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A novel lanthanum metal-assisted reaction of diaryl ketones and electrophiles

Rui Umeda, Masashi Ninomiya, Toshiaki Nishino, Makoto Kishida, Shunsuke Toiya, Tomoki Saito, Yutaka Nishiyama *, Noboru Sonoda

Department of Chemistry and Material Engineering, Faculty of Chemistry, Materials and Bioengineering, Kansai University, Suita, Osaka 564-8680, Japan

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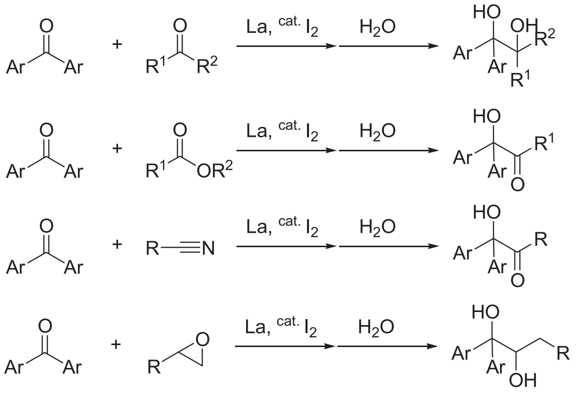
ABSTRACT

A novel and efficient lanthanum metal-assisted carbon-carbon bond formation of diaryl ketones and various electrophiles, such as carbonyl compounds, esters, nitriles, and epoxides, has been developed. When diaryl ketones were allowed to react with dialkyl ketones in the presence of lanthanum metal and a catalytic amount of iodine, the cross pinacol coupling reaction proceeded to give the corresponding unsymmetrical 1,2-diols in moderate to good yields. α-Hydroxy ketones were prepared by the lanthanum metal-assisted reaction of diaryl ketones with esters or nitriles, followed by hydrolysis with aq HCl. It is interesting to note that for the epoxides, the coupling reaction proceeded via the Meinwald rearrangement of epoxides to give the corresponding 1,2-diols.

1. Introduction

The utilization of lanthanoid metal salts and organolanthanoid compounds as synthetic reagents or catalysts in organic synthesis has been steadily increasing due to their unique chemical properties. In particular, low-valent, trivalent, and tetravalent lanthanoid compounds have been widely used in organic reactions.[1] On the hand, although it is expected that zero-valent lanthanoid metals bear a potential reducing ability could be used as the reducing agent in organic synthesis, the direct use of lanthanoid metals in organic synthesis is still rare due to their low solubility in an organic solvent or to their instability under aerobic conditions.[2–5]

We have recently succeeded in the direct use of lanthanum metal as a reagent in the presence of a catalytic amount of iodine in organic synthesis.[6] During the course of our study on the direct use of lanthanum metal in organic synthesis, it was found that various electrophiles were efficiently introduced onto the carbonyl carbon of diaryl ketones in the presence of lanthanum metal and a catalytic amount of iodine.[7] When diaryl ketones were treated with dialkyl ketones in the presence of lanthanum metal and a catalytic amount of iodine, the corresponding unsymmetrical 1,2-diols, the cross pinacol coupling products, were formed in moderate to good yields.[10,11] For the reaction of nitriles[12] and esters,[13] α-hydroxy ketones were obtained. It is interesting to note that for the epoxides, the coupling reaction proceeded via the Meinwald rearrangement of epoxides to give the corresponding 1,2-diols (Scheme 1).[14] Fujiwara et al. have already reported ytterbium metal promoted the cross-coupling reaction of diaryl ketones with a various electrophiles to give the corresponding products.[4a–c] However, in the case of Yb, two-step procedures (time integration[15]), including (i) the reaction of diaryl ketones with Yb metal and (ii) the addition of electrophiles to the resulting solution of (i), were used on the reaction. On the other hand, in the case of La metal, the cross pinacol coupling products were formed in good yields by a simple



Scheme 1.

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* Corresponding author. Tel.: +81 6 6368 0902; fax: +81 6 6339 4026; e-mail address: nishiya@kansai-u.ac.jp (Y. Nishiyama).

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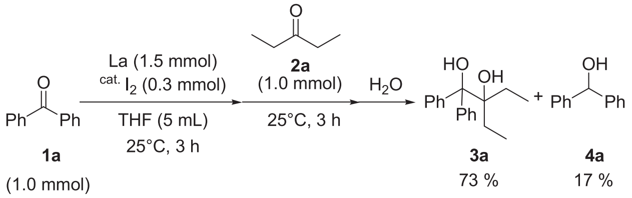
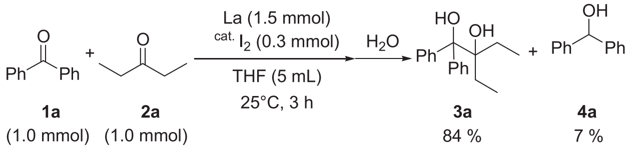
procedure. Furthermore, in the case of epoxide, it is interesting to note that the reaction proceeded via the Meinwald rearrangement of epoxides.

2. Results and discussion

When benzophenone (**1a**) was allowed to react with lanthanum metal in a presence of a catalytic amount of iodine in THF solvent at 25 °C, the solution initially showed a ketyl-like blue color that gradually turned brown. After stirring for 3 h, 3-pentanone (**2a**) was added to the resulting solution, and the solution was stirred for additional 3 h. Subsequent hydrolysis of the reaction mixture with aq HCl formed 2-ethyl-1,1-diphenyl-1,2-butanediol (**3a**), a cross-coupling product between **1** and **2**, in 73% yield along with benzhydrol (**4a**), the reduction product of **1a** (17%) (Scheme 2). This cross-coupling reaction could be conducted by a convenient one-step procedure (time and space integration[15]). As shown in Scheme 3, in the case of the one-pot procedure (time and space integration), cross-coupling between **1a** and **2a** produced a higher selectivity than that of the two-step procedures (time integration), and the yield of **3a** had increased to 84%.

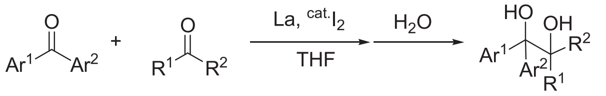


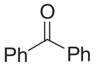
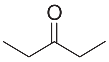
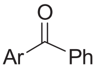
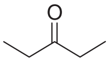
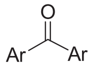
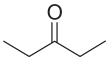
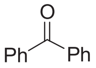
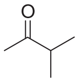
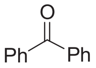
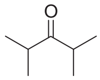
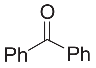
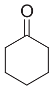
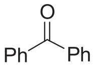
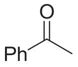
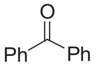
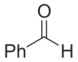
Scheme 2.



Scheme 3.

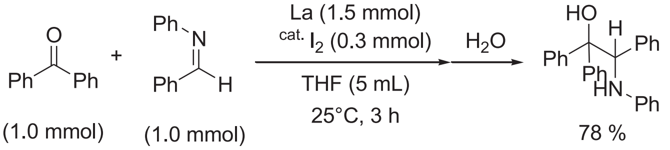
Table 1
La-assisted reaction of diaryl ketones with carbonyl compounds[a]



Entry	Diaryl ketone	Carbonyl compound	Yield[b] (%)
1			**3a** 84
			
2	Ar=4-$CH_3C_6H_4$		**3b** 67
3	Ar=3-$CH_3C_6H_4$		**3c** 90
4	Ar=2-$CH_3C_6H_4$		Trace
5[c]	Ar=4-$CH_3OC_6H_4$		**3d** 90
6	Ar=4-ClC_6H_4		**3e** 37
7	Ar=2-Naphthyl		**3f** 74
			
8	Ar=4-$CH_3C_6H_4$		**3g** 74
9	Ar=4-$CH_3OC_6H_4$		**3h** 74
10	Ar=4-ClC_6H_4		trace
11[d]			**3i** 61
12[d,e]			**4a** 87
13			**3j** 47
14[f]			**3k** 44
15[e]			**4a** 64

[a] Reaction conditions: La (1.5 mmol), diaryl ketone (1.0 mmol), carbonyl compound (1.0 mmol), I_2 (0.3 mmol), THF (5 mL) at 25 °C for 3 h.
[b] Isolated yield.
[c] 3-Pentanone (2.0 mmol) was used.
[d] At 67 °C for 9 h.
[e] The yield of benzhydrol.
[f] At 67 °C for 15 h.

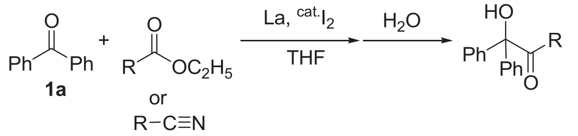
To elucidate the scope and limitation of the lanthanum metal-assisted coupling reaction of diaryl ketones and carbonyl compounds, various diaryl ketones were treated with carbonyl compounds in the presence of lanthanum metal and a catalytic amount of iodine, and these results are shown in Table 1. The coupling of 4-methyl-, 3-methyl-, 4-methoxy-, 4,4′-dimethyl-, and 4,4′-dimethoxybenzophenone, in which the electron donating group was substituted on the aromatic ring, gave the corresponding unsymmetrical 1,2-diols **3b**,**c**,**d**,**g**,**h** in 67–90% yield (entries 2, 3, 5, 8, and 9). In the case of 4-chloro- and 4,4′-dichlorobenzophenones bearing an electron withdrawing group, the yields of the corresponding unsymmetrical 1,2-diols were significant decreased (entries 6 and 10). For the sterically hindered diaryl ketone, such as 2-methylbenzophenone, the cross-coupling product was not obtained at all (entry 4). 2-Ethyl-1-(2-naphthyl)-1-phenyl-1,2-butanediol **(3f)** was obtained in 74% yield by the reaction between 2-naphthyl phenyl ketone and 3-pentanone (entry 7). When cyclohexanone was used as an aliphatic ketone instead of **2a**, the cross pinacol coupling reaction also proceeded to form 1,2-diol **3j** in 47% yield (entry 13). In the case of a sterically hindered dialkyl ketone, such as 2,4-dimethyl-3-pentanone, the coupling reaction did not proceed at all and benzhydrol (**4a**), the reduction product of **1a**, was formed in 87% yield (entry 12). For the reaction of 3-methyl-2-butanone and acetophenone, the yields of the cross-coupling products decreased, however, the product yields **3i**,**k** were improved by extending the reaction time at a higher reaction temperature (67 °C) (entries 11 and 14). In the case of benzaldehyde, **4a** was formed in 64% yield along with the formation of various complicated by-products (entry 15). When an imine was used as the electrophile instead of carbonyl compounds, α-amino alcohol was also synthesized by this protocol (Scheme 4).[16,17]

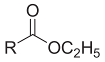
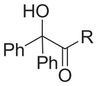
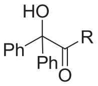


Scheme 4.

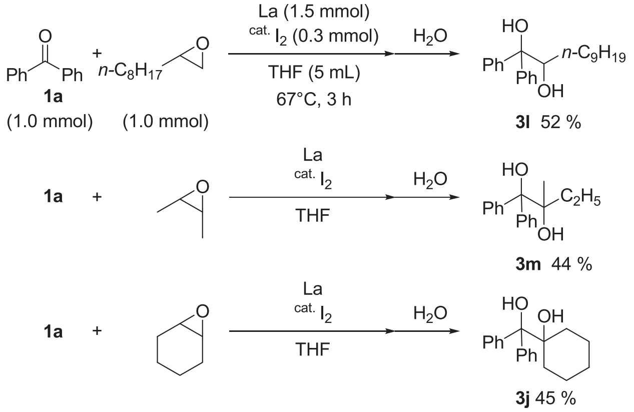
In order to determine the applicability of the lanthanum metal-assisted carbon–carbon bond formation of diaryl ketones, the reaction of benzophenone (**1a**) with esters or nitriles was next examined in the presence of lanthanum metal and a catalytic amount of iodine. These results are shown in Table 2. When **1a** was allowed to react with ethyl benzoate in the presence of lanthanum metal at 25 °C, a benzoyl group was efficiently introduced onto the carbonyl carbon of **1a** to give 2-hydroxy-1,2,2-triphenylethanone (**5a**) in 60% yield along with the formation of diphenylmethyl benzoate (6%) (entry 1). Compound **5a** was also prepared by the treatment of **1a** with benzonitrile followed by hydrolysis with HCl aq in 60% yield (entry 5). For the reaction with benzoyl chloride, the yield of **5a** was low (2%) due to preparation of various complicated by-products. Similarly, **1a** was coupled with various esters or nitriles to give the corresponding α-hydroxy ketones in moderate yields, however, for the α-disubstituted ester, the reaction did not proceed (entries 2–4 and 6–9). On the other hand, for the reaction with 2-octyloxirane, the 1,3-diol, such as 1,1-diphenylundecane-1,3-diol or 2-octyl-1,1-diphenyl-propane-1,3-diol, was not formed. It is interesting to note that the reaction proceeded via the Meinwald rearrangement of epoxides to give the corresponding 1,2-diol, 1,1-diphenyldecane-1,2-diol (**3l**), was formed in 52% yield (Scheme 5). In order to determine the scope and limitation of the reaction, the treatment of **1a** and 2,3-dialkyl substituted and cyclic oxiranes in the presence of lanthanum metal formed the corresponding 1,2-diols **3m** and **3j**, respectively, in which **1a** was coupled with the Meinwald rearrangement products of the epoxides, in moderate yields.

Table 2
La-assisted synthesis of α-hydroxy ketones[a]



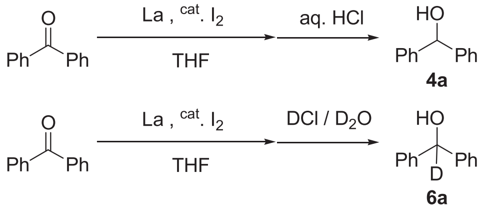
Entry	Electrophile	Product	Yield[b] (%)
			
1	R=Ph		**5a** 60
2	R=Bn		**5b** 60
3	R=n-C_6H_{13}		**5c** 59
4	R=$(CH_3)_2CH$		trace
	R−C≡N		
5	R=Ph		**5a** 60
6	R=4-$CH_3C_6H_4$		**5d** 58
7[c]	R=2-Naphthyl		**5e** 88
8	R=CH_3		**5f** 53
9	R=Bn		**5b** 63

[a] Reaction conditions: La (1.5 mmol), **1a** (1.0 mmol), ester or nitrile (2.0 mmol) I_2 (0.3 mmol), THF (5 mL) at 25 °C for 3 h.
[b] Isolated yield.
[c] At 67 °C.



Scheme 5.

Fujiwara et al. reported that the ytterbium–diaryl ketone complex, which was prepared by the treatment of an diaryl ketone with ytterbium metal, reacted with various electrophiles to give the corresponding coupling products.[4a–c] After then, Hou and co-workers succeeded in the isolation of the Yb(II) benzophenone dianion complex by the reaction of benzophenone with ytterbium metal in the presence of HMPA.[4e,18] We have already shown that the treatment of benzophenone (**1a**) with lanthanum metal followed by quenching with HCl/H_2O afforded benzhydrol (**4a**). In addition, when the reaction mixture was quenched with DCl/D_2O instead of HCl/H_2O, the corresponding C-deuterated benzhydrol (**6a**) was formed (Scheme 6).[6a] Based on these results, at the present time, while the reaction pathway is not clearly shown, the reaction pathway including the addition of electrophiles to the lanthanum–diaryl ketone dianion intermediate formed by the reduction of diaryl ketone with lanthanum metal was suggested.



Scheme 6.

3. Conclusion

In summary, we developed a lanthanum metal-assisted cross-coupling method of diaryl ketones with ketones, esters, nitriles, and epoxides. The present method has the following noteworthy features: (i) direct introduction method of electrophiles onto the carbonyl carbon of the diaryl ketones, (ii) simple procedure, and (iii) moderate to good yields of the products.

4. Experimental section

4.1. Reagents

Benzophenone, 4-methylbenzophenone, 4-chlorobenzophenone, 4-methoxybenzophenone, 2-benzoyl naphthalene, 3-pentanone, cyclohexanone, esters, nitriles, and iodine were commercially available high-grade products and used without purification. The lanthanum metal was a commercially available high-grade product and used as a fine powder grained by metal file in a glove box. THF was purified by the usual methods before use. 2-Methylbenzophenone and 3-methylbenzophenone were prepared by the reaction of benzene with aroyl chlorides in the presence of $AlCl_3$. N-Benzylideneaniline was prepared by the reaction of benzaldehyde with aniline. The other chemical agents were commercially obtained and purified by distillation prior to use if necessary.

4.2. General procedure for the reaction of diaryl ketones with electrophiles

Lanthanum powder (1.5 mmol, 208 mg) was placed in a two-necked flask. The diaryl ketone (1.0 mmol), iodine (0.3 mmol, 76 mg), electrophile (1.0 or 2.0 mmol), and THF (5 mL) were added to the flask, and the mixture was stirred at 25 °C or 67 °C for 3 h under nitrogen atmosphere. After the reaction, aq HCl (1 M) was added to the reaction mixture, and the resulting solution was extracted with diisopropyl ether (five times). The organic layer was dried over $MgSO_4$. The resulting mixture was filtered, and the organic solvent was removed under reduced pressure. Purification of the residue by column chromatography on silica gel afforded the corresponding coupling products. Products (2-ethyl-1,1-diphenyl-1,2-butanediol (**3a**),[19] 1-(diphenylhydroxymethyl)cyclohexanol (**3j**),[4b,19] 1,1,2-triphenyl-1,2-propanediol (**3k**),[19] 2-methyl-1,1-diphenyl-1,2-butanediol (**3m**),[19] 2-hydroxy-1,2,2-triphenylethanone (**5a**),[4b] 1-hydroxy-1,1,3-triphenylpropan-2-one (**5b**),[4b] 1-hydroxy-1,1-diphenyloctan-2-one (**5c**),[4b,20] 1-hydroxy-1,1-diphenyl-2-(4-methylphenyl)ethanone (**5d**),[21] 2-hydroxy-2,2-diphenyl-1-(2-naphthyl)-1-ethanone (**5e**),[22] and 1-hydroxy-1,1-diphenyl-2-propanone (**5f**)[23]) were characterized by comparison of their spectra data (^{1}H and ^{13}C NMR and IR) to those of authentic samples.

*4.2.1. 2-Ethyl-1-(4-methylphenyl)-1-phenyl-1,2-butanediol (**3b**).* Colorless oil; ^{1}H NMR δ 0.86 (t, J=7.6 Hz, 3H), 0.88 (t, J=7.6 Hz, 3H), 1.69–1.75 (m, 4H), 1.98 (br s, 1H), 2.31 (s, 3H), 2.70 (br s, 1H), 7.09–7.11 (m, 2H), 7.20–7.30 (m, 3H), 7.52–7.54 (m, 2H), 7.63–7.65 (m, 2H); ^{13}C NMR δ 8.9, 21.1, 28.7, 79.1, 83.9, 126.9, 127.7, 128.2, 128.5, 128.5, 136.6, 142.1, 145.2; IR 3544, 2967, 2938, 2879, 1726, 1509, 1446, 1379, 1256, 1155, 1033, 964, 808 cm^{-1}; MS (EI) m/z 284 (M$^+$). HRMS (ESI) m/z: [M+Na]$^+$ calcd for $C_{19}H_{24}O_2Na$: 307.1674. Found 307.1689.

*4.2.2. 2-Ethyl-1-(3-methylphenyl)-1-phenyl-1,2-butanediol (**3c**).* Colorless oil; ^{1}H NMR δ 0.87 (t, J=7.2 Hz, 6H), 1.70–1.76 (m, 4H), 1.94 (br s, 1H), 2.32 (s, 3H), 2.72 (br s, 1H), 7.03–7.05 (m, 1H), 7.15–7.30 (m, 4H), 7.45 (s, 2H), 7.64–7.66 (m, 2H); ^{13}C NMR δ 8.8, 8.9, 21.8, 21.8, 28.7, 78.9, 83.8, 125.2, 126.7, 127.4, 127.5, 128.0, 128.6, 137.1, 144.7, 144.8; IR 3546, 2968, 2939, 2880, 1602, 1491, 1459, 1446, 1380, 1321, 1148, 1034, 965, 850 cm^{-1}; MS (EI) m/z 284 (M$^+$). HRMS (FAB) m/z: [M+Na]$^+$ calcd for $C_{19}H_{24}O_2Na$: 307.1674. Found 307.1678.

*4.2.3. 2-Ethyl-1-(4-methoxyphenyl)-1-phenyl-1,2-butanediol (**3d**).* Colorless oil; ^{1}H NMR δ 0.85 (t, J=7.6 Hz, 3H), 0.87 (t, J=7.6 Hz, 3H), 1.68–1.73 (m, 4H), 1.98 (br s, 1H), 2.67 (br s), 1H 3.78 (s, 3H), 6.81–6.86 (m, 2H), 7.23–7.30 (m, 3H), 7.56–7.64 (m, 4H); ^{13}C NMR δ 8.9, 8.9, 28.6, 28.7, 55.2, 79.0, 83.6, 112.8, 126.7, 127.5, 128.0, 129.4, 137.1, 144.9, 158.2; IR 3520, 2966, 2938, 2880, 1608, 1510, 1462, 1445, 1296, 1251, 1182, 1035, 965, 824, 748, 705 cm^{-1}; MS (EI) m/z 300 (M$^+$). HRMS (FAB) m/z: [M+Na]$^+$ calcd for $C_{19}H_{24}O_3Na$: 323.1623. Found 323.1624.

*4.2.4. 2-Ethyl-1-(4-chlorophenyl)-1-phenyl-1,2-butanediol (**3e**).* Colorless oil; ^{1}H NMR δ 0.86 (t, J=7.6 Hz, 3H), 0.87 (t, J=7.6 Hz, 3H), 1.65–1.89 (m, 4H), 1.89 (br s, 1H), 2.74 (br s, 1H), 7.23–7.31 (m, 5H), 7.60–7.92 (m, 4H); ^{13}C NMR δ 8.915.4, 28.7, 79.2, 83.7, 127.2, 127.9, 127.9, 128.2, 129.9, 132.9, 143.8, 144.6; IR 3567, 2969, 2939, 2880, 1598, 1490, 1446, 1398, 1319, 1159, 1094, 1013, 965, 815, 703 cm^{-1}; MS (EI) m/z 304 (M$^+$). HRMS (FAB) m/z: [M+Na]$^+$ calcd for $C_{19}H_{21}{}^{35}ClO_2Na$ and $C_{19}H_{21}{}^{37}ClO_2Na$: 327.1128 and 329.1098. Found 327.1133 and 329.1092.

*4.2.5. 2-Ethyl-1-(2-naphthyl)-1-phenyl-1,2-butanediol (**3f**).* Colorless oil; ^{1}H NMR δ 0.89 (t, J=7.6 Hz, 3H), 0.90 (t, J=7.6 Hz, 3H), 1.75–1.83 (m, 4H), 1.99 (br s, 1H), 2.75 (br s, 1H), 7.23–7.31 (m, 3H), 7.36–7.46 (m, 2H), 7.67–7.83 (m, 6H), 8.19 (s, 1H); ^{13}C NMR δ 9.0, 29.0, 79.3, 84.2, 126.0, 126.1, 126.9, 127.0, 127.1, 127.2, 127.4, 127.9, 128.4, 128.5, 128.6, 132.4, 132.9, 142.5, 144.9; IR 3568, 3056, 2966, 2937, 2879, 1744, 1598, 1492, 1446, 1381, 1152, 1121, 1032, 963, 820, 704 cm^{-1}; MS (EI) m/z 320 (M$^+$). HRMS (FAB) m/z: [M+Na]$^+$ calcd for $C_{22}H_{24}O_2Na$: 343.1674. Found 343.1677.

*4.2.6. 2-Ethyl-1,1-di(4-methylphenyl)-1,2-butanediol (**3g**).* White solid; mp 64–65 °C; ^{1}H NMR δ 0.86 (t, J=7.6 Hz, 6H), 1.67–1.74 (m, 4H), 2.00 (s, 1H), 2.30 (s, 6H), 2.69 (s, 1H), 7.07–7.09 (m, 4H), 7.50–7.52 (m, 4H); ^{13}C NMR δ 8.8, 20.9, 28.5, 78.9, 83.7, 128.0, 128.3, 136.3, 142.0; IR 3565, 2968, 2939, 2880, 1509, 1457, 1379, 1156, 1037, 1022, 964, 811, 784 cm^{-1}; MS (EI) m/z 298 (M$^+$). HRMS (ESI) m/z: [M+Na]$^+$ calcd for $C_{20}H_{26}O_2Na$: 321.1831. Found 321.1846.

*4.2.7. 2-Ethyl-1,1-di(4-methoxyphenyl)-1,2-butanediol (**3h**).* White solid; mp 77–78 °C; ^{1}H NMR δ 0.85 (t, J=7.6 Hz, 6H), 1.66–1.72 (m, 4H), 2.05 (s, 1H), 2.70 (s, 1H), 3.77 (s, 6H), 6.79–6.82 (m, 4H), 7.53–7.55 (m, 4H); ^{13}C NMR δ 8.8, 28.5, 55.1, 79.0, 83.4, 128.0, 129.3, 137.3, 158.2; IR 3526, 2965, 2835, 1608, 1508, 1457, 1297, 1249, 1179, 1034, 823, 584 cm^{-1}; MS (EI) m/z 330 (M$^+$). HRMS (ESI) m/z: [M+Na]$^+$ calcd for $C_{20}H_{26}O_4Na$: 353.1729. Found 353.1746.

*4.2.8. 2,3-Dimethyl-1,1-diphenyl-1,2-butanediol (**3i**).* Colorless oil; ^{1}H NMR δ 0.81 (d, J=6.8 Hz, 3H), 0.91 (d, J=6.8 Hz, 3H), 1.23 (s, 2H), 2.02 (s, 1H), 2.05–2.16 (m, 1H), 2.80 (s, 1H), 7.21–7.31 (m, 6H), 7.63–7.65 (m, 2H), 7.71–7.73 (m, 2H); ^{13}C NMR δ 18.5, 19.3, 20.4, 34.0, 79.4, 83.8, 126.8, 126.9, 127.5, 127.7, 127.9, 128.1, 144.1, 145.3; IR 3540, 3056, 2962, 2876, 1491, 1446, 1388, 1158, 1079, 1024, 749, 704, 636 cm^{-1}; MS (EI) m/z 270 (M$^+$). HRMS (ESI) m/z: [M+Na]$^+$ calcd for $C_{18}H_{22}O_2Na$: 293.1517. Found 293.1531.

*4.2.9. 2-Methyl-1,1-diphenyl-1,2-undecanediol (**3l**).* Colorless oil; ^{1}H NMR δ 0.87 (t, J=6.8 Hz, 3H), 1.23–1.26 (m, 14H), 1.46–1.48 (m, 2H), 1.66–1.69 (m, 1H), 2.10 (br s, 1H), 2.87 (br s, 1H), 7.22–7.29 (m, 6H), 7.59–7.63 (m, 4H); ^{13}C NMR δ 14.1, 22.6, 22.9, 23.5, 29.2, 29.7, 30.3, 31.8, 37.4, 78.1, 83.1, 126.8, 126.9, 127.5, 127.6, 128.3, 128.4, 144.5, 144.6; IR 3476, 2923, 2853, 1491, 1446, 1388, 1158, 1079, 1024, 749, 704, 636 cm^{-1}; MS (EI) m/z 340 (M$^+$). HRMS (ESI) m/z: [M+Na]$^+$ calcd for $C_{24}H_{34}O_2Na$: 377.2457. Found 377.2475.

4.3. Two-step procedure for the reaction of benzophenone with 3-pentanone

Lanthanum powder (1.5 mmol, 208 mg) was placed in a two-necked flask. Benzophenone (1.0 mmol, 182 mg), iodine (0.3 mmol, 76 mg), and THF (5 mL) were added to the flask, and the mixture was stirred at 25 °C for 3 h under nitrogen atmosphere. 3-Pentanone (1.0 mmol, 86 mg) was added to the resulting solution, and the mixture was stirred at 25 °C for 3 h. After the reaction, aq HCl (1 M) was added to the reaction mixture, and the resulting solution was extracted with diisopropyl ether (five times). The organic layer was dried over $MgSO_4$. The resulting mixture was filtered, and the organic solvent was removed under reduced pressure. Purification of the residue by column chromatography on silica gel afforded 2-ethyl-1,1-diphenyl-1,2-butanediol (**3a**).

4.4. General procedure for the reaction of benzophenone with *N*-benzylideneaniline

Lanthanum power (1.5 mmol, 208 mg) was placed in a two-necked flask. Benzophenone (1.0 mmol, 182 mg), iodine (0.3 mmol, 76 mg), *N*-benzylideneaniline (1.0 mmol, 181 mg), and THF (5 mL) were added to the flask, and the mixture was stirred at 25 °C for 3 h under nitrogen atmosphere. After the reaction, aq HCl

(1 M) was added to the reaction mixture, and the resulting solution was extracted with diisopropyl ether (five times). The organic layer was dried over $MgSO_4$. The resulting mixture was filtered, and the organic solvent was removed under reduced pressure. Purification of the residue by column chromatography on silica gel afforded 1,1,2-triphenyl-2-(*N*-phenylamino)ehtanol. 1,1,2-Triphenyl-2-(*N*-phenylamino)ehtanol[17h,i] was characterized by comparison of their spectra data (^{1}H and ^{13}C NMR and IR).

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Supplementary data

Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.tet.2014.12.089.

References and notes

1. For recent reviews concerning the chemistry of lanthanoid compounds, see: (a) Kagan, H. B. *New J. Chem.* **1990**, *14*, 453; (b) Curran, D. P.; Fevig, T. L.; Jasperse, C. P.; Totleben, M. J. *Synlett* **1992**, 943; (c) Molander, G. A. *Chem. Rev.* **1992**, *92*, 29; (d) Kobayashi, S. *Synlett* **1994**, 689; (e) Kamachi, Y.; Kubo, T. *J. Synth. Org. Chem. Jpn.* **1994**, *52*, 285; (f) Imamoto, T. In *Lanthanides in Organic Synthesis*; Katrizky, A. R., Meth-Cohn, O., Ress, C. W., Eds.; Academic: London, UK, 1994; (g) Matsuda, Y. *J. Synth. Org. Chem. Jpn.* **1995**, *53*, 987; (h) Anwander, R.; Edelmann, F. T.; Herrmann, W. A. In *Topics in Current Chemistry*; Herrmann, W. A., Ed.; Springer: Berlin, Germany, 1996; Vol. 179; (i) Molander, G. A.; Harris, C. R. *Chem. Rev.* **1996**, *96*, 307; (j) Herrmann, W. A. In *Synthetic Methods of Organometallic and Inorganic Chemistry*; Edelmann, F. T., Ed.; Thieme: Stuttgart, Germany, 1997; Vol. 6; (k) Ito, Y.; Fujiwara, Y.; Yamamoto, T. *Kikan Kagaku Sousetu*; Gakkai Center, Press Center: Tokyo, 1998; (l) Kobayashi, S. In *Lanthanide: Chemistry and Use in Organic Synthesis*; Springer: Berlin/Heidelberg, Germany, 1999; Vol. 2; (m) Yanada, R.; Ibuka. *J. Synth. Org. Chem. Jpn.* **2000**, *58*, 597; (n) Steel, P. G. *J. Chem. Soc., Perkin Trans. 1* **2001**, 2727; (o) Molander, G. A.; Antoinette, J.; Romero, C. *Chem. Rev.* **2002**, *102*, 2161; (p) Shibasaki, M.; Yoshikawa, N. *Chem. Rev.* **2002**, *102*, 2187; (q) Inanaga, J.; Furuno, H.; Hayano, T. *Chem. Rev.* **2002**, *102*, 2211; (r) Mikami, K.; Terada, M.; Matsuzawa, H. *Angew. Chem., Int. Ed.* **2002**, *41*, 3554; (s) Sumino, Y.; Ogawa, A. *J. Synth. Org. Chem. Jpn.* **2003**, *61*, 201; (t) Kagan, H. B. *Tetrahedron* **2003**, *59*, 10351; (u) Dahlen, A.; Hilmersson, G. *Eur. J. Inorg. Chem.* **2004**, 3393 and references therein.
2. Ce: (a) Imamoto, T.; Kusumoto, T.; Hatanaka, Y.; Yokoyama, M. *Tetrahedron Lett.* **1982**, *23*, 1353; (b) Fukuzawa, S.; Fujinami, T.; Sakai, S. *J. Chem. Soc., Chem. Commun.* **1986**, 475; (c) Fukuzawa, S.; Sumimoto, N.; Fujinami, T.; Sakai, S. *J. Org. Chem.* **1990**, *55*, 1328.
3. Sm: (a) Yanada, R.; Bessho, K.; Yanada, K. *Chem. Lett.* **1994**, 1279; (b) Komachi, Y.; Kudo, T. *Chem. Pharm. Bull.* **1994**, *42*, 402; (c) Yanada, R.; Bessho, K.; Yanada, K. *Synlett* **1995**, 443; (d) Yanada, R.; Bessho, K.; Yanada, K. *Synlett* **1995**, 1261; (e) Komachi, Y.; Kudo, T. *Chem. Pharm. Bull.* **1995**, *43*, 1422; (f) Yanada, R.; Negoro, N.; Yanada, K.; Fujita, T. *Tetrahedron Lett.* **1996**, *37*, 9313; (g) Yanada, R.; Negoro, N.; Yanada, K.; Fujita, T. *Tetrahedron Lett.* **1997**, *38*, 3271; (h) Ding, Z.-B.; Wu, S.-H. *Youji Huaxue* **1997**, *17*, 165; (i) Wang, L.; Zhang, Y. *Tetrahedron* **1998**, *54*, 11129; (j) Banik, B. K.; Mukhopadhyay, C.; Venkatraman, M. S.; Becker, F. F. *Tetrahedron Lett.* **1998**, *39*, 7243; (k) Yanada, R.; Negoro, M.; Okaniwa, M.; Ibuka, T. *Tetrahedron* **1999**, *55*, 13947; (l) Chatak, A.; Becker, F. F.; Banik, B. K. *Tetrahedron Lett.* **2000**, *41*, 3793; (m) Talukdar, S.; Fang, J.-M. *J. Org. Chem.* **2001**, *66*, 330 See also Ref. 2a.
4. Yb: (a) Hou, Z.; Takamine, K.; Fujiwara, Y.; Taniguchi, H. *Chem. Lett.* **1987**, 2061; (b) Hou, Z.; Takamine, K.; Aoki, K.; Shiraishi, O.; Fujiwara, Y.; Taniguchi, H. *J. Org. Chem.* **1988**, *53*, 6077; (c) Hou, Z.; Takamine, K.; Aoki, K.; Shiraishi, O.; Fujiwara, Y.; Taniguchi, H. J. C. S. *J. Chem. Soc., Chem. Commun.* **1988**, 668; (d) Takaki, K.; Beppu, F.; Tanaka, S.; Tsubaki, Y.; Jintoku, T.; Fujiwara, Y. *J. Chem. Soc., Chem. Commun.* **1990**, 516; (e) Hou, Z.; Yamazaki, H.; Kobayashi, K.; Fujiwara, Y.; Taniguchi, H.; Taniguchi, Y. *J. Chem. Soc., Chem. Commun.* **1992**, 722; (f) Makioka, Y.; Uebori, S.; Tsuno, M.; Taniguchi, Y.; Takaki, K.; Fujiwara, Y. *Chem. Lett.* **1994**, 611; (g) Nagafuji, A.; Makioka, Y.; Takaki, K.; Fujiwara, Y. *Tetrahedron Lett.* **1994**, *35*, 6897; (h) Makioka, Y.; Tsuno, M.; Takaki, K.; Taniguchi, Y.; Fujiwara, Y. *Chem. Lett.* **1995**, 821; (i) Taniguchi, Y.; Kuno, T.; Nakanishi, M.; Takaki, Y.; Fujiwara, Y. *Appl. Organomet. Chem.* **1995**, *9*, 491; (j) Taniguchi, Y.; Kuno, T.; Makahashi, M.; Takaki, K.; Fujiwara, Y. *Appl. Organomet. Chem.* **1995**, 949; (k) Makioka, Y.; Tsuno, M.; Uebori, S.; Taniguchi, Y.; Takaki, K.; Fujiwara, Y. *J. Org. Chem.* **1996**, *61*, 372; (l) Jin, W.; Makioka, Y.; Kitamura, Y.; Fujiwara, Y. *J. Org. Chem.* **2001**, *66*, 514; (m) Taniguchi, Y.; Takaki, K.; Fujiwara, Y. In *Reviews on Heteroatom Chemistry*; Oae, S., Ed.; MY: Tokyo, 1995; Vol. 12, p 163.
5. Others: (a) Ogawa, A.; Sumino, T.; Nanke, S.; Ohya, S.; Sonoda, N.; Hirao, T. *J. Am. Chem. Soc.* **1997**, *119*, 2745; (b) Ogawa, A.; Ohya, S.; Hirao, T. *Chem. Lett.* **1997**, 275; (c) Sumino, Y.; Harato, N.; Tomisaka, Y.; Ogawa, A. *Tetrahedron* **2003**, *59*, 10499; (d) Tomisaka, Y.; Tsuchii, K.; Ogawa, A. *J. Alloys Compd.* **2006**, *408–412*, 427; (e) Bian, Y.-J.; Yu, X.-G.; Peng, H.-W.; Li, J.-T. *Synth. Commun.* **2006**, *36*, 2513; (f) Li, Z.-F.; Tomisaka, Y.; Nomoto, A.; Zhang, Y.; Ogawa, A. *Chem. Lett.* **2009**, 16; (g) Tomisaka, Y.; Yoshimura, A.; Nomoto, A.; Sonoda, M.; Ogawa, A. *Res. Chem. Intermed.* **2013**, *39*, 43.
6. (a) Nishino, T.; Nishiyama, Y.; Sonoda, N. *Heteroat. Chem.* **2000**, *11*, 81; (b) Nishino, T.; Nishiyama, Y.; Sonoda, N. *Heteroat. Chem.* **2002**, *13*, 131; (c) Nishino, T.; Watanabe, T.; Okada, M.; Nishiyama, Y.; Sonoda, N. *J. Org. Chem.* **2002**, *67*, 966; (d) Kawabata, H.; Nishino, T.; Nishiyama, Y.; Sonoda, N. *Tetrahedron Lett.* **2002**, *43*, 4911; (e) Nishiyama, Y.; Kawabata, H.; Nishino, T.; Sonoda, N. *Tetrahedron Lett.* **2003**, *43*, 4911; (f) Nishiyama, Y.; Okada, M.; Nishino, T.; Sonoda, N. *Bull. Chem. Soc. Jpn.* **2005**, *78*, 341; (g) Nishiyama, Y.; Tanimizu, H.; Tomita, T. *Tetrehedron Lett.* **2007**, *48*, 6405; (h) Umeda, R.; Yuasa, T.; Anahara, N.; Nishiyama, Y. *J. Organomet. Chem.* **2011**, *696*, 1916.
7. In order to increase the reactivity of lanthanoid metal, the reaction was carried out in the presence of some additives, such as a catalytic amount of iodine[1-m,2a,3k] or methyl iodide,[4] excess amount of HMPA,[3i,l] and HCl aq[3m] or under photoirradiation,[5d,f] sonication,[8] and DMF solvent[9] conditions.
8. (a) Concellon, J. M.; Rodriguez-Solla, H.; Bardales, E.; Huerta, M. *Eur. J. Org. Chem.* **2003**, 1775; (b) Concellon, J. M.; Bernad, P. L.; Huerta, M.; Garcia-Granda, S.; Diaz, M. R. *Chem.—Eur. J.* **2003**, *9*, 5343; (c) Teprovich, J. A., Jr.; Antharjanam, P. K. S.; Prasad, E.; Pesciotta, E. N.; Flowers, R. A., II. *Eur. J. Inog. Chem.* **2008**, 5015.
9. (a) Liu, Y.; Liu, X.; Zheng, Y. *Tetrahedron Lett.* **2003**, *44*, 1667; (b) Liu, Y.; Zheng, Y. *Tetrahedron* **2003**, *59*, 8429; (c) Liu, Y.; Zheng, Y. *Tetrahedron Lett.* **2004**, *45*, 1295; (d) Liu, Y.; Zheng, F.; Qi, Y.; Zhang, S. *Eur. J. Org. Chem.* **2008**, 5470.
10. Fujiwara et al. have already reported the ytterbium metal-assisted the coupling reaction of diaryl ketones various electrophiles. See: Refs. 4a–c.
11. For recent reports, see: (a) Kraynack, E. A.; Pedersen, S. F. *J. Org. Chem.* **1993**, *58*, 6114; (b) Konradi, A. W.; Kemp, S. J.; Pedersen, S. F. *J. Am. Chem. Soc.* **1994**, *116*, 1316; (c) Nowitzki, O.; Munnich, I.; Stucke, H.; Hoffmann, H. M. R. *Tetrahedron* **1996**, *52*, 11799; (d) Hoffmann, H. M. R.; Munnich, I.; Nowitzki, O.; Stucke, H.; Williams, D. J. *Tetrahedron* **1996**, *52*, 11783; (e) Kang, M.; Park, J.; Pedersen, S. F. *Synlett* **1997**, 41; (f) Fujiwara, T.; Tsuruta, Y.; Arizono, K.; Takeda, T. *Synlett* **1997**, 962; (g) Hu, Y.; Du, Z.; Wang, J.-X.; Xi, Y.; Gu, S. *Synth. Commun.* **1998**, *28*, 3299; (h) Nair, V.; Ros, S.; Jayan, C. N.; Rath, N. P. *Tetrahedron Lett.* **2002**, *43*, 8967; (i) Takai, K.; Morita, R.; Matsusita, H.; Toratsu, C. *Chirality* **2003**, *15*, 17; (j) Maekawa, H.; Yamamoto, Y.; Shimada, H.; Yonemura, K.; Nishiguchi, I. *Tetrahedron Lett.* **2004**, *45*, 3869; (k) Groth, U.; Jung, M.; Vogel, T. *Synlett* **2004**, 1054; (l) Groth, U.; Jung, M.; Vogel, T. *Chem.—Eur. J.* **2005**, *11*, 3127; (m) Fischer, S.; Groth, U.; Jumg, M.; Lindenmaier, M.; Vogel, T. *Tetrahedron Lett.* **2005**, *46*, 6679; (n) KIse, N.; Shiozawa, Y.; Ueda, M. *Tetrahedron* **2007**, *63*, 5415 See also Ref. 4b and references cited therein.
12. (a) Guijarro, D.; Mancheno, B.; Yus, M. *Tetrahedron* **1993**, *49*, 1327; (b) Guijarro, D.; Yus, M. *Tetrahedron* **1994**, *50*, 3447; (c) Zhou, L.; Zhang, Y.; Shi, D. *Tetrahedron Lett.* **1998**, *39*, 8491 See also Ref. 4b and references cited therein.
13. Liu, Y.; Zhang, Y. *Tetrahedron Lett.* **2001**, *42*, 5745 See also Ref 4b and references cited therein.
14. Rearrangement of epoxides to carbonyl compounds is an important reaction in organic synthesis. Several catalysts have been employed for this rearrangement. See Wang, Z. In *Comprehensive Organic Name Reactions and Reagents*; Herrmann, W. A., Ed.; John Wiley & Sons: 2009; p 1880; and references therein.
15. Suga, S.; Yamada, D.; Yoshida, J. *Chem. Lett.* **2010**, *39*, 404.
16. Bergmeier, S. C. *Tetrahedron* **2000**, *56*, 2561 and references cited therein.
17. There are some reports on the formation of α-amino alcohols using pinacoltype coupling reaction. For examples, see: (a) Roskamp, E. J.; Pedersen, S. F. *J. Am. Chem. Soc.* **1987**, *109*, 6551; (b) Imamoto, T.; Nishimura, S. *Chem. Lett.* **1990**, 1141; (c) Shono, T.; Kise, N.; Kunimi, N.; Nomura, R. *Chem. Lett.* **1991**, 2191; (d) Murakami, M.; Ito, H.; Ito, H.; Ito, Y. *J. Org. Chem.* **1993**, *58*, 6766; (e) Guijarro, D.; Yus, M. *Tetrahedron* **1993**, *49*, 7761; (f) Clerici, A.; Clerici, L.; Porta, O. *Tetrahedron Lett.* **1995**, *36*, 5955; (g) Machrouhi, F.; Namy, J.-L. *Tetrahedron Lett.* **1999**, *40*, 1315; (h) Ma, Y.; Zhang, Y. *Org. Prep. Proced. Int.* **2000**, *32*, 567; (i) Fan, G.; Liu, Y. *Tetrahedron Lett.* **2012**, *53*, 5084.
18. Hou, Z.; Yamazaki, H.; Fujiwara, Y.; Taniguchi, H. *Organometallics* **1992**, *11*, 722.
19. Scheffler, U.; Stößer, R.; Mahrwald, R. *Adv. Synth. Catal.* **2012**, *354*, 2648.
20. Kise, N.; Agui, S.; Morimoto, S.; Ueda, N. *J. Org. Chem.* **2005**, *70*, 9407.
21. Yoshida, N.; Ohwada, T. *Synthesis* **2001**, 1487.
22. Buckland, S. J.; Halton, B.; Stang, P. J. *Aust. J. Chem.* **1988**, *41*, 845.
23. Stavber, G.; Iskra, J.; Zupan, M.; Stavber, S. *Green Chem.* **2009**, *11*, 1262.