DMAP-Organocatalyzed *O*-Silyl–*O*-(or *C*-)-Benzoyl Interconversions by Means of Benzoyl Fluoride

Thomas Poisson,[a] Vincent Dalla,[b] Cyril Papamicaël,[a] Georges Dupas,[a] Francis Marsais,[a] Vincent Levacher*[a]

[a] Laboratoire de Chimie Organique Fine et Hétérocyclique, UMR 6014, IRCOF, CNRS, Université et INSA de Rouen, B.P. 08, 76131 Mont-Saint-Aignan Cédex, France
Fax +33(2)35522962; E-mail: vincent.levacher@insa-rouen.fr

[b] Laboratoire de Chimie, URCOM, EA 3221, Faculté des Sciences et Techniques de l'Université du Havre, 25, Rue Philippe Lebon, BP 540, 76058 Le Havre Cédex, France

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Abstract: A mild and efficient transprotection of alcohols from silyl ethers **1a**–**f** to benzoates **2a**–**f** is reported in fair to good yields (50–98%). This silyl–acyl exchange reaction proceeds readily in acetonitrile at room temperature in the presence of benzoyl fluoride and DMAP as an acyl transfer catalyst. A two-step 'one-pot' DMAP-catalyzed silylcyanation–transprotection sequence which gives the corresponding *O*-benzoyl cyanohydrines **2g**–**l** in high yields (72–98%) from various benzaldehyde and ketone derivatives is also reported. This original organocatalytic acyl transfer process was also found to be effective in the O-benzoylation of trimethysilyl enolates **1m**–**o**, providing enol esters **2m**–**o**. Lastly, the potential of this strategy is also illustrated by a DMAP-mediated Claisen condensation between ketene silyl acetals **1p**–**r** and benzoyl fluoride.

Key words: organocatalysis, DMAP, transprotection, acid fluorides, silyl ethers, benzoylation, alcohols, cyanohydrins, Claisen condensation

The need for highly selective transformations in organic synthesis has stimulated chemists to develop a wide range of protecting groups for the preparation of multifunctional molecules.[1] Since a given protective group can, on rare occasions, survive several synthetic steps, recurrent costly and time-consuming deprotection–reprotection sequences are frequently required in the construction of sophisticated molecules. Straightforward methodologies enabling the transformation of a protecting group into another one in mild, and preferably, one-pot procedures are therefore highly appealing tools in organic synthesis due to the simple fact that both deprotection–reprotection steps, generally needed in a classical approach, are replaced by a single transformation (Figure 1).[1]

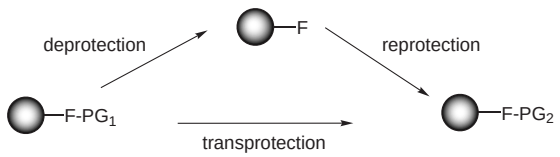

Figure 1 Transprotection methodology: a useful alternative to the deprotection–reprotection classical sequence

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Although the common use of such a transprotection strategy may represent a real advance in synthesis, only a few reports address this issue, with the most representative ones referring to transacetalisation of dithianes to *O*,*O*-acetals,[2] conversion of *N*-benzyl to *N*-carbamate derivatives,[3] direct conversion of *N*-[(fluorenylmethoxy)carbonyl] (Fmoc) to *N*-(*tert*-butoxycarbonyl) (Boc),[4] and interconversion of silyl ethers into acetates.[5] Obviously, the scarcity of literature reports does not match the great benefit that such interconversions could have in synthesis. In this context, we turned our interest in the one-step conversion of alcohols from silyl ethers into acetates. The reported catalytic procedures make use of Lewis acids such as Tin(II) bromide,[5a] $Cu(OTf)_2$,[5b] $FeCl_3$,[5c] $Sc(OTf)_3$,[5e] and $FeCl_3$.[5f] Many of these methods suffer from modest yields and lack of selectivity. With the aim of developing a new catalytic strategy under mild, neutral and more environmentally friendly metal-free conditions, we sought to examine the use of 4-(dimethylamino)pyridine (DMAP) as an organocatalyst in silyl–acyl exchange reactions. DMAP is routinely used as nucleophilic acyl transfer catalyst in the acylation of alcohols and related transformations.[6] The currently accepted mechanism involves the formation of a *N*-acylpyridinium salt as the key reactive intermediate.[6a,7] It is well known that during acylation of alcohols, DMAP is more effective when used in combination with anhydrides rather than with acid chlorides, pointing out a probable assistance of the acetate counterion in the deprotonation of the alcohol.[6a,7] With this scenario in mind, we questioned whether the reactivity of these electrophilic *N*-acylpyridinium salts could be controlled by tuning the nature of the counterion. As a result from the high affinity of silicon for the fluoride ion,[8] we indeed anticipated a specific activation of the 'naked-alcoholate' silyl ether **1** through the uncommon use of an acid fluoride as the acylating agent. This specific oxa-activation mode should ultimately promote a selective silyl–acyl exchange reaction (Figure 2).

On the basis of this working hypothesis, various benzoylating agents were first examined to ascertain the crucial role played by the fluoride counterion of the *N*-acyl pyridinium. Thus, silyl ether **1a**[9] was reacted separately with benzoyl fluoride, benzoic anhydride and benzoyl chloride in the presence of DMAP (10 mol%) in acetonitrile at room temperature (Table 1). While transprotection

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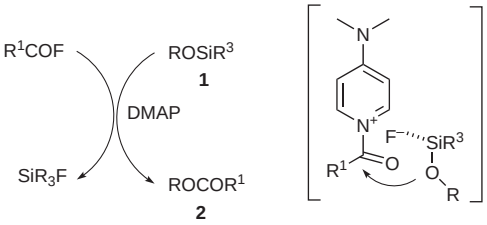
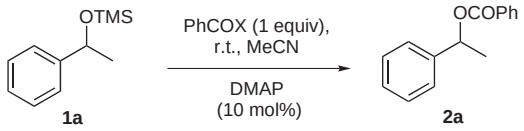


Figure 2 DMAP-organocatalyzed silyl–acyl exchange reaction

proceeded smoothly with benzoyl fluoride, no reaction could be detected when using benzoyl chloride, whereas the use of benzoic anhydride led to an incomplete conversion within the same period of time (Table 1, entries 1–3). These observations confirm the expected requirement of a fluoride counterion for the specific activation of silyl ethers. No reaction took place in the absence of DMAP, even after prolonged reaction time (>6 h), indicating that this was indeed an organocatalyzed reaction.

Table 1 Silyl–Acyl Exchange Reaction from **1a** by Means of Various Benzoylating Agents



Entry	PhCOX	Reaction time (h)	Yield of **2a** (%)[a]
1	PhCOF	1	28
		3	73
		5.5	100
2	$(PhCO)_2O$	2	26
		5.5	49
3	PhCOCl	5.5	0

[a] Yield of isolated products.

Having evidenced the catalytic efficiency of DMAP in this silyl–benzoyl exchange reaction, we next focused on reaction parameters that can influence the reaction rate.

Reducing the catalyst loading to 5 mol% did not significantly affect the reaction time, with the silyl–acyl exchange being completed within 7 hours. However, the transprotection progressed very sluggishly in the presence of 1 mol% of DMAP, affording **2a** in only 23% yield within 5 hours (Figure 3). Further investigations on the solvent employed indicated that higher conversion rates were obtained in polar solvents. Whereas acetonitrile afforded the transprotected product **2a** in quantitative yield within 5.5 hours, less polar solvents such as THF revealed to be poorly effective, giving **2a** in only 15% yield.[10] Attempts to use acetone and CH_2Cl_2 gave moderate conversion rates, although still satisfactory compared to THF (Figure 4).

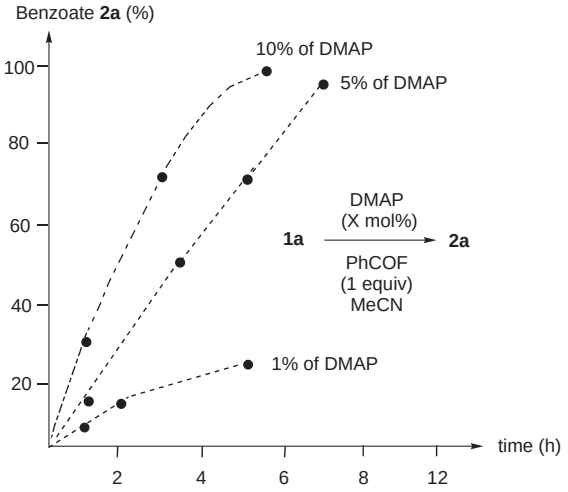


Figure 3 Influence of DMAP loading on the rate of the reaction

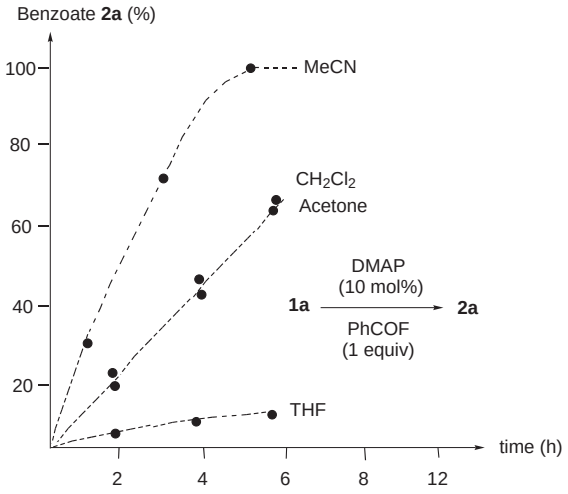


Figure 4 Solvent survey for the transprotection of silyl ether **1a** into benzoate **2a**

We next explored the scope of this interconversion process with various silyl ethers **1a**–**e** under optimized conditions (Table 2).[11] In all the cases examined, quantitative conversions were obtained and the resulting benzoates **2a**–**e** were isolated in fair to excellent yields. Increasing the steric demand of the silicon led to a significant diminution of the reaction rate as demonstrated by the use of TES ether **1b** (Table 2, entry 1, 2). Interestingly, when the reaction was performed from bis-TMS ether **1d**, monotransprotection took place exclusively at the primary TMS ether affording **2d** in 50% yield (Table 2, entry 4). Likewise, it was observed that primary TMS ethers could be selectively transprotected in the presence of phenolic TMS ether (Table 2, entry 6). However, prolonged reaction times led to transprotection of aryl TMS ether in good yields as well (Table 2, entry 5).

We then turned our interest into the transprotection of *O*-trimethylsilyl cyanohydrins. This class of compounds is usually prepared by silylcyanation of activated carbonyl

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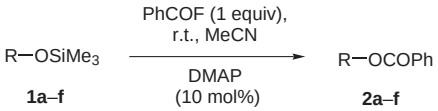
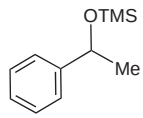
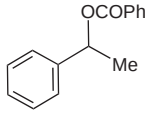
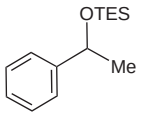
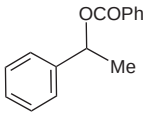
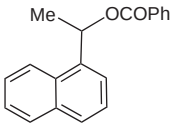
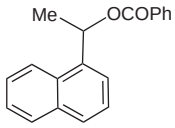
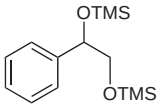
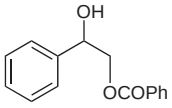
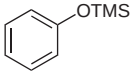
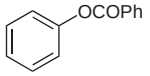
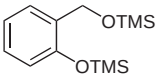
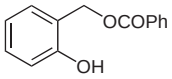
Table 2 Scope of Silyl Ethers (**1a**–**e**)–Benzoates (**2a**–**e**) Transprotection



Entry	Silyl ether **1**	Benzoate **2**	Yield (%)[a]	Time (h)
1	 **1a**	 **2a**	96	5.5
2	 **1b**	 **2a**	17 42 65	2 5 9
3	 **1c**	 **2c**	96	6
4	 **1d**	 **2d**	50[b]	8
5	 **1e**	 **2e**	98	12
6	 **1f**	 **2f**	62[b]	8

[a] Yield of isolated products.
[b] Hydrolysis of the residual silyl ether protecting group occurred during the work-up of the reaction.

compounds. Various catalytic methods have been developed including nucleophilic activation of TMSCN. Recently, DMAP was found to be effective in the silylcyanation of aldehydes.[12] Therefore, we speculated that DMAP could possibly catalyze both catalytic silylcyanation–transprotection steps in a 'one-pot' procedure. A series of aryl aldehydes were subjected to the silylcyanation–transprotection sequence in acetonitrile in the presence of 10 mol% of DMAP at room temperature. After addition of TMSCN, the reaction mixture was stirred for 1 hour and subsequent monitoring by GC-MS analyses revealed complete conversion for the various aldehydes examined to the *O*-trimethylsilyl cyanohydrins **1g**–**k**. The transprotection was next accomplished in the same pot by adding benzoyl fluoride affording after 12 hours the desired *O*-benzoyl cyanohydrins **2g**–**k** in 72–98% over the two steps (Table 3, entries 1–5). Under identical reaction conditions, the less electrophilic cyclohexanone gave, without apparent loss of reactivity, **2l** in 85% yield (Table 3, entry 6).[13]

Methods for clean and selective O-acylation of ketone-derived enolates are lacking. Although silyl–acyl exchange reaction from silyl enol ethers may afford an attractive alternative to prepare enol esters under neutral conditions, only a few papers have reported mild and simple procedures.[14] In this context, our catalytic conditions would make available a new procedure under neutral and mild conditions for such interesting interconversions. The effectiveness and the future potential of this approach have been illustrated by the conversion of silyl enol ethers **1m**–**o** into enol esters **2m**–**o**. Employing optimal conditions,[11] DMAP was found to catalyze the desired silyl enol ether–enol benzoate interconversion in 70–84% yields, respectively, free from competing C-benzoylation products (Table 4).[15]

In a last set of experiments, we briefly considered the *N*-acyl pyridinium fluoride intermediate as a potential acyl acceptor in the Claisen condensation with ketene silyl acetals. Beside the conventional method using strong bases, alternative approaches making use of ketene silyl

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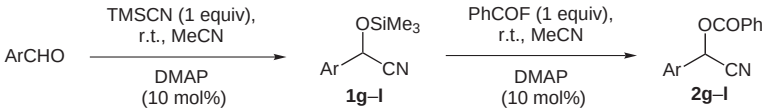
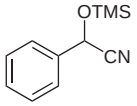
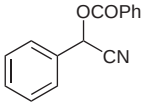
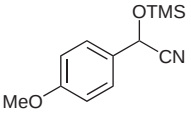
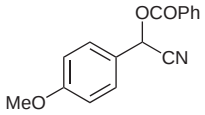
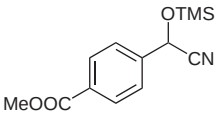
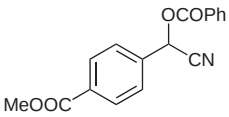
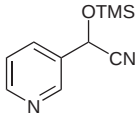
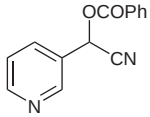
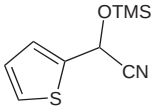
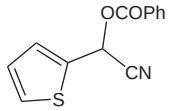
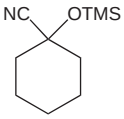
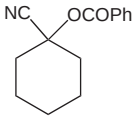
Table 3 'One-pot' Silylcyanation–Transprotection Sequence



Entry	Silyl ether **1**	Benzoate **2**	Yield from ArCHO (%)[a]
1	 **1g**	 **2g**	80[b]
2	 **1h**	 **2h**	72
3	 **1i**	 **2i**	98
4	 **1j**	 **2j**	79
5	 **1k**	 **2k**	72
6	 **1l**	 **2l**	85

[a] Yield of the isolated products.
[b] Transprotection from enantiopure **1g** provided **2g** without any significant loss of optical purity, demonstrating that this silyl–acyl exchange reaction is a non-racemizing transprotection process.

acetals and acid chlorides or anhydrides[16,17a] usually afford crossed-Claisen condensation products in better yields and selectivity with respect to the undesired self-Claisen condensation products which are generally formed in the base-promoted approach. Our strategy would therefore extend this efficient approach to the use of the more stable acid fluorides under neutral conditions. Interestingly, under our optimized catalytic conditions,[11] benzoyl fluoride was found to react with ketene silyl acetals **1p**–**r** to afford β-keto esters **2p**–**r** in 62–73% yields. As previously demonstrated with other substrates **1a**–**n**, the catalytic activity of DMAP was confirmed by conducting a blank experiment where formation of the Claisen condensation product **2p** was not observed (Table 5).

In summary, we have developed a simple, room temperature and metal-free catalytic transprotection of alcohols from silyl ethers **1a**–**f** to benzoates **2a**–**f**. This interconversion is catalyzed by DMAP and proceeds through what appears to be an activation of the silyl ethers **1** by the fluoride counterion of the *N*-acyl pyridinium intermediate. This silyl–acyl exchange reaction was also found to be effective in the conversion of silyl enol ethers **1m**–**o** into enol esters **2m**–**o**. Lastly, this acyl-transfer process opens the route to the development of new Claisen condensation procedures under mild and neutral conditions. An attractive perspective of this organocatalytic transprotection of alcohols is the resolution of chiral racemic silyl ethers **1** by means of chiral DMAPs.[17]

Acknowledgment

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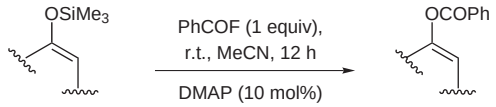
Table 4 DMAP-Catalyzed O-Benzoylation of Silyl Enol Ethers **1m–o** with Benzoyl Fluoride



1m–o **2m–o**

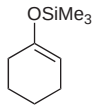
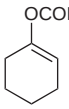
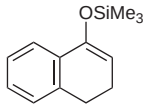
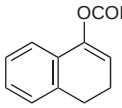
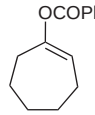
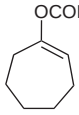
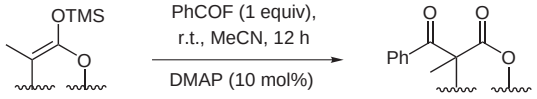
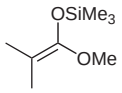
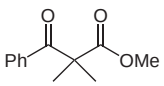
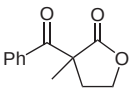
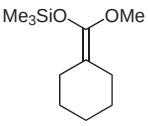
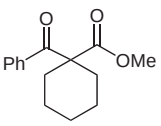
Entry	Silyl enol ethers **1m–o**	Enol benzoates **2m–o**	Yield (%)
1	 **1m**	 **2m**	84
2	 **1n**	 **2n**	72
3	 **1o**	 **2o**	70

Table 5 DMAP-Catalyzed Claisen Condensation Between Ketene Silyl Acetals **1p–r** and Benzoyl Fluoride



1p–r **2p–r** 62–73% yield

Entry	Ketene silyl acetals **1p–r**	Claisen condensation products **2p–r**	Yield (%)
1	 **1p**	 **2p**	65
2	 **1q**	 **2q**	73
3	 **1r**	 **2r**	62

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(9) **General Procedure for the Preparation of Silyl Ethers 1a–f.**
To a solution of 1-phenylethanol (122 mg, 1 mmol) and Et_3N (120 mg, 1.1 mmol) in CH_2Cl_2 (5 mL) was added TMSCl (115 mg, 1.05 mmol). The reaction was stirred at r.t. overnight. The solvent was removed under reduced pressure and the resultant residue was diluted with pentane (10 mL). Simple filtration through a short pad of Celite® provided silyl ether **1a** in 95% yield which could be used in the silyl ether exchange reaction without further purification.

(10) One can notice that acylation of alcohols with DMAP/AC_2O is reported to be more effective in less polar solvents; see ref. 6. There is apparently no rational explanation for this opposite solvent effect.

(11) **General Procedure for the Transprotection of Silyl Ethers 1a–f, Silyl Enol Ethers 1m–o and Ketene Silyl Acetals 1p–r.**
To a solution of silylated alcohol **1f** (268 mg, 1 mmol) and DMAP (12 mg, 0.1 mmol) in MeCN (2 mL) was added benzoyl fluoride (130 mg, 1.05 mmol). The resulting solution was stirred for 6 h at r.t., followed by addition of sat. aq $NaHCO_3$ (4 mL). After phase separation, the aqueous phase was extracted with EtOAc (3 × 10 mL). The combined organic layers were washed with sat. aq NH_4Cl (10 mL) and brine (10 mL). After drying ($MgSO_4$) and evaporation of the organic solvents under vacuum, the resulting residue was chromatographed on silica gel (cyclohexane–EtOAc, 9:1) affording benzoate **2f** in 62% yield.
Selected Data for Benzoate 2f.
^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.01 (s, 1 H), 7.97 (d, 2 H, *J* = 8.3 Hz), 7.46 (t, 1 H, *J* = 5.4 Hz), 7.27 (m, 3 H), 7.16 (m, 1 H), 6.85 (m, 2 H), 5.27 (s, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 168.56, 155.39, 133.52, 131.89, 130.91, 129.86, 129.28, 128.40, 121.88, 120.55, 117.38, 63.53. IR (KBr): ν_{max} = 1693, 3317 cm^{-1}. Mp 64–66 °C.
Selected Data for 2q.
^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.95 (d, 2 H, *J* = 7.9 Hz), 7.52 (m, 1 H), 7.44 (t, 2 H, *J* = 7.9 Hz), 4.40 (t, 2 H, *J* = 6.9 Hz), 3.05 (m, 1 H), 2.22 (m, 1 H), 1.67 (s, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 196.65, 177.48, 134.88, 133.40, 129.50, 128.87, 66.39, 55.30, 35.70, 22.01. IR (KBr): ν_{max} = 1766, 1678 cm^{-1}.

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Selected Data for 2r.
^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.78 (d, 2 H, *J* = 7.3 Hz), 7.49 (m, 1 H), 7.38 (m, 2 H), 3.63 (s, 3 H), 2.09 (t, 4 H, *J* = 6.2 Hz), 1.53 (m, 6 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 198.56, 174.71, 136.50, 132.67, 128.73, 128.62, 58.35, 52.72, 32.68, 25.71, 22.58. IR (KBr): 1735, 1682 cm^{-1}. All other synthesized compounds are in accordance with the literature data.

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(13) **General 'One-Pot' Procedure for the Preparation of *O*-Benzoyl Cyanohydrins 2g–l.**
To a solution of methyl 4-formylbenzoate (164 mg, 1 mmol) and DMAP (12 mg, 0.1 mmol) in MeCN (2 mL) was added TMSCN (241 mg, 1.05 mol). The resulting solution was stirred for 1 h at r.t., after which benzoyl fluoride (130 mg, 1.05 mmol) was added and the solution was stirred for a further 12 h. The solution was treated with sat. aq $NaHCO_3$ (4 mL). After dilution with H_2O, the aqueous phase was extracted with EtOAc (3 × 10 mL). The combined organic phases were washed with sat. aq NH_4Cl (10 mL), brine (10 mL) and dried ($MgSO_4$). The solvents were evaporated under vacuum and the residue was chromatographed on silica gel (cyclohexane–EtOAc, 9:1).

Selected Data for *O*-Benzoyl Cyanohydrine (2i).
^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.05 (d, 2 H, *J* = 7.3 Hz), 7.56 (m, 3 H), 7.45 (m, 2 H), 6.97 (d, 2 H, *J* = 8.6 Hz), 6.62 (s, 1 H), 3.84 (s, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.43, 164.85, 136.66, 134.70, 132.40, 130.89, 130.51, 129.14, 128.27, 128.15, 116.17, 63.19, 52.86. IR (KBr): 1732, 1729 cm^{-1}. All other synthesized *O*-benzoyl cyanohydrins are in accordance with the literature data.

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