Pergamon

SCIENCE DIRECT®

Tetrahedron 59 (2003) 6739–6750

TETRAHEDRON

N-tert-Butylbenzenesulfenamide-catalyzed oxidation of alcohols to the corresponding carbonyl compounds with *N*-chlorosuccinimide

Jun-ichi Matsuo,[a,b] Daisuke Iida,[a,b] Hiroyuki Yamanaka[a,b] and Teruaki Mukaiyama[a,b,*]

[a]*Center for Basic Research, The Kitasato Institute, 6-15-5 (TCI), Toshima, Kita-ku, Tokyo, 114-0003, Japan*
[b]*Kitasato Institute for Life Sciences, Kitasato University, 5-9-1 Shirokane, Minato-ku, Tokyo 108-8641, Japan*

Received 7 February 2003; revised 22 March 2003; accepted 22 March 2003

This paper is dedicated to Professor K. C. Nicolaou on the occasion of his receipt of the 2002 Tetrahedron Prize

Abstract—*N-tert*-Butylbenzenesulfenamide (**1**)-catalyzed oxidation of various primary and secondary alcohols to the corresponding aldehydes and ketones was efficiently carried out by using *N*-chlorosuccinimide (NCS) in the coexistence of potassium carbonate and molecular sieves 4 Å at easy-to-control temperatures ranging from 0°C to room temperature. The present catalytic oxidation was performed without giving any damage to the functional groups in alcohols, and was particularly effective in the oxidation of alcohols that formed labile aldehydes because of its mild reaction conditions. Further, selective oxidation of primary hydroxy groups took place in **1**-catalyzed oxidation of several diols. Mechanistic investigation suggested that the chlorination of the sulfenamide **1** by NCS led to the formation of a key species, *N-tert*-butylbenzenesulfinimidoyl chloride (**2**), which in turn oxidized alcohols in the presence of potassium carbonate to afford carbonyl products by accompanying regeneration of the catalyst **1**.

1. Introduction

Oxidation of primary and secondary alcohols to the corresponding aldehydes and ketones[1] is one of the most important reactions in organic synthesis since the formed carbonyl compounds are quite useful synthetic intermediates especially for the construction of carbon-skeletons. There are many methods for stoichiometric oxidation of alcohols by using following oxidants: e.g. chromium(VI)-based oxidants,[2] manganese dioxide,[3] activated dimethylsulfoxides,[4,5] hypervalent iodines.[6,7] Although these methods are useful in organic synthesis, each contains problems to be solved: e.g. stoichiometric oxidations using heavy metals or activated dimethylsulfoxides accompany such co-products as poisonous heavy metal residues or bad-smelling dimethylsulfide, respectively. In Swern oxidation,[5] a commonly-employed oxidation method using dimethylsulfoxide and oxalyl chloride, the reaction temperature should be controlled strictly in low temperature (<-20°C) for the generation of a key intermediate, chlorodimethylsulfonium chloride. Concerning hypervalent iodine oxidants, it was reported that Dess–Martin periodinane (1,1,1-triacetoxy-1,1-dihydro-1,2-benziodo-3(1*H*)-one)[6] and IBX (1-hydroxy-1,2-benziodoxol-3(1*H*)-one)[7] were sometimes explosive on impact or on heating to >200°C.

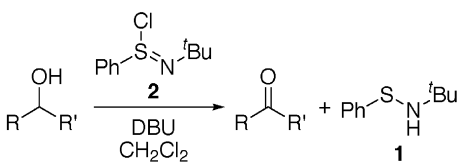
For oxidation of alcohols, catalytic oxidation with a common oxidant is now considered most desirable especially in large-scale synthesis, and numerous catalytic methods[1] using transition metal catalysts[8,9] or non-metal organic catalysts[10–12] have intensively been studied. Among them, tetrapropylammonium perruthenate (TPAP)-catalyzed oxidation[9] and 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO)-catalyzed oxidation[10,11] are well known to be versatile for oxidizing various primary and secondary alcohols to the corresponding aldehydes and ketones under mild conditions. However, TPAP-catalyzed oxidation sometimes turns unsuccessful when a substrate alcohol has a strong coordinating group though it is carried out in simple procedures and has been utilized in the synthesis of complex molecules.[9] Also, the TEMPO-bleach oxidation[10] which is the most useful for large-scale oxidation of alcohols does not work well with unsaturated alcohols.[11] Therefore, it is worthwhile to develop a new and more practical method applicable to catalytic oxidation of various alcohols to carbonyl compounds.

Recently, a new method was reported from our laboratory for the oxidation of primary and secondary alcohols to the corresponding carbonyl compounds by using more than a stoichiometric amount of *N-tert*-butylbenzenesulfinimidoyl chloride (**2**) (Eq. (1)).[13] It was further revealed that the new oxidizing agent **2** was also applicable to other oxidation

Keywords: oxidation; alcohols; catalysis.
* Corresponding author. Address: Center for Basic Research, The Kitasato Institute, 6-15-5 (TCI), Toshima, Kita-ku, Tokyo, 114-0003, Japan. Tel.: +81-3-3911-3111; fax: +81-3-3911-3482;
e-mail: mukaiyam@abeam.ocn.ne.jp

0040–4020/$ - see front matter © 2003 Elsevier Ltd. All rights reserved.
doi:10.1016/S0040-4020(03)00479-4

reactions such as oxidation of secondary amines to imines,[14] oxidation of *N*,*N*-dialkylhydroxylamines to nitrones,[15] one-pot dehydrogenation of saturated ketones to α,β-unsaturated ketones.[16] Despite its easy handling and wide-applicability, a reduced product, *N*-*tert*-butylbenzenesulfenamide (**1**), and other co-products formed by decomposition of **1** or by hydrolysis of **2** had to be removed during purification procedures in the stoichiometric oxidation of using **2**. Therefore, a study on a catalytic oxidation mediated by a catalytic amount of **2** with a suitable oxidant was tried in order to establish a more useful oxidation method.



(1)

It was considered that the catalytic oxidation would be established when in situ chlorination of sulfenamide **1** with an appropriate chlorinating agent smoothly proceeded to regenerate the oxidizing agent **2** (Fig. 1). This assumption led us to study on a new method for the catalytic oxidation of alcohols to the corresponding carbonyl compounds by employing *N*-chlorosuccinimide (NCS) as a chlorinating agent in the presence of a catalytic amount of **1**, which had been reported briefly in our previous communication.[17] In this paper, we would like to describe the convenient **1**-catalyzed oxidation of various alcohols with NCS to the corresponding carbonyl compounds in detail.

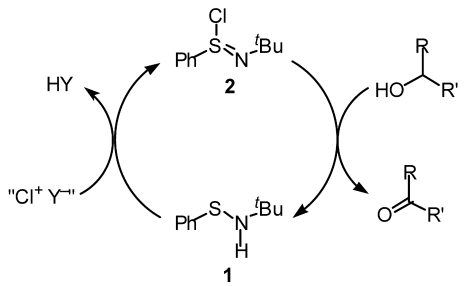


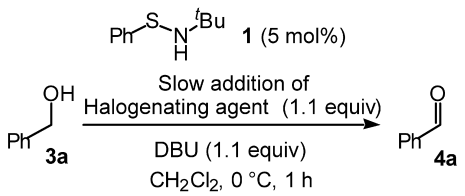
Figure 1. Outline of the catalytic cycle of sulfenamide **1**-catalyzed oxidation of alcohol.

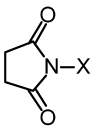
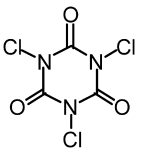
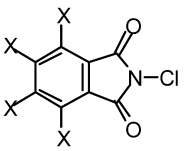
2. Results and discussion

2.1. Optimization of reaction conditions (halogenating agent, base, and additive)

Oxidation of benzyl alcohol (**3a**) to benzaldehyde (**4a**) was chosen as a model reaction to optimize the reaction conditions for **1**-catalyzed oxidation of alcohols. In the first place, several halogenating agents which in situ chlorinated **1** to regenerate sulfinimidoyl halides were screened (Table 1, entries 1–9). NCS was then employed as the chlorinating agent and 1.1 equiv. of 1,8-diazabicyclo-[5.4.0]undec-7-ene (DBU) was used as a base to trap hydrogen chloride. When one portion of NCS was added to the dichloromethane solution of 5 mol% of the catalyst **1**, alcohol **3a**, and DBU, the catalytic oxidation took place and

Table 1. Effect of halogenating agent on **1**-catalyzed oxidation of **3a** to **4a** in the presence of DBU



Entry	Halogenating agent		Yield (%)
1[a]		X = Cl	61
2		X = Cl	86
3		X = Br	87
4			85
5		X = H	40
6		X = Cl	9
7	*t*-BuOCl		3
8	Cl_2		7
9	Br_2		30

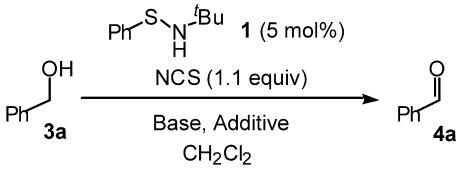
[a] NCS was added in one portion.

aldehyde **4a** was detected in 61% yield (entry 1). It was further found that the slow addition of NCS improved the yield of **4a** up to 86% probably because the operation suppressed the interaction of NCS with DBU. Investigations on other halogenating agents proved that trichloroisocyanuric acid and *N*-bromosuccinimide (NBS) were also effective in the **1**-catalyzed oxidation of **3a** in the presence of DBU while *tert*-butyl hypochlorite, chlorine, and bromine were not (entries 3–9).

In order to establish more efficient catalytic oxidation, it is important to choose a suitable base which is inert to NCS and is effective in trapping hydrogen chloride. Then, sterically hindered amine, diisopropylethylamine, was employed instead of DBU, but the yield of **4a** dropped down unexpectedly to 35% (Table 2, entry 1). Solid bases were next examined since they were insoluble and were thus considered difficult to interact with NCS. Zinc oxide, an effective solid base in the **2**-mediated stoichiometric oxidation of alcohols,[13b] did not work well in the present catalytic oxidation. After screening other solid bases, potassium carbonate was found to be most effective, and the slow addition of NCS was not required in this case (entry 4).

Addition of dehydrating agents such as molecular sieves and Drierite® improved the yield of oxidation product **4a** while sodium or magnesium sulfate showed no effects (entries 6–11). All molecular sieves that were tested (MS3A, 4A and 5A) improved the yield of **4a**, which worked to trap a trace amount of water involved in this reaction system.

Table 2. Effect of base and additive on the **1**-catalyzed oxidation of **3a** to **4a** with NCS



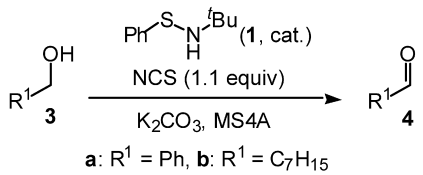
Entry	Base (equiv.)	Additive	Reaction conditions	GC-yield (%)
1[a]	*i*-Pr_2NEt (1.1)	None	0°C, 1 h	35
2	ZnO (5.0)	None	0°C, 1 h	24
3	Na_2CO_3 (10)	None	0°C, 1 h	56
4	K_2CO_3 (10)	None	0°C, 1 h	90
5	Cs_2CO_3 (10)	None	0°C, 1 h	44
6	K_2CO_3 (10)	Na_2SO_4 (10 equiv.)	0°C, 2 h	91
7	K_2CO_3 (10)	Mg_2SO_4 (10 equiv.)	0°C, 2 h	88
8	K_2CO_3 (10)	Drierite (1 g/mmol)	0°C, 1 h	94
9	K_2CO_3 (10)	MS3A (1 g/mmol)	0°C, 1 h	97
10	K_2CO_3 (10)	MS4A (1 g/mmol)	0°C, 1 h	98 (<1)[b]
11	K_2CO_3 (10)	MS5A (1 g/mmol)	0°C, 1 h	95
12	K_2CO_3 (10)	MS4A (1 g/mmol)	−78°C, 1 h	31
13	K_2CO_3 (10)	MS4A (1 g/mmol)	−45°C, 1 h	33
14	K_2CO_3 (10)	MS4A (1 g/mmol)	−23°C, 1 h	75
15	K_2CO_3 (10)	MS4A (1 g/mmol)	rt, 1 h	74

[a] *i*Pr_2NEt was added slowly.
[b] The catalyst **1** was not used.

Therefore, catalytic oxidation was successfully carried out by simply adding the catalyst **1** to the mixture of **3a**, NCS, potassium carbonate, and MS4A. Since the oxidation of **3a** with NCS[18] did not take place in the absence of the catalyst **1**, the present catalytic oxidation was clearly mediated by **1**.

Effects of solvents in the present catalytic oxidation of alcohols were investigated taking oxidation of benzyl alcohol (**3a**) and 1-octanol (**3b**) as a model. As shown in Table 3, both catalytic oxidations proceeded in the solvents other than dichloromethane such as dichloroethane, THF, *tert*-butylmethylether, or toluene to afford the desired carbonyl compounds in high yields. It was found that the oxidation proceeded most rapidly in dichloromethane while longer reaction time and more than 5 mol% of the catalyst **1** were required in other solvents.

Table 3. Effect of solvents



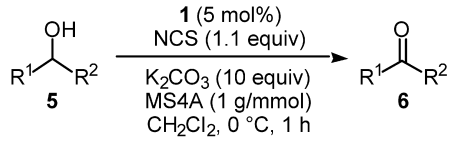
Entry	Alcohol	Solvent	**1** (mol%)	Conditions	Yield (%)[a]
1	**3a**	CH_2Cl_2	5	0°C, 1 h	98
2	**3a**	$ClCH_2CH_2Cl$	5	0°C, 3 h	94
3	**3a**	THF	10	0°C, 6 h	97
4	**3a**	^{t}BuOMe	10	0°C, 24 h	87
5	**3a**	Toluene	10	0°C, 24 h	90
6	**3b**	CH_2Cl_2	5	rt, 1 h	94
7	**3b**	$ClCH_2CH_2Cl$	5	rt, 3 h	91
8	**3b**	THF	10	rt, 3 h	93
9	**3b**	^{t}BuOMe	10	rt, 10 h	93
10	**3b**	Toluene	10	rt, 8 h	85

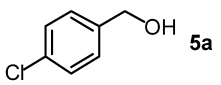
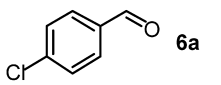
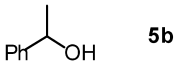
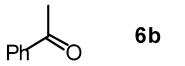
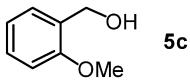
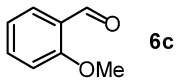
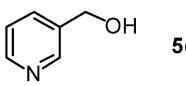
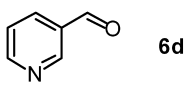
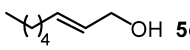
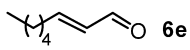
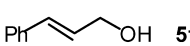
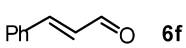
[a] Determined by GC-analysis using an internal standard.

2.2. Catalytic oxidation of various alcohols

As shown in Tables 4–8, various primary and secondary alcohols involving simple allylic and benzylic alcohols were efficiently oxidized by using 5 mol% of the catalyst **1** and 1.1 equiv. of NCS in the coexistence of 10 equiv. of potassium carbonate and 1.0 g/mmol of MS4A in

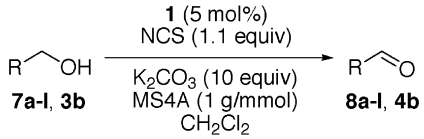
Table 4. Catalytic oxidation of simple allylic and benzylic alcohols by using the catalyst **1** and NCS in the coexistence of K_2CO_3 and MS4A

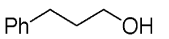
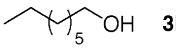
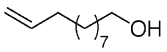
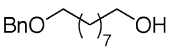
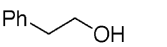
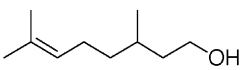
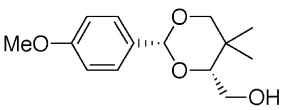
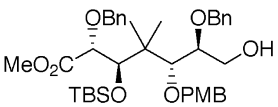
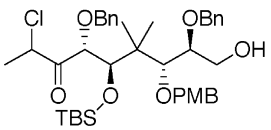
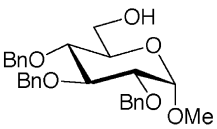
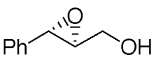
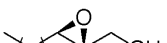
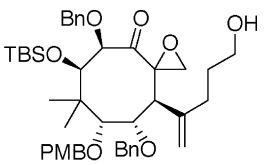


Entry	Alcohol[a]	Product	GC-yield (%)
1	 **5a**	 **6a**	93
2	 **5b**	 **6b**	83
3	 **5c**	 **6c**	86
4[b]	 **5d**	 **6d**	87
5	 **5e**	 **6e**	>99
6	 **5f**	 **6f**	80

[a] Alcohols (0.5 mmol) were used.
[b] Conditions: −78°C∼0°C, 2 h.

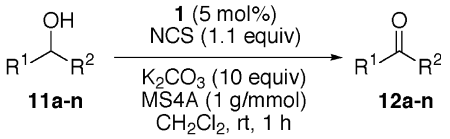
Table 5. Catalytic oxidation of various primary alcohols to aldehydes

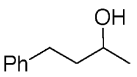
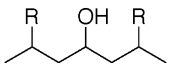
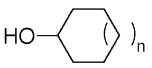
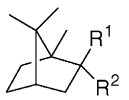
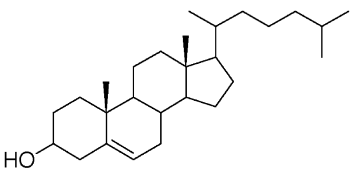
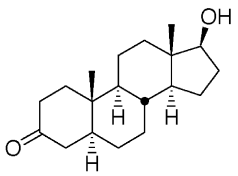
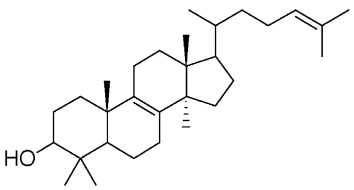
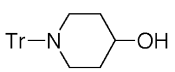
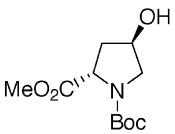
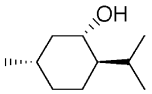
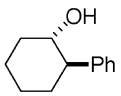


Entry	Alcohol	Conditions	Yield (%)[a]
1	 **7a**	rt, 1 h	95[b]
2[c]	 **3b**	rt, 3 h	99
3	 **7b**	rt, 30 min	>99[b]
4	 **7c**	rt, 1 h	93
5	 **7d**	0°C, 1 h	>99[b]
6	 **7e**	rt, 1 h	88[b]
7	 **7f**	0°C, 1.5 h	94
8[d]	 **7g**	rt, 30 min	88
9[d]	 **7h**	rt, 1 h	92
10	 **7i**	rt, 1 h	88[e]
11	 **7j**	0°C, 1 h	80[e]
12[f]	 **7k**	−23°C, 3 h	90
13[f]	 **7l**	rt, 2 h	93

[a] Isolated yields unless otherwise noted.
[b] Determined by GC-analysis using an internal standard.
[c] The catalyst **1** (0.5 mol%) was used.
[d] The catalyst **1** (10 mol%) was used.
[e] Isolated yield after Wittig reaction using (carbethoxymethylene)triphenylphosphorane.
[f] The catalyst **1** (20 mol%) was used.

Table 6. Catalytic oxidation of various secondary alcohols to ketones

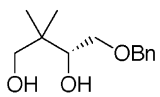
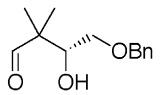
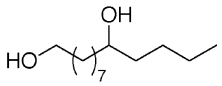
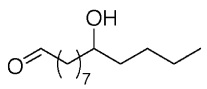
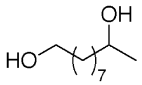
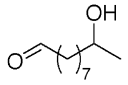


Entry	Secondary alcohol	Yield (%)[a]
1	 **11a**	96
2	 **11b**: R = H	>99
3[b]	**11c**: R = Me	90
4	 **11d**: n = 1	93
5	**11e**: n = 3	99
6	 **11f**: R^1 = OH, R^2 = H	91
7	**11g**: R^1 = H, R^2 = OH	>99
8[b]	 **11h**	92
9[b]	 **11i**	96[c]
10[b]	 **11j**	94[c]
11	 **11k**	>99[c]
12	 **11l**	92[c]
13[b,d]	 **11m**	98
14[b,d]	 **11n**	92[c]

[a] Determined by GC-analysis using an internal standard unless otherwise noted.
[b] The catalyst **1** (10 mol%) was used.
[c] Isolated yield.
[d] NBS was employed instead of NCS, and the reaction time was 24 h.

dichloromethane. Simple allylic and benzylic alcohols were smoothly oxidized at 0°C (Table 4), and primary[19] and secondary[20] alcohols were oxidized to aldehydes and ketones at 0°C–room temperature (Tables 5 and 6). Since primary alcohols were more smoothly oxidized than the

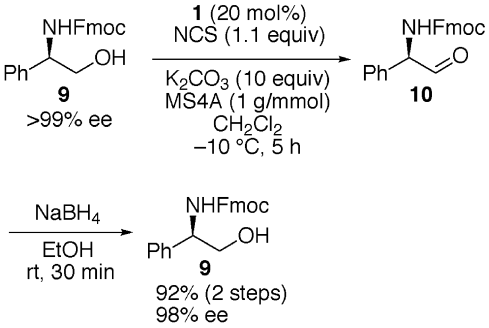
Table 7. Selective oxidation of primary hydroxy group of diol **13a–c**

Entry	Diol	Product (yield (%))[a]
1[b]	 **13a**	 **14a** (72)
2	 **13b**	 **14b** (69)
3	 **13c**	 **14c** (72)

Conditions: **1** (10 mol%), NCS (1.1 equiv.), K_2CO_3 (10 equiv.), MS4A (1 g/mmol), CH_2Cl_2. 0°C, 2 h.
[a] Isolated yield.
[b] Conditions: room temperature, 1.5 h.

secondary ones, selective oxidation of primary hydroxy group[21] took place in the catalytic oxidation of diols which had primary and secondary hydroxy groups within the same molecule, and hydroxyaldehydes were obtained in moderate yields (Table 7). In addition to small-scale oxidation, preparative scale oxidation was successfully carried out as well (Table 8),[22] and oxidation products were isolated after purification by silica gel column chromatography or distillation.

The catalytic oxidation of 2-phenylethanol (**7d**),[13b] highly functionalized primary alcohol **7h** which is a synthetic intermediate for our total synthesis of Taxol®,[23] and **7l**[24] proceeded efficiently to give the corresponding aldehydes in high yields. Also, the oxidation of *N*-Fmoc phenylglycinol **9** (>99% ee) gave a highly epimerizable[25] aldehyde **10** by keeping its high enantiomeric excess (98% ee, Eq. (2)). Double bonds in alcohols were not damaged during the oxidation, and no detectable loss of the geometric integrity of the carbon–carbon double bond was observed. Therefore, the **1**-catalyzed catalytic oxidations proceeded without giving any damage to the functional groups in alcohols and the results shown in Tables 4–7 suggest this method is applicable to the preparation of various types of aldehydes and ketones.



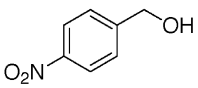
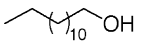
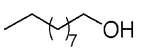
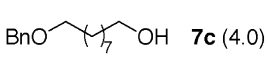
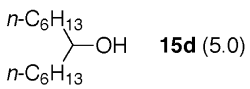
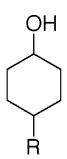
(2)

The exception is the oxidation of alcohols which form stabilized carbocationes. In the cases of **1**-catalyzed oxidation of allylic and benzylic alcohols such as *p*-methoxybenzyl alcohol (**17a**), diphenylmethanol (**17c**), and 2-cyclohexenol (**17d**) under standard oxidation conditions where the corresponding carbonyl compounds were obtained in low yields (Table 9, entries 1–4, yields shown in parentheses) while those oxidations were satisfactorily improved by using DBU as a base.

3. Mechanism

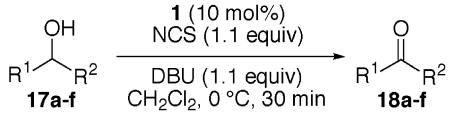
Figure 2 shows a proposed catalytic cycle in the present catalytic oxidation of alcohols by using NCS, potassium carbonate, MS4A, and a catalytic amount of sulfenamide **1**. The key oxidant **2** is first formed by chlorination of the catalyst **1** with NCS together with succinimide. It subsequently reacts with alcohol to form the key intermediate **19** in the presence of potassium carbonate.

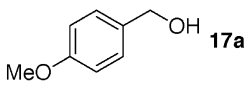
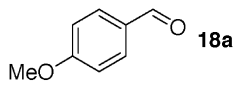
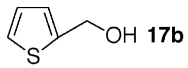
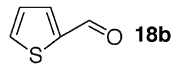
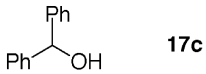
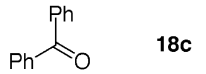
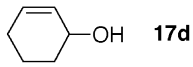
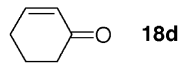
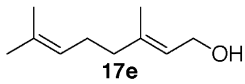
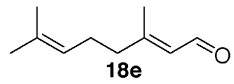
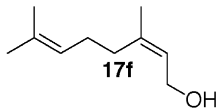
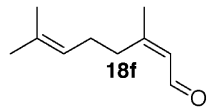
Table 8. Gram-scale catalytic oxidation of various alcohols **15a–f** and **7c** to the corresponding carbonyl compounds **16a–f** and **8c**

Entry	Alcohol (mmol)	K_2CO_3 (equiv.)	MS4A (g/mmol)	Conditions	Isolated yield (%)
1	 **15a** (6.5)	10	0.1	0°C, 3 h	98
2	 **15b** (5.0)	10	0.1	rt, 1 h	91
3	 **15c** (100)	10	0.1	rt, 1 h	91
4	 **7c** (4.0)	5	0	rt, 3 h	95
5	 **15d** (5.0)	10	0.1	rt, 1 h	>99
6	 **15e**: R = Ph (5.7)	5	0.1	rt, 2 h	>99
7	**15f**: R = ^{t}Bu (6.4)	5	0.1	rt, 2 h	98

The catalyst **1** (5 mol%) was used.

Table 9. Catalytic oxidation of allylic and benzylic alcohols by using the catalyst **1** and NCS in the coexistence of DBU



Entry	Alcohol	Product	Yield (%)[a]
1	 **17a**	 **18a**	95 (24)
2	 **17b**	 **18b**	87 (31)
3[b]	 **17c**	 **18c**	94 (12)
4	 **17d**	 **18d**	79 (14)
5	 **17e**	 **18e**	92
6	 **17f**	 **18f**	88

[a] Determined by GC-analysis using an internal standard except entry 3. Yields in entry 3 were isolated yields. Numbers in parentheses were yields which were obtained under the standard conditions of using K_2CO_3 and MS4A instead of DBU.
[b] Reaction temperature: −23°C.

Oxidation proceeds by intramolecular proton-transfer via five-membered transition state[13c] of **19** to give a carbonyl compound by accompanying regeneration of the catalyst **1**. Since 0.5 mol% of the catalyst **1** was enough to catalyze the oxidation of octanol (**3b**), this catalytic cycle worked quite efficiently (Table 5, entry 2).

Formation of sulfinimidoyl chloride **2** by the chlorination of sulfenamide **1** with NCS was confirmed by ^{1}H NMR experiment. It was observed that an equimolar mixture of sulfenamide **1** and NCS in $CDCl_3$ was quantitatively converted to **2** and succinimide at room temperature.[26] The formation of sulfinimidoyl chloride **2** by mixing **1** and NCS was suggested also by the change of color of the solution to yellow which corresponded to **2**.

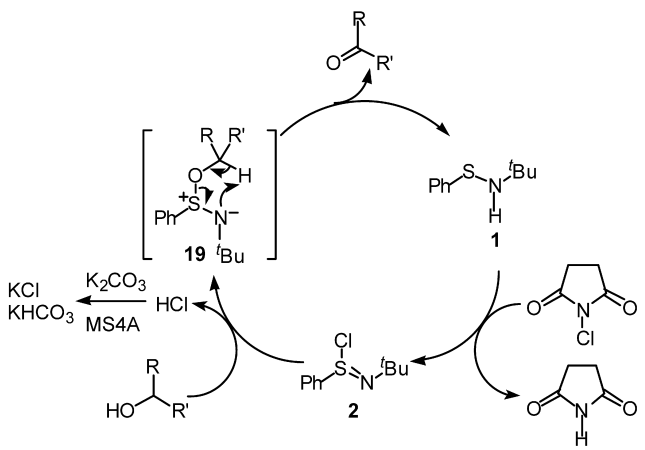
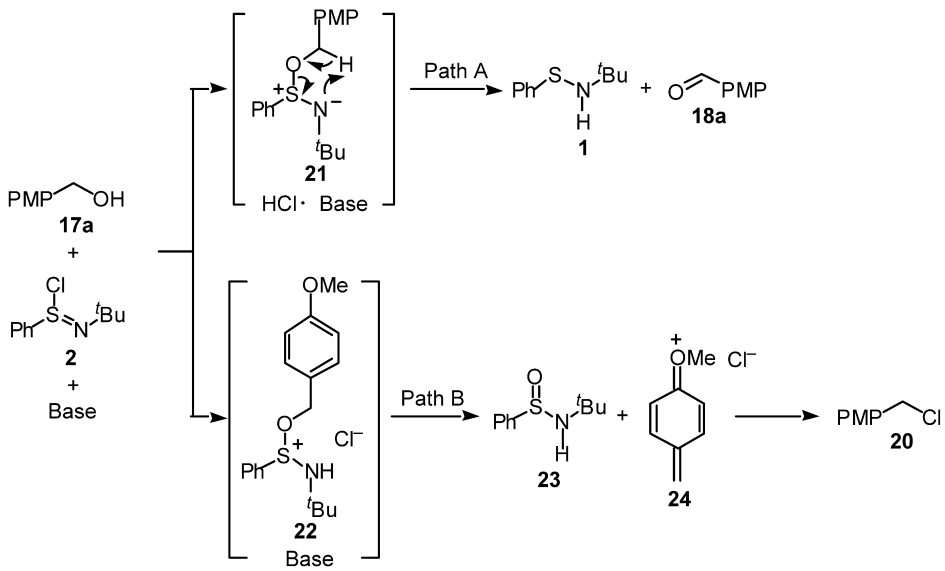


Figure 2. Assumed catalytic cycle of **1**-catalyzed oxidation of alcohols with NCS in the coexistence of K_2CO_3 and MS4A.

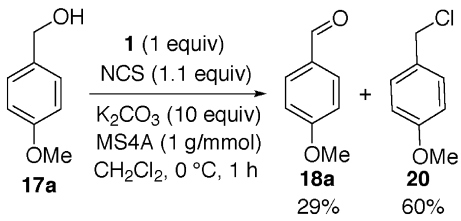
Investigation on reaction temperature revealed that the present catalytic oxidation of benzyl alcohol (**3a**) proceeded in good to exellent yields above −23°C (Table 2, entry 10 and entries 12–15). It was then assumed that the rate-determining step in the catalytic oxidation of **3b** was the chlorination of **1** with NCS which took place smoothly above −23°C because **2** oxidized **3a** rapidly at −78°C.[13] On the other hand, the rate-determining step in the catalytic oxidation of normal primary and secondary alcohols was the formation of **19** since the oxidation of those alcohols proceeded at higher temperature (0°C–room temperature) than that required for chlorination of **1** with NCS.

In order to clarify the reason for the unsuccessful oxidation of *p*-methoxybenzyl alcohol (**17a**) under the standard conditions (Table 9, entry 1), an equimolar amount of sulfenamide **1** was used in the oxidation of **17a** with NCS (Eq. (3)). It was then found that the oxidation product, *p*-methoxybenzaldehyde (**18a**), was formed in only 29% yield together with 60% of *p*-methoxybenzyl chloride (**20**).[27] It was then considered that there were two reaction pathways in the reaction of **17a** with sulfinimidoyl chloride **2** (Scheme 1). When hydrogen chloride was trapped by a base, alkyl sulfinimidate **21** immediately decomposed to afford the oxidation product **18a** and sulfenamide **1** (Path A). On the other hand, sulfonium chloride intermediate **22** was formed when hydrogen chloride was insufficiently trapped, and **22** decomposed to give sulfinamide **23** together



Scheme 1. Possible two pathways in the oxidation of *p*-methoxybenzyl alcohol (**17a**). PMP: *p*-$MeOC_6H_4$.

with stabilized cation **24** which was in turn converted to **20** (Path B). The use of DBU instead of potassium carbonate improved the catalytic oxidation of **17a** probably because DBU trapped hydrogen chloride more effectively than potassium carbonate.



(3)

4. Conclusion

N-tert-Butylbenzenesulfenamide (**1**)-catalyzed oxidation of various primary and secondary alcohols with NCS proceeded smoothly in the coexistence of potassium carbonate and MS4A to afford the corresponding aldehydes and ketones in high yields under mild conditions. Many functional groups in alcohols are tolerated under the oxidation conditions, and labile aldehydes such as phenylacetaldehyde (**8d**) and *N*-Fmoc phenylglycinal (**10**) were prepared in high yields. The present oxidation is carried out at easy-to-control reaction temperatures ranging from 0°C to room temperature by using common reagents as NCS, potassium carbonate, and MS4A. Thus, the sulfenamide **1**-catalyzed oxidation would widely be employed in organic synthesis.

5. Experimental

5.1. General

All melting points were determined on a Yanagimoto micro melting point apparatus (Yanaco MP-S3) and are uncorrected. Infrared (IR) spectra were recorded on a Horiba FT300 FT-IR spectrometer. ^{1}H NMR spectra were recorded on a JEOL EX270 (270 MHz) or a JEOL JNM-LA500 (500 MHz) spectrometer; chemical shifts (δ) are reported in parts per million relative to tetramethylsilane. Splitting patterns are designated as s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad. ^{13}C NMR spectra were recorded on a JEOL EX270 (68 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in parts per million relative to tetramethylsilane with the solvent resonance as the internal standard ($CDCl_3$; δ 77.0 ppm). High resolution mass spectra (HRMS) were recorded on a HITACHI M-80B or a JEOL JMS-AX505HA mass spectrometer. Analytical gas–liquid chromatography (GLC) was performed on a Shimadzu GC-9A instrument equipped with a flame ionizing detector and a capillary column of OV-101 (0.25 mm×50 m) or CBP10 (0.25 mm×25 m) using helium as carrier gas. Analytical TLC was performed on Merk precoated TLC plates (silica gel 60 GF254, 0.25 mm). Silica-gel column chromatography was carried out on Merk silica gel 60 (0.063–0.200 mm). Preparative thin-layer chromatography (PTLC) was carried out on silica gel Wakogel B-5F. All reactions were carried out under an argon atmosphere in anhydrous solvents unless otherwise mentioned.

5.2. Materials

Potassium carbonate was purchased from Nakalai tesque and dried in vacuo with heating just before use. Molecular sieves 4 Å (powder, <5 μm, activated) was purchased from Aldrich Chemical Company, Inc. and dried in vacuo at 250°C for 8 h. Dry solvents were prepared by distillation under appropriate drying agents. Organic bases, DBU and diisopropylethylamine, were purified by distillation. The primary alcohol **7f** was prepared according to the reported procedure.[23c] Unless otherwise noted, commercially available reagents were used as received.

5.2.1. *N-tert*-Butylbenzenesulfenamide (1).[13c,28] To a stirred solution of *tert*-butylamine (13.6 g, 185 mmol) in dry ether (150 mL), a solution of benzenesulfenyl chloride[29] (12.2 g, 84.2 mmol) in dry ether (30 mL) was added dropwise during 30 min at 0°C. After the reaction mixture

was stirred for 2 h at room temperature, the resulting white suspension was filtered and the filtrate was concentrated. The crude product was distilled (94–95°C/7 mm Hg) to give **1** (9.53 g, 62%) as a colorless oil; ^{1}H NMR (270 MHz, $CDCl_3$) δ=1.18 (9H, s), 2.79 (1H, brs), 7.0–7.1 (1H, m), 7.2–7.3 (2H, m), 7.3–7.4 (2H, m); ^{13}C NMR (68 MHz, $CDCl_3$) δ=29.1, 54.7, 122.4, 124.4, 128.3, 144.4.

5.2.2. Methyl (2*R*,3*R*,5*R*,6*S*)-2,6-dibenzyloxy-3-(*tert*-butyldimethylsiloxy)-5-(*p*-methoxybenxyloxy)-7-hydroxy-4,4-dimethylheptanonate (7g). To a stirred solution of methyl (2*R*,3*R*,5*R*,6*S*)-2,6-dibenzyloxy-3,7-bis(*t*-butyldimethylsiloxy)-5-(*p*-methoxybenxyloxy)-4,4-dimethylheptanonate[23c] (210 mg, 0.27 mmol) in THF (5.1 mL) was added 1 M hydrochloric acid (1.6 mL) at 0°C. After the mixture was stirred for 11 h at room temperature, hexane was added to the reaction mixture until two layers were separated. The resulting mixture was neutralized with saturated aqueous $NaHCO_3$ solution (ca. 7 mL), extracted with CH_2Cl_2. The combined extracts were washed with saturated aqueous $NaHCO_3$ solution and brine, dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The crude product was purified by preparative TLC (hexane/ethyl acetate=2/1) to give **7g** (168 mg, 94%) as a colorless oil: TLC R_f 0.57 (hexane/ethyl acetate=2/1); $[\alpha]_D^{25}$=+0.54 (*c* 1.0, EtOH); IR (neat, cm^{-1}) 2923, 1751, 1250, 1088; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.05 (3H, s), 0.08 (3H, s), 0.92 (9H, s), 1.02 (3H, s), 1.04 (3H, s), 2.29 (1H, brs), 3.65–3.68 (1H, m), 3.68 (3H, s), 3.77–3.87 (2H, m), 3.80 (3H, s), 3.91 (1H, d, *J*=4.3 Hz), 4.23 (1H, d, *J*=2.4 Hz), 4.29 (1H, d, *J*=11.3 Hz), 4.33 (1H, d, *J*=2.4 Hz), 4.50 (1H, d, *J*=11.6 Hz), 4.52 (1H, d, *J*=10.7 Hz), 4.56 (1H, d, *J*=11.6 Hz), 4.65 (1H, d, *J*=11.3 Hz), 4.76 (1H, d, *J*=10.7 Hz), 6.86 (2H, d, *J*=8.5 Hz), 7.26–7.33 (12H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ −4.4, −3.5, 18.4, 18.9, 21.2, 26.1, 44.2, 51.5, 55.3, 61.8, 71.4, 72.6, 74.7, 77.3, 80.6, 82.2, 83.0, 113.7, 127.7, 127.7, 127.8, 128.0, 128.2, 128.4, 129.1, 130.8, 137.5, 138.0, 159.1, 171.4; MS (EI) *m*/*z* 665 (M+); HRMS calcd for $C_{38}H_{53}O_8Si$ (M−H)$^+$: 665.3510, found *m*/*z* 665.3521.

5.2.3. (5*S*,6*R*,8*R*,9*S*,10*S*)-6-(*tert*-Butyldimethylsiloxy)-5,9-dibenzyloxy-7,7-dimethyl-10-(5-hydroxypent-1-en-2-yl)-8-(4-methoxybenzyloxy)-1-oxa-4-oxospiro[2.7]-decane (7l). Colorless oil; TLC R_f 0.45 (20% EtOAc in benzene); IR (neat, cm^{-1}) 3247, 3062, 1712, 1095; $[\alpha]_D^{15.4}$=−24.0 (*c* 0.5, EtOH); ^{1}H NMR (400 MHz, C_6D_6) δ 0.00 (3H, s) 0.03 (3H, s), 0.82 (9H, s), 1.01 (6H, s), 1.43–1.36 (2H, m), 2.00–1.93 (1H, m), 2.19–2.26 (2H, m), 2.53 (1H, d, *J*=3.1 Hz), 2.92 (1H, d, *J*=11.2 Hz), 3.08 (3H, s), 3.21 (2H, brs), 3.36 (1H, s), 3.86 (1H, d, *J*=10.7 Hz), 4.04 (1H, d, *J*=11.2 Hz), 4.20–4.32 (4H, m), 4.45 (1H, d, *J*=11.2 Hz), 4.77 (1H, s), 4.83 (1H, d, *J*=10.7 Hz), 5.16 (1H, s), 6.61 (2H, d, *J*=8.8 Hz), 6.88–7.28 (12H, m); ^{13}C NMR (75 MHz, C_6D_6) δ −4.6, −3.8, 18.5, 26.4, 31.0, 32.6, 44.5, 51.1, 52.2, 54.7, 62.3, 63.0, 72.8, 74.1, 75.3, 80.9, 89.2, 112.9, 113.9, 127.8, 127.9, 128.1, 128.3, 128.5, 130.2, 130.9, 138.8, 149.3, 159.7, 206.3; HRMS calcd for $C_{44}H_{60}NaO_8Si$ (M+Na$^+$): 767.3955, found *m*/*z* 767.3986.

5.2.4. *N*-Triphenylmethyl-4-hydroxypiperidine (11k). To the solution of 4-hydroxypiperidine (61 mg, 0.60 mmol) in dichloromethane was added triethylamine (61 mg, 0.60 mmol) and triphenylmehylchloride (167 mg, 0.60 mmol). After stirring the mixture at room temperature for 14 h, saturated $NaHCO_3$ solution was added and the mixture was extracted with dichloromethane. The combined organic extracts were washed with water, dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by preparative TLC (silica gel, hexane/AcOEt=2/1) to give **11k** (169 mg, 82%) as a colorless amorphous; TLC R_f 0.36 (hexane/AcOEt=2/1); IR (neat, cm^{-1}) 3255, 1489; ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.26–1.87 (8H, m), 2.96 (1H, brs), 3.45 (1H, brs), 6.93–7.45 (15H, m); ^{13}C NMR (68 MHz, $CDCl_3$) δ 35.3, 46.0, 69.2, 77.1, 125.9, 127.4, 128.2, 129.1; MS (EI) *m*/*z* 343 (M$^+$), 243 (Tr$^+$).

5.2.5. Preparation of (3*R*)-4-benzyloxy-2,2-dimethyl-1,3-butanediol (13a). To a stirred suspension of NaH (55%, 328 mg, 7.51 mmol) in DMF (15 mL) was added to a solution of **7f**[23c] (1.58 g, 6.26 mmol) in DMF (10 mL). After the mixture was stirred at 50°C for 1 h, benzyl bromide (1.18 g, 6.89 mmol) was added to the mixture, and the reaction mixture was stirred at 50°C for 2 h and 80°C for 1 h. After cooling to room temperature, DMF was evaporated in vacuo, and saturated $NaHCO_3$ solution (25 mL) was added to the residue. The mixture was extracted with AcOEt, and the combined organic extracts were washed with water and brine, dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The obtained crude product was purified by column chromatography (silica gel, hexane/AcOEt=10/1–5/1) to give (2*R*,4*R*)-2-(4-methoxyphenyl)-5,5-dimethyl-4-benzyloxymethyl-1,3-dioxane (1.86 g, 87%) as a colorless oil; TLC R_f 0.69 (hexane/AcOEt=2/1); $[\alpha]_D^{20}$=−28.1 (*c* 1.0, EtOH); IR (neat, cm^{-1}) 1111, 1011; ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.83 (3H, s), 1.10 (3H, s), 3.50–3.69 (4H, m), 3.79 (3H, s), 3.79–3.84 (1H, m), 4.51 (1H, d, *J*=12.0 Hz), 4.63 (1H, d, *J*=12.0 Hz), 5.48 (1H, s), 6.86–6.90 (2H, m), 7.24–7.46 (7H, m); ^{13}C NMR (68 MHz, $CDCl_3$) δ 18.9, 21.6, 31.8, 55.3, 69.9, 73.4, 78.8, 84.5, 101.6, 113.5, 127.5, 127.5, 127.6, 128.3, 131.1, 138.2, 159.9; HRMS calcd for $C_{21}H_{26}O_4$ (M+): 342.1831, found *m*/*z* 342.1826.

To the solution of (2*R*,4*R*)-2-(4-methoxyphenyl)-5,5-dimethyl-4-benzyloxymethyl-1,3-dioxane (811 mg, 2.37 mmol) in THF (15 mL) was added 1 M HCl solution (5 mL), and the mixture was stirred at room temperature for 20 h. After neutralization with K_2CO_3 at 0°C, the solvent was evaporated. The residue was extracted with CH_2Cl_2, and the combined organic extracts were dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The obtained crude product was purified by column chromatography (silica gel, hexane/AcOEt=10/1–1/1) to give **13a** (456 mg, 86%) as a colorless oil; TLC R_f 0.46 (hexane/AcOEt=1/1); $[\alpha]_D^{20}$=−15.4 (*c* 1.0, EtOH); IR (neat, cm^{-1}) 3471, 1088; ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.90 (3H, s), 0.91 (3H, s), 2.82 (1H, brs), 2.86 (1H, brs), 3.46 (2H, s), 3.48 (1H, dd, *J*=8.4, 9.4 Hz), 3.62 (1H, dd, *J*=3.0, 9.4 Hz), 3.75 (1H, dd, *J*=3.0, 8.4 Hz), 4.56 (2H, s), 7.30–7.37 (5H, m); ^{13}C NMR (68 MHz, $CDCl_3$) δ 19.4, 22.4, 37.4, 71.1, 71.7, 73.5, 77.1, 127.7, 127.9, 128.5, 137.7; HRMS calcd for $C_{13}H_{20}O_3$ (M+): 224.1412, found *m*/*z* 224.1415.

5.2.6. Preparation of tridecane-1,9-diol (13b). 13-Benzyloxy-5-tridecanol was prepared in 64% yield by using **8c**

and *n*-butyllithium according to the preparation of 10-benzyloxy-2-decanol (vide infra); TLC R_f 0.43 (hexane/AcOEt=4/1); IR (neat, cm^{-1}) 3325, 1103; ^1H NMR (270 MHz, $CDCl_3$) δ 0.90 (3H, t, J=6.6 Hz), 1.30–1.64 (21H, m), 3.46 (2H, t, J=6.6 Hz), 3.54–3.58 (1H, m), 4.50 (2H, s), 7.25–7.34 (5H, m); ^{13}C NMR (68 MHz, $CDCl_3$) δ 14.0, 22.7, 25.6, 26.1, 27.8, 29.4, 29.5, 29.6, 29.7, 37.1, 37.4, 70.4, 71.9, 72.8, 127.4, 127.5, 128.3, 138.6; MS (EI) *m/z* 306 (M^+); HRMS calcd for $C_{20}H_{34}O_2$ (M+): 306.2559, found *m/z* 306.2567.

Tridecane-1,9-diol (**13b**) was then prepared in 87% yield by deprotection of 13-benzyloxy-5-tridecanol according to the preparation of decane-1,9-diol (**13c**) (vide infra); TLC R_f 0.40 (hexane/AcOEt=1/1); IR (KBr, cm^{-1}) 3363, 3248; ^1H NMR (270 MHz, $CDCl_3$) δ 0.91 (3H, t, J=6.8 Hz), 1.26–1.59 (22H, m), 3.56–3.61 (1H, m), 3.64 (2H, t, J=6.6 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ 14.0, 22.7, 25.6, 25.7, 27.8, 29.3, 29.5, 29.6, 32.7, 37.1, 37.4. 62.8, 71.9; MS (EI) *m/z* 215 (M^+); HRMS calcd for $C_{13}H_{28}O_2$ (M+): 216.2089, found *m/z* 216.2076.

5.2.7. Preparation of decane-1,9-diol (13c).[30] To the solution of MeLi (1.04 M in ether, 1.55 mL, 1.61 mmol) in ether (5 mL) was added a solution of **8c** (400 mg, 1.61 mmol) in ether (5 mL) at −78°C. After stirring the mixture at −78°C for 30 min, the reaction was quenched by adding saturated NH_4Cl solution. The mixture was extracted with ether, and the combined organic extracts were washed with water and brine, dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The crude product was purified by column chromatography (silica gel, hexane/AcOEt) to give 10-benzyloxy-2-decanol (321 mg, 75%) as a colorless oil; TLC R_f 0.54 (hexane/AcOEt=2/1); IR (neat, cm^{-1}) 3340, 1110; ^1H NMR (270 MHz, $CDCl_3$) δ 1.17 (3H, d, J=6.3 Hz), 1.22–1.66 (15H, m), 3.46 (2H, t, J=6.6 Hz), 3.74–3.81 (1H, m), 4.50 (2H, s), 7.23–7.39 (5H, m); ^{13}C NMR (68 MHz, $CDCl_3$) δ 23.4, 25.7, 26.1, 29.3, 29.5, 29.5, 29.7, 39.3, 68.1, 70.4, 72.8, 127.4, 127.6, 128.3, 138.6; MS (EI) *m/z* 264 (M^+); HRMS calcd for $C_{17}H_{28}O_2$ (M+): 264.2089, found *m/z* 264.2095.

Under a hydrogen atmosphere (balloon, 1 atm), a suspension of 10-benzyloxy-2-decanol (310 mg, 1.17 mmol) and 10% Pd/C in acetic acid (10 mL) was stirred at room temperature for 15 h. After the mixture was filtered through Celite pad, the filtrate was concentrated in vacuo. 10% NaOH solution was added to the residue, and the mixture was extracted with ether. The combined organic extracts were washed with water and brine, dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The obtained crude product was purified by column chromatography (silica gel, hexane/AcOEt=2/1–1/1) to give **13c** (184 mg, 90%) as a colorless oil; ^1H NMR (270 MHz, $CDCl_3$) δ 1.18 (3H, d, J=6.3 Hz), 1.21–1.58 (14H, m), 2.05–2.23 (2H, m), 3.61 (2H, t, J=6.8 Hz), 3.72–3.81 (1H, m); ^{13}C NMR (68 MHz, $CDCl_3$) δ 23.3, 25.6, 29.3, 29.5, 32.6, 39.1, 62.7, 68.0.

5.3. Typical procedure for the catalytic oxidation of alcohols (Table 5, entry 4)

To a stirred mixture of potassium carbonate (691 mg, 5.0 mmol), molecular sieves 4 Å (500 mg), and *N*-chlorosuccinimide (73 mg, 0.55 mmol) in dichloromethane (1 mL) were added a solution of 9-benzyloxy-1-nonanol (**7c**) (125 mg, 0.50 mmol) in dichloromethane (1.5 mL) and a solution of **1** (4.5 mg, 25 μmol) in dichloromethane (1.5 mL) at 0°C. After the reaction mixture was stirred at 0°C for 1 h, the mixture was filtered through Celite-pad, and 10% sodium carbonate solution was added to the filtrate. The mixture was then extracted with dichloromethane, and the combined organic extracts were dried over anhydrous Na_2SO_4, filtered, and concentrated. The crude product was purified by column chromatography (silica gel, hexanes/ethyl acetate=15/1–5/1) to give 9-benzyloxy-1-nonanal (**8c**) (116 mg, 93%) as a colorless oil: ^1H NMR (270 MHz, $CDCl_3$) δ 1.26–1.31 (8H, m), 1.50–1.68 (4H, m), 2.40 (2H, td, J=7.0, 1.6 Hz), 3.46 (2H, t, J=6.5 Hz), 4.50 (2H, s), 7.25–7.37 (5H, m), 9.75 (1H, t, J=1.6 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ 22.0, 26.0, 29.0, 29.2, 29.2, 29.6, 43.8, 70.4, 72.8, 127.4, 127.5, 128.3, 138.6, 202.8.

5.3.1. Methyl (2*R*,3*R*,5*R*,6*S*)-2,6-dibenzyloxy-3-(*tert*-butyldimethylsiloxy)-5-(*p*-methoxybenzyloxy)-6-formyl-4,4-dimethylhexanoate (8g). Colorless oil: TLC R_f 0.50 (hexane/ethyl acetate 4/1); $[\alpha]_D^{24}$=+4.18 (*c* 1.4, EtOH); IR (neat, cm^{-1}) 1736, 1250, 1095; ^1H NMR (270 MHz, $CDCl_3$) δ 0.06 (3H, s), 0.91 (9H, s), 0.98 (3H, s), 1.05 (3H, s), 3.68 (3H, s), 3.78 (3H, s), 3.88 (1H, s), 4.11–4.12 (1H, m), 4.21–4.27 (2H, m), 4.30 (1H, d, J=11.8 Hz), 4.42 (1H, d, J=11.8 Hz), 4.44 (1H, d, J=10.9 Hz), 4.62–4.69 (3H, m), 6.84–6.87 (2H, m), 7.21–7.32 (12H, m), 9.71 (1H, d, J=1.7 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ −4.5, −3.6, 18.3, 19.0, 20.8, 26.1, 44.0, 51.5, 55.2, 72.3, 72.7, 73.4, 77.2, 82.0, 84.2, 85.5, 113.6, 127.7, 127.8, 127.8, 127.9, 128.2, 128.4, 129.1, 130.3, 137.3, 137.4, 159.0, 171.1, 201.4; MS (FAB) *m/z* 688 $(M+Na)^+$; HRMS calcd for $C_{38}H_{52}O_8SiNa$ $(M+Na)^+$: 687.3329, found *m/z* 687.3327.

5.3.2. (2*R*,3*R*,5*R*,6*R*)-2,6-Bis(benzyloxy)-5-(*tert*-butyldimethylsilyloxy)-8-chloro-3-(4-methoxybenzyloxy)-4,4-demethyl-7-oxo-nonanal (8h).[23c] ^{13}C NMR (68 MHz, $CDCl_3$) δ −5.1, −2.9, 18.5, 18.9, 19.0, 20.8, 26.2, 44.1, 51.2, 55.2, 72.5, 73.1, 75.1, 78.1, 83.9, 84.6, 86.6, 113.7, 127.8, 127.9, 128.0, 128.2, 128.4, 128.4, 129.0, 130.1, 137.1, 137.3, 159.1, 201.5, 205.7.

5.3.3. Ethyl (methyl 2,3,4-tri-*O*-benzyl-6,7-dideoxy-α-D-gluco-octo-6(*Z*)-enopyranosid)uronate. Alcohol (**7l**)[31] was oxidized according to the general procedure. (Carbethoxymethylene)triphenylphosphorane (241 mg, 0.69 mmol) was added to the solution of crude product in benzene, and the mixture was stirred at room temperature for 11.5 h. After evaporation of the solvent, the residue was purified by column chromatography (silica gel, hexane/AcOEt=7/1–3/1) to give ethyl (methyl 2,3,4-tri-*O*-benzyl-6,7-dideoxy-α-D-gluco-octo-6(*Z*)-enopyranosid)-uronate (234 mg, 88%) as a colorless solid; mp 60°C (lit. 69°C);[32] ^1H NMR (500 MHz, $CDCl_3$) δ 1.29 (3H, t, J=7.3 Hz), 3.24 (1H, dd, J=9.8, 9.8 Hz), 3.35 (3H, s), 3.52 (1H, dd, J=3.7, 9.8 Hz), 4.01 (1H, dd, J=9.2, 9.2 Hz), 4.20 (2H, q, J=7.0 Hz), 4.25 (1H, ddd, J=1.6, 4.9, 10.1 Hz), 4.56 (1H, d, J=10.7 Hz), 4.60 (1H, d, J=3.7 Hz), 4.67 (1H, d, J=10.7 Hz), 4.80 (1H, J=12.2 Hz), 4.82 (1H,

d, J=10.7 Hz), 4.83 (1H, d, J=10.7 Hz), 4.97 (1H, d, J=11.0 Hz), 6.11 (1H, dd, J=1.5, 15.6 Hz), 7.02 (1H, dd, J=4.9, 15.9 Hz), 7.26–7.37 (15H, m); ^{13}C NMR (68 MHz, $CDCl_3$) δ 14.2, 55.3, 60.4, 69.2, 73.4, 75.4, 75.9, 79.7, 81.6, 81.8, 98.1, 122.0, 127.7, 127.9, 128.0, 128.1, 128.1, 128.4, 128.4, 128.5, 137.6, 138.0, 138.5, 143.8, 166.2.

5.3.4. (4*R*,5*R*)-Ethyl 4,5-epoxy-5-phenylpent-2-enoate. After alcohol (**7l**)[33] was oxidized according to the general procedure, (carbethoxymethylene)triphenylphosphorane (241 mg, 0.69 mmol) was added to the solution of the crude product in benzene. The reaction mixture was stirred at room temperature for 2 h, and the solvent was evaporated. The residue was purified by column chromatography (silica gel, hexane/AcOEt=3/1) to give (4*R*,5*R*)-ethyl 4,5-epoxy-5-phenylpent-2-enoate (*E*/*Z*=76/24, 87 mg, 80%) as a colorless oil; TLC R_f 0.71 (hexane/AcOEt=2/1); ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.23 (0.72H, t, J=7.3 Hz), 1.30 (2.28H, t, J=7.3 Hz), 3.46 (0.76H, ddd, J=0.66, 1.8, 6.9 Hz), 3.82–3.83 (1H, m), 4.16 (0.48H, q, J=7.3 Hz), 4.22 (1.52 Hz, q, J=7.3 Hz), 4.63 (0.24H, ddd, J=0.66, 1.8, 7.9 Hz), 5.91 (0.24H, dd, J=7.9, 11.5 Hz), 6.04 (0.24H, dd, J=0.66, 11.5 Hz), 6.18 (0.76H, dd, J=0.66, 15.8 Hz), 6.81 (0.76H, dd, J=6.9, 15.8 Hz) 7.26–7.40 (5H, m); ^{13}C NMR (68 MHz, $CDCl_3$) δ 14.0, 14.2, 58.2, 59.7, 60.4, 60.5, 60.6, 61.0, 124.0, 124.2, 125.5, 125.8, 128.4, 128.5, 128.6, 136.1, 136.2, 143.5, 145.5, 165.5, 165.7.

5.3.5. (2*R*,3*R*)-2,3-Epoxyundecanal (8k). Colorless oil; TLC R_f 0.50 (hexane/ethyl acetate=6/1); $[\alpha]_D^{17}$=−21.4 (*c* 1.0, EtOH); IR (neat, cm^{-1}) 1728, 1450; ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.88 (3H, t, J=6.4 Hz), 1.20–1.60 (12H, m), 1.62–1.71 (2H, m), 3.13 (1H, dd, J=2.0, 6.3 Hz), 3.23 (1H, td, J=5.3, 2.0 Hz), 9.01 (1H, d, J=6.3 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ 14.0, 22.6, 25.7, 29.1, 29.2, 29.3, 31.2, 31.8, 56.7, 59.1, 198.4; MS (EI) *m*/*z* 184 (M^+).

5.3.6. (5*S*,6*R*,8*R*,9*S*,10*S*)-6-(*tert*-Butyldimethylsiloxy)-5,9-dibenzyloxy-7,7-dimethyl-10-(4-formylbut-1-en-2-yl)-8-(4-methoxybenzyloxy)-1-oxa-4-oxospiro[2.7]-decane (8l). Colorless oil; TLC R_f 0.51 (30% EtOAc in hexanes); $[\alpha]_D^{15.7}$=−33.0 (*c* 1.0, EtOH); IR (neat, cm^{-1}) 3424, 3070, 2954, 2892, 1720, 1087; ^{1}H NMR (270 MHz, C_6D_6) δ −0.03 (3H, s), 0.00 (3H, s), 0.79 (9H, s), 0.99 (6H, s), 1.74–1.83 (2H, m), 1.90–2.01 (1H, m), 2.14 (1H, d, J=4.8 Hz), 2.29–2.40 (1H, m), 2.47 (1H, d, J=4.8 Hz), 2.82 (1H, d, J=11.1 Hz), 3.05 (3H, s), 3.31 (1H, s), 3.79 (1H, d, J=10.9 Hz), 3.90 (1H, d, J=11.2 Hz), 4.16–4.29 (4H, m), 4.41 (1H, d, J=10.9 Hz), 4.50 (1H, s), 4.76 (1H, d, J=11.4 Hz), 4.84 (1H, brs), 5.07 (1H, s), 6.59 (1H, d, J=8.7 Hz), 6.79–7.27 (12H, m), 9.04 (1H, t, J=1.3 Hz); ^{13}C NMR (75 MHz, C_6D_6) δ −4.6, −3.8, 18.5, 26.4, 28.8, 41.4, 44.5, 51.0, 52.0, 54.7, 62.7, 72.7, 74.1, 75.4, 80.8, 89.1, 113.3, 114.1 127.7, 127.8, 127.8, 128.1, 128.3, 128.6, 129.8, 130.9, 138.6, 138.7, 147.9, 159.7, 200.4, 206.1; HRMS calcd for $C_{44}H_{58}NaO_8Si$ (M+Na^+): 765.3799, found *m*/*z* 765.3834.

5.3.7. 5-Cholesten-3-one (12h). Mp 125–126°C. (lit.[34] 124–129°C).

5.3.8. 5α-Androstane-3,17-dione (12i). Mp 129–130°C. (lit.[35] 130°C).

5.3.9. 5α-Lanosta-8,24-dien-3-one (12j). Mp 87–89°C. (lit.[36] 87–89°C).

5.3.10. *N*-Triphenylmethyl-4-piperidone (12k). Colorless solid; mp >200°C; IR (KBr, cm^{-1}) 1705, 1219; ^{1}H NMR (270 MHz, $CDCl_3$) δ 2.43–2.71 (8H, m), 7.15–7.53 (15H, m); ^{13}C NMR (68 MHz, $CDCl_3$) δ 42.1, 47.7, 77.3, 126.3, 127.7, 128.8, 142.4, 209.1.

5.3.11. Methyl N^{α}-Boc-4-keto-prolinate (12l).[37] ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.42–1.47 (9H, m), 2.54–2.62 (1H, m), 2.88–3.02 (1H, m), 3.77 (3H, s), 3.83–3.90 (2H, m), 4.70–4.82 (1H, m); ^{13}C NMR (68 MHz, $CDCl_3$) δ 28.1, 40.7, 41.1, 52.4, 52.7, 55.5, 56.2, 81.2, 153.4, 154.3, 172.2, 207.5, 208.3.

5.3.12. (3*R*)-4-Benzyloxy-2,2-dimethyl-3-hydroxy-1-butanal (14a). Colorless oil; TLC R_f 0.71 (hexane/AcOEt=1/1); $[\alpha]_D^{17}$=−1.29 (*c* 0.5, EtOH); IR (neat, cm^{-1}) 3417, 1720, 1095; ^{1}H NMR (270 MHz, CDCl3) δ 1.08 (3H, s), 1.09 (3H, s), 2.75 (1H, brs), 3.46 (1H, dd, J=7.4, 9.6 Hz), 3.57 (1H, dd, J=3.1, 9.6 Hz), 3.92 (1H, dd, J=3.1, 7.4 Hz), 4.53 (2H, s), 7.26–7.39 (5H, m), 9.59 (1H, s); ^{13}C NMR (68 MHz, $CDCl_3$) δ 17.6, 18.9, 48.6, 70.5, 73.4, 74.2, 127.7, 127.8, 128.4, 137.5, 205.3; HRMS calcd for $C_{13}H_{18}O_3$ (M+): 222.1256, found *m*/*z* 222.1257.

5.3.13. 9-Hydroxy-1-tridecanal (14b). Colorless oil; TLC R_f 0.70 (hexane/AcOEt=1/1); IR (neat, cm^{-1}) 3340, 1720; ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.91 (3H, t, J=6.8 Hz), 1.32–1.66 (19H, m), 2.43 (2H, td, J=1.8, 7.3 Hz), 3.57–3.60 (1H, m), 9.77 (1H, t, J=1.8 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ 14.1, 22.0, 22.7, 25.5, 27.8, 29.1, 29.3, 29.4, 37.2, 37.4, 43.9, 71.9, 202.9; MS (EI) *m*/*z* 213 (M^+); HRMS calcd for $C_{13}H_{26}O_2$ (M−H)$^+$: 213.1855, found *m*/*z* 213.1857.

5.3.14. 9-Hydroxy-1-decanal (14c).[38] ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.18 (3H, d, J=6.1 Hz), 1.21–1.80 (13H, m), 2.43 (2H, td, J=7.3, 1.5 Hz), 3.75–3.82 (1H, m), 9.76 (1H, t, J=1.5 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ 22.0, 23.4, 25.6, 29.0, 29.2, 29.3, 39.2, 43.8, 68.0, 202.9.

5.4. Large-scale catalytic oxidation of 1-decanol (15c) (Table 8, entry 3)

To a mechanically stirred suspension of potassium carbonate (138.2 g, 1.0 mol), molecular sieves 4 Å (10 g), and NCS (14.7 g, 110 mmol) in dichloromethane (400 mL) was added a solution of 1-decanol (**15c**) (15.8 g, 100 mmol) in dichloromethane (70 mL) at room temperature. After 1 h at room temperature, the reaction mixture was filtered through Celite pad, and the filtrate was concentrated by a rotary evaporator. Ether (200 mL) was added to the residue, and the ether layer was washed with 20% KOH solution (50 mL×2), 1 M HCl solution (50 mL×2), H_2O (50 mL×2), and brine (50 mL×2), dried over anhydrous Na_2SO_4, filtered, and concentrated. The crude product was purified by distillation (65°C, 2 mm Hg) to give 1-decanal (**16c**) (14.2 g, 91%) as a colorless oil.

5.5. Synthesis of *N*-Fmoc phenylglycinal (10) (Eq. (2))[25]

N-Fmoc-(*S*)-phenylglycinol (**9**)[39] (>99% ee, 108 mg,

0.30 mmol) was added to a suspension of powdered molecular sieves 4 Å (300 mg), powdered potassium carbonate (415 mg, 3.0 mmol), and NCS (44 mg, 0.33 mmol) in dichloromethane (2 mL) at −10°C. A solution of **1** (11 mg, 0.06 mmol) in dichloromethane (2 mL) was added successively to the above suspension and the resulting mixture was stirred at −10°C for 5 h. No remaining starting material was detected by TLC analysis (hexanes/ethyl acetate, 1:1) after 5 h. The reaction mixture was filtered through a pad of Celite into saturated aqueous ammonium chloride solution. The filtrate-mixture was extracted with ethyl acetate, and the combined organic extracts were washed with brine, dried over anhydrous sodium sulfate, filtered, and concentrated. The crude product was dissolved in ethanol (8 mL), and sodium borohydride (95%, 143 mg, 3.6 mmol) was added in one portion. After 30 min at room temperature, TLC analysis showed complete disappearance of *N*-Fmoc phenylglycinal (**10**), and the reduction was quenched by the addition of saturated aqueous ammonium chloride solution (30 mL). The mixture was concentrated, and the residue was extracted with ether and the organic extracts were washed with water and brine, dried over anhydrous sodium sulfate and concentrated. The residue was purified by silica gel column chromatography (hexnanes–ethyl acetate, 2:1–1:1) to give *N*-Fmoc-phenylglycinol (**9**) as a colorless solid (99 mg, 0.28 mmol, 92%). HPLC analysis (Chiralcel OD, 2-propanol–hexanes, 2:1, 0.75 mL/min, 265 nm, t_R (*N*-Fmoc-(*S*)-phenylglycinol)=8.6 min, t_R (*N*-Fmoc-(*R*)-phenylglycinol)=23.6 min) established an ee of 98%.

5.6. Catalytic oxidation of *p*-methoxybenzylalcohol (17a) using 1, NCS, and DBU (Table 9, entry 1)

To a solution of *p*-methoxybenzylalcohol (**17a**, 69 mg, 0.50 mmol), DBU (84 mg, 0.55 mmol), and the catalyst **1** (9 mg, 50 μmol) in dichloromethane (3.5 mL) was added a solution of NCS (73 mg, 0.55 mmol) in dichloromethane (1.5 mL) within 20 min at 0°C. After stirring for 30 min at the same temperature, the reaction was quenched by adding 1% hydrochloric acid (5 mL). *p*-Methoxybenzaldehyde (**18a**) was detected in 95% yield by GC-analysis using naphthalene as an internal standard.

Acknowledgements

The present work was partially supported by Grant-in-Aids for the 21st Century COE Program from the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan.

References

1. (a) Hudlicky, M. *Oxidations in Organic Chemistry*; American Chemical Society: Washington, DC, 1990. (b) Hains, A. H. *Methods for the Oxidation of Organic Compounds*; Academic: New York, 1988. (c) *Organic Synthesis by Oxidation with Metal Compounds*; Mijs, W. J., de Jonge, C. R. H. I., Eds.; Plenum: New York, 1986. (d) Sheldon, R. A.; Kochi, J. K. *Metal-Catalysed Oxidations of Organic Compounds*; Academic: New York, 1981. (e) Wiberg, W. B. *Oxidation in Organic Chemistry*; Academic: New York, 1965.
2. (a) Cainelli, G.; Cardillo, G. *Chromium Oxidations in Organic Chemistry*; Springer: New York, 1984. (b) Ley, S. V.; Madin, A. *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon: Oxford, 1991; Vol. 7, p 251. (c) Bowden, K.; Heilbron, I. M.; Jones, E. R. H.; Weedon, B. C. L. *J. Chem. Soc.* **1946**, 39. (d) Bowers, A.; Halsall, T. G.; Jones, E. R. H.; Lemin, A. J. *J. Chem. Soc.* **1953**, 2548. (e) Collins, J. C.; Hess, W. W.; Frank, F. J. *Tetrahedron Lett.* **1968**, 3363. (f) Corey, E. J.; Suggs, J. W. *Tetrahedron Lett.* **1975**, 2647. (g) Piancatelli, G.; Scettri, A.; D'Auria, M. *Synthesis* **1982**, 245. (h) Corey, E. J.; Schmidt, G. *Tetrahedron Lett.* **1979**, 399. (i) Czernecki, S.; Georgoulis, C.; Stevens, C. L.; Vijayakumaran, K. *Tetrahedron Lett.* **1985**, *26*, 1699.
3. (a) Fatiadi, A. J. *Synthesis* **1976**, *65*, 133. (b) *Encyclopedia of Reagents for Organic Synthesis*; Paquette, L. A., Ed.; Wiley: Chichester, 1995.
4. (a) Lee, T. V. *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon: Oxford, 1991; Vol. 7, p 291. (b) Pitzner, K. E.; Moffatt, J. G. *J. Am. Chem. Soc.* **1965**, *87*, 5661, 5670. (c) Albright, J. D.; Goldman, L. *J. Am. Chem. Soc.* **1965**, *87*, 4214. (d) Parikh, J. R.; Doering, W. E. *J. Am. Chem. Soc.* **1967**, *89*, 5505. (e) Omura, K.; Sharma, A. K.; Swern, D. *J. Org. Chem.* **1976**, *41*, 957. (f) Epstein, W. W.; Sweat, F. W. *Chem. Rev.* **1967**, *67*, 247.
5. (a) Omura, K.; Swern, D. *Tetrahedron* **1978**, *34*, 1651. (b) Mancuso, A. J.; Swern, D. *Synthesis* **1981**, 165. (c) Tidwell, T. T. *Synthesis* **1990**, 857. (d) Tidwell, T. T. *Org. React.* **1990**, *39*, 297.
6. (a) Dess, D. B.; Martin, J. C. *J. Org. Chem.* **1983**, *48*, 4155. (b) Dess, D. B.; Martin, J. C. *J. Am. Chem. Soc.* **1991**, *113*, 7277. (c) Meyer, S. D.; Schreiber, S. L. *J. Org. Chem.* **1994**, *59*, 7549. (d) Plumb, J. B.; Harper, D. J. *Chem. Engng News* **1990**, 3.
7. (a) Frigerio, M.; Santagostino, M. *Tetrahedron Lett.* **1994**, *35*, 8019. (b) Corey, E. J.; Palani, A. *Tetrahedron Lett.* **1995**, *36*, 3485. (c) Frigerio, M.; Santagostino, M.; Sputore, S.; Palmisano, G. *J. Org. Chem.* **1995**, *60*, 7272. (d) De Munari, S.; Frigerio, M.; Santagostino, M. *J. Org. Chem.* **1996**, *61*, 9272.
8. For selected recent reviews: (a) Sheldon, R. A.; Arends, I. W. C. E.; Dijksman, A. *Catal. Today* **2000**, *57*, 157. (b) Hayashi, M.; Kawabata, H. *J. Synth. Org. Chem., Jpn* **2002**, *60*, 137.
9. (a) Griffith, W. P.; Ley, S. V.; Whitcombe, G. P.; White, A. D. *J. Chem. Soc., Chem. Commun.* **1987**, 1625. (b) Griffith, W. P.; Ley, S. V. *Aldrichim. Acta* **1990**, *23*, 13. (c) Ley, S. V.; Morman, J.; Griffith, W. P.; Marsden, S. P. *Synthesis* **1994**, 639.
10. (a) Anelli, P. L.; Biffi, C.; Montanari, F.; Quici, S. *J. Org. Chem.* **1987**, *52*, 2559. (b) Anelli, P. L.; Banfi, S.; Montanari, F.; Quici, S. *J. Org. Chem.* **1989**, *54*, 2970. (c) Siedlecka, R.; Skarzewski, J.; Mlochowski, J. *Tetrahedron Lett.* **1990**, *31*, 2177. (d) Anelli, P. L.; Montanari, F.; Quici, S. *Org. Synth.* **1991**, *69*, 212. (e) Leanna, M. R.; Sowin, T. J.; Morton, H. E. *Tetrahedron Lett.* **1992**, *33*, 5029.
11. For TEMPO-catalyzed oxidation of alcohols using other stoichiometric oxidants, see: (a) Cella, J. A.; Kelley, J. A.; Kenehan, E. F. *J. Org. Chem.* **1975**, *40*, 1860. (b) Semmelhack, M. F.; Schmid, C. R.; Cortés, D. A.; Chou, C. S. *J. Am. Chem. Soc.* **1984**, *106*, 3374. (c) Einhorn, J.; Einhorn, C.; Ratajczak, F.; Pierre, J.-L. *J. Org. Chem.* **1996**, *61*, 7452. (d) Mico, A. D.; Margarita, R.; Parlanti, L.; Vescovi, A.; Piancatelli, G. *J. Org.*

Chem. **1997**, *62*, 6974. (e) Rychnovsky, S. D.; Vaidyanathan, R. *J. Org. Chem.* **1999**, *64*, 310. (f) Luca, L. D.; Giacomelli, G.; Porcheddu, A. *Org. Lett.* **2001**, *3*, 3041. Review: (g) Inokuchi, T.; Matsumoto, S.; Torii, S. *J. Synth. Org. Chem., Jpn* **1993**, *51*, 910. (h) de Nooy, A. E. J.; Besemer, A. C.; van Bekkum, H. *Synthesis* **1996**, 1153.

12. (a) Shimizu, M.; Kuwajima, I. *Tetrahedron Lett.* **1979**, 2801. (b) Shimizu, M.; Urabe, H.; Kuwajima, I. *Tetrahedron Lett.* **1981**, *22*, 2183. (c) Kuwajima, I.; Shimizu, M.; Urabe, H. *J. Org. Chem.* **1982**, *47*, 837. (d) Taylor, R. T.; Flood, L. A. *J. Org. Chem.* **1983**, *48*, 5160. (e) Onami, T.; Ikeda, M.; Woodard, S. S. *Bull. Chem. Soc. Jpn* **1996**, *69*, 3601.
13. (a) Mukaiyama, T.; Matsuo, J.-i.; Yanagisawa, M. *Chem. Lett.* **2000**, 1072. (b) Matsuo, J.-i.; Kitagawa, H.; Iida, D.; Mukaiyama, T. *Chem. Lett.* **2001**, 150. (c) Matsuo, J.-i.; Iida, D.; Tatani, K.; Mukaiyama, T. *Bull. Chem. Soc. Jpn* **2002**, *75*, 223.
14. (a) Mukaiyama, T.; Kawana, A.; Fukuda, Y.; Matsuo, J.-i. *Chem. Lett.* **2001**, *390*, 00. (b) Matsuo, J.-i.; Kawana, A.; Fukuda, Y.; Mukaiyama, T. *Chem. Lett.* **2001**, 712.
15. Matsuo, J.-i.; Shibata, T.; Kitagawa, H.; Mukaiyama, T. *ARKIVOC* **2001**, 58.
16. Mukaiyama, T.; Matsuo, J.-i.; Kitagawa, H. *Chem. Lett.* **2000**, 1250.
17. Mukaiyama, T.; Matsuo, J.-i.; Iida, D.; Kitagawa, H. *Chem. Lett.* **2001**, 846.
18. Filler, R. *Chem. Rev.* **1963**, *63*, 21.
19. The formed aldehydes were not overoxidized to carboxylic acids in the oxidation of primary alcohols.
20. Hydroxy groups at sterically hindered positions were slowly oxidized under the standard reaction conditions. The oxidation of those groups was found to proceed smoothly by increasing the amount of the catalyst **1** (to 10 mol%), extending reaction time (to 24 h), and using NBS instead of NCS (Table 6, entries 13 and 14).
21. For selective oxidation of primary alcohols in the presence of secondary ones, see: (a) Tomioka, H.; Takai, K.; Oshima, K.; Nozaki, H. *Tetrahedron Lett.* **1981**, *22*, 1605. (b) Kaneda, K.; Kawanishi, Y.; Teranishi, S. *Chem. Lett.* **1984**, 1481. (c) Singh, J.; Kalsi, P. S.; Jawanda, G. S.; Chhabra, B. R. *Chem. Ind.* **1986**, 751. (d) Nakano, T.; Terada, T.; Ishii, Y.; Ogawa, M. *Synthesis* **1986**, 774. (e) Ishii, Y.; Osakada, K.; Ikariya, T.; Saburi, M.; Yoshikawa, S. *J. Org. Chem.* **1986**, *51*, 2034. (f) Murahashi, S.-I.; Naota, T.; Ito, K.; Maeda, Y.; Taki, H. *J. Org. Chem.* **1987**, *52*, 4319. (g) Hanyu, A.; Takezawa, E.; Sakaguchi, S.; Ishii, Y. *Tetrahedron Lett.* **1998**, *39*, 5557. (h) Miyata, A.; Murakami, M.; Irie, R.; Katsuki, T. *Tetrahedron Lett.* **2001**, *42*, 7067. See also Refs. 9–11.
22. Smaller amounts of potassium carbonate (5–10 equiv.) and MS4A (0–0.1 g/mmol) were used in order to perform the gram-scale oxidations efficiently. It was noted that the oxidation of 9-benzyloxynonanol (**7c**) proceeded in 95% yield in the absence of MS4A.
23. (a) Mukaiyama, T.; Shiina, I.; Iwadare, H.; Sakoh, H.; Tani, Y.; Hasegawa, M.; Saitoh, K. *Proc. Jpn Acad.* **1977**, *73B*, 95. (b) Mukaiyama, T.; Shiina, I.; Iwadare, H.; Saitoh, M.; Nishimura, T.; Ohkawa, N.; Sakoh, H.; Nishimura, K.; Tani, Y.; Hasegawa, M.; Yamada, K.; Saitoh, K. *Chem. Eur. J.* **1999**, *5*, 121. (c) Shiina, I.; Shibata, J.; Ibuka, R.; Imai, Y.; Mukaiyama, T. *Bull. Chem. Soc. Jpn* **2001**, *74*, 113.
24. TPAP-NMO oxidation of **7l** gave the corresponding aldehyde **8l** in 58% yield.
25. The optical purity of **10** was determined after reduction of the formed aldehyde **10** to **9** with sodium borohydride. See: Myers, A. G.; Zhong, B.; Movassaghi, M.; Kung, D. W.; Lanman, B. A.; Kwon, S. *Tetrahedron Lett.* **2000**, *41*, 1359.
26. Haake reported that alkylamino-succinimidosulfonium chlorides were obtained on treatment of *N*,*N*-dialkylsulfenamide with NCS. See: Haake, M.; Benack, H. *Synthesis* **1976**, 308.
27. The similar formation of chlorides was observed in Corey–Kim oxidation. See: Corey, E. J.; Kim, C. U. *J. Am. Chem. Soc.* **1972**, *94*, 7586.
28. Miura, Y.; Asada, H.; Kinoshita, M. *Bull. Chem. Soc. Jpn* **1977**, *50*, 1855.
29. Barrett, A. G. M.; Dhanak, D.; Graboski, G. G.; Taylor, S. J. *Org. Synth.* **1990**, *68*, 8.
30. Dragovich, P. S.; Prins, T. J.; Zhou, R. *J. Org. Chem.* **1995**, *60*, 4922.
31. Litak, A.; Jodal, I.; Nanasi, P. *Carbohydr. Res.* **1975**, *44*, 1.
32. Postema, M. H. D.; Calimente, D.; Liu, L.; Behrmann, T. L. *J. Org. Chem.* **2000**, *65*, 6061.
33. Gao, Y.; Hanson, R. M.; Klunder, J. M.; Ko, S. Y.; Masamune, H.; Sharpless, K. B. *J. Am. Chem. Soc.* **1987**, *109*, 5765.
34. (a) *Beilsteins Handbuch der Organischen Chemie*; Boit, H.-G., Ed.; Springer: Berlin, 1968; p 1608 3Erg., Bd. 7. (b) Fieser, L. F. *Organic Syntheses*; Wiley: New York, 1963; Collect. Vol. IV, p 195.
35. Pearson, A. J.; Chen, Y.; Han, G. R.; Hsu, S.; Ray, T. *J. Chem. Soc., Perkin Trans. 1* **1985**, 267.
36. Boar, R. B.; Lewis, D. A.; McGhie, J. F. *J. Chem. Soc., Perkin Trans. 1* **1973**, 1583.
37. Tamaki, M.; Han, G.; Hruby, V. J. *J. Org. Chem.* **2001**, *66*, 3593.
38. Bestmann, H. J.; Kellermann, W.; Pecher, B. *Synthesis* **1993**, 149.
39. (a) Dondoni, A.; Perrone, D.; Semola, T. *Synthesis* **1995**, 181. (b) Carpino, L. A.; Han, G. Y. *J. Org. Chem.* **1972**, *37*, 3404.