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# On the regioselectivity of the PIFA-mediated bis(trifluoroacetoxylation) of styrene-type compounds

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## Abstract

The addition of the hypervalent iodine reagent PIFA [phenyliodine(III) bis(trifluoroacetate)] to a series of styrene-type compounds results in the bis(trifluoroacetoxylation) of the double bond as two possible 1,2- and 1,1-regioisomers. We found that 1,1-regioisomers resulted to be unstable during chromatographic purification yielding the related arylacetaldehydes. In this paper, we show our efforts to explore the regioselectivity of this reaction, and to rationalize the results with respect to the electronic nature of the corresponding aryl ring through alternative mechanistic pathways.

*Keywords:* Hypervalent iodine; Styrenes; PIFA; Phenonium ions

## 1. Introduction

Olefins are probably one of the organic functional groups with the highest diverse reactivity. Stepwise additions, with initial attack of a nucleophile, an electrophile, or free radical species, and concerted processes compile a plethora of synthetic strategies for the formation of a diverse array of organic compounds clearly dominated by a number of important oxidative transformations.[1] Among them, the centennial[2] $OsO_4$ mediated *cis*-dihydroxylation of olefins has gained an enormous popularity over the years for its reliability and, more recently, for its evolution into an effective asymmetric strategy for the preparation of enantiomerically pure vicinal diols when used in the presence of chiral ligands.[3] Although used under substoichiometric conditions, the toxicity of the osmium reagents has led to the exploration of novel systems with the same synthetic purpose. In particular, and among others, the use of hypervalent iodine reagents, such as propyliodine(III) bis(trifluoroacetate)[4] or iodine(III) tris(trifluoroacetate),[5] performs the bis(trifluoroacetoxylation) of the C–C double bond although with limited success. More recently,[6] Çelik and Balci have demonstrated the efficiency of PIFA [phenyliodine(III) bis(trifluoroacetate)] in the direct transformation of acyclic as well as cyclic alkenes into 1,2- and/or 1,3-bis(trifluoroacetoxy) derivatives.[7] Particularly, under such conditions, styrene was transformed into 1-phenyl-1,2-ethanediol in a 90% yield after ammonolysis of the bis(trifluoroacetoxylated) intermediate generated. Additionally, in a previous connected study, Koser had reported 2 years earlier, in 2004, on the oxidative rearrangement of 1,1-disubstituted alkenes with HTIB [hydroxy(tosyloxy)iodo]benzene] in methanol as a protocol for the synthesis of α-arylketones.[8]

At the same time when these works were being published, we were involved in a related long lasting project on the search for novel applications of PIFA in organic synthesis, and more precisely on the intramolecular PIFA-mediated olefin amidation of conveniently substituted styrene-type substrates as a new entrance to the synthesis of quinoline and isoindoline derivatives.[9] In fact, we consider that the synthetic power of PIFA has been quantitatively underestimated with respect to

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other hypervalent iodine reagents (i.e., HTIB or PIDA—phenyliodine(III)diacetate), and in this particular context, we expect that the high electrophility of the iodine center in PIFA, as well as the lability of the trifluoroester groups that are eventually transferred to the substrates, might have important consequences in the outcome of the reaction. Thus, in this communication we report additional results on the action of PIFA on such kind of derivatives to show that the regioselectivity of the reaction (1,1- vs 1,2-diester formation) depends mostly on the activation of the aryl ring.

## 2. Results and discussion

We have previously mentioned that styrene (**1a**) affords 1-phenyl-1,2-bis(trifluoroacetoxy)ethane (**2a**) in the presence of PIFA in almost quantitative yield when the reaction is carried out in $CH_2Cl_2$ as solvent. Considering the importance of the 1-aryl-1,2-ethanodiol skeleton in organic synthesis,[10] it is surprising that the study on the action of PIFA has not been extended to other members of the family of styrene compounds. Alerted by the absence of research in this area, and continuing with our interest in discovering novel applications of PIFA in organic synthesis,[11] we started our study by exploring the action of this iodine(III) reagent on a series of commercially available styrenes **1a**–**g** (see Chart 1).

Styrenes **1a** and **1b** were selected to optimize the reaction conditions. Our preliminary observations led us to conclude that the nature of the aryl ring, and also the dilution of the reaction at some extent, had a critical effect on the regioselectivity of the process. Thus, while treatment of styrene **1a** with PIFA (0.3–0.5 M in $CH_2Cl_2$ at room temperature)[12] rendered exclusively the 1,2-diester **2a** in 4 h, styrene **1b** afforded the related 1,1-diester **3b** with complete regioselectivity in few minutes. It has to be mentioned that, unlike **2a**, diester **3b** happened to be unstable during column chromatography resulting in the formation of 2-(2-methoxyphenyl)acetaldehyde (**4b**). Thus, in order to optimize the work up, and prior to its purification, the non-isolated diester **3b** was treated with silica gel and the stirring was continued overnight to afford aldehyde **4b** in 74% yield.[13] This completely regioselective one-pot transformation can be considered as a metal-free alternative to the Wacker process for which the highly selective formation of aldehydes through catalytic oxidation of styrene-type compounds without CC double bond cleavage remains a challenge.[14,15] Later, and looking for an even simpler way to perform this conversion, we considered exploring the behavior of this family of substrates with PIFA also under solvent-free conditions. In particular, under such circumstances, we found that styrene **1a** reacted with PIFA yielding a mixture of regioisomers **2a** and **3a** in a 1.7/1 ratio,[16] and contrarily, styrene **2b** was transformed into aldehyde **4b** in the absence of solvent, but with a moderate 51% yield.

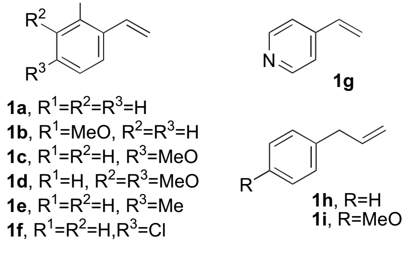


Chart 1.

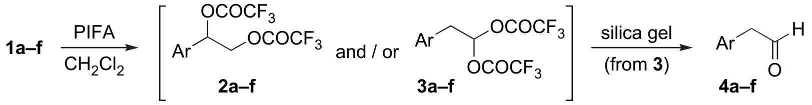
Therefore, in order to gain more information about the insights of this transformation, the behavior of a series of styrenes **1c**–**g** with different activation pattern with the iodine(III) reagent was studied both in solution and under solvent-free conditions. From the information summarized in Table 1, it can be deduced that 1,1-addition to the double bond dominates when starting from activated substrates (**1b**–**e**), and contrarily, non-activated styrenes tend to afford the 1,2 adducts **2a**,**f**.[17] Besides, in some cases (entries 3, 4, 5, 9–12), the generation of the corresponding arylacetaldehydes **4** is detected at some extent in the reaction mixture even before the addition of silica gel. It was also noticeable that vinylpyridine **1g** reacts violently with PIFA under solvent-free conditions, and extremely quickly in solution. In both cases, the dark residue that was obtained could not be analyzed. Finally, in none of these cases under study, we found a benefit from performing the experiment in the absence of solvent apart from the shorten reaction times that were usually needed.[18]

To the view of these results, the following mechanism can be postulated (see Scheme 1). Due to its electrophilic character, the hypervalent iodine reagent reacts with the olefinic double bond in substrates **1a**–**f** to afford the iodonium intermediates **I**, which are opened by a nucleophilic attack of the trifluoroacetate group. Final displacement of iodobenzene by a second trifluoroacetate group[20] (route A) affords the 1,2-bis(trifluoroacetates) **2**. Alternatively, activated aryl rings (in substrates **1b**–**e**)[21] can proceed as a second nucleophilic competitor giving rise, in this cases, to intermediates **III** following route B. These phenonium intermediates recover their aromaticity by reacting with a trifluoroacetate group at their most activated benzylic position furnishing the 1,1-bis(trifluoroacetates) **3**, which, on standing on silica gel, are transformed into the arylacetaldehydes of type **4**. It has to be mentioned that the generation of phenonium ion intermediates had already been postulated[22] and their existence demonstrated,[23] even under the action of hypervalent iodine species.[24]

The extension of our research to allylbenzenes **1h**,**i** offers coherent results, as they perfectly matched our original mechanistic proposal. As expected, allylbenzene (**1h**) was transformed into the 1,2-bis(trifluoroacetate) **2h** by the action of PIFA in $CH_2Cl_2$ at room temperature in an excellent 93% yield, and coherently, *p*-methoxyallylbenzene (**1i**) afforded an inseparable 1:1 mixture of the corresponding 1,2-bis(trifluoroacetate) **2i** and 1,3-bis(trifluoroacetate) **5i** in a combined 83% yield as the result of the lack of regioselectivity in the opening of the phenonium ion **VI** (see Scheme 2).[25] Similarly to our previous routine, the synthesis of diester **2h** under solvent-free conditions took place in almost quantitative yield, but contrarily, a more complex mixture was obtained when **1i** was treated with PIFA in the absence of solvent.

It should be noted the different regiochemistry in the ring opening of intermediates **I** and **IV**. We propose that iodonium

Table 1
Selected synthetic and spectroscopic information for the action of PIFA on styrenes **1a–f**



| Entry | Styrene | Method[a] | **2** (%) | Ratio **2/3/4**[b] | **3** ($\delta_{H\text{-}1}$, $\delta_{H\text{-}2}$, $J_{H\text{-}1/H\text{-}2}$) | **4**[c] (%) |
|---|---|---|---|---|---|---|
| 1 | **1a** | A | 82 | 100/0/0 | 7.08 ppm, 3.30 ppm, 6.1 Hz | |
| 2 | | B | 50 | 63/37/0 | | 23 |
| 3 | **1b** | A | 0 | 0/88/12 | 7.22 ppm, 3.31 ppm, 5.7 Hz | 74 |
| 4 | | B | 0 | 0/80/20 | | 51 |
| 5 | **1c** | A | 0 | 0/75/25 | 7.04 ppm, 3.24 ppm, 5.9 Hz | 85 |
| 6 | | B | 0 | 0/100/0 | | 64 |
| 7 | **1d** | A | 0 | 0/100/0 | 7.04 ppm, 3.23 ppm, 5.7 Hz | 39 |
| 8 | | B | 0 | 0/100/0 | | —[d] |
| 9 | **1e** | A | Traces | 5/73/22 | 7.04 ppm, 3.25 ppm, 6.0 Hz | 69 |
| 10 | | B | Traces | 5/90/5 | | 63 |
| 11 | **1f** | A | 87[17] | 95/0/5 | | Traces |
| 12 | | B | 77[17] | 95/0/5 | | Traces |

[a] Method A: styrene/PIFA (1/1.2), 0.40 M in $CH_2Cl_2$; method B: styrene/PIFA (1/1.2), under solvent-free conditions.

[b] This selectivity was determined from the $^1H$ NMR spectra of the crude mixture before addition of silica gel.

[c] Arylacetaldehydes **4** are extremely unstable, and they were isolated as oils by column chromatography. Some of them are commercially available and others have been described previously. In any case, their spectroscopic data match literature values.[19]

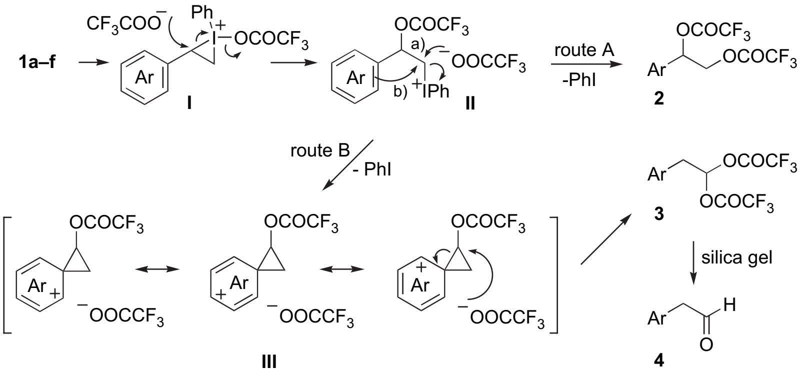
[d] A complex mixture of compounds is obtained.

**I** is opened in an $S_N1$ type process by localizing the positive charge at the most stabilized benzylic position and, conversely, the trifluoroacetate group attacks iodonium **IV** at its most accessible position following an $S_N2$ pathway.

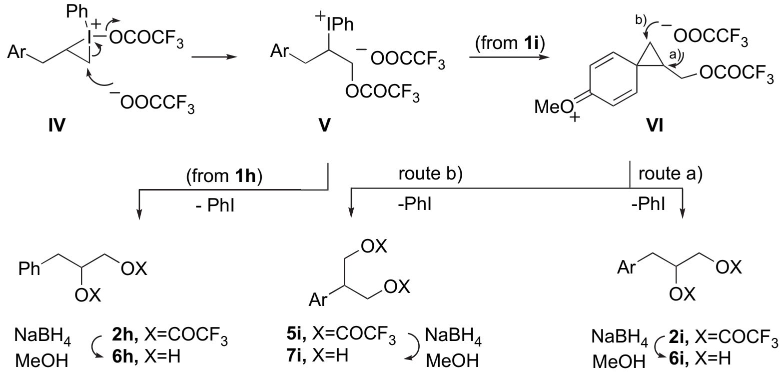
Finally, in order to expand the limits of our study, α-methylstyrenes **1j**,**k** and *trans*-anethole **1l** were submitted to the action of PIFA under both diluted and solvent-free reaction conditions. Three of them followed the general mechanistic proposal, shown in Scheme 1, giving rise in less than 10 min to the formation of the carbonyl compounds **4j–l** in 93%, 89%, and 42% yield, respectively (see Table 2).[26] These results indicate that the preliminary formation of phenonium intermediates of type **VII** and **VIII** had to occur (see Chart 2) to render, after 1,2-aryl migration, *gem*-diesters **3j–l**, which on treatment with silica gel furnished the reported compounds **4j–l**.[27] The simplicity of the method (addition of PIFA and further addition of silica gel), and the equally excellent yields obtained, encourage to perform the synthesis of the ketones **4j**,**k** from styrenes **3j**,**k** under solvent-free conditions, although the discordant result from **1l** does not allow rationalizing the actual effect of structure of the substrate on the reactivity in the absence of solvent.

## 3. Conclusions

The behavior of a series of styrenes in the presence of PIFA has been studied to conclude that non-activated substrates suffer 1,2-addition of trifluoroacetate groups across the olefinic double bound, whilst a related 1,1-addition dominates the reactivity on activated ones. A mechanistic description of this reaction includes the generation of a phenonium ion with concomitant 1,2-migration of the aryl ring. Taking advantage of the lability of such *gem*-diesters, they can be transformed into the corresponding carbonyl compounds on standing with silica gel.



Scheme 1. Proposed alternative mechanisms for the action of PIFA on styrenes **1a–f**.



Scheme 2. Proposed explanation for the action of PIFA on olefins **1h** (Ar=Ph) and **1i** (Ar=*p*-MeOC$_6$H$_4$).

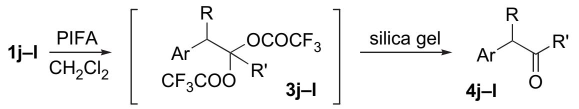
This unprecedented procedure for the direct generation of arylacetaldehydes from 1-arylethenes can be considered a competitive metal-free alternative to the Wacker reaction.

## 4. Experimental section

### 4.1. General procedure for the synthesis of bis(trifluoroacetates) *2*

To a magnetically stirred solution of the corresponding styrene (1 mmol) in $CH_2Cl_2$ (5 mL), PIFA (1.2 mmol) was added in one portion and the stirring continued at room temperature until total consumption of the starting material. After removal of the solvent, the residue was chromatographed on silica gel eluting with hexane/ethyl acetate (80:20) to give the 1,2-diesters as colorless oils.

Table 2
Selected synthetic and spectroscopic information for the action of PIFA on styrenes **1j–l**



**3/4j**, Ar=Ph, R=H, R'=Me
**3/4k**, Ar=*p*-MeC$_6$H$_4$, R=H, R'=Me
**3/4l**, Ar=*p*-OMeC$_6$H$_4$, R=Me, R'=H

| Styrene | Method[a] | Ratio **3/4**[b] | **3** ($\delta_{OCHO}$, $\delta_{ArCH}$, $\delta_{Me}$) | **4** (%)[c] |
|---|---|---|---|---|
| **1j** | A | 90/10 | —, 3.56 ppm, 2.05 ppm | 93 |
| | B | 65/35 | | 91 |
| **1k** | A | 85/15 | —, 3.50 ppm, 2.02 ppm | 89 |
| | B | 90/10 | | 91 |
| **1l** | A | 100/0 | 6.98 ppm, 3.30 ppm, 1.44 ppm | 42 |
| | B | —[d] | | |

[a] Method A: styrene/PIFA (1/1.2), 0.40 M in $CH_2Cl_2$; method B: styrene/PIFA (1/1.2), under solvent-free conditions.

[b] This composition was determined from the $^1H$ NMR spectra of the crude mixture before addition of silica gel.

[c] Carbonyl compounds **4j–l** were isolated as oils by column chromatography. They are all commercially available or have been described previously, and their spectroscopic data match literature values.

[d] A complex mixture of compounds is obtained.

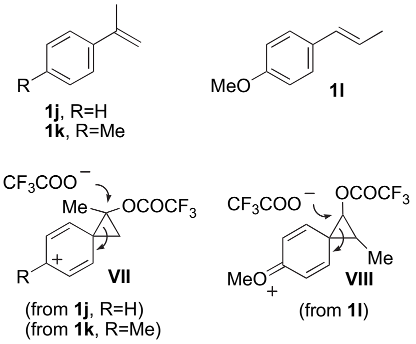


Chart 2.

### 4.2. General procedure for the synthesis of carbonyl compounds *4*

To a magnetically stirred solution of the corresponding styrene (1 mmol) in $CH_2Cl_2$ (3 mL), PIFA (1.2 mmol) was added at once. After 15 min, silica gel was added and the stirring continued overnight. The mixture was purified by column chromatography on silica gel eluting with hexane/ethyl acetate (90:10) to give the related carbonyl compounds **4** as yellowish oils.

### 4.3. General procedure for the synthesis of diols *6f*, *6i*, *6j*, and *7j*

Some 1,2-diesters (**2f**) resulted to be partially unstable and, therefore, they were identified as the corresponding 1,2-diols. To a cooled (0 °C) magnetically stirred solution of the corresponding 1,2- or 1,3-diester (1 mmol) in MeOH (10 mL), $NaBH_4$ (5 mmol) was added slowly. The stirring continued overnight at room temperature, water was added, and the mixture extracted with $CH_2Cl_2$. The corresponding diols were purified by column chromatography on silica gel eluting with hexane/ethyl acetate (80:20).

The selected spectroscopic data for new products are shown below. The characterization data for known products **2a**, **4a–e**, **4j–l** and copies of $^1H$ and $^{13}C$ NMR spectra are provided in Supplementary data.

### *4.4. Characterization data for new products*

#### *4.4.1. 1,2-Bis(trifluoroacetoxy)-3-phenylpropane (**2h**)*

$^{1}$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.41−7.20 (m, 5H), 5.50 (ddd, $J$=9.8, 6.9, 2.8 Hz, 1H), 4.58 (dd, $J$=12.2, 2.8 Hz, 1H), 4.37 (dd, $J$=12.2, 6.9 Hz, 1H), 3.14−2.99 (m, 2H); $^{13}$C NMR (300 MHz, CDCl$_3$) $\delta$ 157.3−156.4 (m, 2×CO), 133.9, 129.2, 129.1, 127.7, 114.2 (q, 2×CF$_3$), 75.4, 66.2, 36.3; MS *m/z* (% rel inten.) 230 ($M^+$−CH$_2$OCOCF$_3$, 67), 117 (53), 91 (100); HRMS calcd for $C_{11}H_{10}F_3O_2$ ($M^+$−CH$_2$OCOCF$_3$) 231.0633, found 231.0628.

#### *4.4.2. 1,2-Bis(trifluoroacetoxy)-3-(4-methoxyphenyl)propane (**2i**) and 1,3-bis(trifluoroacetoxy)-2-(4-methoxyphenyl) propane (**5i**)*

$^{1}$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.16−7.10 (m, 2H-**5i**, 2H-**2i**), 6.91−6.85 (m, 2H-**2i**, 2H-**5i**), 5.45 (ddd, $J$=9.6, 7.2, 2.6 Hz, 1H-**2i**), 4.65−4.54 (m, 1H-**2i**, 4H-**5i**), 4.36 (dd, $J$=12.2, 6.9 Hz, 1H-**2i**), 3.81 (s, 3H, **2i**/**5i**), 3.80 (s, 3H, **5i**/**2i**), 3.57−3.48 (m, 1H, **5i**), 3.07−2.93 (m, 2H, **2i**); $^{13}$C NMR (300 MHz, CDCl$_3$) $\delta$ 158.6, 158.1, 157.0−155.2 (m, 4×CO), 129.2, 127.8, 126.3, 124.8, 119.1, 115.3, 113.5, 113.4 (q, 4×CF$_3$), 113.3, 74.6 (**2i**), 66.6 (**5i**), 65.2 (**2i**), 54.1, 54.0, 41.4 (**5i**), 34.4 (**2i**); HRMS calcd for $C_{14}H_{12}F_6O_5$ 374.0589, found 374.0591.

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## Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2007.12.045.

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12. At higher dilution, the reaction time was prolonged excessively.
13. Diesters **3a**−**e** were identified by the aid of selective TOCSY experiments from the crude reaction prior to the addition of silica gel. See selected information in Table 1.
14. (a) The oxidation of alkenes to carbonyl compounds catalyzed by palladium(II) salts (known as the Wacker reaction) normally proceeds with Markovnikov regioselectivity. For a novel anti-Markovnikov regioselectivity (leading to aldehydes from terminal olefins) in the Wacker reaction of styrenes, see: Wright, J. A.; Gaunt, M. J.; Spencer, J. B. *Chem.—Eur. J.* **2005**, *12*, 949−955 and more recently, Muzart, J. *Tetrahedron* **2007**, *63*, 7505−7521; (b) The catalytic anti-Markovnikov hydration of terminal alkynes to aldehydes has been also described. See: Grotjahn, D. B.; Lev, D. A. *J. Am. Chem. Soc.* **2004**, *126*, 12232−12233.
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17. Diester **2f** resulted to be very unstable on silica gel. Therefore, it was identified from the crude $^{1}$H NMR by the distinctive A$_2$M system of its aliphatic protons [selected absorptions: 6.20 (dd, $J$=8.3, 3.6, 1H, H-1); 4.69 (dd, $J$=12.2, 8.3, 1H, H-2a); 4.59 (dd, $J$=12.2, 3.6, 1H, H-2b)], and by its transformation into the corresponding known 1-(*p*-chlorophenyl)-1,2-ethanediol **6f** (Tsujigami, T.; Sugai, T.; Ohta, H. *Tetrahedron: Asymmetry* **2001**, *12*, 2543−2549) using NaBH$_4$ in MeOH. The yield given in Table 1 is referred to the combined steps.
18. It must be pointed out that a control experiment carried out with styrene **1c** using PIDA [phenyliodine(III) diacetate], instead of PIFA, under the same reaction conditions resulted in the recovery of the starting material completely unchanged. This result evidences the superior activity of PIFA over PIDA.
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21. In these cases, donating methoxy groups are placed at 2- and 4-positions, an electronic feature required to stabilize positively charged species III. Consequently, the methoxy group located at the *meta* position in styrene **1d** disfavors the stability of intermediate III, which explains the dramatic decrease in the yield for its transformation into **4d**.
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25. (a) In both cases, olefins **1h**,**i** required 12–14 h for their complete conversion instead of the standard 3–4 h; (b) Aliphatic olefins behave in a similar way with PIFA to afford 1,2-bistrifluoroacetates. See Ref. 6; (c) These three diesters were identified by their spectroscopic behavior, but for additional authentication purposes, they were transformed into the corresponding known 1,2-diols **6h**,[26] **6i**,[27] and 1,3-diol **7i** by reductive treatment with $NaBH_4$ in methanol. For spectroscopic data of diol **6h**, see: Tanaka, Y.; Nishimura, K.; Tomioka, K. *Tetrahedron* **2003**, *59*, 4549–4556; For diol **6i**, see: Pinard, E.; Alanine, A.; Bourson, A.; Büttelmann, B.; Gill, R.; Heitz, M. P.; Jaeschke, G.; Mutel, V.; Trube, G.; Wyler, R. *Bioorg. Med. Chem. Lett.* **2001**, 2173–2176 and also Wang, L.; Seiders, J. R., II; Floreancig, P. E. *J. Am. Chem. Soc.* **2004**, *126*, 12596–12603; For diol **7i**, see: Katz, C. E.; Aubé, J. *J. Am. Chem. Soc.* **2003**, *125*, 13948–13949.
26. Carbonyl compounds **4j**–**l** were spectroscopically identified by comparison with the reported data. For ketone **4j**, see: Khanh-Van Tran, K.-V.; Bickar, D. *J. Org. Chem.* **2006**, *71*, 6640–6643; For **4k**, see: Molinaro, C.; Mowat, J.; Gosselin, F.; O'Shea, P. D.; Marcoux, J. F.; Angelaud, R.; Davies, I. W. *J. Org. Chem.* **2007**, *72*, 1856–1858 and for aldehyde **4l**, see: Baumann, T.; Vogt, H.; Bräse, S. *Eur. J. Org. Chem.* **2007**, 266–282.
27. At this stage, there is no clear explanation to the fact that no 1,2-addition of trifluoroacetate groups to styrene **1j** is detected, as it would have been anticipated considering the lack of activation of the phenyl ring.