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Indium-Catalyzed Reductive Coupling of Aromatic Carbonyl Compounds and Imines in the Presence of Aluminum and Chlorosilanes

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ABSTRACT: *Reductive homocoupling of aromatic aldehydes, ketones, and imines has been achieved in tetrahydrofuran (THF) at room temperature using a catalytic amount of $InCl_3$ (0.5–3.0 mol %) under a nitrogen atmosphere in the presence of chlorotrimethylsilane (TMSCl) and aluminum metal (Al) to provide the corresponding 1,2-diols and 1,2-diamines, respectively, in good to moderate yields. Other indium compounds such as $In(NO_3)_3$, cyclopentadienylindium, and indium metal have also been revealed to be effective as catalysts. The catalytic effect of the indium compound is remarkable, and, thus, without it, no reaction occurs in the case of aromatic aldehydes and aldimines, and an induction period is quite long in the case of aromatic ketones. Without either TMSCl or Al, no reaction proceeds even in the presence of the catalyst. Unfortunately, the diastereoselectivity of the products (dl and meso) is not high. Although the precise reaction scheme is not yet clear, we tentatively propose that a redox-active In-Al alloy might be formed on the surface of aluminum in the presence of TMSCl, and an electron transfer from the alloy to substrate might occur.* © 2001 John Wiley & Sons, Inc. Heteroatom Chem 12:309–316, 2001

INTRODUCTION

The organic chemistry of indium is of current interest from the viewpoint of organic synthesis [1]. Thus, indium and its compounds have worked as reagents as well as catalysts in some carbon–carbon bond-forming reactions, such as allylation of carbonyl compounds [2], Reformatsky reactions [3], aldol reactions [4], Diels-Alder reactions [5], Michael reactions [6], Friedel-Crafts reactions [7], and reductive coupling reactions [8]. In the cases of catalytic reactions, however, a rather large amount of indium salts (10–20 mol %) has normally been employed. We have now disclosed a new and quite efficient catalytic activity of indium(III) chloride (0.5–3.0 mol %) in reductive homocoupling of carbonyl compounds and imines. It has so far been reported that the use of a stoichiometric amount of indium metal induced the reductive homocoupling of aromatic aldehydes [8a] and imines [8b] in water or water-alcohol mixture. Our new system consists of the combination of chlorotrimethylsilane (TMSCl), aluminum (Al), and a catalytic amount of an indium compound for this reductive coupling reaction. It is worth noting that catalytic systems for the reductive coupling using a catalytic amount of transition metal complex (mainly Ti and V), and TMSCl with a co-reductant

Dedicated to Prof. Naoki Inamoto on the occasion of his 72nd birthday.

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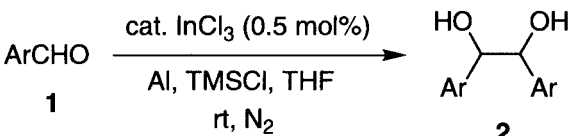
metal such as Zn, Al, and Mg have recently been developed by several groups [9].

RESULTS AND DISCUSSION

Reductive Homocoupling of Aromatic Aldehydes

Treatment of benzaldehyde (**1a**) with aluminum metal (Al, 4 equiv), chlorotrimethylsilane (TMSCl, 4 equiv), and a catalytic amount of $InCl_3$ (5 mol %) in tetrahydrofuran (THF) under a nitrogen atmosphere at room temperature for 2 hours afforded 1,2-diphenyl-1,2-ethanediol (**2a**) in 45% yield (*dl*/*meso* = 52/48) (Scheme 1). Without either Al or TMSCl, the reaction did not occur even in the presence of $InCl_3$. On the other hand, without the addition of $InCl_3$, no reaction proceeded in the presence of both TMSCl and Al [10] even under sonication. It was found that the amount of $InCl_3$ can be reduced to 0.5 mol % with the yield of **2a** being increased to 61%. The yield of the expected diols was somewhat low despite a complete conversion of **1a**, and a small amount of benzyl alcohol and small amounts of many unidentified compounds were detected. It was also disclosed that other several indium(III) and (I) compounds and indium metal (powder) work as effective catalysts like $InCl_3$ (Table 1). We examined the effect of other metals such as Zn [11], Mg [12], and In [8] as a reductant. In the cases of Zn and Mg, the reaction proceeded to give **2a** in moderate yield (up to 45%), but no catalytic effect of $InCl_3$ was observed in the cases of Zn and In, as shown in Table 1. The diastereoselectivity was not affected much by changing the reaction temperature in the range between reflux (58/42) to 0°C (61/39), while the reaction did not proceed at much lower temperature. Similarly, a great change of selectivity was not observed when the reaction was carried out in a variety of solvents, such as dimethylformamide, 1,4-dioxane, acetonitrile, and dichloromethane, as shown in Table 2, the product yield being highest in the reaction using THF. Many chlorosilanes, such as chlorotriisopropylsilane, chlorodiphenylmethylsilane, chlorotriphenylsilane, dichlorodimethylsilane and bis(dimethyl-



1 **2**

1a Ar = Ph
1b Ar = *p*-ClC_6H_4
1c Ar = *p*-$CH_3C_6H_4$
1d Ar = *p*-$CH_3OC_6H_4$

SCHEME 1

TABLE 1 Effect of Reductant for Reductive Coupling of Benzaldehyde (**1a**)[a]

Entry	Reductant (equiv)[b]	Time (h)[c]	Yield (%) of **2a**[d]	*dl*/*meso*[e]
1	Al (4)	24[f]	0	—
2[g]	Al (4)	5[f]	0	—
3[h]	$InCl_3$ (0.001) + Al (4)	8	39	59/41
4[h]	$InCl_3$ (0.005) + Al (4)	2	61	57/43
5	$InCl_3$ (0.01) + Al (4)	2	56	55/45
6	$InCl_3$ (0.02) + Al (4)	2	52	54/46
7	$InCl_3$ (0.05) + Al (4)	2	45	52/48
8	$InCl_3$ (0.1) + Al (4)	2	18	55/45
9[h]	In (0.005) + Al (4)	2	54	53/47
10[g,h]	In (0.005) + Al (4)	4	34	59/41
11[h]	InCl (0.005) + Al (4)	2	59	56/44
12[h]	InCp (0.005) + Al (4)	5	54	57/43
13[h]	$In(NO_3)_3$ (0.005) + Al (4)	5	57	57/43
14	Zn (4)	1	43	52/48
15	Mg (4)	20	42	59/41
16	In (4)	24[i]	0	—
17[h]	$InCl_3$ (0.005) + Zn (4)	4	40	59/41
18[h]	$InCl_3$ (0.005) + In (4)	7	0	—

[a]Reaction conditions: **1a** (0.106 g, 1 mmol), TMSCl (0.5 mL, 4 mmol), THF (10 mL), rt, N_2.
[b]Al, foil; In, powder; Zn, powder; Mg, ribbon.
[c]The time for 100% conversion of **1a**.
[d]Isolated yield. The formation of 0.5 mmol of **2a** corresponds to 100% yield.
[e]Determined by ^1H NMR.
[f]No reaction.
[g]Under sonication in a BRANSONIC ultrasonic cleaner bath, which delivered a 47 kHz wave, with a fixed electrical power of 125 W.
[h]Five-fold scale reaction.
[i]The conversion was not determined.

TABLE 2 Effect of Solvent for Reductive Coupling of Benzaldehyde (**1a**)[a]

Entry	Solvent	Time (h)[b]	Yield (%) of **2a**[c]	*dl*/*meso*[d]
1	THF	2	45	52/48
2	Et_2O	48[e]	18	24/76
3	1,4-dioxane	24	21	48/52
4	DME	18	14	45/55
5	DMF	6	33	60/40
6	MeCN	6	21	49/51
7	CH_2Cl_2	2	18	27/73
8	$CHCl_3$	24[f]	0	—
9	toluene	24[f]	0	—

[a]Reaction conditions: **1a** (0.106 g, 1 mmol), $InCl_3$ (11 mg, 0.05 mmol), Al (0.108 g, 4 mmol), TMSCl (0.5 mL, 4 mmol), THF (10 mL), rt, N_2.
[b]The time for 100% conversion of **1a**. The formation of 0.5 mmol of **2a** corresponds to 100% yield.
[c]Isolated yield.
[d]Determined by ^1H NMR.
[e]The conversion was not determined.
[f]No reaction.

chlorosilyl)ethane, could be used in the place of TMSCl, but the product yield was somewhat lower with almost the same diastereoselectivity. From all these experiments, we decided the optimum condition for this coupling reaction to be the use of the combination of TMSCl, Al, cat $InCl_3$ (0.5 mol %), and THF at room temperature. The results of the application of this optimized condition to *p*-substituted benzaldehydes are shown in Table 3. In these cases, although the reaction became slow, the corresponding coupling product was obtained in 50–68% yields. Without the addition of $InCl_3$, no reaction occurred in all these cases.

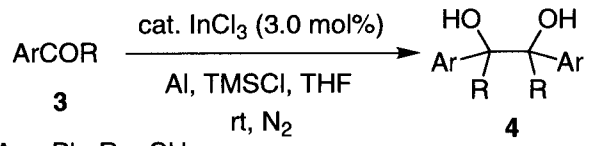
Since Nicholas et al. have reported the enantioselective reductive coupling of benzaldehyde using a stoichiometric amount of a chiral titanium complex [13], we attempted the above reductive coupling in the presence of either chiral monophosphine ((*R*)-MeO-MOP), diphosphine ((*R*)-BINAP), diphosphine oxide ((*R*)-BINAPO), diphosphinite or bisoxazoline (*i*Pr-Phebox), but enantioselectivity was not observed in the formation of the *dl*-isomer.

Reductive Homocoupling of Aromatic Ketones

Reductive coupling similarly proceeded with acetophenone (**3a**) as a substrate to afford 2,3-diphenyl-2,3-butanediol (**4a**) in good yield, the use of 3 mol % $InCl_3$ being revealed to be the best (Scheme 2, Table 4). In this case, the reaction occurred even in the absence of $InCl_3$ catalyst, but a long induction period was observed, and also, the product yield was much lower. Figure 1 shows the relationship between the reaction time and the isolated yield of **4a** in this coupling. Here, Zn and Mg were also revealed to work as a reductant, but the catalytic effect of $InCl_3$ was not observed in the Zn case (Table 4). Results of the reductive coupling of various aromatic ketones are summarized in Table 5 where the effect of $InCl_3$ was generally remarkable.

Reductive Homocoupling of Aliphatic Carbonyl Compounds and Aromatic Imines

In the cases of aliphatic carbonyl compounds, such as *n*-octanal (**5a**), cyclohexanone (**5b**), and 3-phenylpropanal (**5c**), the corresponding 1,2-diols could not be formed (Table 6). However, α,β-unsaturated carbonyl compounds, such as *trans*-cinnamaldehyde (**5d**) and crotonaldehyde (**5e**), yielded the corresponding 1,2-diols in moderate yields. Next, we performed the reductive coupling of various aromatic imines (Scheme 3), typical results of which are sum-



3a Ar = Ph, R = CH_3
3b Ar = *p*-ClC_6H_4, R = CH_3
3c Ar = *p*-BrC_6H_4, R = CH_3
3d Ar = *p*-$CH_3C_6H_4$, R = CH_3
3e Ar = Ph, R = Ph
3f Ar = 2-naphthyl, R = CH_3

SCHEME 2

TABLE 3 $InCl_3$-Catalyzed Reductive Coupling of Aromatic Aldehydes (**1**)[a]

Entry	*Substrate*	*Product*	*Time (h)*[b]	*Isolated Yield (%)*	*dl/meso*[c]
1	**1a**	**2a**	4	61	57/43
2[d]	**1a**	**2a**	24[e]	0	—
3	**1b**	**2b**	18	68	41/59
4[d]	**1b**	**2b**	24[e]	0	—
5	**1c**	**2c**	20	56	62/38
6[d]	**1c**	**2c**	24[e]	0	—
7	**1d**	**2d**	17	50	59/41
8[d]	**1d**	**2d**	24[e]	0	—

[a]Reaction conditions: **1** (5 mmol), $InCl_3$ (5.5 mg, 0.025 mmol), Al (0.54 g, 20mmol), TMSCl (2.5 mL, 20 mmol), THF (50 mL), rt, N_2.
[b]The time for 100% conversion of **1**. The formation of 2.5 mmol of **2** corresponds to 100% yield.
[c]Determined by ^1H NMR.
[d]Reaction without $InCl_3$.
[e]No reaction.

TABLE 4 Effect of Reductant for Reductive Coupling of Acetophenone (**3a**)[a]

Entry	*Reductant (eq)*	*Time (h)*[b]	*Yield (%) of* **4a**[c]	*dl/meso*[d]
1	Al (4)	24[e]	29	68/32
2[f]	Al (4)	18[e]	13	74/26
3[g]	$InCl_3$ (0.005) + Al (4)	8	57	71/29
4[g]	$InCl_3$ (0.01) + Al (4)	7	58	70/30
5	$InCl_3$ (0.03) + Al (4)	4	74	62/38
6	$InCl_3$ (0.05) + Al (4)	2	64	64/36
7	$InCl_3$ (0.10) + Al (4)	2	51	57/43
8	Zn (4)	9	65	49/51
9	Mg (4)	24[e]	29	52/48
10	$InCl_3$ (0.03) + Zn (4)	4	45	56/44

[a]Reaction conditions: **3a** (0.12 g, 1 mmol), TMSCl (0.5 mL, 4 mmol), THF (10 mL), rt, N_2.
[b]The time for 100% conversion of **3a**.
[c]Isolated yield. The formation of 0.5 mmol of **3a** corresponds to 100% yield.
[d]Determined by ^1H NMR.
[e]The conversion was not determined.
[f]Under sonication in a BRANSONIC ultrasonic cleaner bath, which delivered a 47 kHz wave, with a fixed electrical power of 125 W.
[g]Five-fold scale reaction.

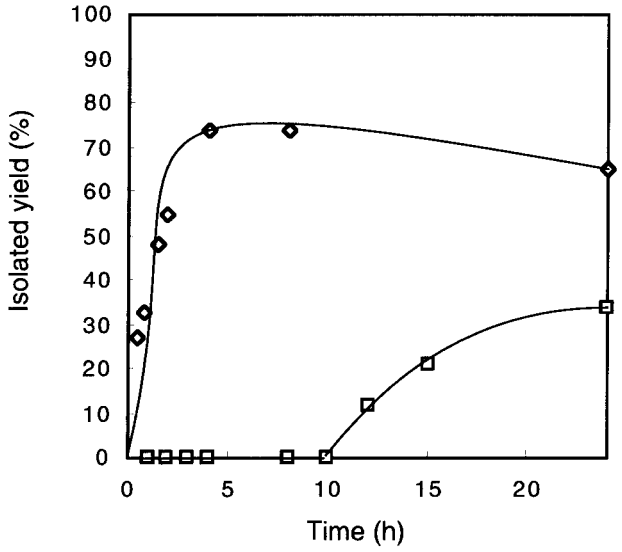


FIGURE 1 Yield of **4a** in the Coupling of Acetophenone in the Presence (◇) and Absence (□) of $InCl_3$.

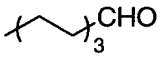
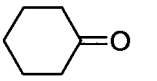
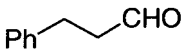
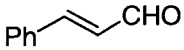
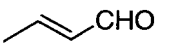
TABLE 5 $InCl_3$-Catalyzed Reductive Coupling of Aromatic Ketones (**3**)[a]

Entry	Substrate	Product	Time (h)[b]	Isolated Yield (%)[c]	dl/meso[d]
1	**3a**	**4a**	4	74	68/32
2[e]	**3a**	**4a**	24[f]	29	62/38
3	**3b**	**4b**	10	76	58/42
4[e]	**3b**	**4b**	10[g]	9	64/36
5	**3c**	**4c**	5[h]	62	61/39
6[e]	**3c**	**4c**	5[h]	48	53/47
7	**3d**	**4d**	5	72	65/35
8[e]	**3d**	**4d**	5[i]	0	—
9	**3e**	**4e**	6[h]	56	—
10[e]	**3e**	**4e**	6[h]	42	—
11	**3e**	**4e**	20	91	—
12[e]	**3e**	**4e**	24	90	—
13	**3f**	**4f**	4	67	58/42
14[e]	**3f**	**4f**	48[h]	34	50/50

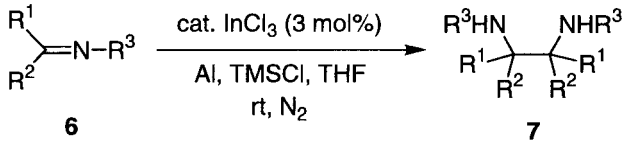
[a]Reaction conditions: **3** (1 mmol), $InCl_3$ (6.6 mg, 0.03 mmol), Al (0.18 g, 4 mmol), TMSCl (0.5 mL, 4 mmol), THF (10 mL), rt, N_2.
[b]The time for 100% conversion of **3**.
[c]The formation of 0.5 mmol of **4** corresponds to 100% yield.
[d]Determined by ^1H NMR.
[e]Reaction without $InCl_3$.
[f]The conversion was not determined.
[g]About 20% conversion of **3**.
[h]About 70–80% conversion of **3**.
[i]No reaction.

marized in Table 7. In the cases of aromatic aldimines such as **6a–6f**, the effect of $InCl_3$ catalyst (3 mol %) was remarkable, while, in the cases of aromatic ketimines such as **6g**, the addition of $InCl_3$ decreased the product yield unexpectedly because of the rapid decomposition of **6g** to the starting ketone (**3a**), probably catalyzed by $InCl_3$.

TABLE 6 $InCl_3$-Catalyzed Reductive Coupling of Aliphatic Aldehydes and Ketones[a]

Entry	Substrate	Time (h)[b]	Isolated Yield (%)[c]	dl/meso[d]	
1		**5a**	24[e]	0	—
2		**5b**	24[e]	0	—
3		**5c**	18	0[f]	—
4			2	27	60/40
5[g]		**5d**	2[h]	0	—
6			3	45	64/36
7[g]		**5e**	2[e]	0	—

[a]Reaction conditions: substrate (1 mmol), $InCl_3$ (6.6 mg, 0.03 mmol), Al (0.108 g, 4 mmol), TMSCl (0.5 mL, 4 mmol), THF (10 mL), rt, N_2.
[b]The time for 100% conversion of **5**.
[c]The formation of 0.5 mmol of 1,2-diol corresponds to 100% yield.
[d]Determined by ^1H NMR.
[e]The conversion was not determined.
[f]3-Phenylpropanol (23% yield) was obtained.
[g]Reaction without $InCl_3$.
[h]No reaction.



6a R^1 = Ph, R^2 = H, R^3 = Ph
6b R^1 = *p*-ClC_6H_4, R^2 = H, R^3 = Ph
6c R^1 = *p*-$CH_3C_6H_4$, R^2 = H, R^3 = Ph
6d R^1 = Ph, R^2 = H, R^3 = *p*-ClC_6H_4
6e R^1 = Ph, R^2 = H, R^3 = *p*-$CH_3C_6H_4$
6f R^1 = Ph, R^2 = H, R^3 = Bn
6g R^1 = Ph, R^2 = CH_3,, R^3 = Ph

SCHEME 3

Plausible Reaction Scheme

Although the precise reaction scheme is not yet clear, we tentatively propose Scheme 4 for this catalytic homocoupling by consideration of the generally accepted scheme for reductive coupling of carbonyl compounds [14] and also by the known fact of activation of aluminum by indium ions in chloride solutions [15]. First, a redox-active In–Al alloy might be formed on the surface of aluminum in the presence of TMSCl. An electron transfer from the alloy to aldehydes generates ketyl radicals, and the carbon–carbon bond formation takes place by the radical coupling. When the coupling was attempted in the presence of *m*-dinitrobenzene (0.5 equiv to **1a**),

TABLE 7 $InCl_3$-Catalyzed Reductive Coupling of Aromatic Imines (**6**)[a]

Entry	*Substrate*	*Product*	*time (h)*[b]	*Isolated Yield (%)*[c]	*dl/meso*[d]
1	**6a**	**7a**	9	71	45/55
2[e]	**6a**	**7a**	12	0	—
3	**5b**	**7b**	8	36	43/57
4[e]	**6b**	**7b**	2	0	—
5	**6c**	**7c**	6	28	42/58
6[e]	**6c**	**7c**	2	0	—
7	**6d**	**7d**	2	48	42/58
8[e]	**6d**	**7d**	4[f]	0	—
9	**6e**	**7e**	2	63	38/62
10[e]	**6e**	**7e**	2[f]	0	—
11	**6f**	**7f**	2	41	—[g]
12[e]	**6f**	**7f**	1	0	—
13	**6g**	**7g**	2	40	50/50
14[e]	**6g**	**7g**	2	79	47/53

[a]Reaction conditions: **6** (1 mmol), $InCl_3$ (6.6 mg, 0.03 mmol), Al (0.108 g, 4 mmol), TMSCl (0.5 mL, 4 mmol), THF (10 mL), rt, N_2.
[b]The time for 100% conversion of **6**.
[c]The formation of 0.5 mmol of **7** corresponds to 100% yield.
[d]Determined by ^1H NMR.
[e]Reaction without $InCl_3$.
[f]The conversion was not determined.
[g]Not determined.

which is considered to be a radical scavenger, the product yield was greatly decreased (45% to 5%) (Table 1, entry 7), suggesting the intervention of a ketyl radical species. Finally, metal–oxygen bond cleavage occurs by the reaction with TMSCl to afford the 1,2-bis(trimethylsiloxy) derivative of the diol, which might be hydrolyzed to the product by the work-up procedure. At this stage, cleavage by the action of a proton, which may be present in TMSCl in a small concentration as HCl, might also be operative to some extent, competitively to afford the diol directly. In fact, a pH indicator showed the reaction mixture to be acidic, and also when the coupling of **1a** or **3a** was attempted using aqueous HCl in the place of TMSCl, the product **2a** or **4a**, respectively, was formed, although the yield was low (see Experimental). Since In(O) metal and In(I) compounds were also effective as catalysts in this system, as recorded in Table 1, we consider that a similar redox-active Al–In species might also be formed from these indium compounds and aluminum.

EXPERIMENTAL

^1H and ^{13}C NMR spectra were measured on JEOL EX-400, JNM-AL300, and JEOL GSX270 spectrometers for solutions in $CDCl_3$ with Me_4Si as an internal standard. Analytical thin-layer chromatography (TLC) was performed with Merck silica gel 60 F-254 plates. Column chromatography was performed with Merck silica gel 60.

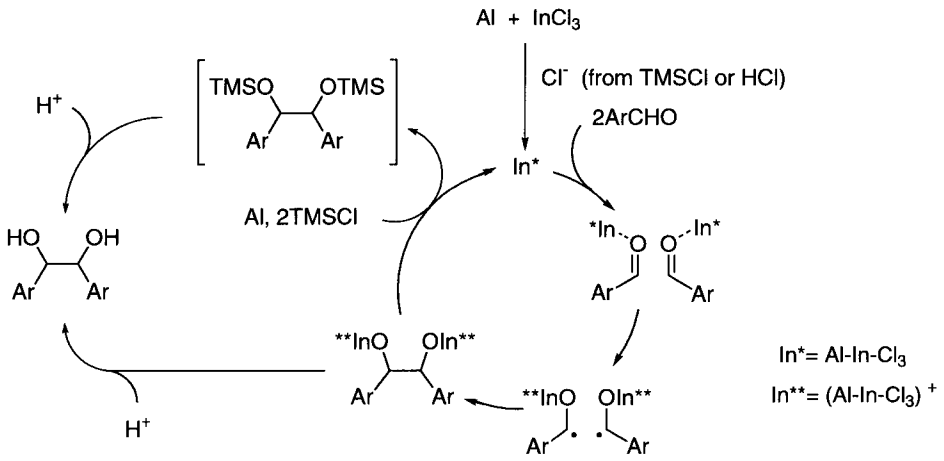
$InCl_3$ was purchased from Aldrich and used without further purification. Aluminum metal (Al foil, 0.1 mm × 0.8 mm) was purchased from Nacalai Tesque and used without further purification. Chlorotrimethylsilane and THF were distilled before use. All of the carbonyl compounds were commercially available and used without further purification. All of the imines were prepared by the condensation of carbonyl compounds with amines. The structures of 1,2-diols and 1,2-diamines were determined by comparison of spectral data with those of the authentic samples reported. The structures of **7e** and **7g** were determined by analogy with other compounds [11,16–26].

*Typical Procedure for Reductive Homocoupling of Benzaldehyde (**1a**) (Table 1, Entry 4)*

To a mixture of $InCl_3$ (5.5 mg, 0.025 mmol), aluminum (0.54 g, 20 mmol), TMSCl (2.5 mL, 20 mmol), and THF (40 mL) in a 200 mL two-necked flask was added **1a** (0.53 g, 5 mmol) in THF (10 mL) at room temperature under N_2. The mixture was kept at room temperature with magnetic stirring for 2 hours. Diethyl ether (100 mL) and aqueous HCl (1.2 M, 50 mL) were added to the resulting mixture, and the organic layer was separated, washed with saturated aqueous $NaHCO_3$ (50 mL × 3), dried over Na_2SO_4, and concentrated. The residue was purified by column chromatography on silica gel (eluent, hexane/ethyl acetate) to obtain 1,2-diphenyl-ethanediol **2a** (325 mg, 1.52 mmol, 61% yield; *dl/meso* = 57/43) and a complex mixture containing benzyl alcohol and many unidentified compounds (56 mg).

*Reductive Homocoupling of Benzaldehyde (**1a**) or Acetophenone (**3a**) in the Presence of HCl in the place of TMSCl*

To a mixture of $InCl_3$ (5.5 mg, 0.025 mmol), aluminum (0.54 g, 20 mmol), and THF (30 mL) in a 200 mL two-necked flask were added a THF (10 mL) solution containing HCl (aqueous 35% HCl, 0.5 mL, 5 mmol) and **1a** (0.53 g, 5 mmol) in THF (10 mL) at room temperature under N_2. The mixture was kept at room temperature with magnetic stirring for 24 hours and treated as described previously in a typical procedure. The product **2a** was obtained in 19% yield (100 mg, 0.467 mmol; *dl/meso* = 58/42) together with benzyl alcohol (60 mg, 0.555 mmol, 11% yield), and **1a** (161 mg, 1.52 mmol) was recovered. When a similar reaction was carried out using 1 mmol of HCl, no reaction occurred.



SCHEME 4 Plausible reaction scheme.

In the case of the coupling of **3a**, using **3a** (1 mmol), $InCl_3$ (0.03 mmol), Al (4 mmol), aqueous 35% HCl (0.1 mL, 1 mmol), and THF (10 mL) at room temperature for 24 hours, **4a** was obtained in 55% yield (67 mg, 0.276 mmol; *dl*/*meso* = 58/42), and **3a** (39 mg, 0.330 mmol) was recovered. Similarly, the reaction using 0.2 mmol HCl did not give any **4a**.

*1,2-Diphenyl-1,2-ethanediol (dl and meso) (***2a***)*

White solid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 2.28 [2.91] (2H, s, br), 4.59 [4.72] (2H, s), 7.01–7.23 (10H, m); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ = 79.0 [78.0], 126.9 [127.0], 127.9 [128.0], 128.2 [128.1], 139.7 [139.8]. The values in brackets are of the *meso*-isomer. The reported ^{1}H NMR data of the benzylic C–H hydrogens are 4.59 and 4.72 for *dl* and *meso*-isomers, respectively [16,17].

*1,2-Bis(4-chlorophenyl)-1,2-ethanediol (dl and meso) (***2b***) [16]*

White solid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 2.55 [3.10] (2H, s, br), 4.56 [4.78] (2H, s), 6.97–7.32 (8H, m); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ = 78.4 [77.1], 128.2, 128.3, 133.8, 137.7 [137.9].

*1,2-Bis(4-methylphenyl)-1,2-ethanediol (dl and meso) (***2c***) [16]*

White solid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 2.22 [2.26] (6H, s), 2.07 [2.77] (2H, s, br), 4.57 [4.65] (2H, s), 6.95–7.18 (8H, m); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ = 21.1 [21.1], 78.8 [78.0], 126.8 [127.0], 128.8 [129.0], 137.0, 137.4 [137.8].

*1,2-Bis(4-methoxyphenyl)-1,2-ethanediol (dl and meso) (***2d***) [16]*

White solid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 2.10 [2.80] (2H, s, br), 3.75 [3.79] (6H, s), 4.63 [4.72] (2H, s), 6.73–7.26 (8H, m); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ = 55.1 [55.2], 78.7 [77.7], 113.5 [113.6], 128.1 [128.3], 132.0, 159.1 [159.4].

*2,3-Diphenyl-2,3-butanediol (dl and meso) (***4a***) [16,17]*

White solid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 1.35 [1.46] (6H, s), 2.23 [2.52] (2H, s, br), 7.06–7.11 (10H, m); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ = 24.9 [25.1], 78.8 [78.6], 126.9, 127.1 [127.0], 127.3 [127.2], 143.4 [143.7].

*2,3-Bis(4-chlorophenyl)-2,3-butanediol (dl and meso) (***4b***) [18]*

White solid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 1.39 [1.47] (6H, s), 2.23 [2.55] (2H, s, br), 7.00–7.15 (8H, m); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ = 24.7 [25.0], 78.5 [78.2], 127.3 [127.3], 128.8 [128.4], 133.1 [133.0], 141.7 [142.2].

*2,3-Bis(4-bromophenyl)-2,3-butanediol (dl and meso) (***4c***) [16]*

White solid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 1.38 [1.46] (6H, s), 2.05 [2.35] (2H, s, br), 6.94–7.30 (8H, m); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ = 24.6 [25.0], 78.4 [78.2], 121.4 [121.2], 129.2 [128.8], 130.2 [130.3], 142.2 [142.7].

*2,3-Bis(4-methylphenyl)-2,3-butanediol (dl and meso) (***4d***) [18]*

White solid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 1.44 [1.51] (6H, s), 2.26 [2.52] (2H, s, br), 2.32 [2.31] (s,

6H), 7.04–7.11 (8H, m); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ = 20.9, 25.0 [25.2], 78.7 [78.5], 127.3 [126.8], 127.8 [128.0], 136.5 [136.3], 140.5 [140.9].

*1,1,2,2-Tetraphenyl-1,2-ethanediol (**4e**) [17]*

White solid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 2.96 (2H, s, br), 7.05–7.25 (20H, m); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ = 83.0, 126.9, 127.3, 128.6, 144.1.

*2,3-Bis(2-naphthyl)-2,3-butanediol (dl and meso) (**4f**) [19]*

White solid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 1.54 [1.61] (6H, s), 2.35 [2.75] (2H, s, br), 7.15–7.77 (14H, m); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ = 25.2 [25.5], 79.2 [78.8], 125.5, 125.8 [125.8], 125.9, 126.4, 126.7, 127.3, 128.3, 132.3 [132.4], 141.0, 141.0.

1,6-Diphenyl-1,5-hexadiene-3,4-diol [20]

White solid; *dl*-isomer: ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 4.27 (2H, d, *J* 5.86 Hz), 6.26 (2H, dd, *J* 5.86 Hz, 15.9 Hz), 6.71 (2H, d, *J* 15.9 Hz), 7.22–7.38 (14H, m); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ = 75.8, 126.6, 127.0, 127.9, 128.6, 132.7, 136.4. *meso*-isomer; ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 4.43 (2H, d, *J* 6.11 Hz), 6.28 (2H, dd, *J* 6.11 Hz, 15.6 Hz), 6.69 (2H, d, *J* 15.6 Hz), 7.22–7.38 (14H, m); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ = 75.7, 126.6, 127.0, 127.6, 128.6, 133.1, 136.4.

2,6-Octadiene-4,5-diol (dl and meso) [11]

White solid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 1.66–1.74 (6H, m), 2.94 (2H, s, br), 3.88 [4.04] (2H, m), 5.35–5.50 (2H, m), 5.63–5.79 (2H, m); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ = 17.8 [17.8], 75.7 [75.5], 128.9 [129.1], 129.7 [129.5].

*N,N′-Diphenyl-1,2-diphenyl-1,2-ethanediamine (dl and meso) (**7a**) [21,22]*

White solid; ^{1}H NMR [$CDCl_3$ + D_2O (few drops), 400 MHz] δ = 4.54 [4.96] (2H, s), 6.49–7.23 (20H, m); ^{13}C NMR [$CDCl_3$ + D_2O (few drops), 75.5 MHz] δ = 63.9 [61.9], 114.2 [113.7], 118.2 [117.8], 127.5, 127.3 [127.5], 128.3 [128.2], 129.0 [129.2], 139.7, 146.8 [146.4].

*N,N′-Diphenyl-1,2-bis(4-chlorophenyl)-1,2-ethanediamine (dl and meso) (**7b**) [23]*

White solid; ^{1}H NMR [$CDCl_3$ + D_2O (few drops), 400 MHz] δ = 4.46 [4.91] (2H, s), 6.49–7.23 (18H, m); ^{13}C NMR [$CDCl_3$ + D_2O (few drops), 75.5 MHz] δ = 61.2 [63.4], 114.1 [113.7], 118.6 [118.3], 128.6 [128.6], 128.7 [128.8], 129.2 [129.3], 133.3 [133.5], 138.2 [136.5], 146.4 [145.9].

*N,N′-Diphenyl-1,2-bis(4-methylphenyl)-1,2-ethanediamine (dl and meso) (**7c**) [23]*

White solid; ^{1}H NMR [$CDCl_3$ + D_2O (few drops), 400 MHz] δ = 2.27 [2.28] (6H, s), 4.52 [4.90] (2H, s), 6.50–7.08 (m, 18H); ^{13}C NMR [$CDCl_3$ + D_2O (few drops), 75.5 MHz] δ = 21.0, 63.3 [61.5], 114.0 [113.6], 117.8 [117.6], 127.2 [127.4], 129.0 [128.9], 129.1 [129.1], 147.1 [146.5].

*N,N′-Bis(4-chlorophenyl)-1,2-diphenyl-1,2-ethanediamine (dl and meso) (**7d**) [24]*

White solid; ^{1}H NMR [$CDCl_3$ + D_2O (few drops), 400 MHz] δ = 4.49 [4.88] (2H, s), 6.40–7.19 (18H, m); ^{13}C NMR [$CDCl_3$ + D_2O (few drops), 75.5 MHz] δ = 63.8 [61.8], 115.2 [114.9], 122.8 [122.5], 127.2 [127.3], 127.7 [127.7], 128.4 [128.3], 128.9 [128.9], 139.1, 145.4 [144.8].

*N,N′-Bis(4-methylphenyl)-1,2-diphenyl-1,2-ethanediamine (dl and meso) (**7e**) [25]*

White solid; ^{1}H NMR [$CDCl_3$ + D_2O (few drops), 400 MHz] δ = 2.14 [2.15] (s, 6H), 4.49 [4.91] (2H, s), 6.40–7.19 (18H, m); ^{13}C NMR [$CDCl_3$ + D_2O (few drops), 75.5 MHz] δ = 20.3, 64.2 [62.1], 114.2 [113.8], 127.2 [126.9], 127.3 [127.4], 127.4 [127.5], 128.3 [128.2], 129.5 [129.7], 140.1 [138.4], 144.8 [144.2].

*N,N′-Dibenzyl-1,2-diphenyl-1,2-ethanediamine (dl and meso) (**7f**) [21]*

White solid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 3.42 (4H, AB system, J_{AB} 13.7 Hz), 3.76 (2H, s), 6.96–7.30 (20H, m); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ = 50.9, 67.1, 126.6, 127.6, 127.9, 128.2, 128.3, 128.6, 140.3, 140.7.

*2,3,N,N′-tetraphenyl-2,3-butanediamine (dl and meso) (**7g**) [26]*

White solid; ^{1}H NMR [$CDCl_3$ + D_2O (few drops), 400 MHz] δ = 1.64 [1.81] (6H, s), 6.17–7.56 (20H, m); ^{13}C NMR [$CDCl_3$ + D_2O (few drops), 75.5 MHz] δ = 20.8, 116.2, 127.4, 127.6, 128.2, 128.5, 128.6, 128.9, 141.2, 145.4.

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