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An atom-efficient and powerful method for direct esterification of silyl ethers catalyzed by $HClO_4$–SiO_2

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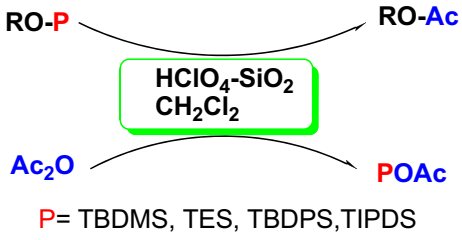
ABSTRACT

An efficient and convenient procedure for direct esterification of alkyl and aryl silyl ethers with Ac_2O and a catalyst system of perchloric acid immobilized on a silica gel ($HClO_4$–SiO_2) has been developed. The silyl protecting groups are directly replaced by acetyls and the protecting groups themselves are transformed into acetates as the sole byproducts, which can be readily recovered and converted back to silylchlorides, the original protecting agents, thus minimizing wastes.

1. Introduction

Green chemistry advocates the need for environmentally benign synthesis, which incorporates high atom efficiency, diminishes or eliminates in the use or generation of hazardous reagents or wastes and the cyclic use of reagents and catalysts.[1] In most cases, protecting groups are indispensable in the multistep synthesis of natural products and medicinal compounds but are the antithesis of atom economy.[2] Silyl groups are the most frequently employed hydroxy protecting group. In the presence of Lewis or protic acids, however, they are labile.[2a,3] On the other hand, esters are quite stable to Lewis and protic acids. The different stability of these two kinds of protecting group often necessitates changing one or more protecting groups.[4] Direct transformation presents an obvious advantage for this purpose as it replaces two steps: cleavage of the primary protecting group(s) and the subsequent installation of the new protecting group(s). Therefore, studies in synthetic methods for direct transforming protecting groups are considered valuable.[5]

A number of methods have been reported for the transformation of *tert*-butyldimethylsilyl (TBDMS) ethers to acetates, using $FeCl_3$–Ac_2O,[6] $Cu(OTf)_2$–Ac_2O,[7] $In(OTf)_3$–Ac_2O,[8] AcBr–$SnBr_2$,[9] AcCl–$ZnCl_2$,[10] $TiCl_4$–Ac_2O,[11] $ZrCl_4$–Ac_2O,[12] or $BF_3{\cdot}Et_2O$–NaI–Ac_2O.[13] Each of these methods is incompatible with some functional groups or delicate structures, limiting their application. This laboratory has found that the $FeCl_3$–Ac_2O combination induces undesired pentofuranose and pentofuranoside chain-opening.[14] Moreover, the high cost and susceptibility to moisture would be a major concern in the industrial applications of a metal salt. The presence of a metal halide also leads to a tedious workup when conducted on large scales.[15] Therefore, a mild, effective, and environmental benign procedure for this purpose would be of value and is still required for green organic synthesis. This report describes an effective and environmental-friendly protocol for direct conversion of silyl ethers into acetates in the presence of $HClO_4$–SiO_2 (Scheme 1), a catalyst, which is readily recovered and reused.[16]



Scheme 1. Direct transformation of silyl ethers to acetates.

2. Results and discussion

2.1. Direct esterification of alkyl silyl ethers

With the concept of waste minimization in mind, we have developed a method for direct transformation of acetonide into acetates using an Ac_2O–$HClO_4$–SiO_2 system.[17] Under the same conditions, the

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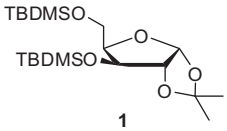
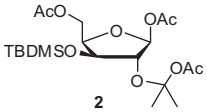
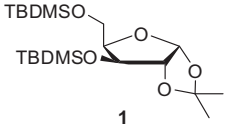
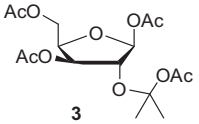
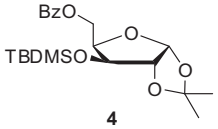
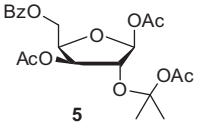
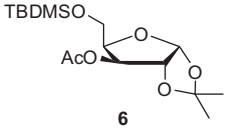
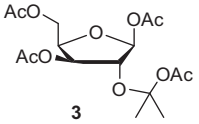
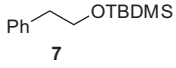
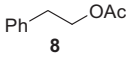
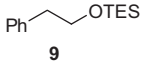
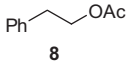
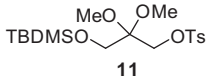
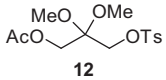
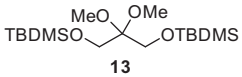
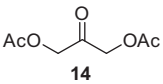
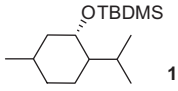
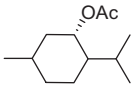
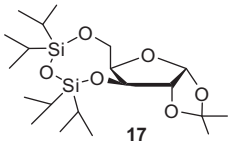
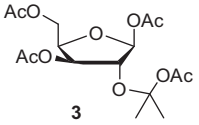
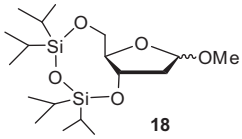
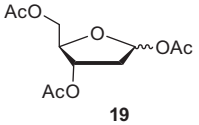
primary TBDMS group in **1** was readily displaced by an acetyl group to give **2** in 94% isolated yield (entry a, Table 1). Furthermore, under reflux in CH_2Cl_2 solution, both TBDMS groups were simultaneously substituted to afford **3** in 89% isolated yield (entry b, Table 1). Encouraged by these results and mild reaction conditions without the use of metal salts, the scope of this protocol was examined further. The steric hindered secondary ether **4** was transformed smoothly under reflux conditions to afford the desired product **5** in 87% isolated yield. Both primary TBDMS ethers **6** and **7** were also successfully transformed at rt (entry d and e, Table 1). In all cases as described above, the anomeric acetonide group was transformed into an open-chain isopropylidene acetal similar to the results obtained as transformation of acetonides.[14,17a] As anticipated, displacement of the TES ether in **9** was more readily achieved as the triethylsilyl (TES) ethers are much more sensitive to acid than TBDMS ethers.[2a,3a]

Moreover, using this one-pot procedure, selective transformation of TBDMS ethers of **11** was successfully achieved without affecting the acid labile dimethyl acetal group (entry g, Table 1).

Table 1
Direct transformation of alkyl silyl ethers into acetates catalyzed by $HClO_4$–SiO_2

Entry	Substrate	Product	Time (h)	Yield[a] (%)
a	 **1**	 **2**	0.5	94[17a]
b	 **1**	 **3**	2 (Reflux)	89[17a]
c	 **4**	 **5**	2 (Reflux)	87[17a]
d	 **6**	 **3**	0.5	89[17a]
e	 **7**	 **8**	0.75	91
f	 **9**	 **8**	0.5	89
g	 **11**	 **12**	2	85
h	 **13**	 **14**	3	81
i	 **15**	 **16**	1 (reflux)	91
j	 **17**	 **3**	5 (reflux)	87
k	 **18**	 **19**	4 (reflux)	84[18]

[a] Isolated yields and reproduced at least twice for each cases.

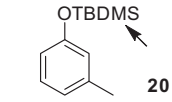
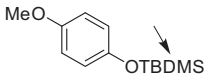
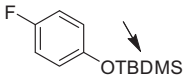
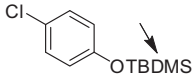
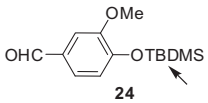
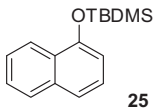
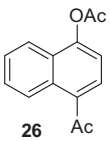
Under the same conditions, however, the dimethyl acetal group in **13** was hydrolyzed during esterification of the TBDMS groups to give the ketone **14** (entry i, Table 1). In view of the single difference between the substrates **11** and **13**, it is reasonable to speculate that the tosylate group gives rise to the different products.[19] The sterically hindered secondary TBDMS ether **15** was also directly converted into the menthol acetate **16** in excellent yield under reflux (entry j, Table 1). Markiewicz's reagent,[20] a useful bifunctional protecting agent, was readily displaced to give the desired products with reasonable yields in both cases (entries j and k, Table 1). The anomeric methoxy group in compound **18** was also substituted by acetate.

2.2. Direct transformation of aryl silyl ethers

Compared with alkyl silyl ethers, aryl silyl ethers are more sensitive to base hydrolysis as phenols are better leaving groups than alcohols.[2a] This means most methodologies for deprotection use more than stoichiometric amounts of fluoride sources (TBAF,[21] KF–Al_2O_3[22]), bases (NaOH,[23] Carbonates,[24] and LiOAc[25]) or strong acids (HF[26]). The protocol described here provides an alternative means of acetylative deprotection of phenol silyl ethers under quite weak acid conditions. To the best of our knowledge, this direct transformation is unprecedented.

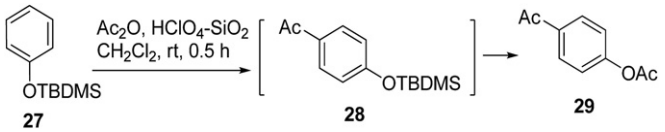
Under similar conditions, *o*-methylphenyl TBDMS ether **20** was directly transformed into corresponding acetate in 91% isolated yield (entry a, Table 2). Substituent effects were observed for this direct conversion reaction. Electron donating groups, such as alkyl and alkoxy groups promote the reaction with high yields (entries a and b, Table 2) and electron withdrawing groups led to much longer reaction times (entries c–e, Table 2). These trends agree with the lower nucleophilicity of electron deficient phenols leading to a lower reaction activity. Additionally, the aldehyde group in **24** was unaffected.[27]

Table 2
Direct esterification of aryl silyl ethers catalyzed by $HClO_4$–SiO_2

Entry	Substrate	Product	Time (h)	Yield[a] (%)
a	 **20**		4	91
b	 **21**		1	93
c	 **22**		10	84
d	 **23**		10	87
e	 **24**		16	86
f	 **25**	 **26**	8	78

[a] Isolated yields and reproduced at least twice for each cases.

4-Acetylnaphthalen-1-ol TBDMS ether, however, was formed and further converted into 4-acetylnaphthalene acetate **26** as the final product when naphthalen-1-ol TBDMS ether **25** was esterified under these conditions as above (entry f, Table 2). Similarly, 4-acetylphenyl TBDMS ether **28** was isolated and identified as an intermediate (Scheme 2) when phenyl TBDMS ether **27** underwent this procedure. It was further transformed with longer reaction times into 4-acetylphenyl acetate **29** in 82% yield. Therefore, both acyl products **26** and **29** might suggest that acetic anhydride is activated by perchloric acid to generate the acylium ion, a very reactive species, acetylizing the aryl ring. Moreover, we observed that, in the absence of perchloric acid, SiO_2–Ac_2O proved ineffective for this purpose. Thus a plausible mechanism involves attack by the oxygen atom of the silyl ethers on the acylium ion rather than protonation of the silyl ether by $HClO_4$[26,28] leading to breaking the RO–Si bond to give the corresponding acetate, a thermodynamically more stable product (Fig. 1). Based on this proposal, the ease of esterification of alkyl silyl ethers over aryl ethers could be attributed to the higher electron density on the alkyl oxygen.



Scheme 2. Direct transformation of silyl ethers to acetates along with acetylizing aryl ring.

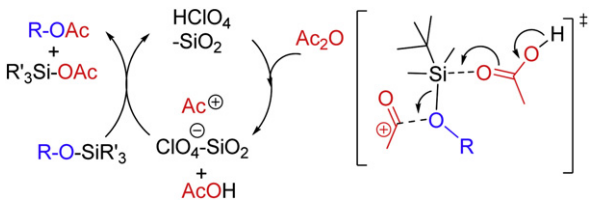
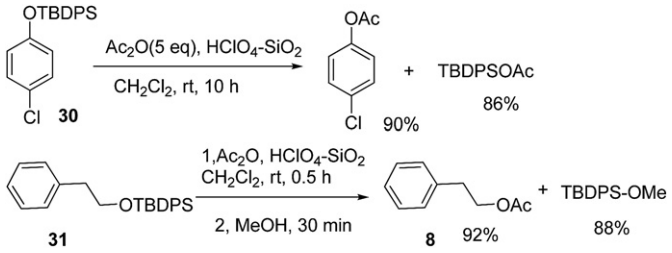


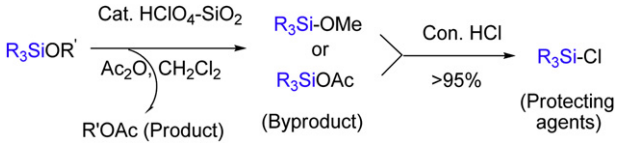
Fig. 1. Catalytic cycle and plausible transition state.

The green and atom-economical features of this method are also exhibited by the sole byproduct, trialkylsilyl acetate. Previous work in this field has isolated the desired acetate products but has failed to find direct evidence of the silyl acetates, namely byproducts.[11,12] Here, TBDPSOAc was isolated in 86% yield after the complete esterification of compound **30** and workup with a saturated aqueous solution of $NaHCO_3$. TBDPSOAc could also be converted into TBDPSOMe (88% yield) shown on the TLC plate when methanol instead of aqueous solution of $NaHCO_3$ was employed in the workup (Scheme 3).[29] Furthermore, TBDPSOAc was conveniently transformed back into its initial form, TBDPS–Cl in 95% yield, when treated with concd HCl at rt. It is well known that both TBDPS ethers and acetates are more stable than the corresponding compounds of other common silyl protecting groups, such as TES, TMS, TBDMS, and TIPS, under acid conditions.[2a,3a] More significantly, methyl silyl ethers can also be conveniently converted back to the protecting agent R_3SiCl in excellent yields by simply stirring with concd HCl without solvent (Scheme 4).[30] This is in contrast to fluoride-mediated desilylation, which affords silylfluorides, a non-recoverable waste.[5b] Thus our protocol makes silyl protecting groups recyclable agents with all the commensurate advantages of atom economy.

The practical and green aspects of this methodology are exhibited in the workup as well. In contrast to fluoride-mediated



Scheme 3. Products and byproducts generated by the direct esterification of silyl ethers.



Scheme 4. Recyclability of the sole byproducts back to silyl protecting agents.

desilylation, our method is feasible with a non-aqueous workup. This is a remarkable advantage as aqueous workup tends to be tedious and leads to large volumes of waste. For large scale reactions, excess Ac_2O, the solvent, and the byproducts R_3SiOAc or R_3SiOMe can be recovered by fractional distillation after the catalyst $HClO_4$–SiO_2 has been recovered via simple filtration.

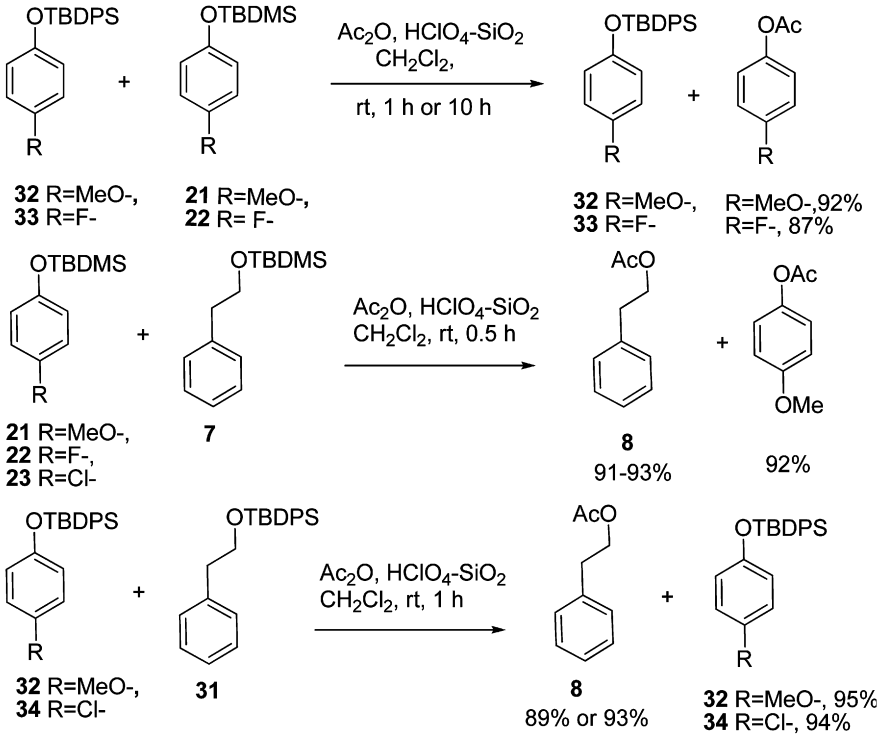
Good chemoselectivity in the cleavage of silyl groups between two different aryl silyl ethers is not easy to achieve.[3a] Our methodology might provide some advantages in this aspect in view of the proposed mechanism (Fig. 1). Treatment of an equimolar mixture of (i) *para*-methoxyphenyl TBDMS ether **21** and TBDPS ether **32** for 1 h or (ii) *para*-fluorophenyl TBDMS ether **22** and TBDPS ether **33** for 10 h afforded the desired acetates as sole products in 92% and 87% without the formation of TBDPS acetate in either case and the TBDPS ethers **32** and **33** were recovered in 97% and 92%, respectively (Scheme 5). Conceivably, similar selectivity should be established between phenyl TBDPS ether and other phenylsilyl ethers, such as phenyl TMS, phenyl TES and phenyl TIPS ethers.[31] This excellent selectivity also encouraged us to examine the selective potentiality between aryl and alkyl ethers. The reaction of a mixture of the relatively active 4-methoxyphenyl ether **21** and phenylethanol TBDMS ether **7** with Ac_2O at rt in half one hour gave 4-methoxyphenyl acetate and phenylethanol acetate **8** in 91% and 92% yields, respectively, without preference (Scheme 5). When either the more sluggish 4-fluorophenyl ether **22** or 4-chlorophenyl TBDMS ether **23** was mixed with **7**, **8** was isolated as the sole products in 93% and 91% yield and substrates **22** and **23** were recovered in 91% and 90%, respectively. These results indicate electron withdrawing substituents inactivate esterification of phenolic silyl ethers under this protocol and lead to good selectivity between aryl and alkyl silyl ethers.

Moreover, displacement of the TBDMS group in glycerol derivative **34** was also achieved selectively in quite good yield without affecting the TBDPS ether group.

To ascertain the selectivity between different TBDPS ethers, equimolar mixtures of **31** and either **32** or 4-chlorophenyl TBDPS ether **36** proceeded at rt in 1 h to afford **8** in 93% and 89% yield and the substrates **32** and **36** were recovered in 95% and 94%, respectively. This remarkable preference could be the result of the different electronic density at the different ether oxygen atoms.

3. Conclusions

In conclusion, silyl protecting groups are commonly used and changed into esters in synthetic chemistry and we have developed a simple, metal, and fluoride-free one-pot procedure for the efficient esterification of silyl ethers in an environmentally benign way. Phenolic silyl ethers could also be direct esterified with excellent selectivity. This method uses $HClO_4$–SiO_2, a cheap, nontoxic, and reusable catalyst previously reported by Chakraborti.[16,32] Significantly, silyl protecting groups were transformed into acetates as the sole byproducts, which were readily recoverable and converted back to silyl protecting agents. Solvent and



Scheme 5. Selective esterification of different silyl ethers with various electronic environment.

excess Ac_2O could also be easily recovered via distillation and wastes were minimized or eliminated. This direct transformation procedure including mild conditions, atom economy, and environmentally benign recycling should provide protecting groups with a new era of usefulness.

4. Experimental

4.1. General

Dichloromethane was dried over P_2O_5 and distilled. Acetic anhydride was distilled before being used. All reactions were monitored by thin layer chromatography (TLC) on gel F_{254} plates. ^1H NMR and ^{13}C NMR spectra were recorded on a Varian Mercury 400 spectrometer or a Bruker AV500 spectrometer in $CDCl_3$ or DMSO-d_6 and using TMS as internal standard. Exact mass measurements were performed on a LCMS2010 spectrometer equipped with a standard electrospray ionization (ESI) interface.

4.2. General procedure for direct transformation

General procedure: $HClO_4$–SiO_2 (0.5 mmol/g; 50 mg) was added to a stirred solution of substrate (1.0 mmol) and Ac_2O (0.45 mL, 5.0 mmol) in CH_2Cl_2 (5 mL) at rt or heated under reflux. After complete conversion and filtration to remove the catalyst, saturated aqueous solution of $NaHCO_3$ (10 mL) was added and separated. The aqueous solution was extracted with CH_2Cl_2 (2×10 mL). The organic layer was combined, washed with brine (10 mL), dried ($MgSO_4$), and concentrated under reduced pressure. The residual was isolated through short column chromatography on silica gel, which was eluted with ethyl acetate–petroleum (bp 60–90 °C) to give the target products.

All new products were characterized by ^1H NMR, ^{13}C NMR and HRMS (ESI) spectra and the NMR data for known compounds matched that reported in literature.

4.2.1. Aceyl 5-O-acetyl-3-O-TBDMS-2-O-(2′-acetoxyisopropyl)-β-D-xylofuranoside ***2***. ^1H NMR ($CDCl_3$): δ_H=0.13 (s, 6H, CH_3), 0.9 (s, 9H, CH_3), 1.48 (s, 6H, CH_3), 2.08 (m, 9H, CH_3), 4.05 (t, J=4.0 Hz, 1H), 4.22 (dd, J=3.6 and 12.0 Hz, 1H), 4.28 (m, 1H), 4.35 (dd, J=3.6 and 12.0 Hz, 1H), 5.19 (t, J=4.0 Hz, 1H), 6.33 (d, J=2.4 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ_C=−0.5, 18.2, 21.0, 21.3, 21.4, 25.7, 25.8, 25.8, 26.8, 69.7, 72.0, 81.9, 96.8, 113.4, 170.5, 170.8.

4.2.2. Aceyl 3,5-di-O-acetyl-2-O-(2′-acetoxyisopropyl)-β-D-xylofuranoside ***3***. ^1H NMR ($CDCl_3$): δ_H=1.45 (s, 3H, CH_3), 1.46 (s, 3H, CH_3), 2.05 (s, 3H, CH_3), 2.06 (s, 3H, CH_3), 2.07 (s, 3H, CH_3), 2.10 (s, 3H, CH_3), 4.10 (dd, J=3.6 and 8.0 Hz, 1H), 4.35 (dd, J=10.4 and 18.4 Hz, 1H), 5.33 (t, J=3.6 Hz, 2H), 6.16 (d, J=1.6 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ_C=13.6, 13.7, 13.8, 14.1, 19.9, 22.7, 54.9, 62.4, 62.5, 73.3, 89.4, 106.8, 162.9, 162.9, 162.9, 163.5.

4.2.3. Acetyl 3-O-acetyl-5-O-benzoyl-2-O-(2′-acetoxyisopropyl)-β-D-xylofuranoside ***5***. ^1H NMR ($CDCl_3$): δ_H=1.48 (s, 3H, CH_3), 1.51 (s, 3H, CH_3), 2.06 (s, 3H, CH_3), 2.09 (s, 3H, CH_3), 2.14 (s, 3H, CH_3), 4.45 (m, 2H), 4.55 (dd, J=4.0 and 12.0 Hz, 1H), 5.45 (dd, J=4.0 and 12.0 Hz, 1H), 5.53 (m, 1H), 6.22 (d, J=2.0 Hz, 1H), 7.46 (m, 2H, C_6H_5), 7.57 (m, 1H, C_6H_5), 8.02 (m, 2H, C_6H_5); ^{13}C NMR ($CDCl_3$): δ_C=20.9, 21.1, 21.4, 26.9, 27.2, 29.9, 62.9, 69.8, 69.8, 80.6, 96.6, 114.1, 128.7, 129.9, 133.6, 170.1.

4.2.4. 1-Acetoxy-3-tosyloxy-2,2-dimethoxypropane ***12***. Colorless oil, ^1H NMR ($CDCl_3$): δ_H=1.94 (s, 3H), 2.45 (s, 3H), 3.17 (s, 6H), 3.99 (s, 2H), 4.05 (s, 2H), 7.35 (d, J=8.0 Hz, 2H), 7.81 (d, J=8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ_C=21.8, 29.9, 48.6, 59.7, 64.5, 98.6, 128.3, 130.1, 145.9, 170.6; HRMS(ESI), calcd for $C_{14}H_{20}O_7S$, m/z 332.0930; found, m/z 355.0921 $(M+Na)^+$.

4.2.5. 1,3-Diacetoxy acetone ***14***. Colorless oil, ^1H NMR ($CDCl_3$): δ_H=2.18 (s, 6H), 4.76 (s, 4H); ^{13}C NMR ($CDCl_3$): δ_C=20.6, 66.5, 170.3, 198.1; HRMS(ESI), calcd for $C_7H_{10}O_5$, m/z 174.0528; found, m/z 197.0519 $(M+Na)^+$.

4.2.6. 4-Acetoxy-3-methoxybenzaldehyde. ^1H NMR ($CDCl_3$): δ_H=2.36 (s, 3H), 3.91 (s, 3H), 7.25 (d, J=8.0 Hz, 1H), 7.52 (m, 2H), 9.98 (s, 1H); ^{13}C NMR ($CDCl_3$): δ_C=20.7, 56.1, 110.8, 123.4, 124.8, 135.2, 144.9, 151.9, 168.4, 191.1; HRMS(ESI), calcd for $C_{10}H_{10}O_4$, m/z 194.0579; found, m/z 217.0569 $(M+Na)^+$.

4.2.7. (R)-3-Acetoxy-2-((tert-butyldiphenylsilyl)oxy)propyl benzoate ***36***. ^1H NMR ($CDCl_3$): δ_H=1.08 (s, 9H), 1.93 (s, 3H), 4.17 (dd, J=1.2 and 4.0 Hz, 2H), 4.23 (m, 1H), 4.34 (m, 2H), 7.34–7.46 (m, 8H), 7.57 (t, J=6.0 Hz, 1H), 7.68 (t, J=6.0 Hz, 4H), 7.94 (d, J=6.0 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ_C=20.7, 26.8, 29.7, 65.4, 65.7, 69.4, 27.7, 128.4, 129.7, 129.9, 133.0, 135.8, 166.2, 170.7; HRMS(ESI), calcd for $C_{28}H_{32}O_5Si$, m/z 476.2019; found, m/z 499.2026 $(M+Na)^+$.

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Supplementary data

Supplementary data related with this article can be found online version at doi:10.1016/j.tet.2010.12.028. These data include MOL files and InChiKeys of the most important compounds described in this article.

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