Diversity-oriented synthesis of 1-hydroxy-2,4-benzodioates by regioselective [3+3] cyclocondensations of 1,3-bis(silyloxy)-1,3-butadienes with 3-alkoxy- and 3-silyloxy-2-alkoxycarbonyl-2-en-1-ones†

Mohanad Shkoor,[a] Abdolmajid Riahi,[a,b] Olumide Fatunsin,[a] Ibrar Hussain,[a] Mirza A. Yawer,[a] Mathias Lubbe,[a] Stefanie Reim,[a] Helmut Reinke,[b] Christine Fischer[b] and Peter Langer*[a,b]

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1-Hydroxy-3,5-dimethyl-2,4-benzodioates (4-hydroxyisophthalates) were prepared by [3+3] cyclocondensation of 1,3-bis(silyloxy)-1,3-butadienes with 3-ethoxycarbonyl-4-trimethylsilyloxy-3-penten-2-one which is synthesized from (symmetrical) ethyl 2-acetylacetoacetate. The [3+3] cyclization of 1,3-bis(silyloxy)-1,3-butadienes with 3-alkoxy-2-alkoxycarbonyl-2-en-1-ones, readily available by reaction of β-ketoesters with trialkyl orthoformiates, provide a convenient and regioselective approach to a great variety of 3-substituted 1-hydroxy-2,4-benzodioates that are not readily available by other methods.

Introduction

Functionalized benzene derivatives, such as hydroxylated benzoates, are of considerable interest as lead structures in medicinal and agricultural chemistry and as synthetic building blocks.[1] Several syntheses of functionalized benzoates rely on electrophilic substitutions, oxidations or transition metal-catalyzed cross-coupling reactions.[2] Despite their great utility, these transformations have several drawbacks. Classical electrophilic substitutions often proceed with poor *o*/*p*-regioselectivity. Oxidations of toluene to benzoic acid derivatives require harsh reaction conditions, which can lead to destruction of more complex, polyfunctionalized substrates. In contrast, transition metal-catalyzed cross-coupling reactions proceed under mild conditions. Despite much progress in this area, cross-coupling reactions of sterically encumbered or functionalized substrates often proceed in low yields or not at all. In addition, the synthesis of more complex starting materials, highly functionalized or substituted aryl halides or triflates, can be a very difficult task.

An alternative approach is based on a building block strategy. Functionalized phenols and benzoates have been prepared, for example, by base-mediated cyclization reactions of activated (symmetrical) 1,3,5-tricarbonyl compounds, *e.g.* diethyl acetone-1,3-dicarboxylate, with enolizable 1,3-dicarbonyl derivatives, ynones or enones.[3] Harris and coworkers reported the (biomimetic) synthesis of densely functionalized phenols by condensation of 1,3-dicarbonyl dianions or 1,3,5-tricarbonyl trianions with carboxylic acid derivatives and subsequent intramolecular aldol reaction of the polyketides thus formed.[4] Other syntheses rely on the [4+2] cycloaddition of electron-rich dienes (*e.g.* 2-silyloxy-1,3-butadienes) with electron-poor alkynes. We have recently reported the synthesis of 4-hydroxy- and 2,4-dihydroxy-homophthalates by [4+2] cycloaddition of 1,3-bis(trimethylsilyloxy)-1,3-butadienes with dimethyl allene-1,3-dicarboxylate.[5] 4,5-Diaryl-1,2,3-benzenetricarboxylates have been prepared by [4+2] cycloaddition of 4-hydroxycyclopent-2-en-1-one-2-carboxylates, precursors of highly reactive fulvenones, with dimethyl acetylenedicarboxylate.[6]

In 1980, Chan and Brownbridge reported[7] the first example of a new approach to salicylates based on the formal [3+3] cyclization of 1,3-bis(silyloxy)-1,3-butadienes, electroneutral 1,3-dicarbonyl dianion equivalents,[8] with dielectrophilic 3-silyloxy-2-en-1-ones. In recent years, this strategy has been applied to the synthesis of various functionalized arenes.[9] However, the scope is limited to 3-silyloxy-2-en-1-ones derived from symmetrical 1,3-diketones. Starting with these substrates, salicylates containing the same substituents located at carbon atoms C3 and C5 can be prepared. Although a few exceptions have been reported,[7] cyclizations of 3-silyloxy-2-en-1-ones derived from *unsymmetrical* 1,3-dicarbonyl compounds often proceed with low regioselectivity. Following an explanation first suggested by Chan and Brownbridge,[7] this is a result of the fact that 3-silyloxy-2-en-1-ones can undergo a $TiCl_4$-mediated isomerization (migration of the TMS-group from one oxygen atom to the other).

In their early work, Chan and Brownbridge mentioned[7] that the cyclocondensation of 1-methoxy-1,3-bis(trimethylsilyloxy)-1,3-butadiene with 1-methoxybut-1-en-3-one proceeds with good regioselectivity. Based on this observation, we recently started a program directed towards the development of new cyclizations of acceptor-substituted 3-*alkoxy*-2-en-1-ones. These cyclizations proceed with very good regioselectivity, which might be explained by the assumption that the substrates do not undergo the above mentioned $TiCl_4$-mediated isomerization process. Our strategy

[a]*Institut für Chemie, Universität Rostock, Albert-Einstein-Str. 3a, 18059, Rostock, Germany. E-mail: peter.langer@uni-rostock.de; Fax: 00 49 381 4986412; Tel: 00 49 381 4986410*
[b]*Leibniz-Institut für Katalyse e. V. an der Universität Rostock, Albert-Einstein-Str. 29a, 18059, Rostock, Germany*

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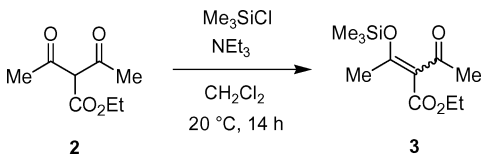
takes advantage of the fact that the required starting materials are readily available by reaction of acceptor-substituted ketones with triethyl or trimethyl orthoformiate.

1-Hydroxy-2,4-benzodioates (4-hydroxyisophthalates) are important core structures of pharmacologically important natural products and also represent versatile building blocks in organic synthesis.[10] The most widely applied synthetic approach to such molecules relies on the oxidation of appropriate benzene derivatives and on the functionalization of phenol or benzoic acid derivatives.[10–14] Recently, we have reported the synthesis of 1-hydroxy-3,5-dimethyl-2,4-benzodioates by $TiCl_4$-mediated [3+3] cyclization of 1,3-bis(silyloxy)-1,3-butadienes with 3-silyloxy-2-en-1-ones derived from (symmetrical) ethyl 2-acetylacetoacetate.[15] Herein, we report full details of this reaction and a significant extension of its scope. In addition, we report, for the first time, the [3+3] cyclocondensation of 1,3-bis(silyloxy)-1,3-butadienes with readily available 3-alkoxy-2-alkoxycarbonyl-2-en-1-ones. These reactions rely on the general concept outlined above and provide a convenient and *regioselective* approach to a great variety of functionalized 1-hydroxy-2,4-benzodioates that are not readily available by other methods.

Results and discussion

The triethylamine-mediated reaction of ethyl 2-acetylacetoacetate (**2**) with trimethylchlorosilane afforded the 2-ethoxycarbonyl-3-silyloxy-2-en-1-one **3** (Scheme 1).

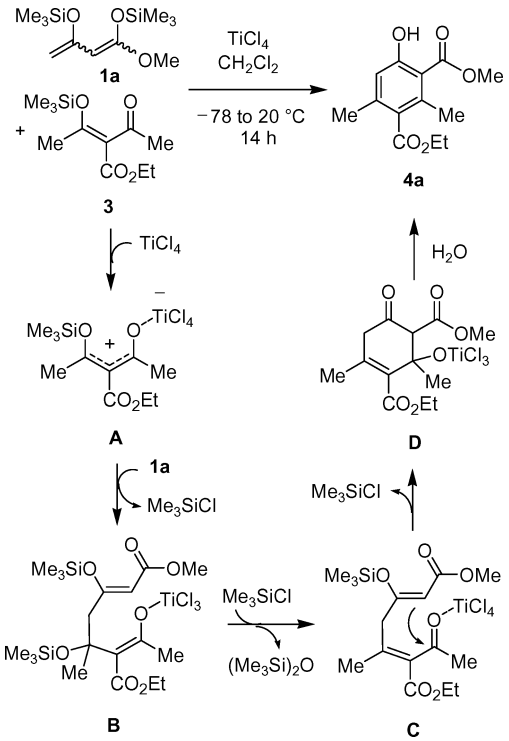


Scheme 1 Synthesis of silyl enol ether **3**.

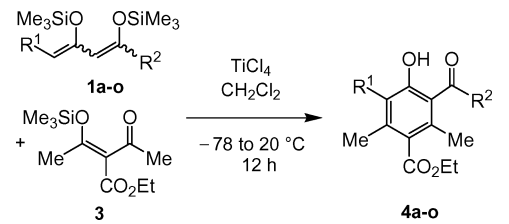
The $TiCl_4$-mediated formal [3+3] cyclization of **3** with 1,3-bis(silyloxy)-1,3-butadiene **1a**, prepared from methyl acetoacetate in two steps,[7] afforded the novel functionalized 1-hydroxy-3,5-dimethyl-2,4-benzodioate **4a** (Scheme 2). The best yield was obtained when (a) the reaction was carried out in a highly concentrated solution (2 mL per 1.0 mmol of **3**), (b) the reagents were added in a stoichiometric ratio and (c) hydrochloric acid (10%) was employed for the aqueous work-up.

The formation of **4a** can be explained by reaction of **3** with $TiCl_4$ to give intermediate **A**. The attack of the terminal carbon atom of **1a** onto **A** afforded intermediate **B**. The elimination of TMS-siloxane generated intermediate **C** and subsequent cyclization gave intermediate **D** (Scheme 2). The elimination of titanium hydroxide (before or during the aqueous work-up) and aromatization resulted in the formation of product **4a**. Due to the symmetrical structure of **A**, the attack of **1a** on either terminal allylic carbon atom would result in the formation of the same product (**4a**).

1,3-Bis(silyloxy)-1,3-butadienes **1a–o** were prepared in analogy to the procedure previously reported.[7] The $TiCl_4$ mediated formal [3+3] cyclization of **3** with 1,3-bis(silyloxy)-1,3-butadienes **1a–m** afforded the 1-hydroxy-2,4-benzodioates **4a–m** (Scheme 3, Table 1). The 2-acetyl- and 2-benzoyl-1-hydroxy-4-benzoates **4n** and **4o** were prepared from dienes **1n** and **1o** which are derived from acetylacetone and benzoylacetone, respectively. The yields



Scheme 2 Possible mechanism of the formation of **4a**.



Scheme 3 Synthesis of **4a–o**.

Table 1 Synthesis of **4a–o**

1,4	R^1	R^2	% (4)[a]
a	H	OMe	30
b	Me	OEt	48
c	Et	OEt	49
d	*n*Hex	OMe	35
e	*n*Non	OMe	40
f	*n*Dec	OMe	41
g	4-MeC_6H_4	OMe	38
h	4-ClC_6H_4	OMe	37
i	4-$(MeO)C_6H_4$	OMe	34
j	OMe	OMe	65
k	OPh	OEt	48
l	O(2-MeC_6H_4)	OEt	42
m	O(3-MeC_6H_4)	OEt	51
n	H	Me	38
o	H	Ph	36

[a] Yields of isolated products.

of products **4b–m**, containing a substituent located at carbon C6, were higher (albeit not in all cases significantly) than the yield of **4a**. The best yield was obtained for product **4j** containing a methoxy group located at carbon C6. The syntheses of

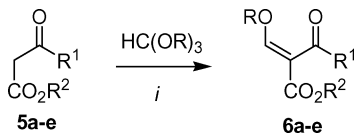
Table 2 Synthesis of **6a–e**

5,6	R	R^1	R^2	% (6)[a]
a	Me	Me	Me	82
b	Me	Et	Me	84
c	Me	*n*Pr	Me	83
d	Et	Ph	Et	81
e	Et	CH_2Cl	Et	80

[a] Yields of isolated products.

2-hydroxy-2,4-benzodioates **4a–o** bear, as discussed above, no issue of regioselectivity.

The regioselective synthesis of 1-hydroxy-2,4-benzodioates derived from *unsymmetrical* substrates was next studied. Our strategy is based, as outlined in the introduction, on the employment of 3-alkoxy- rather than 3-silyloxy-2-en-1-ones as dielectrophilic building blocks. 2-Alkoxycarbonyl-3-methoxy-2-en-1-ones **6a–e** were prepared, following a known procedure,[16] by reaction of β-ketoesters **5a–e** with trimethyl orthoformiate and acetic anhydride (Scheme 4, Table 2). The synthesis of **6a** has been previously reported.[16] All products, including the chlorinated enone **6e**, were prepared in good yields.

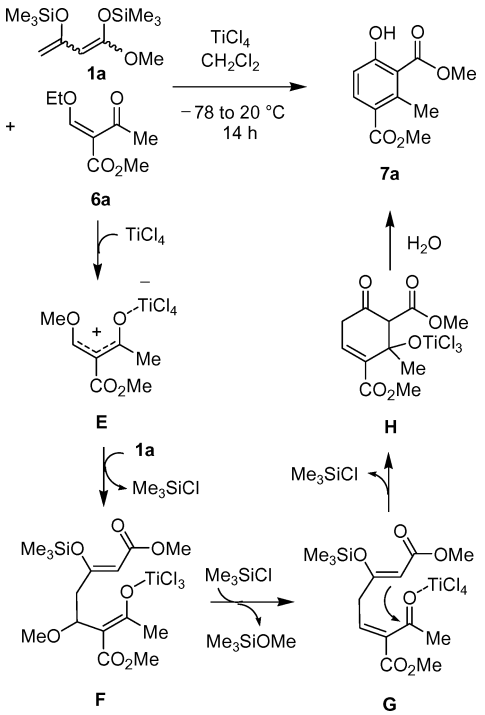


Scheme 4 Synthesis of **6a–e**; (i) **5a–e** (1.0 equiv.), $HC(OR)_3$ (1.2 equiv.), Ac_2O, reflux, 2 h.

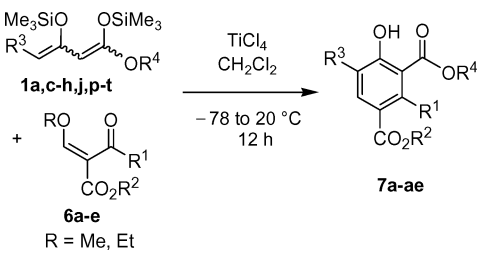
The $TiCl_4$-mediated cyclization of **6a** with **1a** afforded the 1-hydroxy-2,4-benzodioate **7a** with excellent regioselectivity (Scheme 5). The best yield was (again) obtained when the reaction was carried out in a highly concentrated solution (2 mL per 1 mmol of **6a**). The yield decreased when the reaction mixture was more dilute (30 mL per 1.0 mmol of **6a**). The starting materials **6a**, **1a** and $TiCl_4$ were employed in a 1.0 : 1.1 : 1.1 ratio. The yield decreased when the stoichiometric ratio was 1.0 : 1.0 : 2.0, 1.0 : 2.0 : 1.0 or 1.0 : 2.0 : 2.0. The temperature had to slowly warm from –78 to 20 °C. No product could be isolated when the reaction was carried out at 0 °C. The regioselectivity can be explained by steric and electronic effects.

The formal [3+3] cyclization of 2-alkoxycarbonyl-3-alkoxy-2-en-1-ones **6a–d** with 1,3-bis(silyloxy)-1,3-butadienes **1a**, **1c–h**, **1j**, and **1p–t** afforded the 1-hydroxy-2,4-benzodioates **7a–ae** in 43–60% yield (Scheme 6, Table 3).

The substituents R^1, located next to the carbonyl group of **6a–d**, have no significant influence on the yields. 1,3-Bis(silyloxy)-1,3-butadienes **1c–e** and **1p–s** contain an alkyl group located at carbon atom C4 of the diene. Products **7a**,**i** have been prepared from the unsubstituted dienes **1a**,**t**. The yields of products **7b–h**, derived from **6a** and from **1c–e** and **1p–s**, are slightly higher than the yields of **7a**,**i**. There are no significant variations in the yields of the products containing the same substituent R^3 but different substituents R^1. Thus, the substituent introduced by the enone has no significant influence on the yield (except for **6e** which failed to give the desired product **7af**).



Scheme 5 Possible mechanism of the formation of **7a**.



Scheme 6 Synthesis of **7a–ae**.

The structures of 1-hydroxy-2,4-benzodioates **7a** and **7i** were easily confirmed based on the large coupling constants (^{1}H NMR) of the neighbouring aromatic hydrogen atoms. The elucidation of the structure of all other derivatives was considerably more difficult and had to rely on 2D NMR experiments (NOESY, HMBC). The structures of **7b** and **7k** were independently confirmed by X-ray crystal structure analyses (Fig. 1 and 2).† In the structure of **7k** the OH group is involved both in an intra- and an intermolecular hydrogen bond. So the distance between the symmetry equivalent atoms O1 is only 277 pm.

Conclusions

In conclusion, we have reported a convenient and regioselective synthesis of a great variety of 1-hydroxy-2,4-benzodioates (4-hydroxyisophthalates) that is, to the best of our knowledge, the first formal [3+3] cyclization of 1,3-bis(silyloxy)-1,3-butadienes with 3-silyloxy- and 3-alkoxy-2-alkoxycarbonyl-2-en-1-ones. The reactions are carried out easily and the starting materials are readily available. The highly functionalized and sterically encumbered benzene derivatives prepared are not readily available by other methods.

Table 3 Synthesis of **7a–ae**

1	6	7	R^1	R^2	R^3	R^4	Yield (%) [a]
a	**a**	**a**	Me	Me	H	Me	43
p	**a**	**b**	Me	Me	Me	Me	57
c	**a**	**c**	Me	Me	Et	Et	50
q	**a**	**d**	Me	Me	*n*Bu	Me	52
d	**a**	**e**	Me	Me	*n*Hex	Me	55
r	**a**	**f**	Me	Me	*n*Hept	Me	51
s	**a**	**g**	Me	Me	*n*Oct	Me	48
e	**a**	**h**	Me	Me	*n*Non	Me	52
t	**a**	**i**	Me	Me	H	$(CH_2)_2OMe$	48
g	**a**	**j**	Me	Me	4-MeC_6H_4	Me	53
h	**a**	**k**	Me	Me	4-ClC_6H_4	Me	48
j	**a**	**l**	Me	Me	OMe	Me	52
p	**b**	**m**	Et	Me	Me	Me	52
c	**b**	**n**	Et	Me	Et	Et	50
q	**b**	**o**	Et	Me	*n*Bu	Me	52
d	**b**	**p**	Et	Me	*n*Hex	Me	52
r	**b**	**q**	Et	Me	*n*Hept	Me	51
s	**b**	**r**	Et	Me	*n*Oct	Me	50
e	**b**	**s**	Et	Me	*n*Non	Me	51
f	**b**	**t**	Et	Me	*n*Dec	Me	49
g	**b**	**u**	Et	Me	4-MeC_6H_4	Me	51
p	**c**	**v**	*n*Pr	Me	Me	Me	51
c	**c**	**w**	*n*Pr	Me	Et	Et	53
q	**c**	**x**	*n*Pr	Me	*n*Bu	Me	51
d	**c**	**y**	*n*Pr	Me	*n*Hex	Me	45
r	**c**	**z**	*n*Pr	Me	*n*Hept	Me	46
s	**c**	**aa**	*n*Pr	Me	*n*Oct	Me	45
e	**c**	**ab**	*n*Pr	Me	*n*Non	Me	50
f	**c**	**ac**	*n*Pr	Me	*n*Dec	Me	55
p	**d**	**ad**	Ph	Et	Me	Me	58
c	**d**	**ae**	Ph	Et	Et	Et	60
a	**e**	**af**	CH_2Cl	Et	H	Me	0

[a] Yields of isolated products.

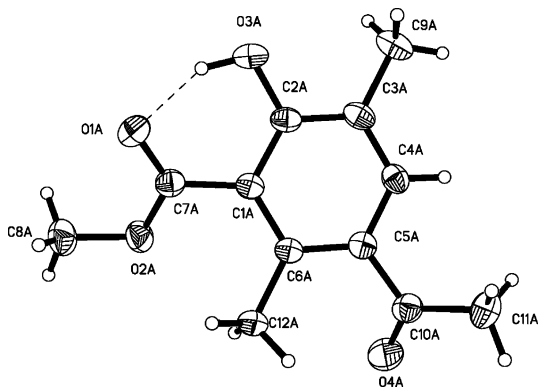


Fig. 1 Ortep plot of **7b** (only one of the symmetry independent molecules shown).

Experimental section

General comments

All solvents were dried by standard methods and all reactions were carried out under an inert atmosphere. For ^1H and ^{13}C NMR spectra, the indicated deuterated solvents were used. Mass spectrometric data (MS) were obtained by electron ionization (EI, 70 eV), chemical ionization (CI, isobutane) or electrospray ionization (ESI). For preparative scale chromatography, silica gel 60 (0.063–0.200 mm, 70–230 mesh) was used.

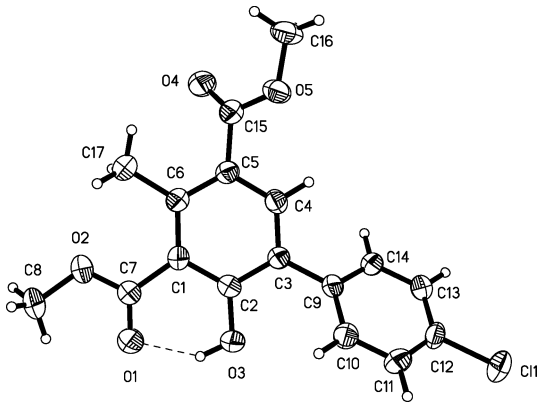


Fig. 2 Ortep plot of **7k**.

General procedure for the synthesis of 1-hydroxy-2,4-benzodioates 4a–o

To a CH_2Cl_2 solution (2 mL per 1.0 mmol of **3**) of **3** (1.0 equiv.) was added **1** (1.0 equiv.) and, subsequently, $TiCl_4$ (1.0 equiv.) at −78 °C. The temperature of the solution was allowed to warm to 20 °C during 14 h with stirring. To the solution was added hydrochloric acid (10%, 20 mL) and the organic and the aqueous layer were separated. The latter was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layers were dried (Na_2SO_4), filtered and the filtrate was concentrated *in vacuo*. The residue was purified by chromatography (silica gel, *n*-heptane–EtOAc) to give product **4**.

1-Ethyl 3-methyl 4-hydroxy-2,6-dimethylisophthalate (4a)

Starting with **3** (0.489 g, 2.0 mmol) and **1a** (0.521 g, 2.0 mmol), **4a** was isolated after chromatography (silica gel, heptanes–EtOAc) as an orange oil (0.149 g, 30%). ^1H NMR ($CDCl_3$, 250 MHz): δ = 1.36 (t, ^3J = 7.1 Hz, 3H, OCH_2CH_3), 2.25 (s, 3H, CH_3), 2.44 (s, 3H, CH_3), 3.94 (s, 3H, OCH_3), 4.36 (q, ^3J = 7.1 Hz, 2H, OCH_2CH_3), 6.69 (s, 1H, CH_{Ar}), 11.23 (s, 1H, OH). ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 14.2 (OCH_2CH_3), 20.0, 20.2 (CH_3), 52.2 (OCH_3), 61.1 (OCH_2CH_3), 110.4 (C_{Ar}), 116.9 (CH_{Ar}), 128.6, 137.8, 141.8 (C_{Ar}), 162.6 (COH), 169.7 (CO), 171.7 (CO). IR (neat, cm^{-1}): ν_{max} = 3421 (br, w), 2983 (m), 2956 (m), 1725 (s), 1666 (s), 1606 (m), 1579 (m), 1444 (s), 1360 (s), 1324 (s), 1259 (s), 1232 (s), 1185 (s), 1115 (s), 1053 (m), 1036 (m). MS (GC/MS, 70 eV): m/z (%) = 252 (M^+, 27), 220 (100), 207 (28), 175 (61). Anal.: calcd. for $C_{13}H_{16}O_5$ (252.26): C, 61.90; H, 6.39. Found: C, 61.69; H, 6.51.

Typical experimental procedure for the synthesis of 7a–ae

To a CH_2Cl_2 solution (2 mL per 1 mmol of **6a–e**) of **6a–e** was added **1** (1.1 mmol) and, subsequently, $TiCl_4$ (1.1 mmol) at −78 °C. The temperature of the solution was allowed to warm to 20 °C during 14 h with stirring. To the solution was added hydrochloric acid (10%, 20 mL) and the organic and the aqueous layer were separated. The latter was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layers were dried (Na_2SO_4), filtered and the filtrate was concentrated *in vacuo*. The residue was purified by chromatography (silica gel, heptanes–EtOAc) to give **7a–ae**.

Dimethyl 4-hydroxy-2-methylisophthalate (7a)

Starting with **6a** (0.237 g, 1.5 mmol) and **1a** (0.429 g, 1.7 mmol), **7a** was isolated after chromatography (silica gel, heptanes–EtOAc) as a yellowish solid (0.144 g, 43%), mp. = 88–90 °C. ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 2.63$ (s, 3H, $PhCH_3$), 3.79 (s, 3H, OCH_3), 3.91 (s, 3H, OCH_3), 6.78 (d, $^3J = 8.7$ Hz, 1H, CH_{Ar}), 7.76 (d, $^3J = 8.9$ Hz, 1H, CH_{Ar}), 10.98 (s, 1H, OH). ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta = 20.0$ (CH_3), 52.0, 52.5 (OCH_3), 114.5 ($CCOOCH_3$), 115.2 (CH_{Ar}), 123.9 ($CCOOCH_3$), 135.8 (CH_{Ar}), 143.6 (C_{Ar}), 163.9 (COH), 168.0, 171.7 (CO). IR (KBr, cm^{-1}): $\nu_{max} = 3339$ (w), 2989 (w), 2959 (w), 2924 (w), 2853 (w), 1715 (m), 1688 (m), 1651 (m), 1583 (m), 1537 (m), 1430 (m), 1386 (m), 1321 (m), 1243 (m), 1195 (s), 1151 (s), 1050 (m), 1018 (m), 960 (m), 944 (m), 858 (m), 797 (s), 754 (m), 707 (s), 652 (m), 560 (m). GC-MS (EI, 70 eV): m/z (%) = 224 ([M]$^+$, 31), 193 (30), 192 (100), 161 (56), 160 (26), 149 (13), 133 (12), 132 (12), 105 (10), 77 (15), 51 (11). HRMS (EI): Calcd. for $C_{11}H_{12}O_5$ ([M]$^+$): 224.06792. Found: 224.067341.

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