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Pinacol couplings of a series of aldehydes and ketones with SmI_2/Sm/Me_3SiCl in DME

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ABSTRACT

The pinacol coupling is one of the most significant methods to synthesize *vic*-diols. The combination of samarium diiodide (SmI_2) and samarium metal successfully induces the selective pinacol couplings of not only aromatic aldehydes and ketones but also aliphatic ones in the presence of trimethylchlorosilane (Me_3SiCl) in 1,2-dimethoxyethane (DME). DME is the most suitable solvent for the reduction system using SmI_2 and Me_3SiCl. Me_3SiCl, a widely available additive, prevents the decomposition of the formed *vic*-diols, i.e., *meso*-isomers, and controls their stereochemistry. In particular, the pinacol couplings of sterically hindered aliphatic aldehydes and ketones proceed with excellent diastereoselectivities to afford *dl*-isomers in good yields.

1. Introduction

The pinacol coupling of carbonyl compounds is an important method for the construction of functionalized carbon–carbon bonds.[1] Since the pinacol coupling was first developed by Fitting in 1859,[2] it has been widely used to synthesize vicinal diols (*vic*-diols). A number of *vic*-diols are found in various important natural products and medicinal chemicals.[3]

Samarium diiodide (SmI_2) is one of the most useful single-electron reducing agents in synthetic organic chemistry. It can be prepared conveniently from samarium metal and 1,2-diiodoethane in THF,[4] and a number of reductive transformations involving single-electron transfer processes have been reported.[5] SmI_2 itself can also induce the pinacol couplings of carbonyl compounds, especially aromatic carbonyl compounds.[5q–x,6] Furthermore, to scope substrates such as aliphatic carbonyl compounds and functionalized ones, and to improve the diastereoselectivity, SmI_2 molar ratios, additives, and solvents were investigated in detail. There have been many reports on pinacol couplings using SmI_2; these reports show that, in spite of similar reaction conditions, the yields and/or diastereoselectivities of pinacol couplings often vary. This is most likely due to (1) the presence/absence of Samarium metal in the reduction system, (2) the methods for quenching the reaction (acid/air-quenching), and (3) the influence of in-situ-formed silyl iodides from SmI_2 and silyl chlorides when silyl chlorides were used as additives.

As to (1), we have revealed that the combination of SmI_2 and samarium metal leads to enhanced reducing ability compared to those of SmI_2 and Samarium metal alone.[7] SmI_2 has occasionally been synthesized using excess amounts of Samarium metal, followed by the subsequent pinacol coupling reaction performed in the same vessel. However, most papers do not clearly describe the details about the presence of Samarium metal. For example, regardless of the use of excess Samarium metal in the preparation of SmI_2, the pinacol coupling reactions are reported as reactions using only SmI_2. Therefore, the presence/absence of Sm metal is an important issue in the SmI_2-induced pinacol coupling reactions of carbonyl compounds.

As to (2), the presence of H_2O is also very important when discussing the reducing ability of SmI_2. Hasegawa and Curran found that water also dramatically enhances the reducing ability of SmI_2, and noted the difference in yield between acid-quenched and air-quenched reactions.[8] Generally, after a reaction using SmI_2, the resulting reaction mixture is quenched with acids. Even if the desired pinacol coupling did not proceed, the addition of water during the workup immediately generates SmI_2/H_2O, which can work quickly as a reducing agent for the carbonyl compounds. However, few papers clearly describe the quenching procedures.[6f,n]

As to (3), pinacol coupling is promoted with high diastereoselectivity in the presence of chlorosilanes as additives.[6] In the case of SmI_2 in THF (a representative solvent for SmI_2), however, undesired reaction of SmI_2 with chlorosilane forms in situ silyl

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iodide, which causes the reductive ring-opening reaction of THF, resulting in the consumption of SmI_2 and the formation of byproducts ($Me_3SiOCH_2CH_2CH_2CH_2SiMe_3$) from THF.[9] To avoid the formation of silyl iodide, we previously developed the pinacol couplings of aromatic carbonyl compounds using Sm metal and Me_3SiCl under sonication in THF in the absence of SmI_2.[10] Furthermore, this ring-opening problem could be solved through the use of 1,2-dimethoxyethane (DME) as solvent, because acyclic ethers do not undergo reductive cleavage of the ethereal C–O bond even in the presence of silyl iodide.[7e] Thus, the reductive coupling of both aromatic and aliphatic carbonyl compounds can be facilitated using the SmI_2/Sm/Me_3SiCl system in DME with high diastereoselectivity. There are a very limited number of systematic studies on SmI_2-induced pinacol couplings of aromatic/aliphatic aldehydes/ketones using the same reduction system. Herein, we report an overview of the pinacol couplings of aromatic and aliphatic carbonyl compounds using SmI_2/Sm/Me_3SiCl in DME.

2. Results and discussion

2.1. Pinacol couplings of aromatic carbonyl compounds with SmI_2/Sm/Me_3SiCl in DME

First, we investigated the reductive coupling of benzaldehyde (**1a**) with SmI_2/Sm/Me_3SiCl in DME (Table 1). When **1a** (1 mmol) was treated with SmI_2 (1.1 mmol), Sm (1.1 mmol), and Me_3SiCl (1.1 mmol) in DME at room temperature for 10 min, corresponding *vic*-diol **2a** was obtained in 61% yield with moderate diastereoselectivity (entry 1). In the absence of Me_3SiCl, the yield of **2a** was 57% (entry 2). When 1.3 equiv of SmI_2/Sm/Me_3SiCl was used, both the yield and diastereoselectivity (*meso*-selectivity) of **2a** increased (entry 3). The best result was obtained when the reaction was conducted using 0.50 mmol of **1a**, 1.0 mmol of SmI_2, 1.0 mmol of Sm, and 1.5 mmol of Me_3SiCl at room temperature for 10 min (entry 4). In contrast, the absence of Sm metal resulted in a very low yield of **2a** (entry 5). However, the pinacol coupling of benzaldehyde proceeded well even in the absence of Me_3SiCl (entry 6). The results clearly indicate that, in the case of aromatic aldehydes, Sm metal strongly induces the pinacol coupling, though Me_3SiCl is not effective.

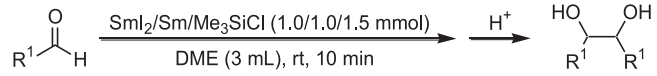
The pinacol couplings of several different aromatic aldehydes were examined under the optimized reaction conditions (Table 1, entry 4). As shown in Table 2, various substituted aromatic aldehydes (**1b**–**1e**) can undergo reductive coupling with SmI_2/Sm/Me_3SiCl in DME to give corresponding *vic*-diol **2** in good to excellent yields with preferential formation of the *meso*-isomers.

Next, we investigated the pinacol couplings of aromatic ketones using SmI_2/Sm/Me_3SiCl in DME (Table 3). Although acetophenone (**3a**), as a model compound, was treated with SmI_2/Sm/Me_3SiCl in DME under the same conditions as those for aromatic aldehydes, corresponding coupling product **4a** was obtained in only 30% yield (entry 1). When the reductive coupling of **3a** was conducted in refluxing DME (85 °C) for a prolonged reaction time (3 h), the yield of **4a** increased; however, interestingly, the diastereoselectivity changed and the formation of the *dl*-isomer was preferred (entry 2). Previously, we reported the reductive dimerization of chlorosilanes using SmI_2/Sm in DME.[7e] This dimerization may influence the pinacol coupling of **3a** when a large excess of Me_3SiCl is used. Thus, we examined the reaction using a slight excess of Me_3SiCl (0.55 mmol), and *vic*-diol **4a** was obtained in 58% yield (entry 3). Prolonging the reaction time further (20 h) decreased the yield of **4a** (entry 4). As some side reactions such as benzoin condensation and the Tishchenko reaction have been reported to occur with higher concentrations of SmI_2,[11] the amounts of both SmI_2 and Sm were reduced to 0.55 mmol, resulting in the increase in the yield of **4a** (71%) (entry 5). However, when a lower amount of SmI_2 than of **3a** was used, the pinacol coupling did not occur sufficiently (entry 6). The best results were achieved under diluted conditions (10 mL of DME), which afforded **4a** in 81% yield (entry 7).

Although the pinacol coupling of **3a** has been reported,[6a,b,g,m,p,r,11] only a very limited number of pinacol couplings of other aromatic ketones with SmI_2 are known.[11a] Thus, we examined the pinacol couplings of several substituted aromatic ketones. The reductive coupling proceeded successfully to give the corresponding *vic*-diols in good yields under the optimized reaction conditions (Table 3, entry 7), as shown in Table 4. In all cases, *dl*-isomers were obtained preferentially.

To clarify the behavior of Me_3SiCl, we performed some control experiments (Scheme 1, A–C). In condition A, the pinacol coupling of benzaldehyde (1.0 mmol) was conducted with 1.0 mmol of both SmI_2 and Sm in DME for 10 min. In condition B, after applying

Table 2
Pinacol couplings of aromatic aldehydes with SmI_2/Sm/Me_3SiCl in DME

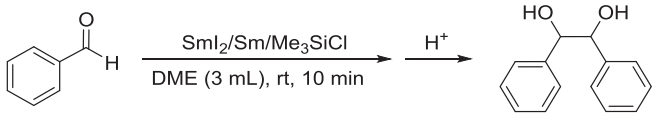


1 2

Entry	R^1	Isolated yield (%)	*dl*/*meso*
1	C_6H_5 (**1a**)	85	18:82
2	*p*-MeC_6H_4 (**1b**)	78	17:83
3[a]	*p*-$MeOC_6H_4$ (**1c**)	71	24:76
4	*p*-BrC_6H_4 (**1d**)	84	36:64
5	*p*-$CF_3C_6H_4$ (**1e**)	75	34:66

[a] DME (10 mL) was used.

Table 1
Pinacol coupling of benzaldehyde with SmI_2/Sm/Me_3SiCl in DME

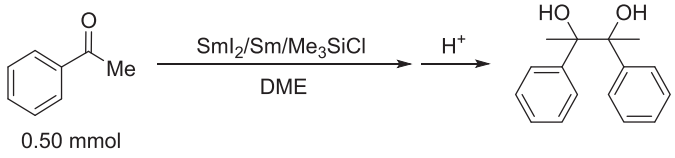


1a 2a

Entry	**1a** (mmol)	SmI_2 (mmol)	Sm (mmol)	Me_3SiCl (mmol)	Yield of **2a**[a] (%)	*dl*/*meso*[a]
1	1.0	1.1	1.1	1.1	61	26:74
2	1.0	1.1	1.1	0	57	27:73
3	0.80	1.1	1.1	1.1	81	19:81
4	0.50	1.0	1.0	1.5	88	18:82
5	0.50	1.0	0	1.5	3	0:100
6	0.50	1.0	1.0	0	81	18:82
7[b]	0.50	1.0	1.0	0	81	30:70

[a] Determined by ^1H NMR.
[b] Use of THF (3 mL) in place of DME.

Table 3
Pinacol coupling of acetophenone with SmI_2/Sm/Me_3SiCl in DME

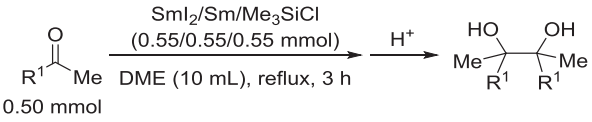


0.50 mmol **3a** **4a**

Entry	SmI_2 (mmol)	Sm (mmol)	Me_3SiCl (mmol)	DME (mL)	Conditions	Yield[a] (%)	*dl*/*meso*
1	1	1	1.5	3	rt, 10 min	30	33:67
2	1	1	1.7	3	Reflux, 3 h	47	62:38
3	1	1	0.55	3	Reflux, 3 h	58	78:22
4	1	1	0.55	3	Reflux, 20 h	38	74:26
5	0.55	0.55	0.58	3	Reflux, 3 h	71	69:31
6	0.25	0.55	0.56	3	Reflux, 3 h	56	66:34
7	0.55	0.55	0.59	10	Reflux, 3 h	81	65:35

[a] Determined by ^1H NMR.

Table 4
Pinacol couplings of aromatic ketones with SmI_2/Sm/Me_3SiCl in DME



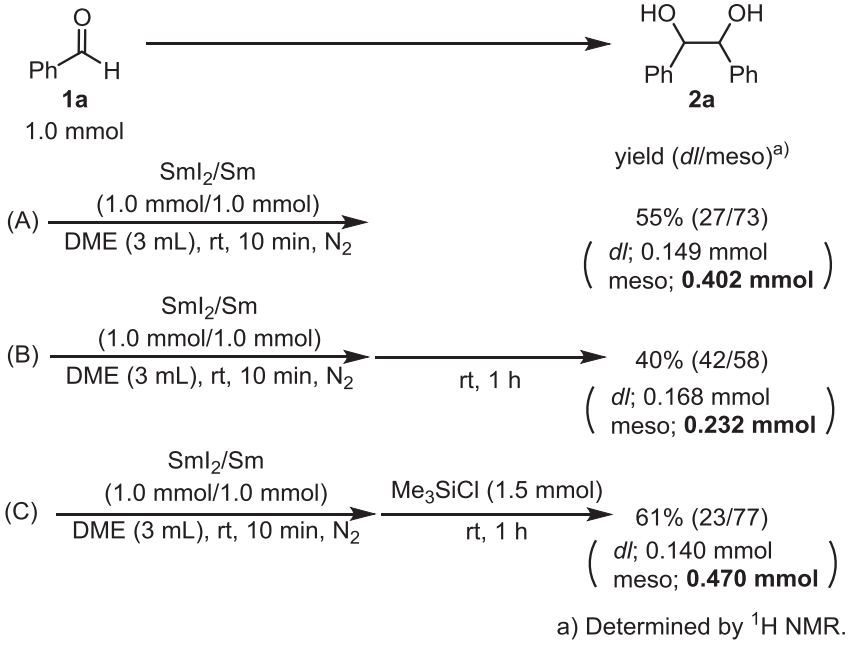
0.50 mmol **3** **4**

Entry	R^1	Isolated yield (%)	*dl*/*meso*
1	C_6H_5 (**3a**)	74	65:35
2[a]	*p*-MeC_6H_4 (**3b**)	70	67:33
3	*p*-$CF_3C_6H_4$ (**3c**)	74	79:21
4	*p*-ClC_6H_4 (**3d**)	73	66:34

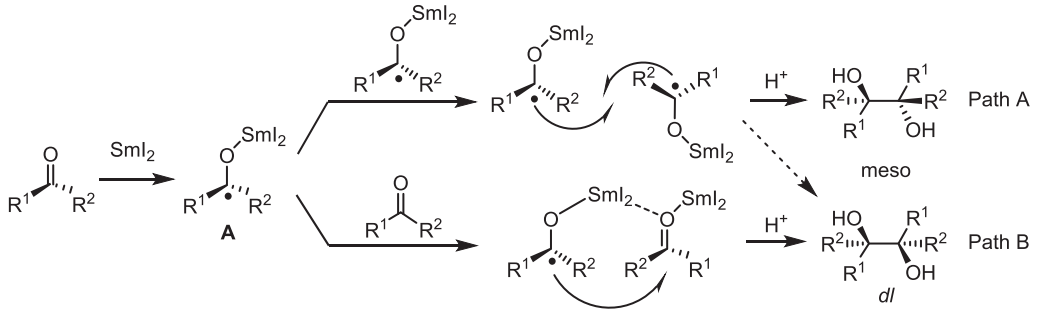
[a] DME (3 mL) was used.

condition A, the reaction continued for another 1 h. In condition C, after applying condition A, Me_3SiCl (1.5 mmol) was added to the solution and the resulting mixture was stirred for 1 h. Product **2a** was obtained in 55% (*dl*/*meso*=27:73), 40% (*dl*/*meso*=42:58), and 61% (*dl*/*meso*=23:77) yields, respectively, with conditions A, B, and C. The yield of the *meso*-isomer with condition B was lower than those with conditions A and C. This strongly suggests decomposition of the *meso*-isomer during the additional 1 h in condition B.[12] In contrast, the *meso*-isomer did not decompose in condition C. These results suggest that the addition of Me_3SiCl can prevent the decomposition of the *meso*-isomer, probably through the bis-silylation of the samarium salt of the pinacol coupling product.

Although several mechanistic pathways of the SmI_2-induced pinacol coupling have been proposed in the literature,[5x,6l,13] its mechanism has not be clarified completely thus far. Mechanistic consideration is shown in Scheme 2. SmI_2-induced pinacol coupling reactions of carbonyl compounds begin with the generation of samarium-coordinated ketyl radical species **A** via single-electron transfer from SmI_2. In path A, the generated ketyl radicals **A** are coupled in an *anti* orientation, avoiding the overlap of the sterically hindered groups, which leads to the *meso*-diol. In path B, coordination of SmI_2 to both the ketyl radical and the substrate carbonyl compound is followed by coupling in a *syn* orientation to give the *dl*-diol. Path A likely operates for the reactions of aromatic



Scheme 1. Behavior of Me_3SiCl.



Scheme 2. Plausible reaction pathways of aromatic carbonyl compounds.

aldehydes because the concentrations of ketyl radical species are higher than those of less-reactive aromatic ketones. Accordingly, the corresponding *meso*-diols are obtained preferentially (Tables 1 and 2). For aromatic ketones, path B likely operates because the corresponding ketyl radical species gradually generate in situ and/or the coupling of ketyl radical species (path A) is inhibited by the steric hindrance of substituents.

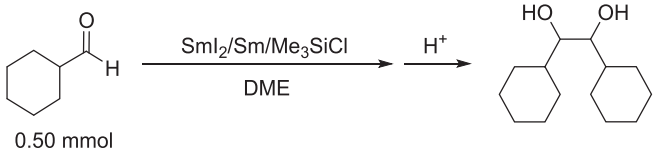
2.2. Pinacol couplings of aliphatic carbonyl compounds with SmI_2/Sm/Me_3SiCl in DME

Compared to aromatic aldehydes and ketones, aliphatic ones are generally less reactive. As to the diastereoselectivities of the hitherto known pinacol couplings of aliphatic carbonyl compounds with SmI_2 in the presence of HMPA,[6j] ferrocene,[6k] or tetraglym[6k] as additives, *dl*-diols were obtained preferentially but not completely. With other additives,[6i,j] lower diastereoselectivities were observed. Thus, we next investigated in detail the pinacol couplings of aliphatic carbonyl compounds (Table 5). When cyclohexanecarboxaldehyde (**5a**) (0.50 mmol), as a model compound, was treated with SmI_2 (1.0 mmol), Sm (1.0 mmol), and Me_3SiCl (1.5 mmol) in DME at room temperature for 20 h, corresponding *vic*-diol **6a** was obtained in 39% yield, surprisingly, with *dl*-selectivity (entry 1). Elevating the temperature did not facilitate the reaction (entry 2). The yield of **6a** did not increase upon prolonging the reaction time or adding 4 equiv of Me_3SiCl (entry 3). When a small excess of Me_3SiCl was used, the yield of **6a** increased slightly (52%) (entry 4). Although using small excesses of SmI_2, Sm, and Me_3SiCl worked well in the reductive couplings of aromatic ketones (Table 4), the coupling of **5a** under similar conditions did not proceed effectively (entry 5). In the absence of Me_3SiCl, the yield of **6a** decreased (28%) and small amounts of the *meso*-isomer was also formed (entry 6). Since the reagent concentrations were important in the pinacol couplings of aromatic ketones, this coupling reaction was examined using 3, 10, and 20 mL of DME. The best results were obtained when 10 mL of DME was used (entries 4, 7, 8). When $Ph_2MeSiCl$ was used in place of Me_3SiCl, the *dl*-diol was obtained in 70% yield with excellent diastereoselectivity (entry 11).[14]

Table 6 presents the reductive couplings of some other aliphatic carbonyl compounds under the optimized reaction conditions (Table 5, entry 7). Aliphatic aldehydes **5a**–**5d** and ketones **5e**–**5i** successfully underwent reductive coupling with SmI_2/Sm/Me_3SiCl in DME to give the corresponding *vic*-diols **6a**–**6i** in moderate to high yields. Although the diastereoselectivity was very substrate-sensitive, complete stereoselectivity (only *dl*-isomer) was observed with several substrates (**5a**, **5c**, **5e**, **5f**, **5h**, and **5i**). In general, the pinacol couplings of aliphatic carbonyl compounds afford *dl*-isomers preferentially, but not exclusively. Notably, the present SmI_2/Sm/Me_3SiCl conditions in DME afford only *dl*-isomers with many substrates. The diastereoselectivities toward products **6e** and **6h** have never been discussed.[6a,b,i]

Since $Ph_2MeSiCl$ promoted the reductive coupling of **5a** efficiently (Table 5, entry 11), we screened various chlorosilanes using 2-methylbutanal (**5b**) as a substrate. As shown in Table 7, Me_3SiCl generated the highest yield of corresponding diol **6b**. However, the bulkiness of chlorosilanes did not influence the diastereoselectivity

Table 5
Pinacol coupling of cyclohexanecarboxaldehyde with SmI_2/Sm/Me_3SiCl

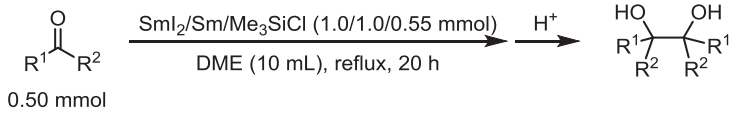


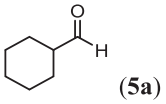
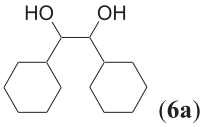
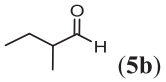
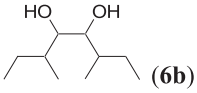
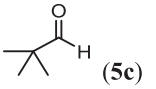
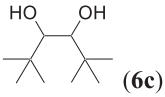
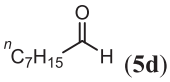
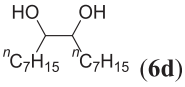
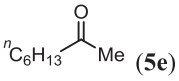
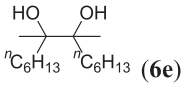
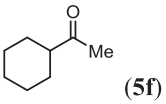
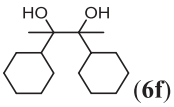
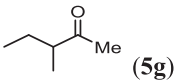
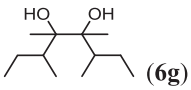
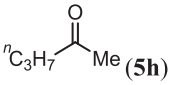
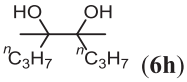
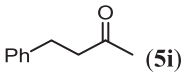
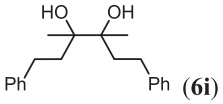
0.50 mmol **5a** **6a**

Entry	SmI_2 (mmol)	Sm (mmol)	Me_3SiCl (mmol)	DME (mL)	Conditions	Yield[a] (%)	*dl*/*meso*
1	1	1	1.5	3	rt, 20 h	39	100:0
2	1	1	1.5	3	Reflux, 20 h	40	100:0
3	1	1	2.0	3	Reflux, 40 h	38	100:0
4	1	1	0.55	3	Reflux, 20 h	52	100:0
5	0.55	0.55	0.56	3	Reflux, 20 h	44	100:0
6	1	1	0	3	Reflux, 20 h	28	93:7
7	1	1	0.55	10	Reflux, 20 h	69	100:0
8	1	1	0.57	20	Reflux, 20 h	63	100:0
9	1	1	0.55	10	rt, 20 h	52	93:7
10	1	1	0	10[b]	Reflux, 20 h	51	100:0
11	1	1	0.55[c]	10	Reflux, 20 h	70	100:0

[a] Determined by ^1H NMR.
[b] Use of THF in place of DME.
[c] $Ph_2MeSiCl$ was used.

Table 6
Pinacol couplings of aliphatic aldehydes and ketones with SmI_2/Sm/Me_3SiCl in DME.



Entry	Substrate	Product	Isolated yield (%)	*dl*/*meso*
1	 (5a)	 (6a)	52	100:0
2	 (5b)	 (6b)	61	65:35
3	 (5c)	 (6c)	65	100:0
4	 (5d)	 (6d)	65	62:38
5	 (5e)	 (6e)	66	100:0[a]
6	 (5f)	 (6f)	46	100:0
7	 (5g)	 (6g)	30	74:26
8	 (5h)	 (6h)	43[b]	100:0
9	 (5i)	 (6i)	62	100:0

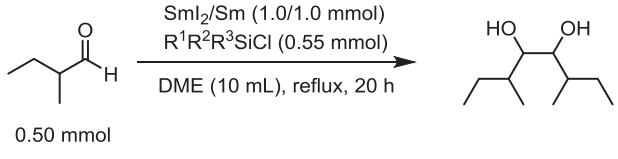
[a] In this case, the *dl*/*meso* ratio determined by ^1H NMR before isolation was 96:4. As to other substrates, the *dl*/*meso* ratios did not change before/after isolation.
[b] Determined by ^1H NMR.

toward **6b**. Since SmI_2/Sm in DME may induce reductive coupling of chlorosilane to give corresponding disilane in situ, the influence of disilane on this pinacol coupling was also investigated (entry 6). By comparison with the results of entries 1 and 6, disilane does not contribute to the yield and diastereo selectivity of the pinacol coupling.

As described in the Introduction, the presence of H_2O is a very important issue concerning the reducing ability of SmI_2. Thus, we investigated the effect of H_2O by quenching the reaction mixture with either 1.5 N HCl or air after the pinacol coupling with SmI_2/Sm/Me_3SiCl in DME was complete. Carbonyl compounds **1a**, **3a**, **5a**, and **5e** were treated under the corresponding optimized conditions, and then the resulting mixtures were quenched with either 1.5 N HCl or air (Table 8). In the case of benzaldehyde (**1a**), which is highly reactive, a higher yield of product **2a** was observed upon quenching with 1.5 N HCl than by air-quenching (entry 1). On the other hand, the pinacol couplings of **3a**, **5a**, and **5e** were not affected by the quenching method (entries 2–4). These results suggest that, in the case of aromatic aldehydes, the influence of water upon quenching with HCl should be considered. To exclude the influence of water on this pinacol coupling, therefore, air-quenching is recommended for the pinacol couplings of aromatic aldehydes.

In general, SmI_2-induced pinacol couplings of aliphatic carbonyl compounds are more difficult than those of aromatic carbonyl compounds. Therefore, the activation of aliphatic carbonyl compounds is essential for pinacol coupling. As shown in path C (Scheme 3), Me_3SiCl coordinates to the oxygen atom of the carbonyl group, and the carbon atom of the carbonyl group is positively charged (intermediate **B**). Depending on this activation by Me_3SiCl, aliphatic carbonyl compounds may receive one electron from SmI_2 easily, and α-siloxy radical species **C** is generated. Although further reduction of radical anion species **A** with SmI_2 in Scheme 2 is difficult, radical species **C** can be reduced easily to corresponding

Table 7
Pinacol coupling of 2-methylbutanal with SmI_2/Sm/chlorosilanes



0.50 mmol

5b **6b**

Entry	$R^1R^2R^3SiCl$	Yield[a] (%)	*dl*/*meso*
1	None	34	63:37
2	$Ph_2MeSiCl$	34	64:36
3	Me_3SiCl	55	62:38
4	$^iPr_3SiCl$	40	62:38
5	$(EtO)_3SiCl$	13	54:46
6	$(Me_3Si)_2$	33	67:33

[a] Determined by ^1H NMR.

anion species **D**. If this process occurs rapidly, the radical coupling process (path D) leading to the *meso*-isomer can be inhibited. The nucleophilic addition of generated anion species **D** to carbonyl compounds may be facilitated because of the intermolecular coordination of SmI_2 to two oxygen atoms. The steric hindrance of the substrate aliphatic carbonyl compounds mainly contributes to the diastereoselectivities.

3. Conclusion

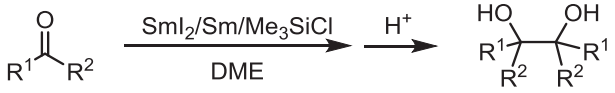
We reported an overview of pinacol couplings of aromatic and aliphatic carbonyl compounds using SmI_2/Sm/Me_3SiCl in DME. The pinacol couplings of aliphatic carbonyl compounds, which have low reactivity, could proceed uneventfully and with diastereoselectivity by adding Me_3SiCl; very interestingly, *dl*-isomers are obtained exclusively in many cases. In fact, a wide range of carbonyl compounds could be efficiently coupled by using SmI_2/Sm/Me_3SiCl in DME. Moreover, it was found that Me_3SiCl prevented the decomposition of *meso*-diols and controlled the stereochemistry of the products.

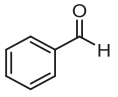
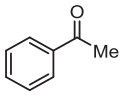
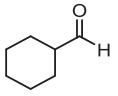
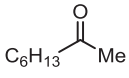
4. Experimental section

4.1. General information

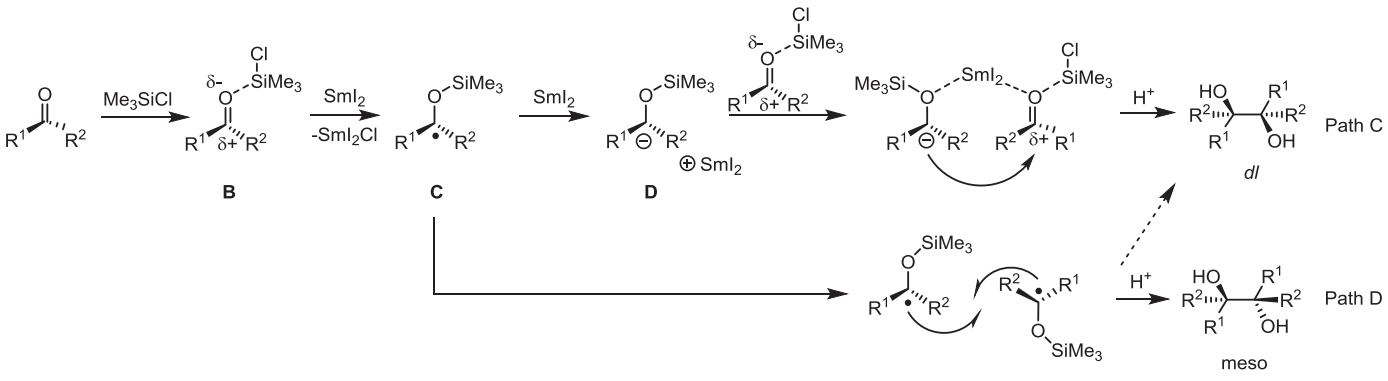
^1H NMR spectra were recorded on a JEOL JNM-ECS or JNM-ECX (400 Hz) spectrometer in $CDCl_3$ with tetramethylsilane (TMS) as

Table 8
Effect of H_2O in the different quenching methods



Entry	$R^1C(O)R^2$	Conditions	Quenched by 1.5 N HCl		Quenched by air	
			Yield[a] (%)	*dl*/*meso*	Yield[a] (%)	*dl*/*meso*
1	 (1a)	Table 1, entry 4	88	18:82	62	20:80
2	 (3a)	Table 3, entry 7	75	69:31	70	70:30
3	 (5a)	Table 5, entry 7	70	100:0	65	100:0
4	 (5e)	Table 5, entry 7	52	96:4	60	>99:1

[a] Determined by ^1H NMR.



Scheme 3. Plausible reaction pathways of aliphatic carbonyl compounds.

the internal standard. ^{13}C NMR spectra were obtained on a JEOL JNM-ECS or JNM-ECX (100 Hz) spectrometer in $CDCl_3$. Chemical shifts in the ^{13}C NMR spectra were measured relative to $CDCl_3$ and converted to δ_{TMS} values using δ 77.0 ppm. Mass spectra were obtained on a Shimadzu GCMS-QP5000 gas chromatograph-mass spectrometer (ionized by electron impact). Melting points were determined using a Yanagimoto micro melting point apparatus. DME was freshly distilled from sodium–benzophenone ketyl prior to use. Unless otherwise noted, chemical reagents were obtained from commercial suppliers and used directly. Samarium powder in oil (99.9%) was purchased from High Purity Chemicals and used after washing with dry pentane followed by drying for 4 h under reduced pressure. 1,2-Diiodoethane was purified by washing its ether solution with saturated sodium thiosulfate aqueous solution followed by removal of ether under reduced pressure.

4.2. Representative procedure for the reductive coupling of aromatic aldehydes mediated by the SmI_2/Sm system in DME

In a 20 mL two-necked flask equipped with a reflux condenser were placed samarium powder (2 mmol), 1,2-diiodoethane (1 mmol), and freshly distilled DME (3 mL) under a nitrogen atmosphere. The mixture was stirred at ambient temperature for 1.5 h, resulting in a dark blue SmI_2 solution. After adding Me_3SiCl (1.5 mmol) and the substrate (0.5 mmol) to the solution, the reaction mixture was stirred for 10 min at room temperature. After that, the reaction mixture was treated with hydrochloric acid (1.5 N, 20 mL) and extracted with diethyl ether (3×10 mL). The combined organic layers were washed with saturated $Na_2S_2O_3$ solution and brine, dried over anhydrous Na_2SO_4, and filtered. The solvent was removed under reduced pressure. Products were isolated by preparative thin-layer chromatography (PTLC) with hexane or a mixture of hexane and ethyl acetate (7:3) as eluent. All products obtained are known compounds, and therefore, the diastereoselectivities of them were unambiguously determined by the comparison of their chemical shifts in NMR spectra with the corresponding literature values.

4.3. Representative procedure for the reductive coupling of aromatic ketones mediated by the SmI_2/Sm system in DME

In a 20 mL two-necked flask equipped with a reflux condenser were placed samarium powder (1.1 mmol), 1,2-diiodoethane (0.55 mmol), and freshly distilled DME (10 mL) under a nitrogen atmosphere. The mixture was stirred at ambient temperature for 1.5 h, resulting a dark blue SmI_2 solution. After adding the substrate (0.5 mmol) and Me_3SiCl (0.55 mmol) to the solution, the flask was set in an oil bath maintained at 97 °C and reaction mixture was treated at reflux for 3 h. After it was cooled to room temperature, the reaction mixture was treated with hydrochloric acid (1.5 N, 20 mL) and extracted with diethyl ether (3×10 mL). The combined organic layers were washed with saturated $Na_2S_2O_3$ solution and brine, dried over anhydrous Na_2SO_4, and filtered. The solvent was removed under reduced pressure. Products were isolated by PTLC with hexane or a mixture of hexane and ethylacetate (7:3) as eluent. All products obtained are known compounds, and therefore, the diastereoselectivities of them were unambiguously determined by the comparison of their chemical shifts in NMR spectra with the corresponding literature values.

4.4. Representative procedure for the reductive coupling of aliphatic aldehydes and ketones mediated by the SmI_2/Sm system in DME

In a 20 mL two-necked flask equipped with a reflux condenser were placed samarium powder (2 mmol), 1,2-diiodoethane (1 mmol), and freshly distilled DME (10 mL) under a nitrogen atmosphere. The mixture was stirred at ambient temperature for 1.5 h, resulting in a dark blue SmI_2 solution. After adding the substrate (0.5 mmol) and Me_3SiCl (0.55 mmol) to the solution, the flask was set in an oil bath maintained at 97 °C and reaction mixture was treated at reflux for 20 h. After it was cooled to room temperature, the reaction mixture was treated with hydrochloric acid (1.5 N, 20 mL) and extracted with diethyl ether (3×10 mL). The combined organic layers were washed with saturated $Na_2S_2O_3$ solution and brine, dried over anhydrous Na_2SO_4, and filtered. The solvent was removed under reduced pressure. Products were isolated by High Performance Liquid Chromatography (HPLC) LC-908 (Japan Analytical Industry Co., Ltd.) with chloroform as an eluent.

4.5. Representative procedure for the reductive coupling of carbonyl compounds mediated by the SmI_2/Sm system in DME (quenching by air)

In a 20 mL two-necked flask equipped with a reflux condenser were placed samarium powder (2 mmol), 1,2-diiodoethane (1 mmol), and freshly distilled DME (3 mL) under a nitrogen atmosphere. The mixture was stirred at ambient temperature for 1.5 h, resulting in a dark blue SmI_2 solution. After adding Me_3SiCl (1.5 mmol) and the substrate (0.5 mmol) to the solution, the reaction mixture was stirred for 10 min at room temperature. After that, the reaction mixture was quenched by air until the color of solution changed to yellow and treated with hydrochloric acid (1.5 N, 20 mL) and extracted with diethyl ether (3×10 mL). The combined organic layers were washed with saturated $Na_2S_2O_3$ solution and brine, dried over anhydrous Na_2SO_4, and filtered. The solvent was removed under reduced pressure. Products were isolated by PTLC with hexane or a mixture of hexane and ethylacetate (7:3) as eluent. Except **6g**, the obtained pinacol coupling products are all known compounds. Therefore, the determination of diastereomers was performed by the comparison of their chemical shifts in NMR spectra with the corresponding literature values. In the cases of the pinacol coupling products **6e**, **6f**, **6g**, and **6h**, which have two methyl groups, the chemical shifts of the methyl groups in *dl*-isomers appear more up-field compared with those in *meso*-isomers. In the case of the pinacol coupling products **6b**, which have two C*H*–OH groups, the chemical shifts of the underlined proton in *dl*-**6b** appear more down-field compared with those in *meso*-**6b**.

4.6. Analytical data

*4.6.1. 1,2-Diphenyl-1,2-ethanediol (**2a**, Table 2).*[15] White solid; mp 133–136 °C; yield 41.1 mg (85%); ^1H NMR (400 MHz, $CDCl_3$/TMS, ppm) (*dl* and [*meso*]) δ 7.33–7.11 (10H, m), 4.72 [4.84] (2H, s), 2.83 [2.19] (2H, br s); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 139.8, 128.1, 128.1 [128.3], 126.9 [127.1], 78.1; MS (EI) *m*/*z* 180 [M^+–2OH].

*4.6.2. 1,2-Bis(4-methylphenyl)-1,2-ethanediol (**2b**, Table 2).*[16] White solid; mp 130–132 °C; yield 48.0 mg (78%); ^1H NMR (400 MHz, $CDCl_3$/TMS, ppm) (*dl* and [*meso*]) δ 7.21–7.19 (4H, d, *J*=8.0 Hz), 7.15–7.13 (4H, d, *J*=7.6 Hz), 4.69 [4.75] (2H, s), 2.30 [2.35] (6H, s), 2.72 [2.04] (2H, br s); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 137.9, 137.0, 128.4 [129.0], 126.8 [127.0], 78.1, 21.2; MS (EI) *m*/*z* 208 [M^+–2OH].

*4.6.3. 1,2-Bis(4-methoxyphenyl)-1,2-ethanediol (**2c**, Table 2).*[15] White solid; mp 163–166 °C; 47.1 mg (71%); ^1H NMR (400 MHz, $CDCl_3$/TMS, ppm) (*dl* and [*meso*]) δ 7.06–7.04 [7.23–7.20] (4H, d, *J*=8.8 Hz), 6.78–6.75 [6.87–6.85] (4H, d, *J*=8.8 Hz), 4.64 [4.74] (2H, s), 3.77 [3.81] (6H, s), 2.76 [2.06] (2H, br s); ^{13}C NMR

(100 MHz, $CDCl_3$, ppm) δ 132.0 [132.0], 128.1 [128.3], 113.5 [113.7], 78.8 [77.8], 55.3 [55.2]; MS (EI) *m*/*z* 256 [M^+−OH].

*4.6.4. 1,2-Bis(4-bromophenyl)-1,2-ethanediol (**2d**, Table 2).*[17] White solid; mp 167–169 °C; 78.0 mg (84%); ^1H NMR (400 MHz, $CDCl_3$/TMS, ppm) (*dl* and [*meso*]) δ 7.38–7.36 [7.42–7.40] (4H, d, *J*=8.8 Hz), 6.98–6.96 [7.06–7.04] (4H, d, *J*=8.8 Hz), 4.60 [4.81] (2H, s), 2.87 [2.31] (2H, br s); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 138.3 [138.5], 131.3 [131.4], 128.7 [128.7], 122.3 [122.1], 78.5 [77.2]; MS (EI) *m*/*z* 338 [M^+−2OH].

*4.6.5. 1,2-Bis[4-(trifluoromethyl)phenyl]-1,2-ethanediol (**2e**, Table 2).*[15] White solid; mp 117–119 °C; 67.6 mg (75%); ^1H NMR (400 MHz, $CDCl_3$/TMS, ppm) (*dl* and [*meso*]) δ 7.54–7.51 [7.56–7.54] (4H, d, *J*=8.0 Hz), 7.25–7.23 [7.31–7.29] (4H, d, *J*=8.0 Hz), 4.76 [4.97] (2H, s), 2.93 [2.41] (2H, br s); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 143.2, 127.3 [127.3], 125.1 [125.2], 125.2 [125.2], 78.4 [77.2]; MS (EI) *m*/*z* 316 [M^+−2OH].

*4.6.6. 2,3-Diphenyl-2,3-buthanediol (**4a**, Table 4).*[18] White solid; mp 87–90 °C; 48.0 mg (74%); ^1H NMR (400 MHz, $CDCl_3$/TMS, ppm) (*dl* and [*meso*]) δ 7.25–7.19 (10H, m), 2.53 [2.37] (2H, br s), 1.51 [1.59] (6H, s); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 143.5 [143.9], 127.1 [127.4], 127.2 [127.2], 126.9 [127.0], 78.8 [78.5], 25.0 [25.2]; MS (EI) *m*/*z* 225 [M^+−OH].

*4.6.7. 2,3-Bis(4-methylphenyl)-2,3-buthanediol (**4b**, Table 4).*[18] White solid; mp 64–67 °C; 44.7 mg (70%); ^1H NMR (400 MHz, $CDCl_3$/TMS, ppm) (*dl* and [*meso*]) δ 7.17–7.05 (8H, m), 2.34 [2.33] (6H, s), 2.52 [2.17] (2H, br s), 1.47 [1.54] (6H, s); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 140.5, 136.6, 127.8 [128.0], 127.3 [126.8], 78.8 [78.5], 25.1, 21.0; MS (EI) *m*/*z* 236 [M^+−OH].

*4.6.8. 2,3-Bis(4-trifluoromethylphenyl)-2,3-buthanediol (**4c**, Table 4).*[18] Yellow oil; 76.4 mg (74%); ^1H NMR (400 MHz, $CDCl_3$/TMS, ppm) (*dl* and [*meso*]) δ 7.52–7.50 (4H, d, *J*=8.0Hz), 7.30–7.28 [7.46–7.44] (4H, d, *J*=8.4 Hz), 2.57 [2.18] (2H, br s), 1.54 [1.57] (6H, s); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 147.1, 127.7 [127.7], 127.4, 124.2 [124.2], 78.5, 24.8; MS (EI) *m*/*z* 361 [M^+−OH].

*4.6.9. 2,3-Bis(4-chlorophenyl)-2,3-buthanediol (**4d**, Table 4).*[18] White solid; mp 114–116 °C; 58.9 mg (73%); ^1H NMR (400 MHz, $CDCl_3$/TMS, ppm) (*dl* and [*meso*]) δ 7.21–7.19 [7.23–7.21] (4H, d, *J*=8.8 Hz), 7.11–7.09 (4H, d, *J*=8.8 Hz), 2.49 [2.20] (2H, br s), 1.48 [1.55] (6H, s); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 133.2, 128.8 [128.8], 128.4, 127.3 [127.3], 78.5, 24.9; MS (EI) *m*/*z* 294 [M^+−OH].

*4.6.10. 1,2-Dicyclohexyl-1,2-ethanediol (**6a**, Table 6).*[19] White solid; mp 145–147 °C; 29.1 mg (52%); ^1H NMR (400 MHz, $CDCl_3$/TMS, ppm) δ 3.35–3.34 [3.88–3.86] (2H, d, *J*=6.0 Hz), 1.90–1.43 (11H, m), 1.33–1.10 (11H, m); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 75.2, 40.4, 29.7, 28.3, 26.5, 26.3, 26.1; MS (EI) *m*/*z* 209 [M^+−OH].

*4.6.11. 3,6-Dimethyl-4,5-octanediol (**6b**, Table 6) [CAS:1139802-30-4].* White solid; mp 67–69 °C; 22.6 mg (61%); ^1H NMR (400 MHz, $CDCl_3$/TMS, ppm) (*dl* and [*meso*]) δ 3.41–3.37 [3.50–3.48] (2H, m), 2.02 (2H, br s), 1.80–1.42 (4H, m), 1.36–1.13 (2H, m), 0.98–0.88 (12H, m); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 70.6, 49.7, 48.2, 34.0, 11.5; MS (EI) *m*/*z* 173 [M^+−H].

*4.6.12. 2,2,5,5-Tetramethyl-3,4-hexanediol (**6c**, Table 6).*[20] White solid; mp 102–106 °C; 27.1 mg (65%); ^1H NMR (400 MHz, $CDCl_3$/TMS, ppm) δ 3.35–3.33 (2H, d, *J*=6.8 Hz), 2.32–2.30 (2H, d, *J*=6.8 Hz), 0.920 (18H, s); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 74.9, 35.2, 25.8; MS (EI) *m*/*z* 174 [M^+].

*4.6.13. 8,9-Hexadecanediol (**6d**, Table 6).*[21] White solid; mp 119–120 °C; 19.1 mg (65%); ^1H NMR (400 MHz, $CDCl_3$/TMS, ppm) (*dl* and [*meso*]) δ 3.40 [3.60] (2H, br s), 1.95 [1.78] (2H, br s), 1.50–1.42 (4H, m), 1.30–1.28 (20H, m), 0.90–0.87 (6H, t, *J*=7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 74.5, 33.6, 31.8, 29.6, 29.2, 25.6, 22.6, 14.1.

*4.6.14. 7,8-Dimethyl-7,8-tetradecanediol (**6e**, Table 6).*[22] White solid; mp 119–120 °C; 43.2 mg (66%); ^1H NMR (400 MHz, $CDCl_3$/TMS, ppm) δ 1.84–1.83 (2H, d), 1.61–1.51 (4H, m), 1.48–1.24 (16H, m), 1.15–1.14 (6H, d, *J*=3.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 77.1 (2C), 36.3, 35.9, 31.9 (2C), 30.2 (2C), 23.7 (2C), 22.7 (2C), 21.1, 20.7, 14.1 (2C); MS (EI) *m*/*z* 241 [M^+−OH].

*4.6.15. 2,3-Dicyclohexyl-2,3-butandiol (**6f**, Table 6).*[11b] Colorless oil; 30.2 mg (46%); ^1H NMR (400 MHz, $CDCl_3$/TMS, ppm) δ 2.27 (2H, s), 2.05–1.90 (2H, m), 1.81–1.51 (10H, m), 1.31–0.78 (10H, m); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 79.3, 79.2, 44.6, 44.1, 30.0, 29.3, 28.2, 28.0, 27.1, 27.00, 26.95, 26.9, 26.6, 26.5, 21.5, 19.7; MS (EI) *m*/*z* 237 [M^+−OH].

*4.6.16. 3,4,5,6-Tetaramethyl-4,5-octandiol (**6g**, Table 6).* Colorless oil; 16.6 mg (34%); ^1H NMR (400 MHz, $CDCl_3$/TMS, ppm) (*dl* and [*meso*]) δ 2.25–2.23 [2.29–2.27] (2H, d, *J*=7.2 Hz), 2.02–1.55 (4H, m), 1.15–1.14, 1.14–1.13 [1.17–1.16] (6H, d, *J*=3.6 Hz), 1.03–0.73 (14H, m); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 79.6, {41.1, 41.0, 40.8}, {40.7, 40.3, 40.2}, {26.2, 26.0}, {25.9, 25.6}, {24.6, 24.5, 24.5}, {21.4, 21.3}, {20.7, 20.4}, {19.3, 19.0, 18.9}, {16.1, 15.8, 15.5}, {14.6, 14.4}, {14.3, 14.2}, {12.9, 12.9, 12.8}; MS (EI) *m*/*z* 185 [M^+−OH]. HRMS (ESI) calcd for $C_{15}H_{25}O_2Na$ [M−H+Na]$^+$: 224.1747, found: 224.1741.

*4.6.17. 4,5-Dimethyl-4,5-octandiol (**6h**, Table 6).*[23] ^1H NMR (400 MHz, $CDCl_3$/TMS, ppm) δ 2.61–1.33 (8H, m), 1.88 (2H, s), 1.15–1.14 (6H, d, *J*=1.6 Hz), 0.97–0.93 (6H, t).

*4.6.18. 3,4-Dimethyl-1,6-diphenyl-3,4-hexanediol (**6i**, Table 6).*[24] Colorless oil; 44.9 mg (62%); ^1H NMR (400 MHz, $CDCl_3$/TMS, ppm) δ 7.31–7.15 (10H, m), 2.86–2.75 (2H, m), 2.73–2.64 (2H, m), 1.98 (2H, s), 1.97–1.87 (2H, m), 1.75–1.64 (2H, m), 1.28–1.26 (6H, d, *J*=4.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 142.8, 142.8, 128.5, 125.9, 77.3, 38.7, 38.4, 30.4, 30.4, 21.2, 20.9; MS (EI) *m*/*z* 281 [M^+−OH].

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