8.6 Hz, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 25.4, 32.4, 61.6, 100.8, 115.6, 128.2, 132.5, 155.5.

MS (EI, 70 eV): *m*/*z* = 194 [M]$^+$.

HRMS (EI): *m*/*z* [M]$^+$ calcd for $C_{11}H_{14}O_3$: 194.0943; found: 194.0950.

2-(4-Hydroxy-2-methylphenyl)-2-methyl-1,3-dioxane (2d)
Mp 129.4–131.6 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.25 (d-like, *J* = 12.8 Hz, 1 H), 1.51 (s, 3 H), 2.09–2.20 (m, 1 H), 2.36 (s, 3 H), 3.76 (t-like, *J* = 12.2 Hz, 2 H), 3.85 (dd-like, *J* = 5.2, 10.4 Hz, 2 H), 4.70 (s, 1 H), 6.67 (d, *J* = 2.8 Hz, 1 H), 6.69 (dd, *J* = 2.8, 8.6 Hz, 1 H), 7.33 (d, *J* = 8.6 Hz, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.0, 25.4, 30.3, 61.0, 101.6, 112.9, 119.0, 130.0, 138.2, 155.1.

MS (EI, 70 eV): *m*/*z* = 208 [M]$^+$.

HRMS (EI): *m*/*z* [M]$^+$ calcd for $C_{12}H_{16}O_3$: 208.1100; found: 208.1093.

2-(4-Acetoxy-3-methoxyphenyl)-2-methyl-1,3-dioxane (2e)
Mp 136.6–138.2 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.27 (d, *J* = 13.5 Hz, 1 H), 1.51 (s, 3 H), 2.07–2.17 (m, 1 H), 2.33 (s, 3 H), 3.81–3.90 (m, 4 H), 3.84 (s, 3 H), 7.00–7.06 (m 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 20.7, 25.3, 32.4, 56.0, 61.2, 100.3, 110.8, 119.1, 122.9, 139.1, 140.2, 151.4, 169.1.

MS (EI, 70 eV): *m*/*z* = 266 [M]$^+$.

HRMS (EI): *m*/*z* [M]$^+$ calcd for $C_{14}H_{18}O_5$: 266.1154; found: 266.1148.

2-[4-Hydroxy-3-(methoxycarbonyl)phenyl]-2-methyl-1,3-dioxane (2f)
Mp 76.0–77.1 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.28 (d-like, *J* = 13.2 Hz, 1 H), 1.49 (s, 3 H), 2.06–2.16 (m, 1 H), 3.77 (t-like, *J* = 13.4 Hz, 2 H), 3.88 (dd, *J* = 4.9, 12.2 Hz, 2 H), 3.97 (s, 3 H), 7.02 (d, *J* = 8.6 Hz, 1 H), 7.52 (dd, *J* = 2.5, 8.6 Hz, 1 H), 7.90 (d, *J* = 2.5 Hz, 1 H), 10.77 (s, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 25.4, 32.1, 52.3, 61.1, 100.0, 112.4, 118.0, 128.3, 132.0, 134.3, 161.0, 170.5

MS (EI, 70 eV): *m*/*z* = 252 [M]$^+$.

HRMS (EI): *m*/*z* [M]$^+$ calcd for $C_{13}H_{16}O_5$: 252.0998; found: 252.0990.

2-Ethyl-2-(2-hydroxyphenyl)-1,3-dioxolane (3a)
Mp 38.2–39.5 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.93 (t, *J* = 7.3 Hz, 3 H), 1.96 (q, *J* = 7.3 Hz, 2 H), 3.86–3.93 (m, 2 H), 4.05–4.12 (m, 2 H), 6.84–6.88 (m, 2 H), 7.20 (dt–like, *J* = 1.5, 7.7 Hz, 1 H), 7.25 (dd, *J* = 1.5, 7.7 Hz, 1 H), 8.27 (s, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 7.5, 32.5, 64.5, 112.0, 116.9, 119.7, 125.3, 127.1, 129.8, 154.8.

MS (EI, 70 eV): *m*/*z* = 194 $[M]^+$.

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{11}H_{14}O_3$: 194.0943; found: 194.0937.

2-Ethyl-2-(4-hydroxyphenyl)-1,3-dioxolane (3b)
Mp 72.5–75.7 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.87 (t, *J* = 7.3 Hz, 3 H), 1.90 (q, *J* = 7.3 Hz, 2 H), 3.75–3.82 (m, 2 H), 3.97–4.04 (m, 2 H), 6.79 (d, *J* = 8.9 Hz, 2 H), 7.31 (d, *J* = 8.9 Hz, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 8.0, 33.3, 64.4, 111.0, 114.8, 127.2, 134.1, 155.4.

MS (EI, 70 eV): *m*/*z* = 165 $[M - C_2H_5]^+$.

HRMS (EI): *m*/*z* $[M - C_2H_5]^+$ calcd for $C_9H_9O_3$: 165.0552; found: 165.0543.

2-Ethyl-2-(2-hydroxyphenyl)-1,3-dioxane (4a)
Mp 43.1–44.7 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.87 (t, *J* = 7.3 Hz, 3 H), 1.34 (d-like, *J* = 13.4 Hz, 1 H), 1.83 (q, *J* = 7.3 Hz, 2 H), 2.12–2.23 (m, 1 H), 3.87–3.99 (m, 4 H), 6.88–6.93 (m, 2 H), 7.19–7.26 (m, 2 H), 8.20 (s, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 7.1, 25.1, 35.3, 61.5, 103.4, 117.0, 119.7, 122.1, 128.9, 129.8, 155.2.

MS (EI, 70 eV): *m*/*z* = 208 $[M]^+$.

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{12}H_{16}O_3$: 208.1100; found: 208.1107.

2-Ethyl-2-(4-hydroxyphenyl)-1,3-dioxane (4b)
Mp 115.2–118.2 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.79 (t, *J* = 7.4 Hz, 3 H), 1.24 (d-like, *J* = 13.1 Hz, 1 H), 1.74 (q, *J* = 7.4 Hz, 2 H), 2.06–2.16 (m, 1 H), 3.78–3.88 (m, 4 H), 5.16 (br, 1 H), 6.87 (d, *J* = 8.6 Hz, 2 H), 7.26 (d, *J* = 8.6 Hz, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 7.3, 25.7, 37.4, 61.0, 102.6, 115.3, 129.1, 131.0, 155.4.

MS (EI, 70 eV): *m*/*z* = 179 $[M - C_2H_5]^+$.

HRMS (EI): *m*/*z* $[M - C_2H_5]^+$ calcd for $C_{10}H_{11}O_3$: 179.0708; found: 179.0717.

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(8) No reaction took place when the reaction was carried out in the absence of ethane-1,2-diol.

(9) Cyclic acetalization of normal ketones such as octan-2-one and acetophenone proceeded smoothly under similar reaction conditions.