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Intermolecular Reductive Coupling of Esters with Benzophenones by Low-Valent Titanium: Synthesis of Diarylmethyl Ketones Revisited

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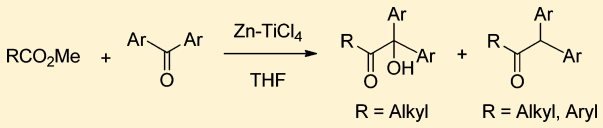
Supporting Information

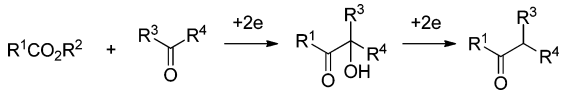
ABSTRACT: The reductive coupling of aliphatic esters with benzophenones by Zn−$TiCl_4$ in THF gave two- and four-electron reduced products, diaryl(hydroxy)methyl ketones, and diarylmethyl ketones selectively by controlling the reaction conditions. In the reaction of aromatic esters with benzophenones, diarylmethyl ketones were obtained as the sole products. *N*-(Alkoxycarbonyl)-(*S*)-α-amino acid methyl esters gave optically active diphenylmethyl ketones by reduction with benzophenone. The obtained diphenylmethyl ketones were transformed to 4,5-*cis*-disubstituted oxazolidin-2-ones stereoselectively.



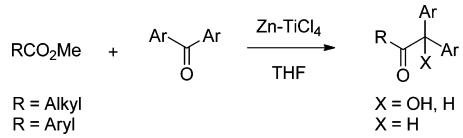
INTRODUCTION

Reductive cross-coupling of carboxylic acid derivatives with ketones is a potent tool for the reductive acylation of ketones to synthesize larger ketones. Of the carboxylic acid derivatives, esters are the most convenient substrates since they are readily accessible and relatively inert. The reductive cross-coupling of esters with ketones have been realized using low-valent titanium as a reducing agent.[1] In these cases, the products were four-electron reduced ketones (Scheme 1).[2] On the other hand, this type of coupling was also effected with SmI_2[3] and electroreduction[4] to give two-electron reduced α-hydroxy ketones. Recently, we reported the reductive coupling of 1,3-dimethyluracils, *N*-methoxycarbonyl lactams, and aliphatic cyclic imides with benzophenones by low-valent titanium generated from Zn−$TiCl_4$ and found that two- and four-electron reduced products were both obtained selectively by controlling the reaction conditions.[5] These results prompted us to reinvestigate the reductive coupling of esters with benzophenones by low-valent titanium. In this paper, we report that the reductive coupling of aliphatic esters and lactones with benzophenones by Zn−$TiCl_4$ gave two- and four-electron reduced products, diaryl(hydroxy)methyl ketones, and diarylmethyl ketones selectively by controlling the reaction conditions; meanwhile, the reductive coupling of aromatic esters with benzophenones afforded only four-electron reduced diarylmethyl ketones (Scheme 2).[6−8] These results show that this reductive coupling provides a useful method for the preparation of diarylmethyl ketones. The synthesis of diarylmethyl ketones still attracts much attention since these compounds are found in various natural and artificial materials.[9,10] In addition, we employed *N*-(methoxycarbonyl)-α-amino acid methyl esters as aliphatic esters to extend the scope of the reductive coupling of esters with benzophenones. From the obtained diphenylmethyl ketones, optically active 4,5-*cis*-disubstituted oxazolidin-2-ones[11] were prepared by stereoselective reduction and following cyclization of resulting alcohols (Scheme 3).

Scheme 1. Reductive Coupling of Esters with Ketones



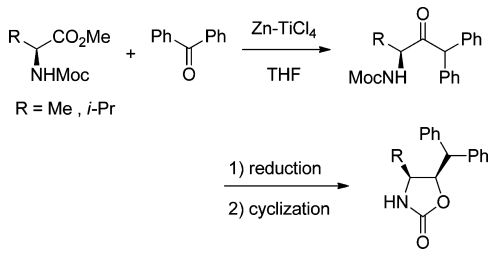
Scheme 2. Reductive Coupling of Esters with Benzophenones by Zn−$TiCl_4$



RESULTS AND DISCUSSION

1. Reductive Coupling of Aliphatic Esters with Benzophenones by Zn−$TiCl_4$. The reaction conditions of

Scheme 3. Reductive Coupling of Amino Acid Methyl Esters with Benzophenone and Transformation to Optically Active 4,5-*Cis*-Disubstituted Oxazolidin-2-ones



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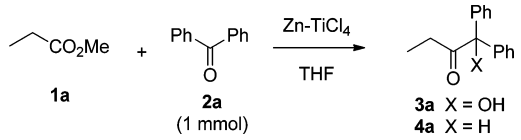
the reductive coupling were examined using methyl propionate (**1a**) and benzophenone (**2a**) as the substrates and the results are summarized in Table 1. Since **2a** is more valuable than **1a**,

Table 1. Reductive Coupling of 1a with 2a by Zn−$TiCl_4$



					% yield[b]	
run	**1a** (mmol)	$TiCl_4$[a] (mmol)	temp (°C)	time (h)	**3a**	**4a**
1	1	1	25	2	64	2
2	2	1	25	2	72	6
3	3	1	25	2	70	5
4	2	2	50	2	5	45
5	2	2	25	12	41	28
6	2	2	25	2	6	77
			50	2		
7	2	2	25	2		80
			50	6		

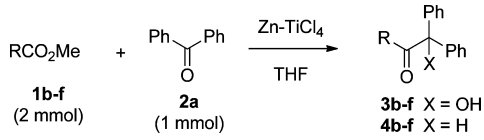
[a]Zn/$TiCl_4$ = 2/1. [b]Isolated yields based on **2a**.

the product yields based on **2a** were optimized. In the previous reports,[2] the reductions were performed with more than 2 equiv of low-valent titanium in refluxing THF. Therefore, we initially investigated the reductive coupling of **1a** with **2a** using equimolar amounts of low-valent titanium at ambient temperature. The molar ratio of Zn/$TiCl_4$ was fixed to 2/1 throughout this study. First, the reaction was carried out with a molar ratio of **1a**/**2a**/$TiCl_4$ of 1/1/1 in THF at 25 °C for 2 h, and then 1-hydroxy-1,1-diphenylbutan-2-one (**3a**) was obtained as the two-electron reduced product in 64% yield together with a small amount (2%) of further reduced product 1,1-diphenylbutan-2-one (**4a**) (run 1). The yield of **3a** increased to 72% and 70% with an increased molar ratio of **1a**/**2a** from 1/1 to 2/1 and 3/1, respectively (runs 2 and 3). These results show that the 2/1 molar ratio of **1a**/**2a** was sufficient to obtain **3a**. Next, to obtain **4a** predominantly, the reaction was carried out with a molar ratio of **1a**/**2a**/$TiCl_4$ as 2/1/2 at 50 °C for 2 h (run 4). Although the yield of **4a** (45%) was much higher than that of **3a** (5%), a considerable amount (40%) of homocoupled product of **2a**, 1,1,2,2-tetraphenylethene, was formed at this temperature. Nevertheless, the further reduction to **4a** seemed to be slow at 25 °C (run 5). Thus, the reaction was performed at 25 °C for 2 h and then continued at 50 °C for 2 h (run 6). The desired **4a** was produced in 77% yield with a small amount of **3a** (6%). Furthermore, the prolonged reaction time (6 h) at 50 °C completed the reduction of **3a** to **4a** (80%) (run 7).

The reductive coupling of aliphatic acid methyl esters **1b−f** with **2a** was carried out under the same conditions as runs 2 and 7 (conditions a and b) in Table 1 (Table 2). In all cases, the two- and four-electron reduced products, **3b−f** and **4b−f**, were produced selectively by choosing between the conditions a and b.

In addition, the reductive coupling of γ-butyrolactone (**1g**) with **2a** under conditions a mainly gave ring-opening γ-hydroxy ketone **3g**, while the reduction under conditions b yielded cyclic enol ether **5** as the major product (Scheme 4). In these cases, the four-electron reduced product was obtained as **5** probably due to the stability of five-membered cyclic enol ether. On the other hand, the reactions of δ-valerolactone (**1h**) and ε-

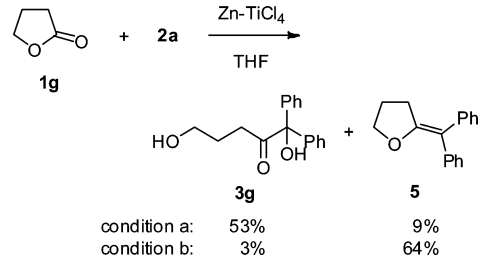
Table 2. Reductive Coupling of Aliphatic Esters 1b−f with 2a by Zn−$TiCl_4$



					% yield[b]	
run	**1**	R	conditions[a]		**3**	**4**
1	**1b**	CH_3	a	**b**	87	4
2	**1b**	CH_3	b	**b**		77
3	**1c**	n-C_3H_7	a	**c**	73	8
4	**1c**	n-C_3H_7	b	**c**		67
5	**1d**	$(CH_3)_2CHCH_2$	a	**d**	66	5
6	**1d**	$(CH_3)_2CHCH_2$	b	**d**		70
7	**1e**	i-C_3H_7	a	**e**	71	4
8	**1e**	i-C_3H_7	b	**e**		68
9	**1f**	$PhCH_2$	a	**f**	75	10
10	**1f**	$PhCH_2$	b	**f**		82

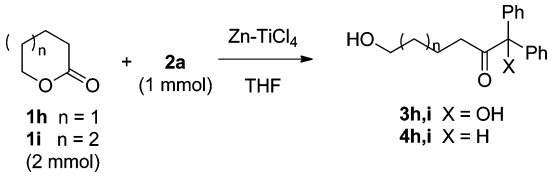
[a]Conditions: (a) **2a**/Zn/$TiCl_4$ = 1/2/1, 25 °C (2 h), (b) **2a**/Zn/$TiCl_4$ = 1/4/2, 25 °C (2 h) and then 50 °C (6 h). [b]Isolated yields based on **2a**.

Scheme 4. Electroreductive Coupling of 1g with 2a by Zn−$TiCl_4$



caprolactone (**1i**) with **2a** under conditions a and b afforded ring-opening δ-hydroxy ketones **3h** and **4h** and ε-hydroxy ketones **3i** and **4i**, respectively (Table 3). Since **1h** and **1i** were reactive substrates for the reductive coupling with **2a**, the reaction proceeded even at 0 °C to give **3h** and **3i**

Table 3. Reductive Coupling of Lactones 1h,i with 2a by Zn−$TiCl_4$



				% yield[b]	
run	**1**	conditions[a]		**3**	**4**
1	**1h**	a	**h**	57	4
2	**1h**	a[c]	**h**	74	
3	**1h**	b	**h**		52
4	**1i**	a	**i**	69	6
5	**1i**	a[c]	**i**	76	
6	**1i**	b	**i**		58

[a]Conditions: (a) **2a**/Zn/$TiCl_4$ = 1/2/1, 25 °C (2 h); (b) **2a**/Zn/$TiCl_4$ = 1/4/2, 25 °C (2 h) and then 50 °C (6 h). [b]Isolated yields based on **2a**. [c]0 °C (6 h).

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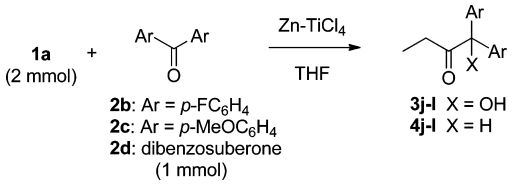
predominantly in 74% and 76% yields, respectively (runs 2 and 5).

In place of **2a**, other benzophenones **2b–d** also reacted with **1a**, and the results are summarized in Table 4. Under

Table 4. Reductive Coupling of 1a with Benzophenones 2b–d by Zn–$TiCl_4$



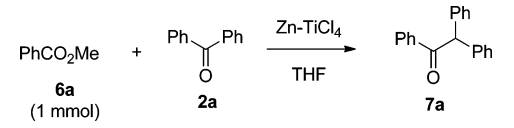
run	2	conditions[a]		% yield[b] 3	% yield[b] 4
1	**2b**	a	**j**	38	10
2	**2b**	b	**j**		45
3	**2c**	a	**k**	57	4
4	**2c**	b	**k**		52
5	**2d**	a	**l**	27	40
6	**2d**	a[c]	**l**	29	55
7	**2d**	b	**l**		63

[a]Conditions: (a) **2**/Zn/$TiCl_4$ = 1/2/1, 25 °C (2 h); (b) **2**/Zn/$TiCl_4$ = 1/4/2, 25 °C (2 h) and then 50 °C (6 h). [b]Isolated yields based on **2**. [c]0 °C (12 h).

conditions a, diaryl(hydroxy)methyl ketones **3j** and **3k** were mainly formed (runs 1 and 3), whereas **3l** was the minor product and further reduced ketone **4l** was the major product (run 5). Unexpectedly, the reaction at 0 °C also gave **4l** as the major product (run 6). These results show that the further reduction of **3l** to **4l** proceeded even at 0 °C. Under conditions b, diarylmethyl ketones **4j–l** were obtained selectively in moderate yields (runs 2, 4, and 7).

2. Reductive Coupling of Aromatic Esters with Benzophenones by Zn–$TiCl_4$. Methyl benzoate (**6a**) was employed as an aromatic ester to survey the reaction conditions for the reductive coupling with **2a** and the results are summarized in Table 5. The yields of the products were calculated on the basis of **6a**, since aromatic esters are usually more valuable than benzophenones. First, the reaction was carried out with the molar ratio of **6a**/**2a**/$TiCl_4$ as 1/1/1 in

Table 5. Reductive Coupling of 6a with 2a by Zn–$TiCl_4$



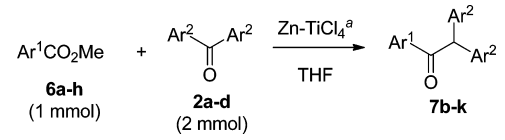
run	**2a** (mmol)	$TiCl_4$[a] (mmol)	temp (°C)	time (h)	% yield[b] of **7a**
1	1	1	25	6	33
2	1	2	25	6	54
3	2	3	25	6	72
4	2	3	25	2	75
			50	2	
5	2	3	50	2	62
6	2	4	25	6	67
7	2	4	25	2	65
			50	2	

[a]Zn/$TiCl_4$ = 2/1. [b]Isolated yields based on **6a**.

THF at 25 °C for 6 h, and 1,2,2-triphenylethanone (**7a**) was obtained as the four-electron reduced product in 33% yield (run 1). In this case, **6a** and **2a** were recovered in 65% and 35% recovery rates, respectively. To complete the reaction, the amount of reducing agent was doubled (**6a**/**2a**/$TiCl_4$ = 1/1/2) (run 2). Although **2a** was completely consumed (54% yield of **7a**), 33% of **6a** was recovered unreacted. Therefore, the reaction was carried out with a molar ratio of **6a**/**2a**/$TiCl_4$ as 1/2/3 (run 3). As expected, almost all of **6a** was consumed and **7a** was obtained in 72% yield. When the reaction was performed at 25 °C for 2 h and then continued at 50 °C for 2 h as run 6 in Table 1, the yield of **7a** slightly increased to 75% (run 4). However, the yield of **7a** somewhat decreased to 62% by the reaction at 50 °C from the start (run 5). Since small amounts of **2a** (<10%) were recovered in runs 3–5, the molar ratio of $TiCl_4$ was increased (**6a**/**2a**/$TiCl_4$ = 1/2/4) (runs 6 and 7). Almost all of **2a** and **6a** was consumed; however, the yields of **7a** were somewhat lowered. Regardless of the reaction conditions, **7a** was obtained as the sole coupled product, and the corresponding two-electron reduced product, 2-hydroxy-1,2,2-triphenylethanone, could not be detected at all.

The reductive coupling of a variety of aromatic acid methyl esters **6b–h** with **2a** was carried out under the same conditions as run 4 in Table 5 (Table 6). In all cases, diphenylmethyl

Table 6. Reductive Coupling of Aromatic Esters 6a–h with 2a–d by Zn–$TiCl_4$



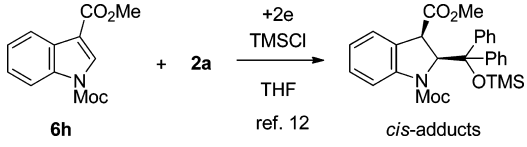
run	**2**	**6**	Ar^1	**7**	% yield[b]
1	**2a**	**6b**	*p*-$MeOC_6H_4$	**7b**	83
2	**2a**	**6c**	3,4-methylenedioxyphenyl	**7c**	77
3	**2a**	**6d**	2-naphthyl	**7d**	60
4	**2a**	**6e**	*E*-$PhCH_2$=CH	**7e**	45
5	**2a**	**6f**	2-furyl	**7f**	63
6	**2a**	**6g**	3-indolyl	**7g**	71
7	**2a**	**6h**	*N*-Moc-3-indolyl	**7h**	80
8	**2b**	**6a**	Ph	**7i**	52
9	**2c**	**6a**	Ph	**7j**	31
10	**2d**	**6a**	Ph	**7k**	85

[a]**2**/Zn/$TiCl_4$ = 1/3/1.5, 25 °C (2 h) and then 50 °C (2 h). [b]Isolated yields based on **6**.

ketones **7b–h** were obtained in moderate to good yields (runs 1–7). The result obtained from **6h** (run 7) is in contrast to the electroreduction of **6h** with **2a**, which afforded the corresponding 1,4-adduct (Scheme 5).[12] Other benzophenones **2b–d** also reacted with **6a** to give diarylmethyl ketones **7i–k**, although the yield of **7j** was low (runs 8–10).

3. Reaction Mechanism of the Reductive Coupling. The presumed reaction mechanism of the reductive coupling of

Scheme 5. Electroreductive Coupling of 6h with 2a



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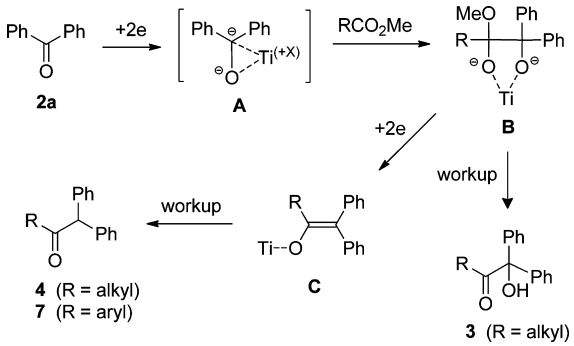
esters with benzophenone (**2a**) is exhibited in Scheme 6. The cyclic voltamograms of **2a** in 0.03 M Bu_4NClO_4/DMF on a

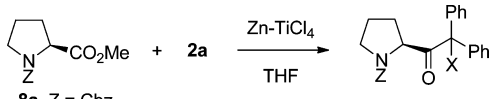
Scheme 6. Presumed Reaction Mechanism of Reductive Coupling of Esters with 2a by Low-Valent Titanium



platinum cathode showed first reduction peaks at −1.90 vs SCE, whereas those of **1a** and **6a** under the same conditions revealed no reduction peak from 0 to −2.5 V vs SCE. These results suggest that this reductive coupling is initiated by the reduction of **2a**. Initially, **2a** is reduced by two-electron transfer from low-valent titanium to give titanate **A**. The nucleophilic addition of **A** to an ester produces adduct **B**. When the ester is aliphatic (R = alkyl), the workup of **B** with water at 25 °C gives **3** since the adduct **B** is stable at this temperature. On the other hand, further two-electron reduction of **B** by low-valent titanium proceeds at 50 °C to afford enolate **C**, which is hydrolyzed to diphenylmethyl ketone **4**. When the ester is aromatic (R = aryl), adduct **B** is immediately reduced to **C** even at 25 °C since enolate **C** is additionally stabilized by the aryl group. Hence, diphenylmethyl aryl ketones **7** were the only products and diphenyl(hydroxy)methyl aryl ketones corresponding to **3** could not be detected as described above.

4. Reductive Coupling of *N*-Alkoxycarbonyl α-Amino Acid Methyl Esters with Benzophenone by Zn−$TiCl_4$. The reduction with benzophenone (**2a**) was attempted by employing *N*-Cbz- and *N*-Moc-(*S*)-proline methyl esters (**8a** and **8b**) as aliphatic esters to prepare optically active diphenylmethyl ketones, and the results are summarized in Table 7, in which the yields based on more valuable esters **8a**,**b** were optimized. The reduction was carried out with the molar ratio of **8a**/**2a**/$TiCl_4$ as 1/1/1 at 25 °C for 2 h according as run 1 in Table 1. The two- and four-electron reduced products **9a** (10%) and **10a** (14%) were obtained in poor yields, and a significant amount (72%) of **8a** was recovered since **8a** was a sterically hindered ester (run 1). In addition, this result shows that it is difficult to control the further reduction of **9a** to **10a** at 25 °C. Therefore, the reaction was performed with a molar ratio of **8a**/**2a**/$TiCl_4$ of 1/2/3 under the same conditions as run 3 in Table 5 to obtain **10a** primarily (run 2). Since an unignorable amount of **8a** (38%) and a small amount of **9a** (8%) still remained, the molar ratio of **2a** and $TiCl_4$ against **8a** was increased twice (**8a**/**2a**/$TiCl_4$ as 1/4/6) (run 3). Moreover, the reaction was carried out at 25 °C for 2 h and subsequently at 50 °C for 1 h, and **10a** was obtained in 72% yield (run 4). Similarly, the reaction of **8b** with **2a** under the same conditions as run 4 afforded **10b** in 69% yield (run 6). Although the optical purities of **10a** and **10b** obtained in runs 4 and 6 could not be determined, they were both estimated to be

Table 7. Reductive Coupling of 8a,b with 2a by Zn−$TiCl_4$



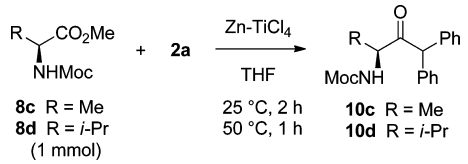
							% yield[b]		
run	**8**	**2a** (mmol)	$TiCl_4$[a] (mmol)	temp (°C)	time (h)		**9**	**10**	**8**
1	**8a**	1	1	25	2	**a**	10	14	72
2	**8a**	2	3	25	2	**a**	8	45	38
3	**8a**	4	6	25	2	**a**	13	58	10
4	**8a**	4	6	25	2	**a**		72	
				50	1				
5	**8b**	4	6	25	6	**b**	8	57	12
6	**8b**	4	6	25	2	**b**		69	
				50	1				

[a]Zn/$TiCl_4$ = 2/1. [b]Isolated yields based on **8**.

>99% ee from the results of transformation to oxazolidin-2-ones as described below.

Next, the reductive coupling of *N*-Moc-(*S*)-alanine methyl ester (**8c**) with **2a** under the same conditions as run 4 in Table 7 produced optically active diphenylmethyl ketone **10c** in 55% yield with more than 20% recovery of **8c** (Table 8, run 1).

Table 8. Reductive Coupling of 8c,d with 2a by Zn−$TiCl_4$



run	**8**	**2a** (mmol)	$TiCl_4$[a] (mmol)	% yield[b] of **10**	ee[c] of **10** (%)
1	**8c**	4	6	**10c**, 55	>99
2	**8c**	5	7.5	**10c**, 68	>99
3	**8d**	5	7.5	**10d**, 62	>99

[a]Zn/$TiCl_4$ = 2/1. [b]Isolated yields based on **8**. [c]Determined by ^{1}H NMR spectra with Eu(hfc)$_3$.

Therefore, the molar ratio of **2a** and $TiCl_4$ against **8c** was increased by 1.25 times (**8c**/**2a**/$TiCl_4$ = 1/5/7.5). The yield of **10c** increased to 68%, and the recovery of **8c** decreased to less than 10% (run 2). The reduction of *N*-Moc-(*S*)-valine methyl ester (**8d**) with **2a** under the same conditions also gave the corresponding diphenylmethyl ketone **10d** in 62% yield (run 3). The optical purities of **10c** and **10d** could be both determined to be >99% ee by ^{1}H NMR analyses with Eu(hfc)$_3$.

The obtained optically active diphenylmethyl ketones **10a** and **10b** were stereospecifically reduced with L-Selectride at −50 °C, and then the resultant β-amino alcohols were cyclized by refluxing in K_2CO_3/MeOH to give oxazolidin-2-one **11a** in 63% and 67% yields, respectively (Scheme 7). The optical purities of these **11a** obtained from **10a** and **10b** were both confirmed to be >99% ee by ^{1}H NMR analyses with Eu(hfc)$_3$. These results suggested that the optical purities of **10a** and **10b** were also >99% ee. Although the single crystal of **11a** could not be obtained, the stereoconfiguration of **11a** was fortunately confirmed to be cis by X-ray crystallography of ***rac*-11a** prepared from ***rac*-8c** by the same procedure. The same sequential transformation of **10c** gave the corresponding

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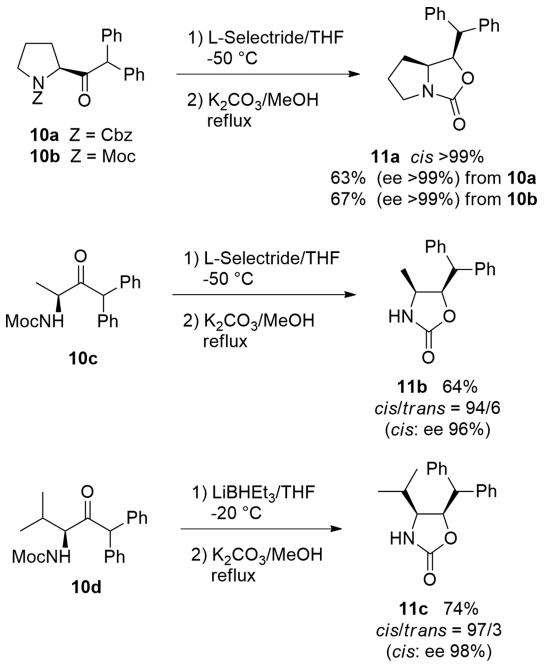
Scheme 7. Transformation of 10a–d to 11a–c

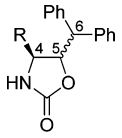


oxazolidin-2-one **11b** in 64% yield with high stereoselectivity (94/6). Although the major isomer of **11b** could be isolated by recrystallization, its single crystal could not be acquired. Similarly to **11a**, the cis configuration of the major isomer of **11b** was confirmed by X-ray crystallography of that of ***rac*-11b**. The optical purity of ***cis*-11b** was determined to be 96% ee by ^{1}H NMR spectra with Eu(hfc)$_3$. However, the reduction of **10d** with L-Selectride did not proceed at all, probably due to the high bulkiness of **10d**. Alternatively, the reduction of **10d** with LiBHEt$_3$ at −20 °C and following cyclization gave **11c** in 74% yield with a 97/3 of cis/trans ratio. The major isomer of **11c** was assigned to be cis by the correlation of ^{1}H NMR spectra between **11b** and **11c** as shown in Table 9. The optical purity of ***cis*-11c** was determined to be 98% ee by ^{1}H NMR spectra with Eu(hfc)$_3$.

CONCLUSION

The reductive coupling of aliphatic esters **1a–f** with benzophenones **2a–d** by Zn−TiCl$_4$ gave two-electron reduced products, diaryl(hydroxy)methyl ketones **3a–f**, and four-electron reduced products, diarylmethyl ketones **4a–f**. The both of two- and four-electron reduced products could be obtained selectively by controlling the amounts of Zn−TiCl$_4$ and reaction temperature. In the reaction of aliphatic lactones **1g–i** with benzophenone **2a**, two-electron reduced products **3g,h** and four-electron reduced products **5** and **4h,i** were also obtained selectively by controlling the reaction conditions. On the other hand, the reductive coupling of aromatic esters **6a–h** with **2a–d** afforded four-electron reduced products, diarylmethyl ketones **7a–k**, as the sole products irrespective of the reaction conditions. In addition, optically active diphenylmethyl ketones **10a–d** were prepared by the reductive coupling of *N*-(alkoxycarbonyl)-*α*-amino acid methyl esters **8a–d** with **2a**. From **8a–d**, optically active 4,5-*cis*-disubstituted oxazolidin-2-ones **11a–c** were synthesized by selective reduction and following cyclization.

Table 9. ^{1}N NMR Chemical Shifts (*δ*, ppm) and Coupling Constants (Hz) of 11b,c



	chemical shift (multitude)				
11	4-H	5-H	6-H	$J_{4,5}$	$J_{5,6}$
***cis*-11b**	3.84 (m)	5.35 (dd)	4.21 (d)	6.8	11.5
***trans*-11b**	3.66 (m)	4.84 (dd)	4.11 (d)	6.0	7.3
***cis*-11c**	3.62 (dd)	5.38 (dd)	4.36 (d)	6.8	11.5
***trans*-11c**	3.35 (t)	4.97 (dd)	4.06 (d)	4.1	8.3

EXPERIMENTAL SECTION

General Methods. Column chromatography was performed on silica gel 60. THF was distilled from sodium benzophenone ketyl radical.

Typical Procedure of Reductive Coupling by Ti-ZnCl$_4$. To a solution of **1a** (0.20 mL, 2 mmol), **2a** (182 mg, 1 mmol), and zinc powder (0.13 g, 2 mmol) in THF (5 mL) was added TiCl$_4$ (0.11 mL, 1 mmol) dropwise at 0 °C, and then the dark blue suspension was stirred for 2 h at 25 °C. To the mixture was added 1 M HCl (20 mL), and the mixture was stirred for 10 min at 25 °C. The mixture was extracted with ethyl acetate three times. The organic layer was washed with aqueous NaCl and dried over MgSO$_4$. After the solvent was removed, the residue was purified by column chromatography on silica gel to give **3a** in 72% yield (173 mg) with small amounts of **4a** (11 mg, 5%). Compounds **3a**,[7] **3b**,[6,7] **3c**,[3,7] **3e**,[6,7] **3f**,[6] **4a**,[9f,10a] **4b**,[13,14] **4c**,[8a,15] **4e**,[9h,16] **4f**,[8b,17,18] **5**,[19] **7a**,[8a,b,9a,d,15,17] **7b**,[8a,b,9e,17] **7d**,[9d] **7f**,[9d] **7i**,[9a,10b,20] and **7j**[9a,b,j,10b,20] were known.

*1-Hydroxy-4-methyl-1,1-diphenylpentan-2-one (**3d**):* colorless paste (177 mg, 66%); R_f 0.35 (hexanes−ethyl acetate, 10:1); IR (neat) 3447, 1705, 1599, 1491, 768, 745, 733, 696, 669 cm^{-1}; ^{1}H NMR (CDCl$_3$) *δ* 0.77 (d, 6H, *J* = 6.7 Hz), 1.95–2.03 (m, 1H), 2.49 (d, 2H, *J* = 6.6 Hz), 4.89 (s, 1H), 7.32–7.39 (m, 10H); ^{13}C NMR (CDCl$_3$) *δ* 22.2 (q), 24.6 (d), 46.6 (t), 85.5 (s), 128.0 (d), 128.1 (d), 128.2 (d), 141.3 (s), 210.2 (s); HRMS (ESI, ion trap) calcd for $C_{18}H_{21}O_2$ (M + H)$^+$ 269.1542, found 269.1541.

*1,5-Dihydroxy-1,1-diphenylpentan-2-one (**3g**):* colorless paste (143 mg, 53%); R_f 0.5 (hexanes−ethyl acetate, 1:1); IR (ATR) 3401, 1707, 1599, 1491, 853, 770, 735, 696, 667 cm^{-1}; ^{1}H NMR (CDCl$_3$) *δ* 1.63–1.69 (m, 2H), 2.45 (brs, 1H), 2.63 (t, 2H, *J* = 7.0 Hz), 3.39 (t, 2H, *J* = 6.3 Hz), 5.04 (s, 1H), 7.26–7.34 (m, 10H); ^{13}C NMR (CDCl$_3$) *δ* 27.0 (t), 34.8 (t), 61.3 (t), 85.5 (s), 127.7 (d), 127.9 (d), 128.2 (d), 141.4 (s), 211.5 (s); HRMS (ESI, ion trap) calcd for $C_{17}H_{19}O_3$ (M + H)$^+$ 271.1334, found 271.1333.

*1,6-Dihydroxy-1,1-diphenylhexan-2-one (**3h**):* colorless paste (162 mg, 57%); R_f 0.45 (hexanes−ethyl acetate, 1:1); IR (ATR) 3379, 1707, 1599, 1491, 914, 764, 746, 733, 696, 667 cm^{-1}; ^{1}H NMR (CDCl$_3$) *δ* 1.35–1.42 (m, 2H), 1.50–1.58 (m, 2H), 1.94 (brs, 1H), 2.60 (t, 2H, *J* = 7.5 Hz), 3.42 (t, 2H, *J* = 6.3 Hz), 4.93 (brs, 1H), 7.31–7.38 (m, 10H); ^{13}C NMR (CDCl$_3$) *δ* 20.2 (t), 31.5 (t), 37.7 (t), 61.8 (t), 85.4 (s), 127.8 (d), 127.9 (d), 128.2 (d), 141.4 (s), 211.2 (s); HRMS (ESI, ion trap) calcd for $C_{18}H_{21}O_3$ (M + H)$^+$ 285.1491, found 285.1490.

*1,7-Dihydroxy-1,1-diphenylheptan-2-one (**3i**):* colorless paste (226 mg, 76%); R_f 0.45 (hexanes−ethyl acetate, 5:1); IR (ATR) 3420, 1709, 1600, 1493, 910, 762, 733, 698, 665 cm^{-1}; ^{1}H NMR (CDCl$_3$) *δ* 1.14–1.22 (m, 2H), 1.35–1.50 (m, 4H), 1.93 (brs, 1H), 2.57 (t, 2H, *J* = 7.5 Hz), 3.47 (t, 2H, *J* = 6.7 Hz), 4.97 (s, 1H), 7.30–7.36 (m, 5H); ^{13}C NMR (CDCl$_3$) *δ* 23.8 (t), 24.9 (t), 31.9 (t), 38.1 (t), 62.0 (t), 54.4 (s), 127.8 (d), 127.9 (d), 128.2 (d), 141.4 (s), 211.2 (s); HRMS (ESI, ion trap) calcd for $C_{19}H_{23}O_3$ (M + H)$^+$ 299.1647, found 299.1645.

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1,1-Bis(4-fluorophenyl)-1-hydroxybutan-2-one (**3j**): colorless paste (105 mg, 38%); R_f 0.3 (hexanes−ethyl acetate, 10:1); IR (ATR) 3429, 1709, 1601, 1504, 982, 831, 812, 772, 727 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.04 (t, 3H, J = 7.3 Hz), 2.55 (q, 2H, J = 7.3 Hz), 4.82 (s, 1H), 7.03−7.09 (m, 4H), 7.28−7.33 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 8.2 (q), 31.7 (t), 84.5 (s), 115.3 (d, J_{CCF} = 20.7 Hz), 129.7 (d, J_{CCCF} = 8.4 Hz), 137.4 (s, J_{CCCCF} = 2.4 Hz), 162.4 (s, J_{CF} = 247.3 Hz), 211.5 (s); HRMS (ESI, ion trap) calcd for $C_{16}H_{15}F_2O_2$ (M + H)$^+$ 277.1040, found 277.1039.

1-Hydroxy-1,1-bis(4-methoxyphenyl)butan-2-one (**3k**): colorless paste (171 mg, 57%); R_f 0.25 (hexanes−ethyl acetate, 5:1); IR (ATR) 3456, 1703, 1655, 1605, 1578, 1506, 982, 964, 827, 800, 772, 733 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.01 (t, 3H, J = 7.5 Hz), 2.54 (q, 2H, J = 7.5 Hz), 3.81 (s, 6H), 4.82 (s, 1H), 6.86−6.90 (m, 4H), 7.24−7.27 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 8.3 (q), 31.4 (t), 55.1 (q), 84.6 (s), 113.5 (d), 129.1 (d), 133.8 (s), 159.1 (s), 212.2 (s); HRMS (ESI, ion trap) calcd for $C_{18}H_{21}O_4$ (M + H)$^+$ 301.1440, found 301.1438.

1-(5-Hydroxy-10,11-dihydro-5H-dibenzo[a,d][7]annulen-5-yl)-propan-1-one (**3l**): white solid (77 mg, 29%); R_f 0.2 (hexanes−ethyl acetate,10:1); mp 109−111 °C; IR (ATR) 3433, 3389, 1703, 1483, 972, 951, 926, 903, 880, 854, 812, 785, 752, 718, 696, 652 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.89 (t, 3H, J = 7.3 Hz), 2.29 (q, 2H, J = 7.3 Hz), 3.07−3.20 (m, 4H), 4.92 (s, 1H), 7.11−7.23 (m, 6H), 7.36−7.40 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 8.3 (q), 30.4 (t), 35.4 (t), 84.5 (s), 126.5 (d), 127.9 (d), 128.6 (d), 130.3 (d), 138.4 (s), 140.8 (s), 210.3 (s); HRMS (ESI, ion trap) calcd for $C_{18}H_{19}O_2$ (M + H)$^+$ 267.1385, found 267.1385.

4-Methyl-1,1-diphenylpentan-2-one (**4d**): colorless paste (176 mg, 70%); R_f 0.5 (hexanes−ethyl acetate, 10:1); IR (neat) 1715, 1597, 1495, 770, 743, 696 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.88 (d, 6H, J = 6.4 Hz), 2.14−2.23 (m, 1H), 2.42 (d, 2H, J = 6.9 Hz), 5.09 (s, 1H), 7.20−7.27 (m, 6H), 7.29−7.34 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 22.3 (q), 24.3 (d), 51.6 (t), 64.3 (d), 127.0 (d), 128.5 (d), 128.8 (d), 138.3 (s), 207.8 (s); HRMS (ESI, ion trap) calcd for $C_{18}H_{21}O$ (M + H)$^+$ 253.1592, found 253.1591.

6-Hydroxy-1,1-diphenylhexan-2-one (**4h**): colorless paste (139 mg, 52%); R_f 0.5 (hexanes−ethyl acetate, 1:1); IR (ATR) 3375, 1711, 1597, 1584, 1493, 986, 932, 745, 696 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.46−1.53 (m, 2H), 1.63−1.71 (m, 2H), 2.61 (t, 2H, J = 7.2 Hz), 3.56 (t, 2H, J = 6.3 Hz), 5.13 (s, 1H), 7.21−7.37 (m, 10 H); ^{13}C NMR ($CDCl_3$) δ 19.8 (t), 31.7 (t), 42.3 (t), 62.0 (t), 64.0 (d), 127.1 (d), 128.6 (d), 128.8 (d), 138.2 (s), 208.8 (s); HRMS (ESI, ion trap) calcd for $C_{18}H_{21}O_2$ (M + H)$^+$ 269.1542, found 269.1541.

7-Hydroxy-1,1-diphenylheptan-2-one (**4i**): colorless paste (164 mg, 58%); R_f 0.55 (hexanes−ethyl acetate, 1:1); IR (ATR) 3375, 1713, 1597, 1584, 1495, 962, 743, 696 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.26−1.34 (m, 2H), 1.47−1.54 (m, 2H), 1.57−1.65 (m, 2H), 2.57 (t, 2H, J = 7.5 Hz), 3.54−3.65 (m, 2H), 5.12 (s, 1H), 7.20−7.37 (m, 10 H); ^{13}C NMR ($CDCl_3$) δ 23.3 (t), 24.9 (t), 32.0 (t), 42.5 (t), 62.0 (t), 63.8 (d), 126.9 (d), 128.4 (d), 128.7 (d), 138.2 (s), 208.7 (s); HRMS (ESI, ion trap) calcd for $C_{19}H_{23}O_2$ (M + H)$^+$ 283.1698, found 283.1696.

1,1-Bis(4-fluorophenyl)butan-2-one (**4j**): colorless paste (117 mg, 45%); R_f 0.3 (hexanes−ethyl acetate, 10:1); IR (ATR) 1717, 1601, 1504, 864, 820, 768, 702 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.06 (t, 3H, J = 7.2 Hz), 2.57 (q, 2H, J = 7.2 Hz), 5.10 (s, 1H), 6.98−7.03 (m, 4H), 7.15−7.20 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 7.9 (q), 36.0 (t), 61.9 (d), 115.5 (d, J_{CCF} = 21.6 Hz), 130.3 (d, J_{CCCF} = 8.4 Hz), 134.2 (s, J_{CCCCF} = 3.6 Hz), 161.9 (s, J_{CF} = 245.9 Hz), 208.9 (s); HRMS (ESI, ion trap) calcd for $C_{16}H_{15}F_2O$ (M + H)$^+$ 261.1091, found 261.1090.

1,1-Bis(4-methoxyphenyl)butan-2-one (**4k**): colorless paste (148 mg, 52%); R_f 0.35 (hexanes−ethyl acetate, 5:1); IR (ATR) 1715, 1607, 1582, 1506, 814, 772 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.05 (t, 3H, J = 7.3 Hz), 2.55 (q, 2H, J = 7.3 Hz), 3.78 (s, 6H), 5.03 (s, 1H), 6.83−6.87 (m, 4H), 7.11−7.15 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 8.0 (q), 35.7 (t), 55.0 (q), 62.0 (d), 113.8 (d), 129.7 (d), 130.9 (s), 158.4 (s), 209.6 (s); HRMS (ESI, ion trap) calcd for $C_{18}H_{21}O_3$ (M + H)$^+$ 285.1491, found 285.1490

1-(10,11-Dihydro-5H-dibenzo[a,d][7]annulen-5-yl)propan-1-one (**4l**): colorless paste (158 mg, 63%); R_f 0.3 (hexanes−ethyl acetate,10:1); IR (ATR) 1717, 1703, 993, 908, 851, 839, 768, 754, 741, 710, 702, 675 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.98 (t, 3H, J = 7.2 Hz), 2.36 (q, 2H, J = 7.2 Hz), 2.78−2.86 (m, 2H), 3.12−3.21 (m, 2H), 4.60 (s, 1H), 7.11−7.24 (m, 8H); ^{13}C NMR ($CDCl_3$) δ 8.0 (q), 32.1 (t), 33.8 (t), 67.6 (d), 126.2 (d), 127.6 (d), 130.3 (d), 131.4 (d), 136.5 (s), 139.3 (s), 209.9 (s); HRMS (ESI, ion trap) calcd for $C_{18}H_{19}O$ (M + H)$^+$ 251.1436, found 251.1436.

1-(Benzo[d][1,3]dioxol-5-yl)-2,2-diphenylethanone (**7c**): white solid (243 mg, 77%); R_f 0.4 (hexanes−ethyl acetate, 5:1); mp 141−143 °C; IR (neat) 1665, 1622, 1601, 1582, 1504, 1487, 997, 924, 903, 887, 807, 800, 743, 729, 723, 694, 669 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.94 (s, 1H), 6.01 (s, 2H), 6.79 (d, 1H, J = 8.2 Hz), 7.22−7.27 (m, 6H), 7.30−7.34 (m, 4H), 7.48 (d, 1H, J = 1.7 Hz), 7.62 (dd, 1H, J = 1.7, 8.2 Hz); ^{13}C NMR ($CDCl_3$) δ 59.1 (d), 101.7 (t), 107.8 (d), 108.6 (d), 125.2 (d), 127.0 (d), 128.6 (d), 129.0 (d), 131.4 (s), 139.2 (s), 148.0 (s), 151.6 (s), 196.1 (s). Anal. Calcd for $C_{21}H_{16}O_3$: C, 79.73; H, 5.10. Found: C, 79.69; H, 5.12.

(E)-1,1,4-Triphenylbut-3-en-2-one (**7e**): colorless paste (134 mg, 45%); R_f 0.55 (hexanes−ethyl acetate, 5:1); IR (neat) 1653, 1624, 1597, 1576, 1493, 968, 908, 772, 752, 731, 694 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.38 (s, 1H), 6.83 (d, 1H, J = 16.0 Hz), 7.23−7.40 (m, 13H), 7.46−7.51 (m, 2H), 7.69 (d, 1H, J = 16.0 Hz); ^{13}C NMR ($CDCl_3$) δ 63.2 (d), 125.1 (d), 127.1 (d), 128.4 (d), 128.6 (d), 128.8 (d), 129.2 (d), 130.4 (d), 134.3 (s), 138.4 (s), 143.2 (d), 197.2 (s); HRMS (ESI, ion trap) calcd for $C_{22}H_{19}O$ (M + H)$^+$ 299.1436, found 299.1435.

1-(1H-Indol-3-yl)-2,2-diphenylethanone (**7g**): white solid (221 mg, 71%); R_f 0.5 (hexanes−ethyl acetate, 2:1); mp 195−197 °C; IR (neat) 1607, 1580, 1520, 1495, 955, 804, 772, 752, 735, 721, 694 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.82 (s, 1H), 7.20−7.36 (m, 12H), 7.75−7.77 (m, 1H), 8.45−8.48 (m, 1H), 8.70 (brs, 1H); ^{13}C NMR ($CDCl_3$, DMSO-*d6*) δ 60.3 (d), 111.6 (d), 116.8 (s), 122.0 (d), 122.1 (d), 123.1 (d), 125.9 (s), 126.5 (d), 128.2 (d), 128.8 (d), 132.8 (d), 136.5(s), 140.0 (s). Anal. Calcd for $C_{22}H_{17}NO$: C, 84.86; H, 5.50; N, 4.50. Found: C, 84.85; H, 5.53; N, 4.40.

Methyl 3-(2,2-diphenylacetyl)-1H-indole-1-carboxylate (**7h**): white solid (296 mg, 80%); R_f 0.4 (hexanes−ethyl acetate, 5:1); mp 157−158 °C; IR (ATR) 1757, 1674, 1604, 1597, 1545, 1497, 1476, 957, 826, 799, 764, 748, 731, 716, 696, 681 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.08 (s, 3H), 5.84 (s, 1H), 7.22−7.29 (m, 2H), 7.30−7.41 (m, 10H), 8.09−8.14 (m, 1H), 8.26 (brs, 1H), 8.44−8.47 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 54.5 (q), 60.7 (d), 114.7 (d), 120.5 (s), 122.8 (d), 124.6 (d), 125.8 (d), 127.0 (d), 127.6 (s), 128.6 (d), 128.9 (d), 132.0 (d), 135.3 (s), 139.1 (s), 150.7 (s), 194.2 (s). Anal. Calcd for $C_{24}H_{19}NO_3$: C, 78.03; H, 5.18; N, 3.79. Found: C, 77.96; H, 5.20; N, 3.73.

(10,11-Dihydro-5H-dibenzo[a,d][7]annulen-5-yl)(phenyl)-methanone (**7k**): pale yellow solid (253 mg, 85%); R_f 0.55 (hexanes−ethyl acetate, 5:1); mp 129−131 °C; IR (neat) 1682, 1595, 1578, 1489, 993, 858, 839, 770, 762, 745, 718, 691, 679 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.75−2.84 (m, 2H), 3.32−3.41 (m, 2H), 5.52 (s, 1H), 7.07−7.12 (m, 2H), 7.13−7.18 (m, 4H), 7.29−7.36 (m, 4H), 7.41−7.45 (m, 1H), 7.90−7.94 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 31.6 (t), 63.7 (d), 126.2 (d), 127.4 (d), 128.0 (d), 128.7 (d), 130.8 (d), 132.2 (d), 136.6 (s), 139.8 (s), 198.9 (s); HRMS (ESI, ion trap) calcd for $C_{22}H_{19}O$ (M + H)$^+$ 299.1436, found 299.1435.

(S)-Benzyl 2-(2-hydroxy-2,2-diphenylacetyl)pyrrolidine-1-carboxylate (**9a**): white solid (42 mg, 10%); R_f 0.25 (hexanes−ethyl acetate, 5:1); mp 149−151 °C; $[\alpha]^{21}_D$ −20.1 (c = 1.21, $CHCl_3$); IR (ATR) 3406, 3281, 1730, 1665, 1597, 1497, 1468, 982, 955, 918, 908, 851, 768, 750, 698, 662 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.53−1.62 (m, 1H), 1.65−1.77 (m, 2H), 1.88−1.98 (m, 1H), 3.46−3.55 (m, 2H), 5.05−5.12 (m, 2H), 5.19 (d, 1H, J = 12.6 Hz), 6.10 (s, 1H), 7.14−7.42 (m, 13H), 7.53−7.57 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 25.0 (t), 31.5 (t), 47.1 (t), 58.6 (d), 67.7 (t), 85.4 (s), 127.3 (d), 127.6 (d), 127.90 (d), 127.94 (d), 127.98 (d), 128.01 (d), 128.1 (d), 128.3 (d), 128.5 (d), 136.2 (s), 138.7 (s), 143.4 (s), 155.7 (s), 210.8 (s); HRMS (ESI, ion trap) calcd for $C_{26}H_{26}NO_4$ (M + H)$^+$ 416.1862, found 416.1860.

(S)-Methyl 2-(2-hydroxy-2,2-diphenylacetyl)pyrrolidine-1-carboxylate (**9b**): white solid (41 mg, 12%); R_f 0.45 (hexanes−ethyl acetate, 2:1); mp 182 °C; $[\alpha]^{21}_D$ −172 (c = 1.03, $CHCl_3$); IR (ATR) 3302, 1724, 1665, 1495, 986, 961, 930, 906, 826, 768, 746, 712, 696, 665

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J. Org. Chem. 2015, 80, 3496−3503

cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.51−1.97 (m, 4H), 3.41−3.59 (m, 2H), 3.72 (s, 3H), 5.06 (t, 1H, J = 6.9 Hz), 6.06 (s, 1H), 7.23−7.43 (m, 8H), 7.53−7.57 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 20.5 (t), 31.5 (t), 47.0 (t), 53.1 (q), 58.7 (d), 85.4 (s), 127.3 (d), 127.5 (d), 127.6 (d), 127.9 (s), 128.0 (s), 128.2 (d), 138.8 (s), 143.3 (s), 156.3 (s), 210.8 (s). Anal. Calcd for $C_{20}H_{21}NO_4$: C, 70.78; H, 6.24; N, 4.13. Found: C, 70.74; H, 6.23; N, 4.04.

*(S)-Benzyl 2-(2,2-diphenylacetyl)pyrrolidine-1-carboxylate (**10a**:).* white solid (288 mg, 72%); R_f 0.25 (hexanes-ethyl acetate, 5:1); mp 122−123 °C; $[\alpha]^{25}_D$ −66.1 (c = 1.05, $CHCl_3$); IR (ATR) 1724, 1699, 1495, 957, 920, 768, 748, 735, 714, 696 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.64−2.12 (m, 4H), 3.29−3.59 (m, 2H), 4.54 (dd, 0.5H, J = 4.4, 8.9 Hz), 4.58 (dd, 0.5H, J = 6.0, 7.0 Hz), 4.81 (d, 0.5H, 12.2 Hz), 5.08 (d, 0.5H, J = 12.2 Hz), 5.13−5.19 (m, 1H), 5.21 (s, 0.5H), 5.50 (s, 0.5H), 7.13−7.40 (m, 15H); ^{13}C NMR ($CDCl_3$) δ 23.2 (t), 24.2 (t), 29.7 (t), 30.2 (t), 44.6 (t), 47.2 (t), 60.2 (d), 61.5 (d), 65.2 (d), 66.90 (t), 66.94 (t), 127.0 (d), 127.12 (d), 127.13 (d), 127.2 (d), 127.7 (d), 127.87 (d), 127.92 (d), 128.1 (d), 128.32 (d), 128.34 (d), 128.4 (d), 128.47 (d), 128.49 (d), 128.6 (d), 128.7 (d), 128.8 (d), 128.9 (d), 129.4 (d), 136.3 (s), 136.6 (s), 137.4 (s), 137.6 (s), 137.8 (s), 138.0 (s), 154.2 (s), 155.0 (s), 206.8 (s), 207.9 (s). Anal. Calcd for $C_{26}H_{25}NO_3$: C, 78.17; H, 6.31; N, 3.51. Found: C, 78.14; H, 6.31; N, 3.47.

*(S)-Methyl 2-(2,2-diphenylacetyl)pyrrolidine-1-carboxylate (**10b**):* white solid (223 mg, 69%); R_f 0.4 (hexanes−ethyl acetate, 2:1); mp 103−104 °C; $[\alpha]^{21}_D$ −55.4 (c = 1.20, $CHCl_3$); IR (ATR) 1707, 1491, 962, 953, 768, 754, 735, 716, 702, 692, 669 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.67−1.94 (m, 3.5H), 2.08−2.17 (m, 0.5H), 3.28−3.34 (m, 0.5H), 3.37−3.44 (m, 0.5H), 3.44 (s, 1.5H), 3.48−3.59 (m, 1H), 3.72 (s, 1.5H), 4.48 (dd, 0.5H, J = 4.8, 8.8 Hz), 4.58 (t, 0.5H, J = 6.7 Hz), 5.29 (s, 0.5H), 5.49 (s, 0.5H), 7.21−7.36 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 23.3 (t), 24.4 (t), 29.8 (t), 30.2 (t), 46.6 (t), 47.2 (t), 52.1 (q), 52.6 (q), 60.0 (d), 61.7 (d), 65.1 (d), 65.4 (d), 127.0 (d), 127.2 (d), 127.26 (d), 127.29 (d), 128.4 (d), 128.5 (d), 128.57 (d), 128.61 (d), 128.8 (d), 128.9 (d), 129.0 (d), 129.4 (d), 137.5 (s), 137.6 (s), 137.9 (s), 138.0 (s), 154.8 (s), 155.7 (s), 207.1 (s), 207.9 (s). Anal. Calcd for $C_{20}H_{21}NO_3$: C, 74.28; H, 6.55; N, 4.33. Found: C, 74.22; H, 6.58; N, 4.27.

*(S)-Methyl (3-oxo-4,4-diphenylbutan-2-yl)carbamate (**10c**):* colorless paste (202 mg, 68%); R_f 0.45 (hexanes−ethyl acetate, 2:1); $[\alpha]^{22}_D$ 32.6 (c = 2.06, $CHCl_3$); >99% ee; IR (ATR) 3325, 1701, 1599, 1508, 1495, 941, 920, 849, 773, 737, 696, 669 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.36 (d, 3H, J = 6.9 Hz), 3.66 (s, 3H), 4.52−4.60 (m, 1H), 5.34 (s, 1H), 5.41 (brs, 1H), 7.21−7.36 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 17.8 (q), 52.0 (q), 55.4 (d), 60.3 (d), 127.2 (d), 127.3 (d), 128.5 (d), 128.69 (d), 128.71 (d), 137.5 (s), 137.6 (s), 156.1 (s), 207.0 (s); HRMS (ESI, ion trap) calcd for $C_{18}H_{20}NO_3$ (M + H)$^+$ 298.1443, found 298.1442.

*(S)-Methyl (4-methyl-2-oxo-1,1-diphenylpentan-3-yl)carbamate (**10d**):* white solid (202 mg, 62%); R_f 0.3 (hexanes−ethyl acetate, 5:1); mp 132−133 °C; $[\alpha]^{23}_D$ 75.8 (c = 1.04, $CHCl_3$); >99% ee; IR (ATR) 3250, 1724, 1701, 1672, 1599, 1497, 1468, 959, 943, 922, 833, 789, 781, 750, 735, 721, 696 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.69 (d, 3H, J = 6.9 Hz), 0.98 (d, 3H, J = 6.9 Hz), 2.19−2.36 (m, 1H), 3.65 (s, 3H), 4.54 (d, 1H, J = 3.9, 9.1 Hz), 5.25 (d, 1H, J = 9.1 Hz), 5.31 (brs, 1H), 7.22−7.36 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 16.3 (q), 19.9 (q), 29.6 (d), 52.1 (q), 61.0 (d), 64.6 (d), 127.2 (d), 127.3 (d), 128.4 (d), 128.6 (d), 128.7 (d), 137.5 (s), 137.6 (s), 156.8 (s), 206.6 (s). Anal. Calcd for $C_{20}H_{23}NO_3$: C, 73.82; H, 7.12; N, 4.30. Found: C, 73.80; H, 7.13; N, 4.23.

Transformarion of 10a to 11a. To a solution of **10a** (100 mg, 0.25 mmol) in THF (5 mL) was added 1 M L-Selectride in THF (0.5 mL, 0.5 mmol) at −50 °C. After being stirred at this temperature for 6 h, the mixture was diluted with 0.5 M HCl (10 mL) and extracted with ethyl acetate three times. The organic layer was washed with aqueous NaCl and dried over $MgSO_4$. After the solvent was removed, the residue was refluxed in MeOH (5 mL) containing K_2CO_3 (35 mg, 0.25 mmol) for 2 h. After the solvent was removed in vacuo, the residue was purified by column chromatography on silica gel to give **11a** in 63% yield (46 mg).

*(1R,7aS)-1-Benzhydryltetrahydropyrrolo[1,2-c]oxazol-3(1H)-one (**11a**):* white solid (136 mg, 67%); R_f 0.4 (hexanes−ethyl acetate, 2:1); mp 176−178 °C; $[\alpha]^{21}_D$ 38.3 (c = 1.01, $CHCl_3$); >99% ee; IR (ATR) 1734, 1599, 1497, 1476, 976, 772, 756, 743, 710, 698, 662 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.33−1.39 (m, 1H), 1.51−1.60 (m, 1H), 1.66−1.76 (m, 1H), 1.98−2.06 (m, 1H), 3.10−3.16 (m, 1H), 3.62−3.75 (m, 2H), 4.18 (d, 1H, J = 11.0 Hz), 5.44 (dd, 1H, J = 6.9, 11.0 Hz), 7.17−7.21 (m, 1H), 7.24−7.36 (m, 9H); ^{13}C NMR ($CDCl_3$) δ 24.8 (t), 25.1 (t), 45.6 (t), 52.4 (d), 63.2 (d), 77.7 (d), 126.9 (d), 127.3 (d), 127.9 (d), 128.0 (d), 128.6 (d), 129.0 (d), 139.9 (s), 140.9 (s), 161.6 (s). Anal. Calcd for $C_{19}H_{19}NO_2$: C, 77.79; H, 6.53; N, 4.77. Found: C, 77.81; H, 6.50; N, 4.71.

*(4S,5R)-5-Benzhydryl-4-methyloxazolidin-2-one (**cis-11b**).* Isomeric mixture (*cis*/*trans* = 94/6): white solid (112 mg, 61%); R_f 0.3 (hexanes−ethyl acetate, 2:1); mp 147−148 °C; $[\alpha]^{21}_D$ 89.8 (c = 1.07, $CHCl_3$); 96% ee (*cis*-form); IR (ATR) 3277, 1742, 1497, 988, 968, 949, 773, 754, 743, 727, 702, 694, 669 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.08 (d, 3H, J = 6.4 Hz), 3.82−3.89 (m, 1H), 4.21 (d, 1H, J = 11.5 Hz), 5.11 (brs, 1H), 5.35 (dd, 1H, J = 6.8, 11.5 Hz), 7.16−7.21 (m, 1H), 7.22−7.36 (m, 9H); ^{13}C NMR ($CDCl_3$) δ 15.8 (q), 50.7 (d), 51.1 (d), 81.3 (d), 126.8 (d), 127.2 (d), 127.7 (d), 128.0 (d), 128.5 (d), 129.1 (d), 139.9 (s), 141.0 (s), 159.5 (s). Anal. Calcd for $C_{17}H_{17}NO_2$: C, 76.38; H, 6.41; N, 5.24. Found: C, 76.37; H, 6.44; N, 5.20.

*(4S,5R)-5-Benzhydryl-4-isopropyloxazolidin-2-one (**cis-11c**).* Isomeric mixture (*cis*/*trans* = 97/3): colorless paste (136 mg, 74%); R_f 0.45 (hexanes−ethyl acetate, 1:1); $[\alpha]^{20}_D$ 68.8 (c = 1.28, $CHCl_3$); 98% ee (*cis*-form); IR (ATR) 3265, 1740, 1491, 982, 964, 812, 772, 754, 712, 700, 669 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.75 (d, 3H, J = 6.9 Hz), 1.06 (d, 3H, J = 6.9 Hz), 1.77−1.87 (m, 1H), 3.62 (dd, 1H, J = 2.1, 6.8 Hz), 4.36 (d, 1H, J = 11.5 Hz), 5.38 (dd, 1H, J = 6.8, 11.5 Hz), 6.48 (brs, 1H), 7.15−7.19 (m, 1H), 7.21−7.36 (m, 9H); ^{13}C NMR ($CDCl_3$) δ 16.2 (q), 20.5 (q), 27.4 (d), 50.2 (d), 60.2 (d), 82.0 (d), 126.7 (d), 127.1 (d), 127.5 (d), 128.0 (d), 128.4 (d), 129.0 (d), 140.0 (s), 141.0 (s), 160.6 (s). Anal. Calcd for $C_{19}H_{21}NO_2$: C, 77.26; H, 7.17; N, 4.74. Found: C, 77.20; H, 7.15; N, 4.67.

Crystal data of 7g: $C_{22}H_{17}NO$, FW = 311.37, mp 195−197 °C, triclinic, $P\bar{1}$ (No. 2), colorless block, a = 7.3392(15) Å, b = 10.293(2) Å, c = 12.030(3) Å, α = 101.890(12)°, β = 102.401(12)°, γ = 95.231(10)°, V = 859.7(3) Å^3, T = 298 K, Z = 2, D_{calcd} = 1.203 g/cm^3, μ = 0.73 cm^{-1}, GOF = 1.064.

Crystal data of 9b: $C_{20}H_{21}NO_4$, FW = 339.38, mp 182 °C, orthorhombic, $P2_12_12_1$ (No. 19), colorless block, a = 8.2810(6) Å, b = 14.3537(10) Å, c = 14.8094(12) Å, V = 1760.3(2) Å^3, T = 298 K, Z = 4, D_{calcd} = 1.281 g/cm^3, μ = 0.89 cm^{-1}, GOF = 1.041.

Crystal data of 10d: $C_{20}H_{23}NO_3$, FW = 325.39, mp 131−132 °C, orthorhombic, $P2_12_12_1$ (No. 19), colorless block, a = 8.9117(8) Å, b = 14.0713(11) Å, c = 14.8382(12) Å, V = 1860.7(3) Å^3, T = 298 K, Z = 4, D_{calcd} = 1.162 g/cm^3, μ = 0.78 cm^{-1}, GOF = 0.890.

Crystal data of *rac*-11a: $C_{19}H_{19}NO_2$, FW = 293.35, mp 212−213 °C, monoclinic, Cc (no 9), colorless block, a = 9.402(3) Å, b = 15.737(3) Å, c = 10.672(3) Å, β = 99.933(1), V = 1555.5(7) Å^3, T = 298 K, Z = 4, D_{calcd} = 1.253 g/cm^3, μ = 0.81 cm^{-1}, GOF = 1.076.

Crystal data of *rac-cis*-11b: $C_{17}H_{17}NO_2$, FW = 267.32, mp 177−179 °C, triclinic, $P\bar{1}$ (No. 2), colorless block, a = 10.452(4) Å, b = 10.453(4) Å, c = 17.077(7) Å, α = 104.04(4), β = 90.81(3), γ = 116.56(3), V = 1602.7(11) Å^3, T = 298 K, Z = 4, D_{calcd} = 1.108 g/cm^3, μ = 0.73 cm^{-1}, GOF = 1.049.

■ ASSOCIATED CONTENT

Supporting Information

^{1}H and ^{13}C NMR spectra of products, X-ray crystallographic data (ORTEP) of **7g**, **9b**, **10d**, ***rac*-11a**, and ***rac-cis*-11b**. X-ray data for **7g**, **9b**, **10d**, ***rac*-11a**, and ***rac-cis*-11b** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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