

Efficient Method for the Preparation of Carboxylic Acid Alkyl Esters or Alkyl Phenyl Ethers by a New-Type of Oxidation–Reduction Condensation Using 2,6-Dimethyl-1,4-benzoquinone and Alkoxydiphenylphosphines

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A new-type of oxidation–reduction condensation proceeded smoothly to afford carboxylic acid alkyl esters or alkyl phenyl ethers in good to high yields by combined use of alkoxydiphenylphosphines (**1**) having primary, bulky secondary or tertiary alkoxy groups, a mild quinone-type oxidant such as 2,6-dimethyl-1,4-benzoquinone (DMBQ) and carboxylic acids or phenols. Generally, alkoxydiphenylphosphines were prepared easily from chlorodiphenylphosphine (**2**) and alcohols in the presence of pyridine, and were isolated by distillation. On the other hand, the phosphines **1** were also prepared in situ from *N*,*N*-dimethylaminodiphenylphosphine (**3a**) and primary or secondary alcohols while primary, bulky secondary or tertiary alkoxydiphenylphosphines were alternatively formed in situ by adding **2** to the ^{n}BuLi-treated alcohols in order to perform the above reactions by a one-pot procedure from alcohols and nucleophiles. The reaction of thus formed **1**, DMBQ and carboxylic acids or phenols afforded the corresponding alkylated products, including hindered secondary and tertiary alkylated ones, in good to high yields at room temperature. In the case of using chiral secondary alcohols, the corresponding carboxylic acid alkyl esters were obtained as well in high yields with perfect inversion of stereochemistry by S_N2 replacement.

Preparation of carboxylic acid esters or phenyl ethers are among the best-established, most fundamental, and most important procedures in organic synthesis.[1] Direct formation of carboxylic esters from the corresponding carboxylic acids and alcohols is generally performed by shifting the equilibrium in favor of the desired ester according to one of the following methods: i) to use a large excess amount of carboxylic acids or alcohols or to remove the formed water from the reaction mixture as an azeotrope mixture with a solvent such as benzene or xylene by using catalysts such as sulfuric acid,[1e] sulfonic acid, hydrochloric acids, Nafion-H,[1f] zirconium oxide sulfate ion,[1g] etc; ii) to use dehydrating agents such as 1-methyl-2-halopyridinium salts,[1h] dicyclohexylcarbodiimide,[1i,1j] 2,4,6-trichlorobenzoyl chloride,[1k] and 2-methyl-6-nitrobenzoic anhydride,[1l] etc. Of these esterification methods, preparation of bulky secondary or tertiary alkyl esters is known to be more difficult compared with the preparation of primary ones. For the synthesis of carboxylic esters from the corresponding carboxylic acids and hindered alcohols, most of all the methods have some problems:[1] for example, long reaction time, need of a large excess amount of carboxylic acids or alcohols, severe reaction conditions with strong acids or bases, side reactions, or poor yields of the desired products.

The fundamental concept of oxidation–reduction condensation is to perform dehydration condensation by removing H_2O as 2[H] and [O] using a combination of weak reductants and oxidants. The important point of this concept is that the reaction proceeded under "mild and neutral" conditions without having any assistance from acids or bases. The first examples of this type of condensation were reported from our laboratory concerning acylation reactions by using combinations of diphenylmercury and tributylphosphine (in 1963),[2] *trans*-1,2-dibenzoylethylene and tributylphosphine (in 1964),[3] and 2,2′-dipyridyl disulfide and triphenylphosphine (in 1970).[4] In 1967, preparation of phosphoric esters was also carried out by using triethyl phosphite and diethyl azodicarboxylate (DEAD) in the presence of alcohols.[5] Mitsunobu developed this concept to an efficient alkylation method by using a combination of triphenylphosphine and DEAD, and achieved a condensation reaction between alcohols and various nucleophiles (Mitsunobu reaction), which is now known very widely.[6] Recently, Tsunoda et al. reported an alkylating reaction by using alcohols and cyanomethylenetributylphosphorane or *N*,*N*,*N*′,*N*′-tetramethylazodicarboxamide (TMAD)[7] which works out well likewise.

The search for a convenient and useful new-type of oxidation–reduction condensation has been a matter of our continued interest ever since the reaction was first reported. In most cases of the current oxidation–reduction condensation, triphenylphosphine is employed as a reductant. Acylations proceeded smoothly to afford the desired products in high yields while the yields of alkylations using bulky secondary or tertiary alcohols stayed generally low, which was probably because of the incomplete formation of the key intermediates, phosphonium alkoxides. Since the alkoxy part of alkoxydiphenylphosphine had been introduced in advance, it was thought to have be-

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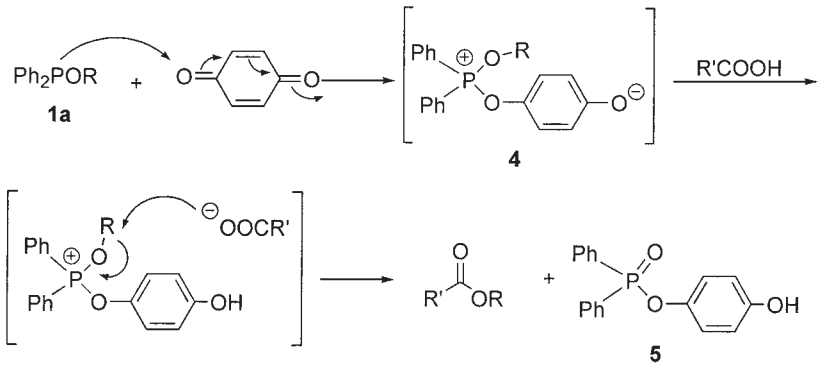
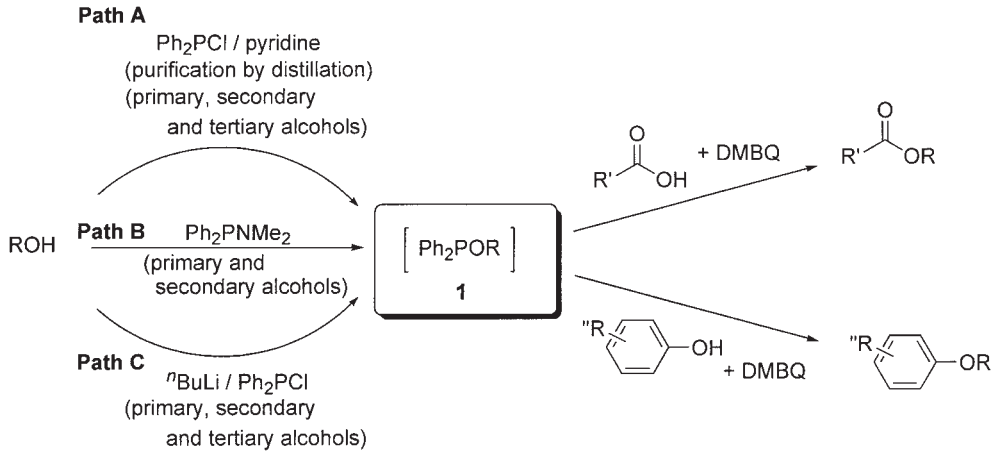
The Present Oxidation-reduction Condensation



Scheme 1.

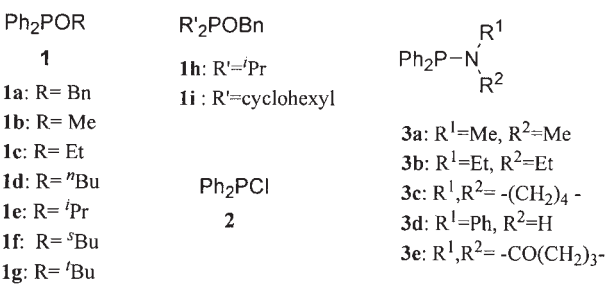


Scheme 2.

haved more effectively in the formation of the important intermediate phosphonium salt. In our another point of view, alkoxydiphenylphosphine would form the key intermediate, phosphonium salt, more smoothly by an interaction even with weaker oxidizing agents such as quinone because of the introduction of one alkoxy group in place of phenyl group of triphenylphosphine, and the subsequent alkylation reaction via the oxidation–reduction process would proceed effectively. Quinone compounds have long been anticipated as effective oxidants in this type of condensation; however, no successful examples have been shown to date. The intermediate phosphonium salt was in turn converted to so-called penta-valent phosphorus by catching one hydrogen atom up with a negatively charged oxygen of the formed quartery phosphonium salt (**4**) from carboxylic acids or phenols. At the same time, thus formed nucleophilic species such as carboxylates or phenolates attacked the alkyl group to form an alkylated product and diphenylphosphinic acid 4-hydroxyphenyl ester (**5**) (Scheme 1). Then, with the consideration that the combination of Ph_2POR and quinones would work well in the oxidation–reduction condensation, benzylation of benzoic acid (**6a**) with benzyloxydiphenylphosphine (**1a**) was tried first by using 1,4-benzoquinone in toluene, and the desired product (**7a**) was obtained in 32% yield. The result prompted us to work further on this new-type of oxidation–reduction condensation by using a combination of alkoxydiphenylphosphine and DMBQ, and the reaction successfully afforded various carboxylic acid alkyl esters or alkyl phenyl ethers including bulky alkyl groups in good to high yield after screening various quinones (Scheme 2).[8–10]

Results and Discussion

Synthesis of Alkoxyphosphines (Scheme 3, 1a–i) and Aminodiphenylphosphines (Scheme 3, 3a–e). Alkoxydiphenylphosphines such as methoxydiphenylphosphine (**1b**) and ethoxydiphenylphosphine (**1c**) have been employed in peptide syntheses or Arbuzov reactions as useful phosphorus compounds.[11] Alkoxydiphenylphosphines having a primary, secondary, or tertiary alkoxy group were generally isolated by distillation. Alkoxydiphenylphosphines (**1a–f**) having a primary or secondary alkoxy group are prepared easily from **2** and alcohols by using a base such as pyridine. Similarly,

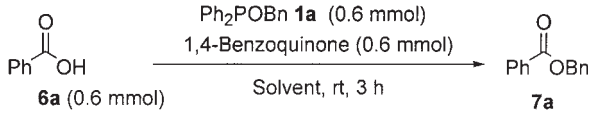


Scheme 3.

benzyloxydialkylphosphines such as benzyloxydiisopropylphosphine (**1h**) and benzyloxycyclohexylphosphine (**1i**) were prepared from alkylchlorophosphine and benzyl alcohol; *t*-butoxydiphenylphosphine (**1g**) was also prepared from **2** and potassium *t*-butoxide in 31% yield. Alkoxydiphenylphosphines were alternatively in situ formed by treating aminodiphenylphosphines (**3a–e**),[12] prepared from **2** and the corresponding amines or 1-(trimethylsilyl)-2-pyrrolidinone,[13] with primary or secondary alcohols.

Esterification of Carboxylic Acids by a New-Type of Oxidation–Reduction Condensation Using Quinones and Alkoxydiphenylphosphines. In the first place, benzylation of **6a** with 1.0 equivalent of **1a** was tried by using 1.0 equivalent of 1,4-benzoquinone in toluene, and the desired ester (**7a**) was obtained in 32% yield within 3 h (Table 1, entry 1). When the reaction was tried under the same conditions in half the quantity of toluene, **7a** was obtained in 43% yield (Table 1, entry 2). Next, after screening the effect of several other solvents such as acetonitrile, diethyl ether, and dichloromethane on the above model reaction, it was found that no significant difference due to the nature of solvent was observed (Table 1, entries 2–5). However, careful observation indicated that a more concentrated solution could be available when dichloromethane was used because of its high solubility. When the concentration was 1.2 mol dm^{-3} in dichloromethane, **7a** was obtained in 75% yield under the above conditions (Table 1, entry 7). Thus, dichloromethane was used as the most preferable solvent for this condensation.

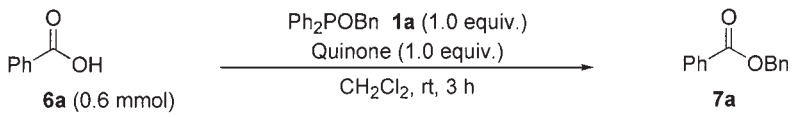
Table 1. Effect of Solvent on Benzylation of **6a**



Entry	Solvent/mL	Yield/%	Entry	Solvent/mL	Yield/%
1	Toluene/3.0	32	5	CH_2Cl_2/1.5	43
2	Toluene/1.5	43	6	CH_2Cl_2/1.0	56
3	CH_3CN/1.5	40	7	CH_2Cl_2/0.5	75
4	Et_2O/1.5	41	8	CH_2Cl_2/0.25	47

When benzylation of **6a** with 1.0 equivalent of **1a** was tried in the absence of quinone type oxidant such as 1,4-benzoquinone in dichloromethane, the reaction hardly took place, as expected (Table 2, entry 1). When the well-known oxidant such as *trans*-1,2-dibenzoylethylene or DEAD mentioned above was used together, **7a** was obtained within 3 h under the above

Table 2. Screening of Quinone Derivatives on Benzylation of **6a**



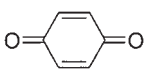
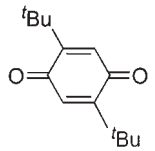
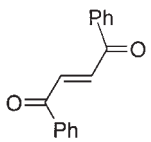
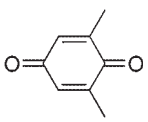
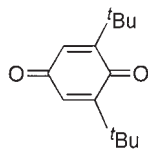
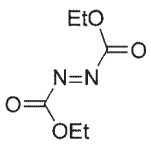
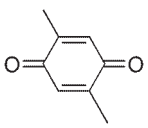
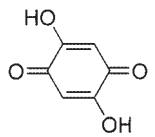
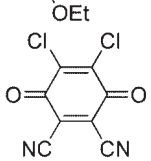
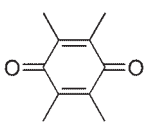
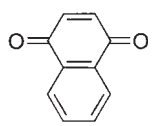
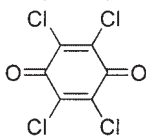
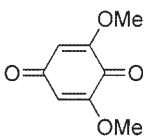
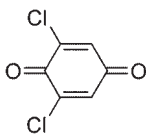
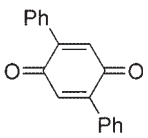
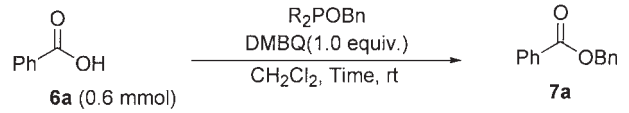
Entry	Quinone	Yield/%	Entry	Quinone	Yield/%	Entry	Quinone	Yield/%
1	none	N.R.	7		75	13		19
2		55	**8**		**90**	14		77
3		73	9		66	15		19
4		N.R.	10		12	16		32
5		N.R.	11		45			
6		N.R.	12		70			

Table 3. Effect of Substituents of Phosphine on Benzylation of **6a**



Entry	R		R_2POBn/equiv.	Time/h	Yield/%
1	^{i}Pr	**1h**	1.0	3	60
2	cyclohexyl	**1i**	1.0	3	57
3	Ph	**1a**	1.0	3	90
4	Ph	**1a**	1.1	3	97
5	Ph	**1a**	1.3	3	97
6	Ph	**1a**	1.1	0.5	98
7	Ph	**1a**	1.1	1	97

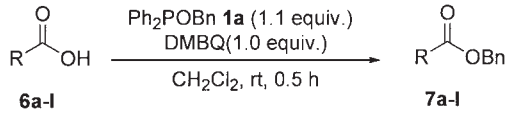
conditions in 55% or 73% yields, respectively (Table 2, entries 2 and 3). It is interesting to note that the carboxylic esters were not obtained when more powerful oxidizing agents such as 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), tetrachloro-1,4-benzoquinone (*p*-chloranil), and 2,6-dichloro-1,4-benzoquinone were used (Table 2, entries 4–6) while the yield of **7a** was 75% when a milder oxidant such as 1,4-benzoquinone was used (Table 2, entry 7). After screening several quinone derivatives, **7a** was obtained in 90% yield under mild condition when DMBQ was used (Table 2, entries 8–16).

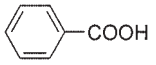
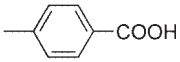
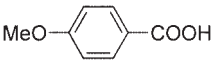
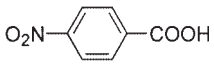
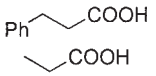
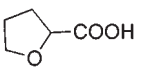
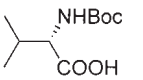
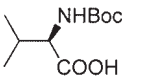
Next, it was thought that the present reaction might be improved by replacing two phenyl groups contained in the abovementioned **1a** by two electron-donating alkyl groups. It was known that chlorodialkylphosphines were generally prepared by treating phosphorus trichloride with the corresponding alkyl Grignard reagents.[14] However, preparation of chlorodialkylphosphine having alkyl groups such as methyl or *n*-butyl group was not successful due to the extreme unstability of the produced phosphines. In the case of secondary alkyl groups such as isopropyl or cyclohexyl group, the corresponding chlorodialkylphosphines were successfully isolated and were converted to **1h** or **1i**; employment of thus prepared **1h** and **1i** afforded the desired ester in 60% and 57% yields, respectively (Table 3, entries 1 and 2).

Benzyloxydiphenylphosphine afforded the ester effectively in 90% yield by treating **1a**, DMBQ, and **6a** (Table 3, entry 3). The reaction proceeded rapidly (0.5 h) at room temperature and the ester was obtained in over 98% yield when 1.1 equivalents of **1a** was used (Table 3, entries 3–7).

The benzylation of various carboxylic acids was then tried by using 1.1 equivalents of **1a** and 1.0 equivalent of DMBQ in dichloromethane (Table 4). As a result, benzylation of various carboxylic acids smoothly proceeded to afford the corresponding carboxylic acid benzyl esters in high yields under mild conditions. When benzoic acids having electron-donating or electron-withdrawing groups were used, the desired products were obtained in excellent yields (Table 4, entries 1–4). The reactions of primary and tertiary aliphatic carboxylic acids also gave the corresponding carboxylic esters in high yields (Table 4, entries 5–7). When a heterocyclic compound such as tetrahydrofuran-2-carboxylic acid was used, the corresponding ester was obtained in 86% yield under the above conditions (Table 4, entry 8). In the cases of *N*-*t*-butoxycarbonyl-L-valine and *N*-*t*-butoxycarbonyl-D-valine, the corresponding

Table 4. Benzylation of Various Carboxylic Acids with **1a** and DMBQ



Entry	RCOOH		Product	Yield/%
1		**6a**	**7a**	98
2		**6b**	**7b**	98
3		**6c**	**7c**	95
4		**6d**	**7d**	95
5		**6e**	**7e**	93
6		**6f**	**7f**	89
7	^{t}BuCOOH	**6g**	**7g**	89
8		**6h**	**7h**	86
9		**6i**	**7i**	90[a]
10		**6j**	**7j**	89[a]
11	$ClCH_2COOH$	**6k**	**7k**	95
12	CCl_3COOH	**6l**	**7l**	93

a) No epimerization was observed by HPLC using Daicel CHIRALPAK AF.[8]

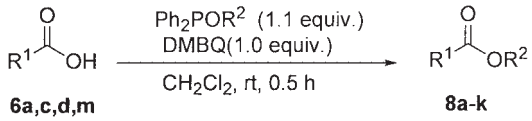
benzyl esters were exclusively obtained in high yields with no epimerizations (Table 4, entries 9 and 10). Carboxylic acids having a chlorine atom at α-position such as chloroacetic acid and trichloroacetic acid, also afforded the desired products in excellent yields (Table 4, entries 11 and 12).

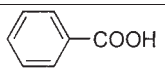
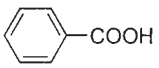
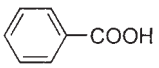
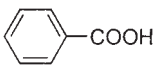
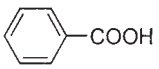
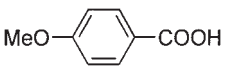
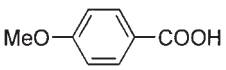
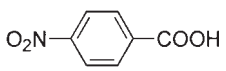
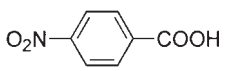
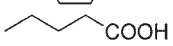
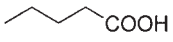
In order to extend the scope of the present reactions, alkylation of several carboxylic acids using DMBQ and alkoxydiphenylphosphines such as **1c**, **1d**, **1e**, **1f**, and **1g** was next tried (Table 5). Esterifications of several aromatic and aliphatic carboxylic acids smoothly proceeded to afford the corresponding carboxylic acid alkyl esters in good to high yields under mild conditions when alkoxydiphenylphosphines having primary or secondary alkoxy groups were used (Table 5, entries 1–4 and 6–11). In the case of using alkoxydiphenylphosphine that has a *t*-butyl group, the desired product was obtained in 73% yield when the reaction was carried out in refluxing dichloromethane for 3 h (Table 5, entry 5).

Thus, an efficient method for esterification of various carboxylic acids was established via the present new-type of oxidation–reduction condensation by combined use of alkoxydiphenylphosphines having primary, secondary or tertiary alkoxy group and DMBQ.

Etherification of Phenols by a New-Type of Oxidation–Reduction Condensation Using Quinones and Alkoxydiphenylphosphines. Benzylation of phenol with 1.1 equivalents of **1a** was examined by using 1.0 equivalent of 1,4-benzoquinone in dichloromethane, and the desired product was

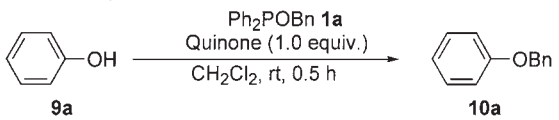
Table 5. Alkylations of Several Carboxylic Acids with Alkoxydiphenylphosphines and DMBQ



Entry	R^1COOH		R_2POR^2		Product	Yield/%	Comparision Yield/%[b]
1		**6a**	Ph_2POEt	**1c**	**8a**	91	85
2		**6a**	Ph_2PO^nBu	**1d**	**8b**	88	—
3		**6a**	Ph_2PO^iPr	**1e**	**8c**	93	90
4		**6a**	Ph_2PO^sBu	**1f**	**8d**	82	27[c]
5		**6a**	Ph_2PO^tBu	**1g**	**8e**	73[a]	—
6		**6c**	Ph_2POEt	**1c**	**8f**	89	—
7		**6c**	Ph_2PO^nBu	**1d**	**8g**	85	—
8		**6d**	Ph_2PO^nBu	**1d**	**8h**	93	—
9		**6d**	Ph_2PO^iPr	**1e**	**8i**	91	—
10		**6m**	Ph_2POEt	**1c**	**8j**	76	34
11		**6m**	Ph_2PO^iPr	**1e**	**8k**	84	43

a) The raction mixture was refluxed for 3 h. b) Comparision of Mitsunobu reaction. See Ref. 6c. c) Mitsunobu reaction was tried.

Table 6. Benzylation of Phenol with **1a** and Quinones



Entry	**1a**/equiv.	Quinone	Yield/%
1	1.1	1,4-benzoquinone	49
2	1.1	DMBQ	85
3	1.1	DMBQ	72[a]
4	1.2	DMBQ	85
5	1.5	DMBQ	92

a) To a mixture of phenol and DMBQ was added **1a** in CH_2Cl_2 at 0 °C and then reacted for 0.5 h at room temperature.

obtained in 49% yield within 0.5 h (Table 6, entry 1). When DMBQ was used under the above conditions, the benzyl phenyl ether was obtained in 85% yield (Table 6, entry 2). The yield lowered to 72% when phenol, 1.1 equivalents of DMBQ and 1.1 equivalents of **1a** were allowed to react in dichloromethane at 0 °C and were stirred for an additional 0.5 h at room temperature (Table 6, entry 3) whereas the desired product was obtained in 92% yield under the above conditions when 1.5 equivalents of **1a** was used (Table 6, entry 5).

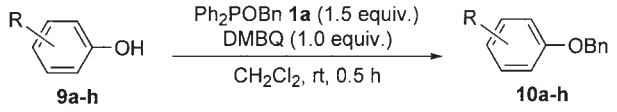
Next, the benzylation of various phenols was tried by using 1.5 equivalent of **1a** and 1.0 equivalent of DMBQ in dichloromethane (Table 7). As a result, the corresponding benzyl phenyl ethers were obtained in good yields under mild conditions when phenols having electron-donating or electron-withdrawing groups were used (Table 7, entries 1–5). The corresponding benzyl phenyl ether was obtained in 70% yield at room temperature (Table 7, entry 6). Similarly, the desired products were obtained in good yields under mild conditions when 1-naphthol and 2-naphthol were used (Table 7, entries 7 and 8).

Further, alkylations of phenol with DMBQ and several alkoxydiphenylphosphines such as **1b**, **1c**, **1d**, and **1e** were tried (Table 8) and the corresponding alkyl phenyl ethers were obtained in good yields. When *p*-nitrophenol and **1g** having a bulky substituent such as *t*-butyl group was used, on the other hand, the yield was 62% after refluxing them in dichloromethane for 10 h.

Thus, an effective method for alkylation of various phenols was established by this new-type of oxidation–reduction condensation with a combination of alkoxydiphenylphosphines having primary, secondary, or tertiary alkoxy group and DMBQ.

One-pot Esterification of Carboxylic Acids by a New-Type of Oxidation–Reduction Condensation Using 2,6-Dimethyl-1,4-benzoquinone and in situ Formed Alkoxydiphenylphosphines from *N*,*N*-Dimethylaminodiphenylphosphine and Primary or Secondary Alcohols. Next, it was thought that the present reaction would afford carboxylic acid

Table 7. Benzylation of Various Phenol with **1a** and DMBQ



9a-h **10a-h**

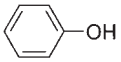
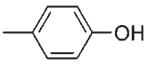
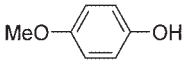
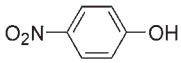
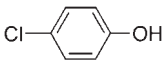
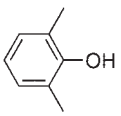
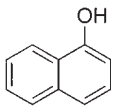
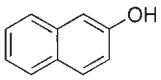
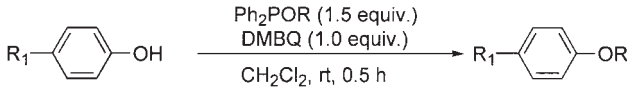
Entry	PhOH derivative		Product	Yield/%
1		**9a**	**10a**	92
2		**9b**	**10b**	82
3		**9c**	**10c**	78
4		**9d**	**10d**	88
5		**9e**	**10e**	84
6		**9f**	**10f**	70
7		**9g**	**10g**	81
8		**9h**	**10h**	84

Table 8. Alkylation of Phenol or *p*-Nitrophenol with Several Alkoxydiphenylphosphines and DMBQ

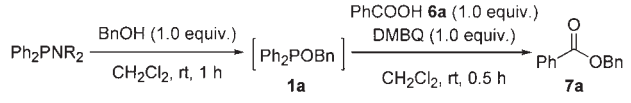


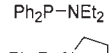
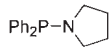
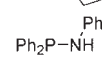
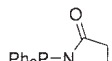
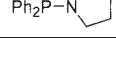
9a,d **11a-e**

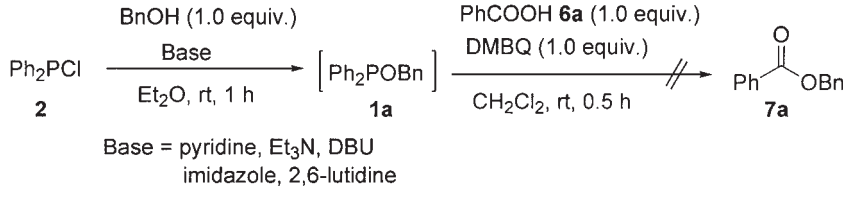
Entry	R_1		Ph_2POR		Product	Yield/%
1	H	**9a**	Ph_2POMe	**1b**	**11a**	88
2	H	**9a**	Ph_2POEt	**1c**	**11b**	84
3	H	**9a**	Ph_2PO^nBu	**1d**	**11c**	87
4	H	**9a**	Ph_2PO^iPr	**1e**	**11d**	81
5	NO_2	**9d**	Ph_2PO^tBu	**1g**	**11e**	62[a]

a) The reaction mixture was refluxed for 10 h.

Table 9. Screening of Aminophosphine Derivatives on Reaction of Benzyl Alcohol and **6a**



Entry	$Ph_2P–NR_2$		Yield/%
1		**3a**	76
2		**3b**	70
3		**3c**	51
4		**3d**	61
5		**3e**	Trace



Scheme 4.

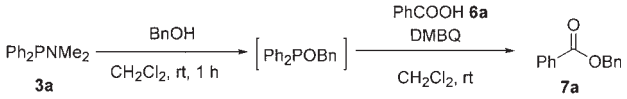
alkyl esters from the corresponding carboxylic acids and alcohols by one-pot procedure without isolation of alkoxydiphenylphosphine.

First, chlorodiphenylphosphine (**2**) (132 mg, 0.6 mmol) was dropped into a mixture of benzyl alcohol (65 mg, 0.6 mmol) and pyridine (48 mg, 0.6 mmol) in Et_2O (1.0 mL) at 0 °C. After stirring the mixture at room temperature for 1 h, salts were filtered off and concentrated in vacuo. A reaction mixture was again stirred at room temperature for 0.5 h after **6a** and DMBQ were added to the residue in dichloromethane. However, benzyl ester **7a** was not obtained when benzoic acid and DMBQ were treated with in situ formed **1a** without purification (Scheme 4). Nor was the ester **7a** obtained when **1a** prepared from **2** and benzyl alcohol by using organic bases such as Et_3N, DBU, imidazole, and 2,6-lutidine, was allowed to react under the above conditions (Scheme 4).

It was known that the phosphorus-nitrogen bond of *N*,*N*-disubstituted diarylphosphines was thermo-stable; therefore, tautomeric transformations of trivalent phosphorus compounds to the corresponding pentavalent phosphorus compounds did not occur.[15] More importantly, the above aminophosphines were easily converted to the alkoxy ones by the replacement of amino group with the alkoxy group of alcohols.[16] Then, it was considered that the alkoxydiphenylphosphines might be formed by alcoholysis of the corresponding aminophosphines with alcohols. Expectedly, the desired product was obtained in 76% yield within 0.5 h when a mixture of 1.0 equivalent of benzyl alcohol and 1.0 equivalent of **3a** was treated with 1.0 equivalent each of DMBQ and of benzoic acid in dichloromethane at room temperature (Table 9, entry 1).

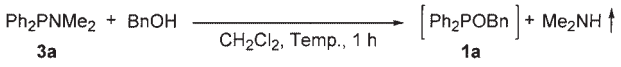
These results indicated that **3a** was the most preferable aminodiphenylphosphine for this purpose because dimethylamine (bp 7 °C) was removed easily from the formed alkoxydiphenylphosphines. However, the removal of other amines such as diethylamine (bp 55 °C), pyrrolidine (bp 87–88 °C), aniline (bp 184 °C), and 2-pyrrolidinone (bp 245 °C) from the reaction mixture was difficult because of their higher boiling points. On the contrary, when amines having lower boiling

Table 10. The Condensation of Benzyl Alcohol and **6a** with **3a**



Entry	BnOH/equiv.	**3a**/equiv.	**6a**/equiv.	DMBQ/equiv.	Time/h	Yield/%
1	1.0	1.0	1.0	1.0	0.5	76
2	1.0	1.0	1.0	1.0	1	82
3	1.0	1.0	1.0	1.0	2	84
4	1.5	1.0	1.0	1.0	1	81
5	1.0	1.5	1.0	1.0	1	74
6	1.5	1.5	1.0	1.0	1	89
7	1.0	1.0	1.0	1.5	1	78
8	1.0	1.0	1.5	1.0	1	82

Table 11. The Preparation Ratio of **in situ** Formed **1a**



Entry	BnOH/equiv.	**3a**/equiv.	Temp./°C	**1a**/BnOH[a)]
1	1.0	1.0	rt	16/84
2	1.0	1.0	40	87/13
3	1.0	1.0	reflux	86/14
4	1.0	1.2	40	88/12
5	1.0	1.5	40	86/14

a) **1a**/BnOH ratios were determined by ^{1}H NMR analysis.

points such as ammonia (bp −33 °C) or methylamine (bp −6.3 °C) were used, the compounds such as aminodiphenylphosphine and *N*-methylaminodiphenylphosphine could not be successfully isolated because aminodiphenylphosphine, *N*,*N*-bis(diphenylphosphino)amine, and tris(diphenylphosphino)amine were formed.

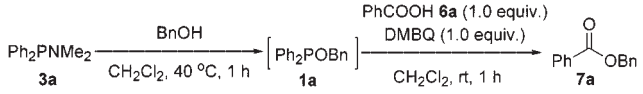
Next, the reaction time and molar ratio of benzyl alcohol, **3a**, **6a**, and DMBQ were investigated (Table 10). Benzyl ester **7a** was obtained in 89% yield after stirring it for 1 h at room temperature when 1.5 equivalents each of benzyl alcohol and of **3a** were used.

The result above shows that the replacement of benzyloxy group with dimethylamine group did not take place smoothly in the preparative procedure. And the ^{1}H NMR analysis (Table 11) indicated that the ratio of in situ formed alkoxydiphenylphosphine and non-reacted benzyl alcohol was almost at max when 1.0 equivalent each of benzyl alcohol and of **3a** were allowed to react for 1 h at 40 °C (Table 11, entry 2).

Product **7a** was obtained in 86% yield by treating in situ formed **1a** with **6a** and DMBQ (Table 12, entry 1). It was further revealed that the desired product was obtained in 96% yield when the reaction was carried out according to method B by using 1.1 equivalents of benzyl alcohol and 1.1 equivalents of **3a** as shown in Table 12 (Table 12, entry 3).

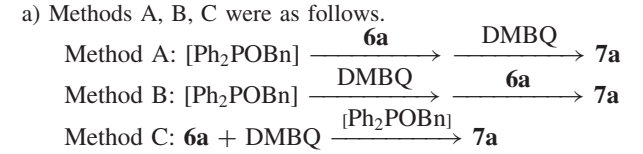
Benzylation of various carboxylic acids with **3a** and benzyl alcohol was tried according to method B (Table 13). The benzylation of benzoic acids having electron-donating or electron-withdrawing groups, saturated or unsaturated aliphatic carboxylic acids and chloroacetic acid, proceeded smoothly to afford the corresponding carboxylic acid benzyl esters in high yields under mild conditions. Similarly, the benzylation of *N*-*t*-butoxycarbonyl-L-valine gave the corresponding esters in high

Table 12. Screening of the Condensation of Benzyl Alcohol and **6a** with **3a**



Entry	BnOH/equiv.	**3a**/equiv.	Method[a)]	Yield/%
1	1.0	1.0	A	86
2	1.0	1.0	B	90
3	1.1	1.1	B	96
4	1.2	1.2	B	95
5	1.5	1.5	B	96
6	1.5	1.5	C	94

a) Methods A, B, C were as follows.

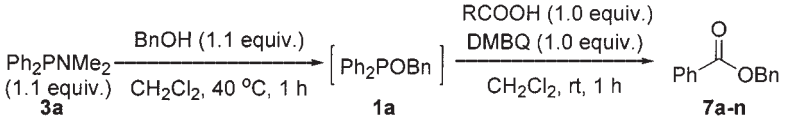


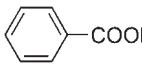
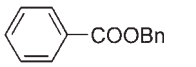
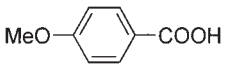
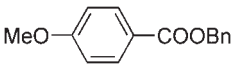
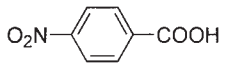
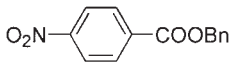
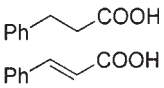
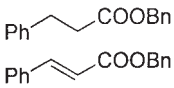
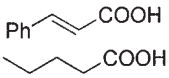
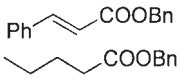
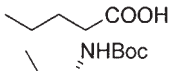
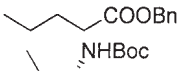
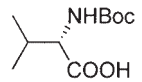
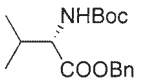
yields where no epimerization took place (Table 13, entry 8).

Next, in order to extend the scope of the present reactions, condensation of **6a** and several alkoxydiphenylphosphines generated from primary alcohols and **3a** was tried under the above conditions (Table 14). When benzyl alcohols having electron-donating or electron-withdrawing groups and saturated or unsaturated aliphatic alcohols were used, the corresponding esters were obtained in excellent yields (Table 14, entries 1–5 and 7). Also, the desired ester was obtained in 86% yield when 2-pyridinemethanol having a heterocyclic moiety was used (Table 14, entry 6).

Next, condensation of **6a** and several bulky secondary alcohols was tried after forming an intermediate Ph_2POR' in situ. Concerning isopropyl alcohol, the ratio of in situ formed isopropoxydiphenylphosphine and non-reacted isopropyl alcohol was first examined by ^{1}H NMR analysis (Table 15). It was revealed that the replacement of isopropoxy group with dimethylamine group did not take place smoothly under the same conditions when dichloromethane was used as a solvent (Table 15, entry 1). Then, the exchange reaction was tried in refluxing dichloromethane, but no significant difference was observed (Table 15, entry 2). A similar result was given when toluene was used for a solvent (Table 15, entry 3). When 1,2-dichloroethane was used, the generation of isopropoxydiphenylphosphine was almost completed after stirring it for 7 h at 100 °C (Table 15, entries 4–8, Fig. 1).

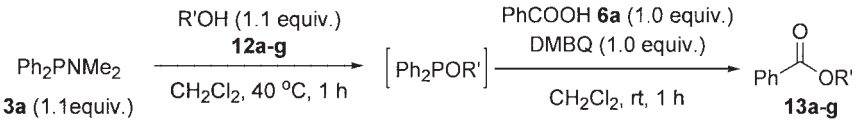
Table 13. Benzylation of Various Carboxylic Acids with **3a** and Benzyl Alcohol

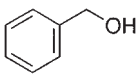
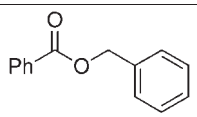
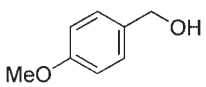
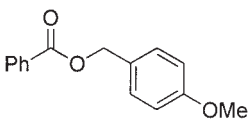
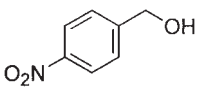
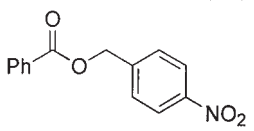
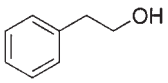
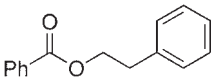
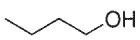
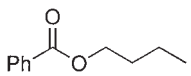
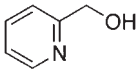
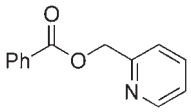
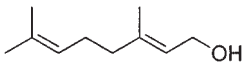
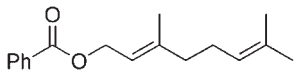


Entry	RCOOH		Product		Yield/%
1		**6a**		**7a**	96
2		**6c**		**7c**	96
3		**6d**		**7d**	90
4		**6e**		**7e**	90
5		**6n**		**7n**	92
6		**6m**		**7m**	93
7		**6i**		**7i**	89[a]
8	$ClCH_2COOH$	**6k**	$ClCH_2COOBn$	**7k**	91

a) No epimerization was observed by HPLC using Daicel CHIRALPAK AF.[8]

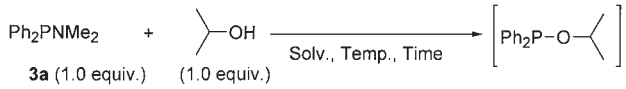
Table 14. Esterification of **6a** with Various Primary Alcohols



Entry	R′OH		Product		Yield/%
1		**12a**		**13a** (**7a**)	96
2		**12b**		**13b**	91
3		**12c**		**13c**	95
4		**12d**		**13d**	94
5		**12e**		**13e** (**8b**)	96
6		**12f**		**13f**	86
7		**12g**		**13g**	96

Next, the condensation of **6a** and several secondary alcohols with **3a** was tried (Table 16). Alkylation of **6a** proceeded smoothly to afford the corresponding alkyl esters in high to excellent yields in 1,2-dichloroethane under the conditions shown in Table 16. In addition, it was noted that the corresponding benzoic acid alkyl esters were obtained in excellent yields with perfect inversion of stereochemistry by S_N2 replacement when chiral secondary alcohols were used

Table 15. The Replacement of Isopropoxy Group with Dimethylamine Group



Entry	Solv.	Temp./°C	Time/h	$Ph_2PO^iPr/^iPrOH$[a)]
1	CH_2Cl_2	40	1	5/95
2	CH_2Cl_2	reflux	1	5/95
3	Toluene	reflux	1	5/95
4	$ClCH_2CH_2Cl$	100	1	23/77
5	$ClCH_2CH_2Cl$	100	3	48/52
6	$ClCH_2CH_2Cl$	100	5	72/28
7	$ClCH_2CH_2Cl$	100	7	98/2
8	$ClCH_2CH_2Cl$	100	9	99/1

a) The ratio of $Ph_2PO^iPr/^iPrOH$ was determined by ^1H NMR.

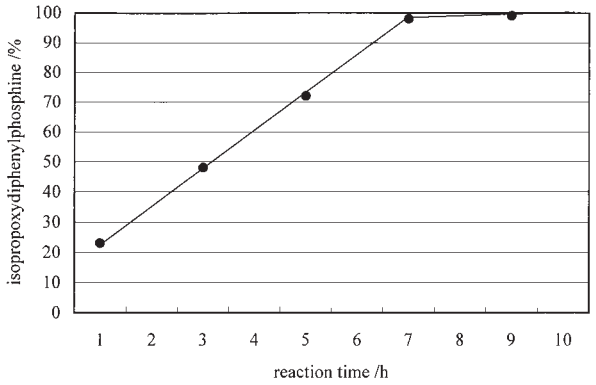
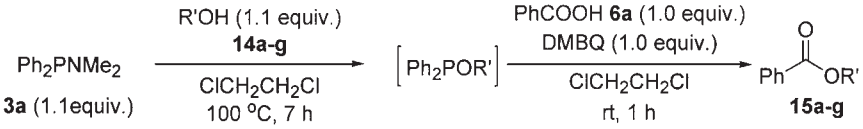
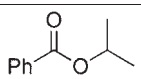
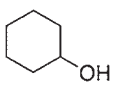
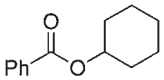
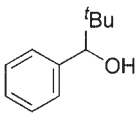
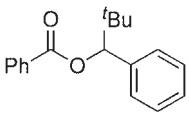
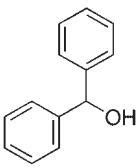
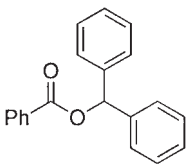
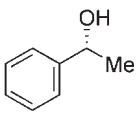
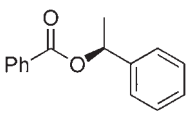
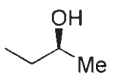
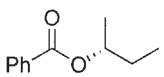
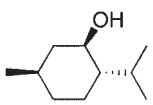
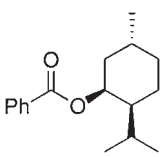


Fig. 1. The replacement isopropoxy group with dimethylamine group.

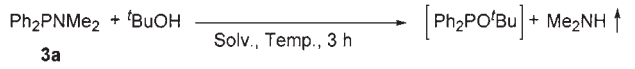
Table 16. Esterification of **6a** with Various Secondary Alcohols



Entry	R′OH		Product		Yield/%	$[\alpha]_D$
1		**14a**		**15a** (**8c**)	94[d)]	—
2		**14b**		**15b**	95	—
3		**14c**		**15c**	96	—
4		**14d**		**15d**	94	—
5[a)]		**14e**		**15e**	94	$[\alpha]_D^{24} = +26.6$ (c 3.08, EtOH)
6[b)]		**14f**		**15f**	88	$[\alpha]_D^{21} = -35.3$ (c 1.10, $CHCl_3$)
7[c)]		**14g**		**15g**	88[e)]	$[\alpha]_D^{23} = +92.0$ (c 1.16, C_6H_6)

a) Isomer authentic sample **15e′**: $[\alpha]_D^{25} = -28.7$ (c 1.02, EtOH) (preparation from PhCOCl, Et_3N, alcohol).[50] In addition, Daicel Chiralcel OD column was used for chiral HPLC analysis. b) Isomer authentic sample **15f′**: $[\alpha]_D^{22} = +34.6$ (c 1.16, $CHCl_3$) (preparation from PhCOCl, Et_3N, alcohol).[51] c) Isomer authentic sample **15g′**: $[\alpha]_D^{24} = -93.5$ (c 1.23, C_6H_6) (preparation from PhCOCl, Et_3N, alcohol). Diastereoselectivities determined by ^1H NMR spectroscopy.[50b,52] Also, intermediate L-menthoxydiphenylphosphine was prepared by mixing **14g** with **3a** and was stirred for 10 h at 100 °C. d) 90% Yield by Mitsunobu reaction. e) 27% Yield by Mitsunobu reaction.

Table 17. The Replacement of *tert*-Butoxy Group with Dimethylamine Group



Entry	Solv.	Temp./°C	Ph_2PO^tBu[a)]
1	$ClCH_2CH_2Cl$	100	N.D.
2	$ClCH_2CH_2CH_2Cl$	130	N.D.

a) Determined by ^1H NMR analysis.

(Table 16, entries 5–7).

Further, the condensation of **6a** and tertiary alcohols by using **3a** was tried; however, replacement of tertiary alcohols did not take place even when they were heated at higher temperatures than those of secondary alcohols (Table 17).

Thus, effective one-pot esterification of various carboxylic acids was established via a new-type of oxidation–reduction condensation using a combination of DMBQ and in situ formed alkoxydiphenylphosphines formed from **3a** and primary or secondary alcohols.

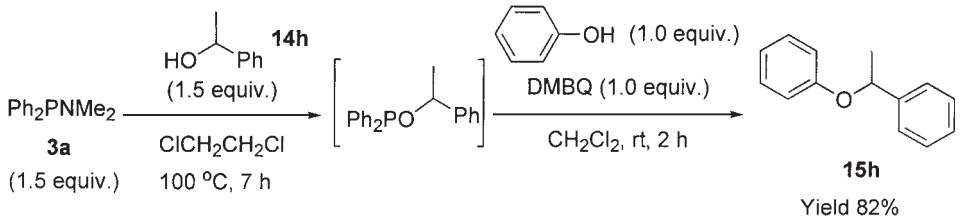
According to this procedure, **3a** and 1-phenylethyl alcohol (**14h**) also gave the corresponding alkoxydiphenylphosphine smoothly; the desired ether (**15h**) was afforded in 82% yield by one-pot procedure on treatment with phenol (Scheme 5).

One-pot Esterification of Carboxylic Acids by a New-Type of Oxidation–Reduction Condensation Using 2,6-Dimethyl-1,4-benzoquinone and Primary, Bulky Secondary, or Tertiary in situ-formed Alkoxydiphenylphosphines by Adding Chlorodiphenylphosphine to ^{n}BuLi-treated Alcohols. The above experiment indicated that the key point of the present reactions was the effective formation of alkoxydiphenylphosphine. Then, preparation of various alkoxydiphenylphosphines from **2** and alcohols using ^{n}BuLi was tried according to Evans's procedure.[17] It was thought that the existence of generated LiCl would not influence the oxidation–reduction condensation reaction in the case when the alkoxydiphenylphosphines were prepared from **2** and alcohols with ^{n}BuLi. First, into a THF (18 mL) solution of alcohol (5.0 mmol) was dropped a hexane solution of ^{n}BuLi (5.0 mmol) at 0 °C; after it was stirred it for 1 h at room temperature, **2** (5.0 mmol) was added at 0 °C. The reaction mixture was then stirred for 1 h at room temperature and was concentrated in vacuo. Immediately, carboxylic acid, DMBQ, and dichloromethane were added to the residue and the mixture was stirred under argon atmosphere at the temperatures between room temperature and 40 °C. The same result was alternatively obtained by the following procedure: that is, after the above mentioned residue was diluted with a mixed solution of hexane (8 mL) and ethyl acetate (1 mL), lithium chloride was removed by filtration through celite (3.0 g) after passing it through alumina (activated, basic) (Wako Pure Chemical Industries, LTD) (20 g). The diluted solution was concentrated in vacuo, and crude alkoxydiphenylphosphine was obtained. It was then allowed to react with carboxylic acid and DMBQ in dichloromethane by a similar procedure to that mentioned above.

When primary alcohols were used, the corresponding alkoxydiphenylphosphines were obtained smoothly, and the desired esters were afforded in excellent yields by one-pot procedure on treatment with **6a** (Table 18).

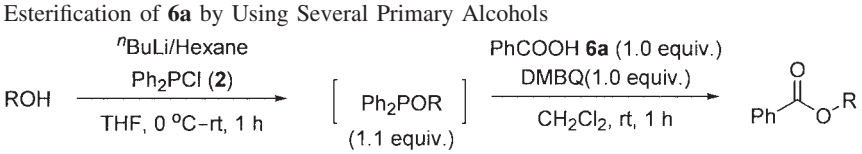
The esterification of various in situ-formed secondary alkoxydiphenylphosphines having sterically hindered bulky alkoxy groups with **6a** was further examined under the same conditions (Tables 19); the corresponding esters were afforded in high yields with perfect inversion of stereochemistry by S_N2 replacement with secondary alcohols (Table 19, entries 1 and 2).

The esterification of in situ formed secondary alkoxydiphenylphosphine having a sterically hindered bulky group such as (L)-(−)-menthol with various carboxylic acids was tried under the above conditions. Preparation of such hindered esters in high yields under mild conditions still remains difficult because it generally needs a long reaction time (24 h) using a



Scheme 5.

Table 18. Esterification of **6a** by Using Several Primary Alcohols



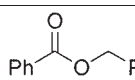
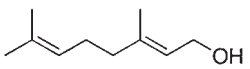
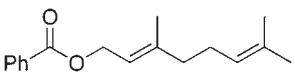
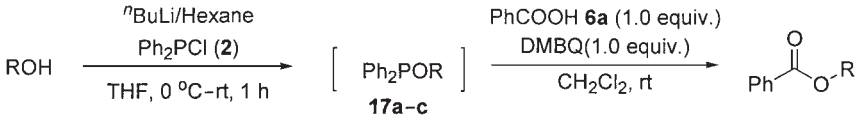
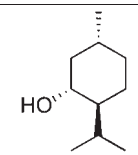
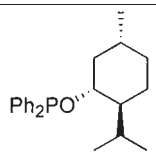
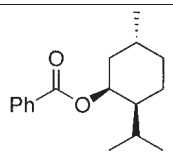
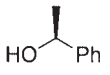
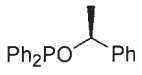
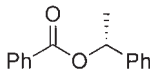
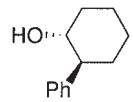
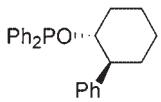
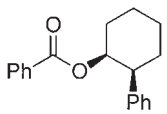
Entry	ROH	Ph_2POR	Product		Yield/%
1		**1a**		**7a**	98
2		**16a**		**13g**	93

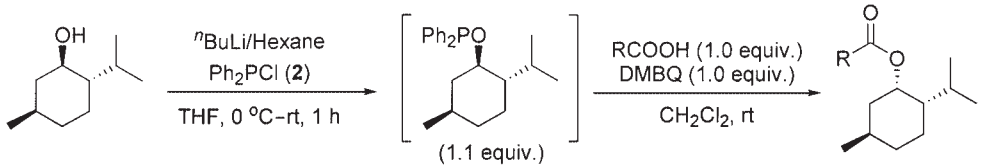
Table 19. Esterification of **6a** by Using Various Bulky Secondary Alcohols



Entry	ROH	Ph_2POR/equiv.		Product	Time/h	Yield/%
1	 **14g**	 **17a**	1.1	 **15g**	3.0	86[a]
2	 **14e**	 **17b**	1.1	 **15e**	1.0	93[b]
3	 **14h**	 **17c**	1.2	 **15i**	3.0	85[c]

a) $[\alpha]_D^{14} = +92.4$ (*c* 1.22, C_6H_6). The corresponding ester was obtained with perfect inversion of stereochemistry by S_N2 replacement. b) $[\alpha]_D^{23} = +27.3$ (*c* 1.22, EtOH). c) Use of racemic compound. 58% yield by Mitsunobu reaction.

Table 20. Comparison of Esterification of Several Carboxylic Acids and (L)-(−)-Menthol by Means of Several Methods



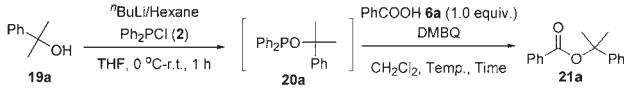
Entry	RCOOH		pK_a	Product	Present reaction Time/h	Present reaction Yield/%(a/%)	Mitsunobu reaction[b] Yield/%(a/%)	Tsunoda method[c] Yield/%(a/%)
1	*o*-NO_2-PhCOOH	**6o**	2.16	**18a**	3	54(>99.9)	33(>99.9)	—
2	*p*-NO_2-PhCOOH	**6d**	3.41	**18b**	1	87(>99.9)	84(>99.9)	26(0.082)
3	*m*-NO_2-PhCOOH	**6p**	3.47	**18c**	3	53(>99.9)	55(>99.9)	—
4[d]	*m*-NO_2-PhCOOH	**6p**	3.47	**18c**	2	86(>99.9)[d]		
5	*o*-MeO-PhCOOH	**6q**	4.09	**18d**	3	53(>99.9)	0	—
6	PhCOOH	**6a**	4.19	**15g**	3	86(>99.9)	27(>99.9)	91(10.6)
7	*p*-MeO-PhCOOH	**6d**	4.47	**18e**	1	88(>99.9)	17(>99.9)	98(>99)

a) Inversion ratio. Diastereoselectivities determined by ^1H NMR spectroscopy. Corresponding isomer (**15g′**, **18a′**, **18b′**, **18c′**, **18d′**, **18e′**) was prepared by using RCOCl (1.0 eq.), (L)-(−)-menthol (1.0 eq.), and Et_3N (1.0 eq.). b) (L)-(−)-menthol (1.0 eq.), RCOOH (4.0 eq.), PPh_3 (4.0 eq.), $EtO_2CN{=}NCO_2Et$ (4.0 eq.), THF, rt, 24 h.[6i,7c] c) (L)-(−)-menthol (1.0 eq.), RCOOH (1.5 eq.), $^tBu_3P$ (1.5 eq.), $Me_2NOCN{=}NCONMe_2$ (1.5 eq.), benzene, 60 °C, 24 h.[7c] d) (L)-(−)-menthoxydiphenylphosphine (1.5 eq.).

large excess amount of carboxylic acids and reagents, as shown in the esterification of carboxylic acids with (L)-(−)-menthol by Mitsunobu and Tsunoda methods (Table 20). The present method using a combination of DMBQ and in situ-formed alkoxydiphenylphosphine from lithium alkoxide and **2** afforded the corresponding esters in good to high yields with perfect inversion of stereochemistry by S_N2 replacement of (L)-(−)-menthol. Similarly, the esterification of **6a** and benzoic acids having electron-donating or electron-withdrawing groups at *p*-positions, such as *p*-nitrobenzoic acid or *p*-methoxybenzoic acid proceeded smoothly to afford the corresponding esters in 86–88% yields under mild conditions within 1–3 h (Table 20, entries 2 and 6–7). The esterification of benzoic acids having electron-donating or electron-withdrawing groups at *o*-position or *m*-position, such as *o*-nitrobenzoic acid, *m*-nitrobenzoic acid, or *o*-methoxybenzoic acid, proceeded to afford the corresponding esters in 53–54% yields after having been allowed to react for 3 h at room temperature (Table 20, entries 1, 3, and 5). On the other hand, the desired ester was obtained in 86% yield when the alkoxydiphenylphosphine, formed from 1.5 equivalents each of lithium salt of (L)-(−)-menthol and **2**, with *m*-nitrobenzoic acid (Table 20, entry 4).

Interestingly, the desired ester **21a** was obtained in 73% yield by treating DMBQ and the above-mentioned crude al-

Table 21. Screening of Esterification of **6a** with Tertiary Alcohols **19a**



Entry	**20a**/equiv.	DMBQ/equiv.	Temp.	Time/h	Yield/%
1	1.1	1.0	rt	12	73
2	1.2	1.0	rt	7	78
3	1.2	1.0	rt	15	81
4	1.5	1.0	rt	15	81
5	1.2	1.1	rt	15	82
6	1.1	1.0	reflux	3	64
7	1.2	1.0	reflux	3	68

koxydiphenylphosphine **20a** with acid **6a** at room temperature for 12 h (Table 21, entry 1). The reaction condition was further screened in order to improve the chemical yield (73%) shown in Table 21. The ester **21a** was obtained in 81% yield when 1.2 equivalents of **20a** and 1.0 equivalent of DMBQ were treated with **6a** at room temperature for 15 h (Table 21, entry 3).

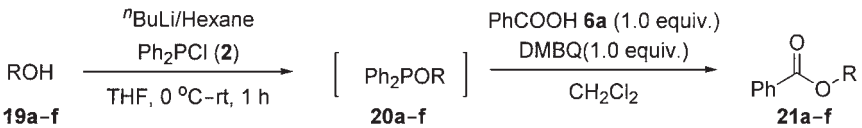
Next, the esterification of various in situ formed tertiary alkoxydiphenylphosphines with **6a** was examined under the above conditions (Tables 22). Alkylation of **6a** with various bulky tertiary alcohols proceeded smoothly to afford the corresponding alkyl esters in good yields under the conditions shown in Table 22.

Esterifications of various in situ-formed tertiary alkoxydiphenylphosphines with various carboxylic acids were tried under the previously mentioned conditions (Table 23). Esterifications of various aliphatic carboxylic acids smoothly proceeded to afford the corresponding carboxylic acid bulky alkyl esters in good yields when various bulky tertiary alcohols were used (Table 23, entries 1–4). When an unsaturated aliphatic carboxylic acid was used, the corresponding ester was also obtained in high yield (Table 23, entry 5). Similarly, the desired products were obtained in high yields by the reactions between carboxylic acids having a chlorine atom at α-position, such as chloroacetic acid, secondary and tertiary carboxylic acids (Table 23, entry 6).

Thus, an effective one-pot esterification of various carboxylic acids was established via a new-type of oxidation–reduction condensation by using a combination of DMBQ and primary, secondary, or bulky tertiary in situ formed alkoxydiphenylphosphines by adding **2** to the ^{n}BuLi-treated alcohols.

According to this one-pot procedure, secondary or tertiary alcohols gave the corresponding alkoxydiphenylphosphines smoothly and the desired ethers were also afforded in good yields on treatment with *p*-nitrophenol (Table 24).

Table 22. Esterification of **6a** Using Various Bulky Tertiary Alcohols



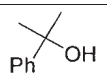
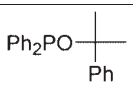
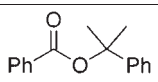
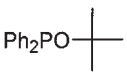
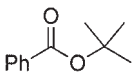
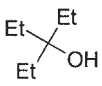
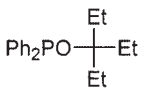
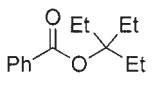
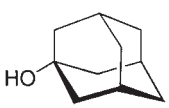
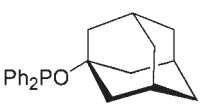
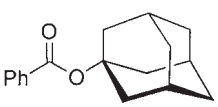
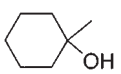
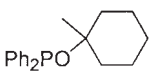
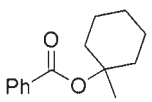
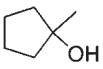
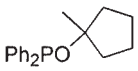
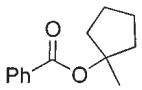
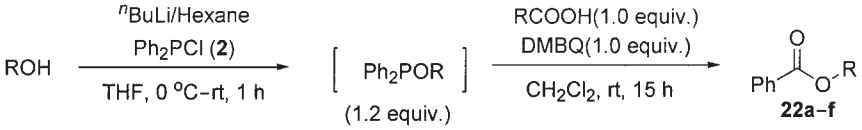
Entry	ROH	Ph_2POR/equiv.		Product	Condition	Yield/%
1	 **19a**	 **20a**	1.2	 **21a**	rt, 15 h	81
2	 **19b**	 **20b (1g)**	1.2	 **21b (8e)**	rt, 15 h reflux, 6 h	69 79
3	 **19c**	 **20c**	1.2	 **21c**	rt, 15 h reflux, 6 h	69 72
4	 **19d**	 **20d**	1.2	 **21d**	reflux, 15 h	83
5	 **19e**	 **20e**	1.2 1.5	 **21e**	rt, 15 h reflux, 3 h reflux, 3 h	23 51 78
6	 **19f**	 **20f**	1.2	 **21f**	rt, 15 h	82

Table 23. Esterifications of Various Carboxylic Acids Using Various Bulky Tertiary Alcohols



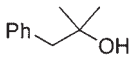
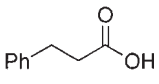
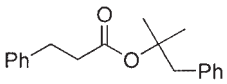
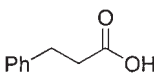
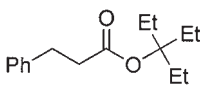
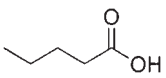
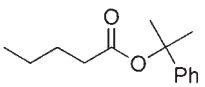
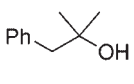
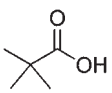
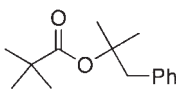
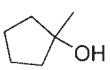
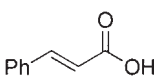
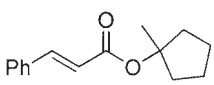
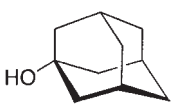
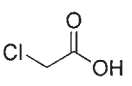
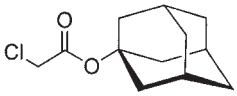
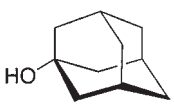
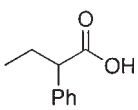
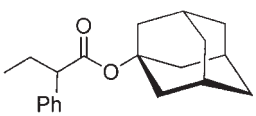
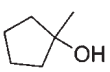
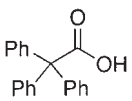
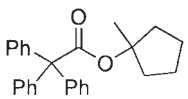
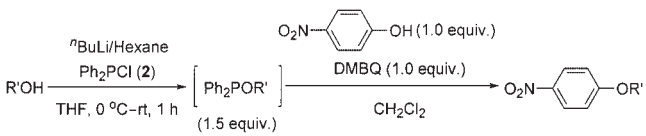
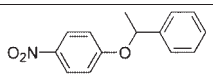
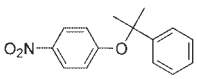
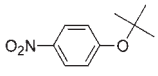
Entry	ROH	Ph_2POR	RCOOH	Product	Yield/%
1	 **19g**	**20g**	 **6e**	 **22a**	82
2	 **19c**	**20c**	 **6e**	 **22b**	76
3	 **19a**	**20a**	 **6m**	 **22c**	85
4	 **19g**	**20g**	 **6g**	 **22d**	85
5	 **19f**	**20f**	 **6n**	 **22e**	92
6	 **19d**	**20d**	 **6k**	 **22f**	94
7	 **19d**	**20d**	 **6o**	 **22g**	96
8	 **19f**	**20f**	 **6p**	 **22h**	91

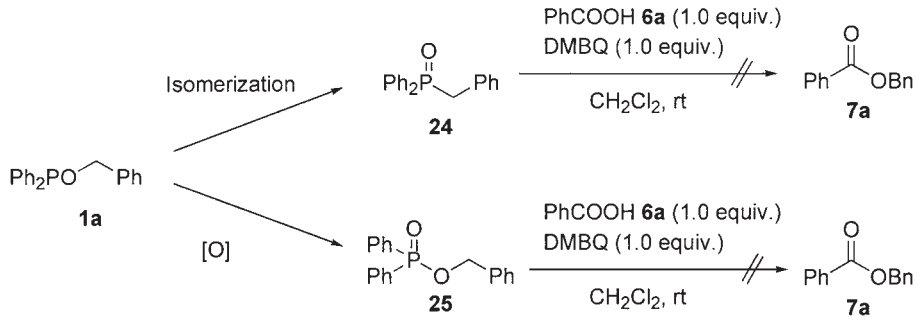
Table 24. Alkylation of *p*-Nitrophenol Using ^{n}BuLi and Several Alcohols



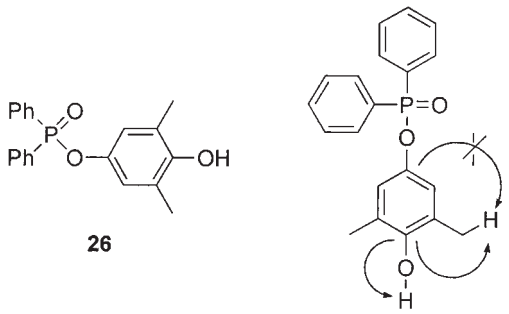
Entry	R′OH	Condition	Product	Yield/%
1		rt, 1 h	 **23a**	71
2		reflux, 3 h	 **23b**	70
3	^{t}BuOH	reflux, 12 h	 **11e**	72

Mechanism for a New-Type of Oxidation–Reduction Condensation Using 2,6-Dimethyl-1,4-benzoquinone and Alkoxydiphenylphosphines. It is considered that **1a** may be isomerized to benzyldiphenylphosphine oxide (**24**) or be oxidized to benzyloxydiphenylphosphine oxide (**25**). Since thus formed compounds were thought to work as reactive species, esterification of **6a** with **24** or **25** under the present conditions was tried (Scheme 6). However, the product **7a** was not detected. Thus, it was made clear that alkoxydiphenylphosphines behaved as important reaction species of the present reaction.

On the other hand, esterification of **6a** also proceeded to afford the desired ester along with diphenylphosphinic acid 4-hydroxy-3,5-dimethylphenyl ester (**26**) and its structure was determined by the correlation of HMBC (Scheme 7).



Scheme 6.

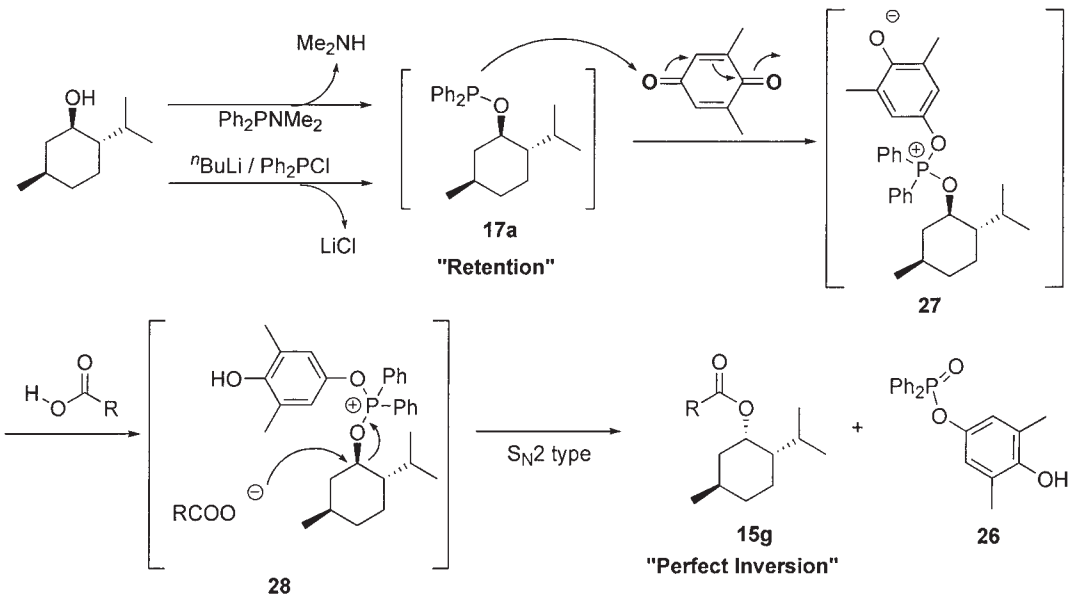


Scheme 7.

Based on the above result, a proposed reaction mechanism of a new-type of oxidation–reduction condensation by combined use of carboxylic acid, DMBQ and (L)-(−)-menthol is shown in Scheme 8. Menthoxydiphenylphosphine (**17a**) was prepared in situ with retention of stereochemistry from **3a** and (L)-(−)-menthol or by adding **2** to the ^{n}BuLi-treated (L)-(−)-menthol. Phosphine **17a** was assumed to react with DMBQ to form intermediate phosphonium salt (**27**), which then transformed to the phosphonium carboxylate by the interaction with carboxylic acid. Intramolecular attack of the carboxylate anion of an intermediate (**28**) to the neighboring carbon of oxygen atom of oxygen–phosphorus bond afforded the corresponding carboxylic acid ester (**15g**) with perfect inversion of stereochemistry by S_N2 replacement along with **26**.

Conclusion

A new and efficient method for the preparations of carboxylic acid alkyl esters or alkyl phenyl ethers from various primary, secondary and tertiary alcohols and carboxylic acids or phenols was established. The corresponding carboxylic acid esters or alkyl phenyl ethers were afforded in good to high yields by way of a new-type of oxidation–reduction condensation using alkoxydiphenylphosphines having a primary, bulky secondary, or tertiary alkoxy group, a mild quinone type oxidant such as DMBQ, and carboxylic acids or phenols. Generally, alkoxydiphenylphosphines were prepared easily from chlorodiphenylphosphine and alcohols in the presence of pyridine, and were isolated by distillation (Scheme 2, Path A). On the other hand, the phosphines **1** were also prepared in situ from *N*,*N*-dimethylaminodiphenylphosphine and primary or secondary alcohols (Scheme 2, Path B) while primary, bulky secondary, or tertiary alkoxydiphenylphosphines were alternatively formed in situ by adding Ph_2PCl to the ^{n}BuLi-treated alcohols (Scheme 2, Path C) in order to perform the above reactions by one-pot procedures from alcohols and nucleophiles.



Scheme 8.

The reaction of thus formed **1**, DMBQ and carboxylic acids or phenols afforded the corresponding alkylated products including hindered tertiary alkylated ones, in good to high yields at room temperature. In the case of using chiral secondary alcohols, the corresponding carboxylic acid alkyl esters were obtained in high yields as well, with perfect inversion of stereochemistry by S_N2 replacement.

Experimental

General. All melting points were determined on a Yanagimoto micro melting point apparatus (Yanaco MP-S3) and are not corrected. Infrared (IR) spectra were recorded on a Nicolet AVATAR360. ^{1}H NMR spectra were recorded on a JEOL JNM EX270L (270 MHz) spectrometer; chemical shifts (δ) are reported in parts per million relative to tetramethylsilane. Splitting patterns are designated as s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad. ^{13}C NMR spectra were recorded on EX270L (68 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in parts per million relative to tetramethylsilane with the solvent resonance as the internal standard ($CDCl_3$; δ77.0 ppm). High resolution mass spectra (HRMS) were recorded on a JEOL LCmate. MS spectra were recorded on a JEOL DX-303HF. The polarimeter used was JASCO P-1020. Analytical high performance liquid chromatography (HPLC) was performed on a Hitachi LC-Organizer (L-4000 UV Detector, L-6200 Intelligent Pump, and D-2500 Chromato-Integrator) equipped with a chiral column (ϕ 4.6 × 250 mm). Analytical TLC was performed on Merck preparative TLC plates (silica gel 60 GF254, 0.25 mm). Column chromatography was carried out on Merck silica gel 60 (0.063–0.200 mm). Preparative thin-layer chromatography (PTLC) was carried out on silica gel Wakogel B-5F. Dry solvents were prepared by distillation under appropriate drying agents. Carboxylic acids were purified by recrystallization.

Benzyloxydiphenylphosphine (1a).[18] To a stirred solution of benzyl alcohol (6.5 g, 60 mmol) and pyridine (4.8 g, 60 mmol) in Et_2O (60 mL) under argon atmosphere was added **2** (13.2 g, 60 mmol) at 0 °C. After the reaction mixture was stirred at room temperature for 1 h, it was filtered and concentrated in vacuo. The resulted residue was purified by distillation under reduced pressure to afford the title compound (**1a**) (9.6 g, 55%) as a colorless oil: bp 155–157 °C/0.2 Pa; IR (ATR, cm^{-1}) 982, 735; ^{1}H NMR (270 MHz, $CDCl_3$) δ7.54–7.47 (m, 4H), 7.37–7.27 (m, 11H), 4.89 (d, J = 9.2 Hz, 2H); ^{13}C NMR (68 MHz, $CDCl_3$) δ141.7, 141.4, 130.5, 130.2, 129.2, 128.3 (d, J = 6.7 Hz), 127.6, 127.4, 71.6 (d, J = 20.1 Hz); MS (APCI$^+$) m/z 293 $[M + H]^+$.

Methoxydiphenylphosphine (1b)[19] **and Ethoxydiphenylphosphine (1c).**[19] These reagents were purchased from Tokyo Kasei Kogyo Co., Ltd., and were used without further purification.

***n*-Butoxydiphenylphosphine (1d).**[19] Isolated as a colorless oil (yield 45%): bp 100–103 °C/0.3 Pa; ^{1}H NMR (270 MHz, $CDCl_3$) δ7.51–7.45 (m, 4H), 7.34–7.27 (m, 6H), 3.88–3.80 (m, 2H), 1.69–1.61 (m, 2H), 1.43–1.35 (m, 2H), 0.89 (t, J = 7.4 Hz, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ142.1 (d, J = 17.9 Hz), 130.1 (d, J = 21.8 Hz), 129.0, 128.1 (d, J = 7.3 Hz), 69.9 (d, J = 19.0 Hz), 33.6 (d, J = 7.8 Hz), 19.1, 13.9.

Isopropoxydiphenylphosphine (1e).[19] Isolated as a colorless oil (yield 52%): bp 98–99 °C/0.8 Pa; ^{1}H NMR (270 MHz, $CDCl_3$) δ7.51–7.45 (m, 4H), 7.36–7.30 (m, 6H), 4.22–4.15 (m, 1H), 1.39 (d, J = 6.2 Hz, 6H); ^{13}C NMR (68 MHz, $CDCl_3$) δ142.8 (d, J = 16.8 Hz), 130.0 (d, J = 21.2 Hz), 128.8, 128.1 (d, J = 6.7 Hz), 73.7 (d, J = 21.2 Hz), 24.4 (d, J = 5.6 Hz).

***s*-Butoxydiphenylphosphine (1f).**[20] Isolated as a colorless oil (yield 45%): bp 100–103 °C/0.6 Pa; ^{1}H NMR (270 MHz, $CDCl_3$) δ7.51–7.46 (m, 4H), 7.33–7.26 (m, 6H), 4.02–3.92 (m, 1H), 1.75–1.51 (m, 2H), 1.26 (d, J = 5.9 Hz, 3H), 0.89 (t, J = 7.6 Hz, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ143.1 (d, J = 17.3 Hz), 142.7 (d, J = 16.3 Hz), 130.3, 129.9 (d, J = 6.1 Hz), 128.8, 128.7, 128.1 (d, J = 7.3 Hz), 79.0, 78.7, 31.2 (d, J = 5.6 Hz), 21.8 (d, J = 5.5 Hz), 10.0.

Benzyloxydiisopropylphosphine (1h). To a stirred solution of benzyl alcohol (6.5 g, 60 mmol) and pyridine (4.8 g, 60 mmol) in Et_2O (60 mL) under argon atmosphere was added chlorodiisopropylphosphine (9.2 g, 60 mmol) at 0 °C. After the reaction mixture was stirred at room temperature for 1 h, it was filtered, and then concentrated in vacuo. The resulted residue was purified by distillation under reduced pressure to afford the title compound (**1h**) (9.4 g, 70%) as a colorless oil: bp 110 °C/5.0 Pa; ^{1}H NMR (270 MHz, $CDCl_3$) δ7.38–7.34 (m, 5H), 5.08 (d, J = 6.8 Hz, 2H), 2.10–1.98 (m, 2H), 1.23–1.12 (m, 12H); ^{13}C NMR (68 MHz, $CDCl_3$) δ137.1, 128.4 (d, J = 13.4 Hz), 127.9 (d, J = 5.6 Hz), 127.6, 66.2 (d, J = 6.7 Hz), 26.6, 25.3, 15.8 (d, J = 3.9 Hz), 15.6 (d, J = 2.9 Hz).

Benzyloxydicyclohexylphosphine (1i). To a stirred solution of benzyl alcohol (6.5 g, 60 mmol) and pyridine (4.8 g, 60 mmol) in Et_2O (60 mL) was added chlorodicyclohexylphosphine (14.0 g, 60 mmol) at 0 °C. After the reaction mixture was stirred at room temperature for 1 h, it was filtered and concentrated in vacuo. The resulted residue was purified by distillation under reduced pressure to afford the title compound (**1i**) (8.0 g, 44%) as a colorless oil: bp 163 °C/2.0 Pa; ^{1}H NMR (270 MHz, $CDCl_3$) δ7.36–7.33 (m, 5H), 5.05 (d, J = 7.0 Hz, 2H), 1.93–1.69 (m, 11H), 1.40–1.21 (m, 11H); ^{13}C NMR (68 MHz, $CDCl_3$) δ137.2 (d, J = 5.6 Hz), 128.2, 127.7 (d, J = 21.8 Hz), 66.1 (d, J = 47.1 Hz), 36.7, 35.4, 26.3 (d, J = 13.5 Hz), 25.8, 25.3 (d, J = 3.3 Hz).

***t*-Butoxydiphenylphosphine (1g).**[19] To a stirred suspension of potassium *tert*-butoxide (5.6 g, 50 mmol) in Et_2O (10 mL) under argon atmosphere was added a Et_2O (20 mL) solution of **2** (11.0 g, 50 mmol) at 0 °C. After the reaction mixture was stirred at room temperature for 1 h, it was filtered, and concentrated in vacuo. The resulted residue was purified by distillation under reduced pressure to afford the title compound (**10g**) (4.0 g, 31%) as a colorless oil: bp 105–106 °C/0.7 Pa; IR (ATR, cm^{-1}) 2970, 931, 738; ^{1}H NMR (270 MHz, $CDCl_3$) δ7.51–7.46 (m, 4H), 7.31–7.28 (m, 6H), 1.40 (s, 9H); ^{13}C NMR (68 MHz, $CDCl_3$) δ143.6 (d, J = 15.6 Hz), 129.9 (d, J = 21.8 Hz), 128.5, 128.1 (d, J = 6.7 Hz), 76.7 (d, J = 12.3 Hz), 30.2 (d, J = 8.4 Hz); MS (FAB$^+$) m/z 259 $[M + H]^+$.

***N*,*N*-Dimethylaminodiphenylphosphine (3a).**[21] Through a stirred solution of **2** (6.6 g, 30 mmol) in benzene (40 mL) under argon atmosphere, dimethylamine gas was bubbled for 45 minutes at 0 °C. After the reaction mixture was stirred at room temperature for 1 h, it was filtered and concentrated in vacuo. The resulted residue was purified by distillation under reduced pressure to afford the title compound (**3a**) (6.0 g, 87%) as a colorless oil: bp 129 °C/0.7 Pa (lit.[21a] bp 106 °C/0.2 Torr); IR (ATR, cm^{-1}) 1053, 960, 744; ^{1}H NMR (270 MHz, $CDCl_3$) δ7.40–7.32 (m, 10H), 2.63 (d, J = 9.7 Hz, 6H); ^{13}C NMR (68 MHz, $CDCl_3$) δ138.6 (d, J = 15.2 Hz), 131.9 (d, J = 19.0 Hz), 128.2, 128.0 (d, J = 5.6 Hz), 41.8 (d, J = 14.6 Hz); MS (FAB$^+$) m/z 229 $[M]^+$.

***N*,*N*-Diethylaminodiphenylphosphine (3b).**[12a] To a stirred solution of **2** (6.6 g, 30 mmol) in benzene (70 mL) under argon atmosphere was added diethylamine (5.1 g, 75 mmol) at 0 °C. Af-

ter the reaction mixture was stirred at room temperature for 1 h, it was filtered and concentrated in vacuo. The resulted residue was purified by distillation under reduced pressure to afford the title compound (**3b**) (6.3 g, 82%) as a colorless oil: bp 122 °C/1.0 Pa (lit.[12a] bp 138 °C/0.3 Torr); IR (ATR, cm^{-1}) 1021, 742; ^1H NMR (270 MHz, $CDCl_3$) δ7.44–7.30 (m, 10H), 3.13–3.02 (m, 4H), 0.95 (t, $J = 7.0$ Hz, 6H); ^{13}C NMR (68 MHz, $CDCl_3$) δ140.2 (d, $J = 14.5$ Hz), 131.9 (d, $J = 19.5$ Hz), 128.0, 127.9 (d, $J = 5.6$ Hz), 44.4 (d, $J = 15.6$ Hz), 14.6 (d, $J = 3.4$ Hz); MS (FAB$^+$) m/z 257 $[M]^+$.

1-(Diphenylphosphonio)pyrrolidine (3c).[12a] Isolated as a colorless oil (yield 53%): bp 128 °C/1.0 Pa (lit.[11a] bprttf 156–160 °C/0.9 Torr); IR (ATR, cm^{-1}) 1063, 1001; ^1H NMR (270 MHz, $CDCl_3$) δ7.38–7.29 (m, 10H), 3.03–3.02 (m, 4H), 1.76–1.72 (m, 4H); ^{13}C NMR (68 MHz, $CDCl_3$) δ139.0 (d, $J = 12.3$ Hz), 132.0 (d, $J = 19.6$ Hz), 128.1, 127.9 (d, $J = 6.1$ Hz), 49.6 (d, $J = 12.3$ Hz), 26.4 (d, $J = 5.6$ Hz); MS (FAB$^+$) m/z 255 $[M]^+$.

(Phenylamino)diphenylphosphine (3d).[12b] Isolated as a white solid (yield 56%): mp 59–61 °C (lit.[12c] mp 69–71 °C); IR (ATR, cm^{-1}) 888, 738; ^1H NMR (270 MHz, $CDCl_3$) δ7.48–7.34 (m, 10H), 7.24–7.16 (m, 2H), 7.02–6.99 (m, 2H) 6.84–6.78 (m, 1H), 4.38 (d, $J = 7.8$ Hz, 1H); ^{13}C NMR (68 MHz, $CDCl_3$) δ146.4 (d, $J = 17.3$ Hz), 140.0 (d, $J = 11.7$ Hz), 131.1 (d, $J = 20.7$ Hz), 129.2 (d, $J = 1.7$ Hz), 129.0, 128.5 (d, $J = 6.7$ Hz), 119.3, 115.8 (d, $J = 12.9$ Hz); MS (FAB$^+$) m/z 277 $[M]^+$.

1-(Diphenylphosphonio)pyrrolidin-2-one (3e).[13] 1-(Trimethylsilyl)-2-pyrrolidinone (4.7 g, 30 mmol) was dropped into **2** (6.6 g, 30 mmol) at 0 °C under argon atmosphere. After the reaction mixture was stirred at room temperature for 1 h, chlorotrimethylsilane (TMSCl) was removed in vacuo. The resulted residue was purified by recrystallization from benzene to afford the title compound (**3e**) (6.1 g, 76%) as a white solid: mp 123–125 °C (lit.[13] mp 129–132 °C); IR (ATR, cm^{-1}) 1691, 1119, 742; ^1H NMR (270 MHz, $CDCl_3$) δ7.40–7.35 (m, 10H), 3.17 (t, $J = 7.0$ Hz, 2H), 2.51 (t, $J = 8.1$ Hz, 2H), 2.08–1.97 (m, 2H); ^{13}C NMR (68 MHz, $CDCl_3$) δ132.3 (d, $J = 21.3$ Hz), 129.4, 128.5 (d, $J = 6.2$ Hz), 128.2, 46.3 (d, $J = 8.9$ Hz), 32.2, 20.3; MS (FAB$^+$) m/z 269 $[M + H]^+$.

Typical Experimental Procedure for Esterification of Various Carboxylic Acids by Using a Combination of 2,6-Dimethyl-1,4-benzoquinone and Alkoxydiphenylphosphines (Tables 4 and 5). To a mixture of carboxylic acid (0.60 mmol) and DMBQ (0.60 mmol) under argon atmosphere was added a solution of alkoxydiphenylphosphine (0.66 mmol) in dichloromethane (0.50 mL) at room temperature. The reaction mixture was stirred for 0.5 h at room temperature. After the reaction that was monitored by TLC was completed, the reaction mixture was quenched by adding water and the aqueous layer was extracted with dichloromethane. The combined organic layer was dried over anhydrous sodium sulfate. After filtration and evaporation, the resulted residue was purified by preparative TLC to afford the corresponding carboxylic esters.

Benzyl Benzoate (7a).[22] Colorless oil; IR (ATR, cm^{-1}) 1715, 1265, 1105, 736; ^1H NMR (270 MHz, $CDCl_3$) δ8.10–8.06 (m, 2H), 7.59–7.53 (m, 1H), 7.46–7.33 (m, 7H), 5.37 (s, 2H); ^{13}C NMR (68 MHz, $CDCl_3$) δ166.3, 135.9, 132.9, 130.0, 129.6, 128.5, 128.3, 128.1, 128.0, 66.7; MS (EI$^+$) m/z 212 $[M]^+$.

Benzyl 4-Methylbenzoate (7b).[23] Colorless oil; IR (ATR, cm^{-1}) 1702, 1264, 1097, 750; ^1H NMR (270 MHz, $CDCl_3$) δ7.98–7.95 (m, 2H), 7.45–7.32 (m, 5H), 7.25–7.21 (m, 2H), 5.35 (s, 2H), 3.40 (s, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ166.3, 143.6, 136.1, 129.6, 129.0, 128.5, 128.1, 128.0, 127.3, 66.5, 21.7; MS (EI$^+$) m/z 226 $[M]^+$.

Benzyl 4-Methoxybenzoate (7c).[24] Colorless oil; IR (ATR, cm^{-1}) 1709, 1604, 1250, 1165, 1097, 768; ^1H NMR (270 MHz, $CDCl_3$) δ8.04–8.01 (m, 2H), 7.45–7.32 (m, 5H), 6.92–6.89 (m, 2H), 5.33 (s, 2H), 3.85 (s, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ166.0, 163.3, 136.2, 131.6, 128.4, 128.0 (×2), 122.4, 113.5, 66.4, 55.4; MS (EI$^+$) m/z 242 $[M]^+$.

Benzyl 4-Nitrobenzoate (7d).[25] Yellow solid; mp 79–81 °C (lit.[25] mp 83–84 °C); IR (ATR, cm^{-1}) 1710, 1519, 1271, 743; ^1H NMR (270 MHz, $CDCl_3$) δ8.21–8.30 (m, 4H), 7.47–7.36 (m, 5H) 5.40 (s, 2H); ^{13}C NMR (68 MHz, $CDCl_3$) δ164.4, 135.4, 135.1, 130.7, 128.6, 128.5, 128.3, 123.4, 67.7; MS (EI$^+$) m/z 257 $[M]^+$.

Benzyl 3-Phenylpropionate (7e).[26] Colorless oil; IR (ATR, cm^{-1}) 1732, 1147, 745; ^1H NMR (270 MHz, $CDCl_3$) δ7.33–7.16 (m, 10H), 5.11 (s, 2H), 2.97 (t, $J = 7.7$ Hz, 2H), 2.68 (t, $J = 7.7$ Hz, 2H); ^{13}C NMR (68 MHz, $CDCl_3$) δ168.8, 140.3, 135.8, 133.9, 128.4 (×2), 128.2, 128.1, 126.2, 66.3, 36.0, 31.0; MS (EI$^+$) m/z 240 $[M]^+$.

Benzyl Propionate (7f).[27] Colorless oil; IR (ATR, cm^{-1}) 1735, 1170, 737; ^1H NMR (270 MHz, $CDCl_3$) δ7.38–7.31 (m, 5H), 5.11 (s, 2H), 2.38 (q, $J = 7.6$ Hz, 2H), 1.16 (t, $J = 7.6$ Hz, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ174.1, 136.0, 128.4, 128.0, 66.1, 27.7, 9.2; MS (EI$^+$) m/z 164 $[M]^+$.

Benzyl Trimethylacetate (7g).[27,28] Colorless oil; IR (ATR, cm^{-1}) 1729, 1142, 735; ^1H NMR (270 MHz, $CDCl_3$) δ7.38–7.27 (m, 5H), 5.10 (s, 2H), 1.23 (s, 9H); ^{13}C NMR (68 MHz, $CDCl_3$) δ178.1, 136.3, 128.3, 127.5, 66.0, 38.8, 27.2; MS (EI$^+$) m/z 192 $[M]^+$.

Benzyl Tetrahydrofuran-2-carboxylate (7h).[29] Yellow oil; IR (ATR, cm^{-1}) 1746, 1169, 1083, 738; ^1H NMR (270 MHz, $CDCl_3$) δ7.35 (s, 5H), 5.17 (s, 2H), 4.52–4.47 (m, 1H), 4.06–3.87 (m, 2H), 2.31–2.20 (m, 1H), 2.07–1.88 (m, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ173.0, 135.5, 128.4, 128.1, 128.0, 76.6, 69.3, 66.5, 30.2, 25.2; MS (EI$^+$) m/z 206 $[M]^+$.

***N*-*t*-Butoxycarbonyl-L-valine Benzyl Ester (7i).**[30] Colorless oil; $[\alpha]_D^{20} = -33.4$ (*c* 1.11, MeOH) (lit.[30b] $[\alpha]_D = -33.3$ (*c* 2, MeOH)); IR (ATR, cm^{-1}) 1711, 1498, 1366, 1243, 1154, 734; ^1H NMR (270 MHz, $CDCl_3$) δ7.35 (m, 5H), 5.16 (q, $J = 11.5$ Hz, 2H), 5.10–5.02 (m, 1H), 4.28 (m, 1H), 2.14–2.04 (m, 1H) 1.44 (s, 9H) 0.94 (d, $J = 6.8$ Hz, 3H), 0.85 (d, $J = 7.0$ Hz, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ172.1, 155.5, 135.3, 128.4, 128.3, 128.2, 79.7, 66.9, 58.6, 31.4, 28.4, 19.1, 17.5; MS (EI$^+$) m/z 307 $[M]^+$; HPLC analysis: DAICEL CHIRALPAK AF (ϕ 4.6 × 250 mm), hexane/isopropyl alcohol = 19/1, flow rate: 1.0 mL/min, Temp.: 25 °C, detector: 254 nm, *N*-*t*-butoxycarbonyl-L-valine benzyl ester (**7i**) ($t_R = 7.8$ min), *N*-*t*-butoxycarbonyl-D-valine benzyl ester (**7j**) ($t_R = 9.6$ min).

***N*-*t*-Butoxycarbonyl-D-valine Benzyl Ester (7j).**[30] Colorless oil; $[\alpha]_D^{20} = +32.1$ (*c* 1.08, MeOH); IR (ATR, cm^{-1}) 1709, 1497, 1366, 1243, 1153, 748; ^1H NMR (270 MHz, $CDCl_3$) δ7.35 (m, 5H), 5.16 (q, $J = 11.5$ Hz, 2H), 5.05–5.02 (m, 1H), 4.29–4.25 (m, 1H), 2.19–2.09 (m, 1H) 1.41 (s, 9H) 0.40 (d, $J = 7.0$ Hz, 3H), 0.85 (d, $J = 7.0$ Hz, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ172.1, 155.5, 135.3, 128.4, 128.2 (×2), 79.7, 66.8, 58.6, 31.3, 28.4, 19.0, 17.5; MS (EI$^+$) m/z 307 $[M]^+$.

Benzyl 2-Chloroacetate (7k).[27] Colorless oil; IR (ATR, cm^{-1}) 1752, 1163, 740; ^1H NMR (270 MHz, $CDCl_3$) δ7.37 (m, 5H), 5.22 (s, 2H), 4.10 (s, 2H); ^{13}C NMR (68 MHz, $CDCl_3$) δ166.9, 134.8, 128.5 (×2), 128.3, 67.8, 40.9; MS (FAB$^+$) m/z 149 $[M - Cl]^+$.

Benzyl 2,2,2-Trichloroacetate (7l).[27] Colorless oil; IR (ATR, cm^{-1}) 1763, 1222, 825; ^1H NMR (270 MHz, $CDCl_3$) δ7.44–7.32 (m, 5H), 5.36 (s, 2H); ^{13}C NMR (68 MHz, $CDCl_3$) δ161.7, 133.6, 128.9, 128.7, 128.4, 128.2, 70.7; MS (FAB$^+$) m/z 254 $[M + H]^+$.

Ethyl Benzoate (8a).[28,31a,31c] Colorless oil; IR (ATR, cm^{-1}) 1714, 1270, 1105; ^1H NMR (270 MHz, $CDCl_3$) δ8.06–8.03 (m, 2H), 7.54–7.40 (m, 3H), 4.38 (q, $J = 7.1$ Hz, 2H), 1.39 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ166.4, 132.6, 130.4, 129.4, 128.2, 60.9, 14.4; MS (EI$^+$) m/z 150 $[M]^+$.

Butyl Benzoate (8b).[22,31a,31c] Colorless oil; IR (ATR, cm^{-1}) 1716, 1270, 1107; ^1H NMR (270 MHz, $CDCl_3$) δ8.06–8.02 (m, 2H), 7.54–7.39 (m, 3H), 4.32 (t, $J = 6.6$ Hz, 2H), 1.78–1.72 (m, 2H), 1.52–1.44 (m, 2H), 0.98 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ166.5, 132.6, 130.4, 129.4, 128.1, 64.8, 30.8, 19.3, 13.8; MS (EI$^+$) m/z 178 $[M]^+$.

Isopropyl Benzoate (8c).[28,31b,31c] Colorless oil; IR (ATR, cm^{-1}) 1712, 1271, 1097; ^1H NMR (270 MHz, $CDCl_3$) δ8.06–8.02 (m, 2H), 7.56–7.39 (m, 3H), 5.30–5.21 (m, 1H), 1.37 (d, $J = 6.5$ Hz, 6H); ^{13}C NMR (68 MHz, $CDCl_3$) δ165.9, 132.5, 130.7, 129.3, 128.1, 68.3, 22.0; MS (EI$^+$) m/z 164 $[M]^+$.

1-Methylpropyl Benzoate (8d).[31c,32] Colorless oil; IR (ATR, cm^{-1}) 1713, 1265; ^1H NMR (270 MHz, $CDCl_3$) δ8.06–8.03 (m, 2H), 7.56–7.50 (m, 1H), 7.45–7.39 (m, 2H), 5.13–5.06 (m, 1H), 1.81–1.64 (m, 2H), 1.34 (d, $J = 6.2$ Hz, 3H) 0.97 (t, $J = 7.6$ Hz, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ166.0, 132.5, 130.8, 129.3, 128.1, 72.8, 29.0, 19.6, 9.8; MS (FAB$^+$) m/z 227 $[M + H]^+$.

***t*-Butyl Benzoate (8e).**[22,28,31a,31c] Colorless oil; IR (ATR, cm^{-1}) 1710, 1288, 1112; ^1H NMR (270 MHz, $CDCl_3$) δ8.01–7.97 (m, 2H), 7.55–7.38 (m, 3H), 1.60 (s, 9H); ^{13}C NMR (68 MHz, $CDCl_3$) δ165.6, 132.3, 131.9, 129.3, 128.0, 80.9, 28.3; MS (FAB$^+$) m/z 149 $[M - 2Me + H]^+$.

Ethyl 4-Methoxybenzoate (8f). Colorless oil; IR (ATR, cm^{-1}) 1707, 1605, 1250, 1166, 1099, 769; ^1H NMR (270 MHz, $CDCl_3$) δ8.01–7.98 (m, 2H), 6.92–6.89 (m, 2H), 4.34 (q, $J = 7.1$ Hz, 2H), 3.85 (s, 3H), 1.38 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ166.2, 163.0, 131.4, 122.8, 113.4, 60.6, 55.4, 14.4; MS (EI$^+$) m/z 180 $[M]^+$.

Butyl 4-Methoxybenzoate (8g).[31c] Colorless oil; IR (ATR, cm^{-1}) 1708, 1605, 1251, 1166, 1100, 769; ^1H NMR (270 MHz, $CDCl_3$) δ8.01–7.98 (m, 2H), 6.92–6.89 (m, 2H), 4.29 (t, $J = 6.6$ Hz, 2H), 3.84 (s, 3H), 1.79–1.68 (m, 2H), 1.51–1.43 (m, 2H), 0.97 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ166.2, 163.0, 131.3, 122.8, 113.4, 64.5, 56.3, 30.8, 19.3, 13.8; MS (EI$^+$) m/z 208 $[M]^+$.

Butyl 4-Nitrobenzoate (8h).[25] Colorless oil; IR (ATR, cm^{-1}) 1721, 1526, 1271, 1101; ^1H NMR (270 MHz, $CDCl_3$) δ8.30–8.19 (m, 4H), 4.39 (t, $J = 6.5$ Hz, 2H), 1.85–1.74 (m, 2H), 1.54–1.46 (m, 2H), 1.00 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ164.5, 150.2, 135.7, 130.5, 123.3, 65.7, 30.6, 19.2, 13.7; MS (EI$^+$) m/z 223 $[M]^+$.

Isopropyl 4-Nitrobenzoate (8i).[33] White solid; mp 104–106 °C (lit.[33b] mp 108.5 °C); IR (ATR, cm^{-1}) 1710, 1520, 1274, 1094; ^1H NMR (270 MHz, $CDCl_3$) δ8.30–8.19 (m, 4H), 5.32–5.27 (m, 1H), 1.41 (d, $J = 6.2$ Hz, 6H); ^{13}C NMR (68 MHz, $CDCl_3$) δ163.9, 150.2, 136.1, 130.5, 123.3, 69.7, 21.9; MS (EI$^+$) m/z 209 $[M]^+$.

Ethyl Pentanoate (8j). Colorless oil; IR (ATR, cm^{-1}) 1735, 1177; ^1H NMR (270 MHz, $CDCl_3$) δ4.12 (q, $J = 7.1$ Hz, 2H), 2.29 (t, $J = 7.6$ Hz, 2H), 1.66–1.55 (m, 2H), 1.42–1.33 (m, 2H), 1.25 (t, $J = 7.2$ Hz, 3H), 0.92 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ173.7, 60.1, 34.1, 27.1, 22.3, 14.3, 13.8; MS (EI$^+$) m/z 130 $[M]^+$.

Isopropyl Pentanoate (8k).[34] Colorless oil; IR (ATR, cm^{-1}) 1731, 1179, 1108; ^1H NMR (270 MHz, $CDCl_3$) δ5.05–4.96 (m, 1H), 2.26 (t, $J = 7.6$ Hz, 2H), 1.66–1.54 (m, 2H), 1.41–1.28 (m, 2H), 1.23 (t, $J = 6.2$ Hz, 6H), 0.92 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ173.2, 67.3, 34.5, 27.2, 22.3, 21.9, 13.8; MS (EI$^+$) m/z 129 $[M - CH_3]^+$.

Typical Experimental Procedure for Etherification of Phenols by Using a Combination of 2,6-Dimethyl-1,4-benzoquinone and Alkoxydiphenylphosphines (Tables 7 and 8). To a stirred solution of phenol (0.60 mmol) and DMBQ (0.60 mmol) in dichloromethane (0.25 mL) under argon atmosphere was added a solution of alkoxydiphenylphosphine (0.90 mmol) in dichloromethane (0.25 mL) at room temperature. The reaction mixture was stirred for 0.5 h at room temperature and was quenched with water after completion of the reaction (detected by TLC). The aqueous layer was extracted with dichloromethane and the combined organic layer was dried over anhydrous sodium sulfate. After filtration and evaporation, the resulted residue was purified by preparative TLC to afford the corresponding ethers.

Benzyl Phenyl Ether (10a).[35a,35b] White solid; mp 39–41 °C (lit.[35b] mp 39–40 °C); IR (ATR, cm^{-1}) 1234, 1011, 742; ^1H NMR (270 MHz, $CDCl_3$) δ7.45–7.24 (m, 7H), 6.99–6.93 (m, 3H), 5.06 (s, 2H); ^{13}C NMR (68 MHz, $CDCl_3$) δ158.6, 136.9, 129.4, 128.5, 127.8, 127.4, 120.8, 114.8, 69.9; MS (EI$^+$) m/z 184 $[M]^+$.

Benzyl 4-Methylphenyl Ether (10b).[36] White solid; mp 35–36 °C; IR (ATR, cm^{-1}) 1507, 1234, 1009, 806, 731; ^1H NMR (270 MHz, $CDCl_3$) δ7.42–7.28 (m, 5H), 7.08–7.05 (m, 2H), 6.87–6.84 (m, 2H), 5.01 (s, 2H), 2.27 (s, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ156.5, 137.1, 130.0, 129.8, 128.4, 127.7, 127.3, 114.6, 70.0, 20.5; MS (EI$^+$) m/z 198 $[M]^+$.

Benzyl 4-Methoxyphenyl Ether (10c).[35c,35d] White solid; mp 64–66 °C; IR (ATR, cm^{-1}) 1503, 1221, 1032, 824, 725; ^1H NMR (270 MHz, $CDCl_3$) δ7.42–7.29 (m, 5H), 6.92–6.80 (m, 4H), 4.99 (s, 2H), 3.74 (s, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ153.8, 152.8, 137.2, 128.4, 127.7, 127.3, 115.7, 114.5, 70.6, 55.7; MS (EI$^+$) m/z 214 $[M]^+$.

Benzyl 4-Nitrophenyl Ether (10d).[37] Yellow solid; mp 102–104 °C; IR (ATR, cm^{-1}) 1493, 1249, 1004, 840, 753; ^1H NMR (270 MHz, $CDCl_3$) δ8.22–8.18 (m, 2H), 7.42–7.36 (m, 5H), 7.04–7.01 (m, 2H), 5.16 (s, 2H); ^{13}C NMR (68 MHz, $CDCl_3$) δ163.5, 135.4, 133.2, 128.7, 128.4, 127.4, 125.8, 114.8, 70.7; MS (EI$^+$) m/z 229 $[M]^+$.

Benzyl 4-Chlorophenyl Ether (10e).[35b] Colorless solid; mp 65–67 °C; IR (ATR, cm^{-1}) 1487, 1243, 1041, 826, 731; ^1H NMR (270 MHz, $CDCl_3$) δ7.39–7.31 (m, 5H), 7.24–7.20 (m, 2H), 6.90–6.87 (m, 2H), 5.02 (s, 2H); ^{13}C NMR (68 MHz, $CDCl_3$) δ157.2, 136.5, 129.2, 128.5, 128.0, 127.3, 125.7, 116.1, 70.3; MS (EI$^+$) m/z 218 $[M]^+$.

Benzyl 2,6-Dimethylphenyl Ether (10f).[38] Colorless oil; IR (ATR, cm^{-1}) 1196, 767; ^1H NMR (270 MHz, $CDCl_3$) δ7.49–7.33 (m, 5H), 7.04–6.91 (m, 3H), 4.81 (s, 2H), 2.31 (s, 6H); ^{13}C NMR (68 MHz, $CDCl_3$) δ155.6, 137.6, 131.0, 128.8, 128.4, 127.8, 127.6, 128.8, 73.9, 16.5; MS (EI$^+$) m/z 212 $[M]^+$.

Benzyl 1-Naphthyl Ether (10g).[39a] Colorless oil; IR (ATR, cm^{-1}) 1267, 1096, 768; ^1H NMR (270 MHz, $CDCl_3$) δ8.36–8.32 (m, 1H), 7.80–7.77 (m, 1H), 7.53–7.32 (m, 9H), 6.88–6.85 (m, 1H), 5.23 (s, 2H); ^{13}C NMR (68 MHz, $CDCl_3$) δ154.3, 137.0, 134.4, 128.5, 127.8, 127.3, 127.2, 126.3, 125.7, 125.1, 122.1, 120.4, 105.1, 70.1; MS (EI$^+$) m/z 234 $[M]^+$.

Benzyl 2-Naphthyl Ether (10h).[39] White solid; mp 96–98 °C (lit.[39b] mp 99–100 °C); IR (ATR, cm^{-1}) 1018, 838, 743; ^1H NMR

(270 MHz, $CDCl_3$) δ7.77–7.70 (m, 3H), 7.49–7.30 (m, 7H), 7.23–7.21 (m, 2H), 5.17 (s, 2H); ^{13}C NMR (68 MHz, $CDCl_3$) δ156.6, 136.8, 134.4, 129.3, 129.0, 128.5, 127.9, 127.54, 127.47, 126.7, 126.3, 123.6, 119.0, 107.1, 70.0; MS (EI$^+$) m/z 234 [M]$^+$.

Methyl Phenyl Ether (11a). Colorless oil; ^{1}H NMR (270 MHz, $CDCl_3$) δ7.33–7.24 (m, 2H), 6.97–6.88 (m, 3H), 3.80 (s, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ159.3, 129.3, 120.5, 113.8, 55.1.

Ethyl Phenyl Ether (11b).[40] Colorless oil; IR (ATR, cm^{-1}) 1241, 1046, 750; ^{1}H NMR (270 MHz, $CDCl_3$) δ7.31–7.23 (m, 2H), 6.95–6.86 (m, 3H), 4.03 (q, $J = 7.0$ Hz, 2H), 1.41 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ158.7, 129.3, 120.4, 114.4, 63.3, 14.9; MS (EI$^+$) m/z 122 [M]$^+$.

Butyl Phenyl Ether (11c).[40] Colorless oil; IR (ATR, cm^{-1}) 1242, 751; ^{1}H NMR (270 MHz, $CDCl_3$) δ7.29–7.22 (m, 2H), 6.94–6.87 (m, 3H), 3.95 (t, $J = 6.4$ Hz, 2H), 1.81–1.71 (m, 2H), 1.56–1.42 (m, 2H) 0.97 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ158.9, 129.3, 120.3, 114.4, 67.5, 31.4, 19.3, 13.9; MS (EI$^+$) m/z 150 [M]$^+$.

Isopropyl Phenyl Ether (11d).[40] Colorless oil; IR (ATR, cm^{-1}) 1239, 1117, 750; ^{1}H NMR (270 MHz, $CDCl_3$) δ7.29–7.23 (m, 2H), 6.94–6.87 (m, 3H), 4.56–4.52 (m, 1H), 1.33 (d, $J =$ 6.2 Hz, 6H); ^{13}C NMR (68 MHz, $CDCl_3$) δ157.7, 129.3, 120.4, 115.8, 69.7, 22.1; MS (EI$^+$) m/z 136 [M]$^+$.

***t*-Butyl 4-Nitrophenyl Ether (11e).**[41] Yellow oil; IR (ATR, cm^{-1}) 1339, 1154; ^{1}H NMR (270 MHz, $CDCl_3$) δ8.18–8.14 (m, 2H), 7.07–7.03 (m, 2H), 1.46 (s, 9H); ^{13}C NMR (68 MHz, $CDCl_3$) δ161.7, 125.1, 121.6, 80.6, 28.9; MS (FAB$^+$) m/z 167 [M $-$ 2Me + H]$^+$.

Typical Experimental Procedure for One-Pot Esterification of Carboxylic Acids by a New-Type of Oxidation–Reduction Condensation Using 2,6-Dimethyl-1,4-benzoquinone and in situ-Formed Alkoxydiphenylphosphines from *N*,*N*-Dimethylaminodiphenylphosphine and Primary Alcohols (Tables 13 and 14). To a stirred solution of primary alcohol (0.66 mmol) in dichloromethane (0.4 mL) under argon atmosphere was added a solution of **3a** (0.66 mmol) in dichloromethane (0.4 mL) at room temperature. The reaction was stirred for 1 h at 40 °C and then the solvent was concentrated in vacuo. To the resulted residue was added a dichloromethane (0.7 mL) solution of carboxylic acid (0.60 mmol) and next a dichloromethane (0.8 mL) solution of DMBQ (0.60 mmol). The reaction was stirred for 1 h at room temperature and was quenched with water after completion of the reaction (detected by TLC). The aqueous layer was extracted with dichloromethane. The combined organic layer was washed with brine and dried over anhydrous sodium sulfate. After filtration and evaporation, the resulted residue was purified by preparative TLC to afford the corresponding esters.

Benzyl (*E*)-3-Phenyl-2-propenoate (7m).[27] Colorless oil; IR (ATR, cm^{-1}) 1704, 1154; ^{1}H NMR (270 MHz, $CDCl_3$) δ7.73 (d, $J = 15.9$ Hz, 1H), 7.53–7.50 (m, 2H), 7.41–7.33 (m, 8H), 6.49 (d, $J = 15.9$ Hz, 1H), 5.25 (s, 2H); ^{13}C NMR (68 MHz, $CDCl_3$) δ166.6, 145.1, 135.9, 134.2, 130.2, 128.8, 128.5, 128.2 (×2), 128.0, 117.8, 66.4; MS (FAB$^+$) m/z 239 [M + H]$^+$.

Benzyl Pentanoate (7n).[31a] Colorless oil; IR (ATR, cm^{-1}) 1734, 1163, 735; ^{1}H NMR (270 MHz, $CDCl_3$) δ7.36–7.30 (m, 5H), 5.11 (s, 2H), 2.35 (t, $J = 7.6$ Hz, 2H), 1.69–1.57 (m, 2H), 1.41–1.28 (m, 2H), 0.91 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ173.5, 136.0, 128.4 (×2), 128.0, 66.0, 34.1, 27.0, 22.3, 13.8; MS (EI$^+$) m/z 192 [M]$^+$.

4-Methoxybenzyl Benzoate (13b).[42] Colorless oil; IR (ATR, cm^{-1}) 1713, 1245, 1025; ^{1}H NMR (270 MHz, $CDCl_3$) δ8.07–8.04 (m, 2H), 7.57–7.51 (m, 1H), 7.44–7.37 (m, 4H), 6.93–6.89 (m, 2H), 5.30 (s, 2H), 3.81 (s, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ166.3, 159.5, 132.8, 130.1, 130.0, 129.6, 128.2, 128.1, 113.9, 66.5, 55.3; MS (FAB$^+$) m/z 242 [M]$^+$.

4-Nitrobenzyl Benzoate (13c).[43] White solid; mp 86–88 °C (lit.[43] mp 88.5 °C); IR (ATR, cm^{-1}) 2721, 1342, 1269, 1119; ^{1}H NMR (270 MHz, $CDCl_3$) δ8.26–8.23 (m, 2H), 8.10–8.07 (m, 2H), 7.62–7.57 (m, 3H), 7.50–7.44 (m, 2H), 5.46 (s, 2H); ^{13}C NMR (68 MHz, $CDCl_3$) δ165.9, 147.5, 143.2, 133.3, 129.6, 129.3, 128.4, 128.2, 123.7, 65.1; MS (FAB$^+$) m/z 258 [M + H]$^+$.

Phenethyl Benzoate (13d).[44] Colorless oil; IR (ATR, cm^{-1}) 1715, 1268, 1110; ^{1}H NMR (270 MHz, $CDCl_3$) δ8.02–7.99 (m, 2H), 7.57–7.23 (m, 8H), 4.53 (t, $J = 7.0$ Hz, 2H), 3.08 (t, $J = 6.9$ Hz, 2H); ^{13}C NMR (68 MHz, $CDCl_3$) δ166.3, 137.8, 132.8, 130.2, 129.4, 128.8, 128.4, 128.2, 126.5, 65.5, 35.3; MS (FAB$^+$) m/z 227 [M + H]$^+$.

2-Pyridylmethyl Benzoate (13f).[45] Colorless oil; IR (ATR, cm^{-1}) 1717, 1269, 1109; ^{1}H NMR (270 MHz, $CDCl_3$) δ8.63–8.61 (m, 1H), 8.14–8.10 (m, 2H), 7.75–7.69 (m, 1H), 7.61–7.55 (m, 1H), 7.48–7.43 (m, 3H), 7.27–7.22 (m, 1H), 5.49 (s, 2H); ^{13}C NMR (68 MHz, $CDCl_3$) δ166.0, 155.8, 149.3, 136.7, 133.1, 129.7, 128.3, 122.8, 121.6, 67.2; MS (FAB$^+$) m/z 214 [M + H]$^+$.

(*E*)-3,7-Dimethyl-2,6-octadienyl Benzoate (13g).[46] Colorless oil; IR (ATR, cm^{-1}) 1717, 1266, 1106; ^{1}H NMR (270 MHz, $CDCl_3$) δ8.08–8.03 (m, 2H), 7.58–7.51 (m, 1H), 7.45–7.39 (m, 2H), 5.47 (t, $J = 7.0$ Hz, 1H), 5.13–5.07 (m, 1H), 4.84 (d $J = 7.0$ Hz, 2H), 2.16–2.03 (m, 4H), 1.77 (s, 3H), 1.68 (s, 3H), 1.60 (s, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ166.5, 142.2, 132.7, 131.7, 129.5, 129.3, 123.6, 118.3, 61.9, 39.6, 26.3, 25.8, 17.8, 16.6; MS (FAB$^+$) m/z 259 [M + H]$^+$.

Typical Experimental Procedure for One-Pot Esterification of Carboxylic Acids by a New-Type of Oxidation–Reduction Condensation Using 2,6-Dimethyl-1,4-benzoquinone and in situ-Formed Alkoxydiphenylphosphines from *N*,*N*-Dimethylaminodiphenylphosphine and Secondary Alcohols (Table 16). Under argon atmosphere, a secondary alcohol (0.66 mmol) and **3a** (0.66 mmol) in 1,2-dichloroethane (0.6 mL) were stirred for 7.0 h at 100 °C. To a mixture of carboxylic acid (0.60 mmol) and DMBQ (0.6 mmol) was added the above reaction solution; then the reaction flask was washed by 1,2-dichloroethane (0.4 mL). The reaction was stirred for 1.0 h at room temperature and was quenched with water after completion of the reaction (detected by TLC). The aqueous layer was extracted with dichloromethane. The combined organic layer was washed with brine and dried over anhydrous sodium sulfate. After filtration and evaporation, the resulting residue was purified by preparative TLC to afford the corresponding esters.

Cyclohexyl Benzoate (15b).[47] Colorless oil; IR (ATR, cm^{-1}) 2935, 1712, 1273, 1110; ^{1}H NMR (270 MHz, $CDCl_3$) δ8.07–8.03 (m, 2H), 7.58–7.51 (m, 1H), 7.46–7.40 (m, 2H), 5.08–4.99 (m, 1H), 1.93–1.65 (m, 4H), 1.61–1.32 (m, 6H); ^{13}C NMR (68 MHz, $CDCl_3$) δ165.8, 132.5, 130.9, 129.4, 128.1, 73.0, 31.7, 25.6, 23.7; MS (FAB$^+$) m/z 205 [M + H]$^+$.

2,2-Dimethyl-1-phenylpropyl Benzoate (15c).[48] Colorless oil; IR (ATR, cm^{-1}) 1708, 1275, 1108; ^{1}H NMR (270 MHz, $CDCl_3$) δ8.12–8.10 (m, 2H), 7.56–7.27 (m, 8H), 5.72 (s, 1H), 1.03 (s, 9H); ^{13}C NMR (68 MHz, $CDCl_3$) δ165.4, 138.3, 132.8, 130.5, 129.5, 128.3, 127.6, 127.5, 127.4, 83.4, 35.4, 26.2; MS (FAB$^+$) m/z 269 [M + H]$^+$.

Benzhydryl Benzoate (15d).[49] White solid; mp 70–72 °C (lit.[49] mp 87–88 °C); IR (ATR, cm^{-1}) 1711, 1262, 1107, 749; ^{1}H NMR (270 MHz, $CDCl_3$) δ8.16–8.13 (m, 2H), 7.60–7.26 (m,

13H), 7.12 (s, 1H); ^{13}C NMR (68 MHz, $CDCl_3$) δ165.4, 140.1, 133.0, 130.1, 129.7, 128.4, 128.3, 127.8, 127.0, 77.4; MS (FAB$^+$) m/z 289 $[M + H]^+$.

(1*S*)-1-Phenylethyl Benzoate (15e).[50] Colorless oil; $[\alpha]_D^{25} = +26.6$ (c 1.10, EtOH) ($[\alpha]_D^{23} = +27.3$ (c 1.22, EtOH) Table 21, Entry 2), [lit.[50a] $[\alpha]_D^{25} = +20.9$ (c 2.78, EtOH)]; IR (ATR, cm^{-1}) 1713, 1264; ^{1}H NMR (270 MHz, $CDCl_3$) δ8.09–8.07 (m, 2H), 7.56–7.28 (m, 8H), 6.13 (q, $J = 6.5$ Hz, 1H), 1.67 (d, $J = 6.5$ Hz, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ165.6, 141.6, 132.8, 130.4, 129.5, 128.4, 128.2, 127.7, 125.9, 72.9, 22.5; MS (FAB$^+$) m/z 227 $[M + H]^+$; HPLC analysis: DAICEL CHIRALCEL OD (ϕ 4.6 × 250 mm), hexane/isopropyl alcohol = 1000/1, flow rate: 0.5 mL/min, Temp.: 25 °C, detector: 254 nm, (1*S*)-1-phenylethyl benzoate (**15e**) ($t_R = 34.4$ min), isomer authentic sample, (1*R*)-1-phenylethyl benzoate (**15e′**) ($t_R = 31.2$ min).

(1*R*)-1-Phenylethyl Benzoate (15e′).[50] Isomer authentic sample; Colorless oil; $[\alpha]_D^{25} = -28.7$ (c 1.02, EtOH); ^{1}H NMR (270 MHz, $CDCl_3$) δ8.10–8.06 (m, 2H), 7.58–7.23 (m, 8H), 6.13 (q, $J = 6.5$ Hz, 1H), 1.67 (d, $J = 6.5$ Hz, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ165.6, 141.6, 132.8, 130.4, 129.5, 128.4, 128.2, 127.7, 125.9, 72.9, 22.5.

(1*R*)-1-Methylpropyl Benzoate (15f).[51] Colorless oil; $[\alpha]_D^{21} = -35.3$ (c 1.10, $CHCl_3$); IR (ATR, cm^{-1}) 1713, 1269, 1096; ^{1}H NMR (270 MHz, $CDCl_3$) δ8.06–8.03 (m, 2H), 7.56–7.50 (m, 1H), 7.45–7.39 (m, 2H), 5.13–5.06 (m, 1H), 1.81–1.64 (m, 2H), 1.34 (d, $J = 6.2$ Hz, 3H) 0.97 (t, $J = 7.6$ Hz, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ166.0, 132.5, 130.8, 129.3, 128.1, 72.8, 29.0, 19.6, 9.8; MS (FAB$^+$) m/z 149 $[M - Et + H]^+$.

(1*S*)-1-Methylpropyl Benzoate (15f′).[51] Isomer authentic sample; Colorless oil; $[\alpha]_D^{22} = +34.6$ (c 1.16, $CHCl_3$); ^{1}H NMR (270 MHz, $CDCl_3$) δ8.07–8.03 (m, 2H), 7.57–7.51 (m, 1H), 7.46–7.40 (m, 2H), 5.13–5.06 (m, 1H), 1.78–1.64 (m, 2H), 1.34 (d, $J = 6.2$ Hz, 3H) 0.97 (t, $J = 7.6$ Hz, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ166.0, 132.6, 130.8, 129.4, 128.1, 72.8, 29.0, 19.6, 9.8.

(1*S*, 2*S*, 5*R*)-2-Isopropyl-5-methylcyclohexyl Benzoate (15g).[50b,52] Colorless oil; $[\alpha]_D^{23} = +92.0$ (c 1.16, C_6H_6), ($[\alpha]_D^{14} = +92.4$ (c 1.22, C_6H_6) Table 21, Entry 1); IR (ATR, cm^{-1}) 1713, 1268, 1111; ^{1}H NMR (270 MHz, $CDCl_3$) δ8.07–8.04 (m, 2H), 7.58–7.41 (m, 3H), 5.46 (s, 1H), 2.11–2.06 (m, 1H), 1.85–1.48 (m, 4H), 1.26–0.78 (m, 13H); ^{13}C NMR (68 MHz, $CDCl_3$) δ165.7, 132.6, 130.9, 129.4, 128.2, 71.7, 47.1, 39.3, 34.9, 29.5, 26.9, 25.5, 22.3, 21.1, 20.9; MS (FAB$^+$) m/z 261 $[M + H]^+$.

(1*R*, 2*S*, 5*R*)-2-Isopropyl-5-methylcyclohexyl Benzoate (15g′).[50b,52] Isomer authentic sample; Colorless oil; $[\alpha]_D^{24} = -93.5$ (c 1.23, C_6H_6); ^{1}H NMR (270 MHz, $CDCl_3$) δ8.06–8.03 (m, 2H), 7.57–7.40 (m, 3H), 4.94 (td, $J = 10.8, 3.9$ Hz, 1H), 2.15–2.11 (m, 1H), 2.03–1.50 (m, 5H), 1.21–0.78 (m, 12H); ^{13}C NMR (68 MHz, $CDCl_3$) δ165.9, 132.6, 130.7, 129.4, 128.2, 74.8, 47.3, 41.0, 34.4, 31.5, 26.5, 23.7, 22.1, 20.9, 16.6.

Phenyl 1-Phenylethyl Ether (15h).[53] Colorless oil; IR (ATR, cm^{-1}) 1419, 1235, 750; ^{1}H NMR (270 MHz, $CDCl_3$) δ7.38–7.15 (m, 7H), 6.88–6.84 (m, 3H), 5.30 (q, $J = 6.4$ Hz, 1H), 1.63 (d, $J = 6.4$ Hz, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ157.7, 143.1, 129.2, 128.5, 127.3, 125.4, 120.5, 115.8, 75.8, 24.6; MS (FAB$^+$) m/z 198 $[M]^+$.

Typical Experimental Procedure for One-Pot Esterification of Carboxylic Acids by a New-Type of Oxidation–Reduction Condensation Using 2,6-Dimethyl-1,4-benzoquinone and Primary, Secondary or Bulky Tertiary in situ-Formed Alkoxydiphenylphosphines by Adding Chlorodiphenylphosphine to ^{n}BuLi-treated Alcohols (Tables 18–23). Into a stirred solution of alcohol (5.0 mmol) in THF (18 mL) was dropped a hexane solution of ^{n}BuLi (5.0 mmol) at 0 °C under argon atmosphere. After the solution was stirred at room temperature for 1.0 h, **2** (5.0 mmol) was added at 0 °C. The reaction mixture was stirred for 1.0 h at room temperature and the solvent was concentrated in vacuo. Immediately, carboxylic acid, DMBQ, and dichloromethane were added to the residue and the mixture was stirred under the conditions shown in Tables 18–23. The same result was alternatively obtained by the following procedure: that is, after the above mentioned residue was diluted with a mixed solution of hexane (8 mL) and ethyl acetate (1 mL), lithium chloride was removed by filtration through celite (3.0 g) after passing it through alumina (activated, basic) (Wako Pure Chemical Industries, LTD) (20 g). The solvent was concentrated in vacuo, and crude alkoxydiphenylphosphine was obtained. To a mixture of carboxylic acid (0.60 mmol) and DMBQ (0.60 mmol) under argon atmosphere was added a dichloromethane (0.50 mL) solution of the above crude alkoxydiphenylphosphine under the conditions shown in Tables 18–23. After the reaction that was monitored by TLC was completed, the reaction mixture was quenched by adding water and the aqueous layer was extracted with dichloromethane. The combined organic layer was dried over anhydrous sodium sulfate. After filtration and evaporation, the resulting residue was purified by preparative TLC to afford the corresponding carboxylic esters.

***cis*-2-Phenylcyclohexyl Benzoate (15i).**[22] Colorless oil; IR (ATR, cm^{-1}) 2953–2842, 1699, 1254; ^{1}H NMR (270 MHz, $CDCl_3$) δ8.01–7.97 (m, 2H), 7.55–7.38 (m, 3H), 7.29–7.09 (m, 5H), 5.42 (s, 1H), 2.93–2.86 (m, 1H), 2.28–2.18 (m, 2H), 2.00–1.83 (m, 2H), 1.75–1.53 (m, 4H); ^{13}C NMR (68 MHz, $CDCl_3$) δ165.4, 143.0, 132.5, 130.7, 129.3, 128.2, 128.0, 127.6, 126.2, 73.9, 46.8, 30.9, 26.3, 26.1, 20.4; MS (FAB$^+$) m/z 281 $[M + H]^+$.

(*E*)-(3,7-Dimethyl-2,6-octadienyloxy)diphenylphosphine (16a). Colorless oil; IR (ATR, cm^{-1}) 1226, 1129, 956, 727; ^{1}H NMR (270 MHz, $CDCl_3$) δ7.86–7.78 (m, 4H), 7.54–7.32 (m, 6H), 5.43–5.38 (m, 1H), 5.06 (m, 1H), 4.58 (t, $J = 7.4$ Hz, 2H), 2.06–2.02 (m, 4H), 1.675 (s, 3H), 1.59 (s, 6H); ^{13}C NMR (68 MHz, $CDCl_3$) δ142.1, 131.9, 131.7, 131.5, 128.4, 128.2, 123.6, 119.2, 61.6, 39.5, 26.2, 25.8, 17.8, 16.5; HRMS (APCI$^+$) calcd for $C_{22}H_{28}OP$ $[M + H]^+$ 339.1878, found m/z 339.1876.

Menthoxydiphenylphosphine (17a). Colorless oil; IR (ATR, cm^{-1}) 1013, 988, 790, 739; ^{1}H NMR (270 MHz, $CDCl_3$) δ7.51–7.44 (m, 4H), 7.36–7.30 (m, 6H), 3.77–3.64 (m, 1H), 2.11–2.07 (m, 2H), 1.65–1.61 (m, 2H), 1.43–1.36 (m, 2H), 0.98–0.75 (m, 9H), 0.63 (d, $J = 7.0$ Hz, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ143.4 (d, $J = 16.3$ Hz), 142.6, 130.8 (d, $J = 22.4$ Hz), 129.9 (d, $J = 22.4$ Hz), 128.9 (d, $J = 31.3$ Hz), 128.3, 128.1 (d, $J = 2.2$ Hz) 128.0 127.9, 81.3 (d, $J = 19.0$ Hz), 49.3 (d, $J = 6.7$ Hz), 43.6 (d, $J = 5.0$ Hz), 34.6 (d, $J = 6.1$ Hz), 31.8 (d, $J = 12.9$ Hz), 22.8 (d, $J = 9.5$ Hz), 22.2 (d, $J = 8.9$ Hz), 21.3 (d, $J = 22.9$ Hz), 15.6 (d, $J = 1.7$ Hz); HRMS (APCI$^+$) calcd for $C_{22}H_{30}OP$ $[M + H]^+$ 341.2030, found m/z 341.2043.

(1*R*)-(1-Phenylethoxy)diphenylphosphine (17b). Colorless oil; IR (ATR, cm^{-1}) 953, 926, 740, 728; ^{1}H NMR (270 MHz, $CDCl_3$) δ7.58–7.52 (m, 2H), 7.41–7.16 (m, 13H), 5.06–4.95 (m, 1H), 1.58 (d, $J = 6.5$ Hz, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ143.5 (d, $J = 16.3$ Hz), 129.8 (d, $J = 22.4$ Hz), 128.5, 128.0 (d, $J = 7.3$ Hz), 76.7, 30.2 (d, $J = 8.4$ Hz); HRMS (APCI$^+$) calcd for $C_{20}H_{20}OP$ $[M + H]^+$ 307.1248, found m/z 307.1252.

***trans*-(2-Phenylcyclohexyloxy)diphenylphosphine (17c).** White solid; mp 81–83 °C; IR (ATR, cm^{-1}) 2930, 1028, 964,

752, 738; ^{1}H NMR (270 MHz, $CDCl_3$) δ7.41–6.69 (m, 13H), 6.66–6.63 (m, 2H), 4.08–4.01 (m, 1H), 2.76–2.68 (m, 1H), 2.22–2.18 (m, 1H), 1.92–1.69 (m, 3H), 1.59–1.20 (m, 4H); ^{13}C NMR (68 MHz, $CDCl_3$) δ144.0, 130.4, 130.1, 129.7 (d, $J = 20.7$ Hz), 128.8, 128.2 (d, $J = 2.2$ Hz), 128.0, 127.9 (×2), 127.6, 127.5, 126.1, 84.1 (d, $J = 19.6$ Hz), 52.4 (d, $J = 6.7$ Hz), 35.2 (d, $J = 5.0$ Hz), 34.3, 25.6 (d, $J = 49.2$ Hz); HRMS (APCI$^+$) calcd for $C_{24}H_{26}OP$ $[M + H]^+$ 361.1717, found m/z 361.1720.

(1*S*, 2*S*, 5*R*)-2-Isopropyl-5-methylcyclohexyl 2-Nitrobenzoate (18a).[6i] Colorless oil; IR (ATR, cm^{-1}) 2950, 1725, 1534, 1287, 1126; ^{1}H NMR (270 MHz, $CDCl_3$) δ7.88–7.84 (m, 1H), 7.76–7.59 (m, 3H), 5.50 (s, 1H), 2.21–2.15 (m, 1H), 1.79–1.74 (m, 2H), 1.64–1.62 (m, 1H), 1.57–1.00 (m, 4H), 0.96–0.82 (m, 10H); ^{13}C NMR (68 MHz, $CDCl_3$) δ164.6, 132.5, 131.4, 129.8, 127.9, 123.6, 74.0, 47.0, 38.8, 34.8, 34.7, 29.1, 26.7, 25.1, 22.3, 21.1, 20.8; MS (FAB$^+$) m/z 306 $[M + H]^+$.

(1*R*, 2*S*, 5*R*)-2-Isopropyl-5-methylcyclohexyl 2-Nitrobenzoate (18a′).[6i] Isomer authentic sample; Colorless oil; ^{1}H NMR (270 MHz, $CDCl_3$) δ7.91 (t, $J = 4.3$ Hz, 1H), 7.72–7.58 (m, 3H), 4.96 (dt, $J = 10.8$, 4.5 Hz, 1H), 2.24–2.20 (m, 1H), 1.94–1.89 (m, 1H), 1.75–1.67 (m, 2H), 1.64–1.41 (m, 2H), 1.16–0.80 (m, 12H); ^{13}C NMR (68 MHz, $CDCl_3$) δ164.9, 132.8, 131.3, 129.5, 123.8, 76.7, 46.9, 40.0, 34.1, 31.5, 26.2, 23.3, 22.1, 20.9, 16.2.

(1*S*, 2*S*, 5*R*)-2-Isopropyl-5-methylcyclohexyl 4-Nitrobenzoate (18b).[6i] White solid; mp 85–87 °C (lit.[6i] mp 93–95 °C); IR (ATR, cm^{-1}) 2960–1867, 1710, 1526, 1275; ^{1}H NMR (270 MHz, $CDCl_3$) δ8.30 (d, $J = 8.9$ Hz, 2H), 8.21 (d, $J = 8.6$ Hz, 2H), 5.50 (s, 1H), 2.13–2.04 (m, 1H), 1.91–1.81 (m, 2H), 1.73–1.62 (m, 1H), 1.55–1.43 (m, 2H), 1.24–0.75 (m, 12H); ^{13}C NMR (68 MHz, $CDCl_3$) δ163.8, 150.2, 136.2, 130.5, 123.5, 73.1, 46.9, 39.1 34.7, 29.5, 26.9, 25.4, 22.2, 21.0, 20.9; MS (FAB$^+$) m/z 306 $[M + H]^+$.

(1*R*, 2*S*, 5*R*)-2-Isopropyl-5-methylcyclohexyl 4-Nitrobenzoate (18b′).[6i] Isomer authentic sample; White solid; mp 58–59 °C; ^{1}H NMR (270 MHz, $CDCl_3$) δ8.30 (td, $J = 7.8$, 2.1 Hz, 2H), 8.21 (td, $J = 7.8$, 2.0 Hz, 2H), 4.97 (dt, $J = 10.9$, 4.5 Hz, 1H), 2.18–2.05 (m, 1H), 1.94–1.89 (m, 1H), 1.78–1.62 (m, 2H), 1.58–1.54 (m, 2H), 1.29–0.79 (m, 12H); ^{13}C NMR (68 MHz, $CDCl_3$) δ164.5, 150.7, 136.5, 131.0, 123.9, 76.6, 47.7, 41.3, 34.7, 32.0, 27.1, 24.1, 22.6, 21.3, 17.0.

(1*S*, 2*S*, 5*R*)-2-Isopropyl-5-methylcyclohexyl 3-Nitrobenzoate (18c).[6i] Colorless oil; IR (ATR, cm^{-1}) 2968, 1721, 1535, 1055; ^{1}H NMR (270 MHz, $CDCl_3$) δ8.84 (t, $J = 1.8$ Hz, 1H), 8.44–8.35 (m, 2H), 7.67 (t, $J = 8.0$ Hz, 1H), 5.51 (s, 1H), 2.12–2.04 (m, 1H), 1.88–1.84 (m, 2H), 1.71–1.60 (m, 1H), 1.57–1.45 (m, 2H), 1.24–0.75 (m, 12H); ^{13}C NMR (68 MHz, $CDCl_3$) δ163.6, 135.1, 132.6, 129.5, 127.1, 124.4, 73.1, 46.9, 39.1, 34.1, 29.5, 26.9, 25.5, 22.2, 21.1, 20.9; MS (FAB$^+$) m/z 306 $[M + H]^+$.

(1*R*, 2*S*, 5*R*)-2-Isopropyl-5-methylcyclohexyl 3-Nitrobenzoate (18c′).[6i] Isomer authentic sample; Colorless oil; ^{1}H NMR (270 MHz, $CDCl_3$) δ8.85 (s, 1H), 8.40 (t, $J = 9.1$ Hz, 2H), 7.70 (t, $J = 8.0$ Hz, 1H), 5.00 (dt, $J = 10.9$, 4.3 Hz, 1H), 2.14–2.10 (m, 1H), 1.98–1.92 (m, 1H), 1.85–1.73 (m, 2H), 1.64–1.56 (m, 2H), 1.26–0.79 (m, 12H); ^{13}C NMR (68 MHz, $CDCl_3$) δ163.8, 148.1, 135.2, 132.4, 129.4, 127.1, 124.4, 76.0, 47.1, 40.9, 34.2, 31.5, 26.6, 23.6, 22.1, 20.8, 16.5.

(1*S*, 2*S*, 5*R*)-2-Isopropyl-5-methylcyclohexyl 2-Methoxybenzoate (18d).[54] Colorless oil; IR (ATR, cm^{-1}) 2947, 1725, 1534, 1287, 1126; ^{1}H NMR (270 MHz, $CDCl_3$) δ7.84 (dd, $J = 5.9$, 1.9 Hz, 1H), 7.49–7.43 (m, 1H), 7.00–6.95 (m, 2H), 5.43 (s, 1H), 3.90 (s, 3H), 2.15–2.09 (m, 1H), 1.81–1.71 (m, 3H), 1.62–1.42 (m, 2H), 1.16–0.85 (m, 12H); ^{13}C NMR (68 MHz, $CDCl_3$) δ165.3, 159.2, 133.2, 131.5, 120.5, 119.9, 111.8, 71.4, 55.8, 47.1, 39.2, 34.9, 29.2, 26.7, 25.4, 22.3, 21.1, 20.9; HRMS (FAB$^+$) calcd for $C_{18}H_{27}O_3$ $[M + H]^+$ 291.1956, found m/z 291.1954.

(1*R*, 2*S*, 5*R*)-2-Isopropyl-5-methylcyclohexyl 2-Methoxybenzoate (18d′).[6i] Isomer authentic sample; Colorless oil; ^{1}H NMR (270 MHz, $CDCl_3$) δ7.75 (dd, $J = 8.0$, 1.8 Hz, 1H), 7.44 (dt, $J = 8.5$, 1.6 Hz, 1H), 6.97 (dd, $J = 7.8$, 6.5 Hz, 2H), 4.92 (dt, $J = 10.8$, 4.3 Hz, 1H), 3.88 (s, 3H), 2.14–2.01 (m, 2H), 1.74–1.70 (m, 2H), 1.56–1.51 (m, 2H), 1.20–0.80 (m, 12H); ^{13}C NMR (68 MHz, $CDCl_3$) δ165.7, 158.8, 133.0, 131.1, 120.9, 119.9, 111.9, 74.6, 55.9, 47.2, 40.9, 34.4, 31.5, 26.1, 23.3, 22.1, 21.0, 16.2.

(1*S*, 2*S*, 5*R*)-2-Isopropyl-5-methylcyclohexyl 4-Methoxybenzoate (18e).[6i] Colorless oil; IR (ATR, cm^{-1}) 2953–2842, 1699, 1254; ^{1}H NMR (270 MHz, $CDCl_3$) δ7.98 (d, $J = 8.9$ Hz, 2H), 6.90 (d, $J = 8.9$ Hz, 2H), 5.39 (s, 1H), 3.83 (s, 3H), 2.10–2.01 (m, 1H), 1.81–1.44 (m, 5H), 1.15–0.73 (m, 12H); ^{13}C NMR (68 MHz, $CDCl_3$) δ165.4, 163.0, 131.3, 123.3, 113.4, 71.2, 55.4, 47.0, 39.3, 34.9, 29.4, 26.8, 25.5, 22.3, 21.0, 20.9; MS (FAB$^+$) m/z 291 $[M + H]^+$.

(1*R*, 2*S*, 5*R*)-2-Isopropyl-5-methylcyclohexyl 4-Methoxybenzoate (18e′).[6i] Isomer authentic sample; Colorless oil; ^{1}H NMR (270 MHz, $CDCl_3$) δ8.00 (td, $J = 9.5$, 2.4 Hz, 2H), 6.90 (td, $J = 9.5$, 2.4 Hz, 2H), 4.90 (dt, $J = 10.8$, 4.3 Hz, 1H), 3.85 (s, 3H), 2.14–2.09 (m, 1H), 1.99–1.93 (m, 1H), 1.74–1.70 (m, 2H), 1.58–1.49 (m, 2H), 1.19–0.78 (m, 12H); ^{13}C NMR (68 MHz, $CDCl_3$) δ165.7, 163.0, 131.4, 123.2, 113.4, 74.4, 55.4, 47.3, 41.1 34.4, 31.5, 26.5, 23.7, 22.1, 20.8, 16.6.

(1-Methyl-1-phenylethoxy)diphenylphosphine (20a). White solid; mp 87–88 °C; IR (ATR, cm^{-1}) 946, 886, 745; ^{1}H NMR (270 MHz, $CDCl_3$) δ7.54–7.44 (m, 6H), 7.34–7.22 (m, 9H), 1.73 (s, 6H); ^{13}C NMR (68 MHz, $CDCl_3$) δ147.3 (d, $J = 2.8$ Hz), 143.2 (d, $J = 15.6$ Hz), 130.1 (d, $J = 22.4$ Hz), 128.7, 128.1 (d, $J = 7.3$ Hz), 126.8, 125.3 (d, $J = 1.2$ Hz), 124.2, 79.7, 30.4 (d, $J = 9.5$ Hz); HRMS (APCI$^+$) calcd for $C_{21}H_{22}OP$ $[M + H]^+$ 321.1404, found m/z 321.1410.

(1,1-Diethylpropoxy)diphenylphosphine (20c). Colorless oil; IR (ATR, cm^{-1}) 929, 734; ^{1}H NMR (270 MHz, $CDCl_3$) δ7.55–7.49 (m, 4H), 7.32–7.23 (m, 6H), 1.70 (q, $J = 7.5$ Hz, 6H), 0.784 (t, $J = 7.5$ Hz, 9H); ^{13}C NMR (68 MHz, $CDCl_3$) δ144.0 (d, $J = 15.6$ Hz), 130.0 (d, $J = 22.9$ Hz), 128.5, 128.0 (d, $J = 7.3$ Hz), 83.9 (d, $J = 8.4$ Hz), 29.5 (d, $J = 7.8$ Hz), 8.15 (d, $J = 1.1$ Hz); HRMS (APCI$^+$) calcd for $C_{19}H_{26}OP$ $[M + H]^+$ 301.1717, found m/z 301.1744.

Adamantyloxydiphenylphosphine (20d). White solid; mp 66–68 °C; IR (ATR, cm^{-1}) 1065, 974, 942, 733; ^{1}H NMR (270 MHz, $CDCl_3$) δ7.52–7.46 (m, 4H), 7.36–7.28 (m, 6H), 2.16 (s, 3H), 1.97 (d, $J = 2.2$ Hz, 6H), 1.62 (d, $J = 3.0$ Hz, 6H); ^{13}C NMR (68 MHz, $CDCl_3$) δ143.8 (d, $J = 16.3$ Hz), 129.9 (d, $J = 22.4$ Hz), 128.5, 128.0 (d, $J = 6.7$ Hz), 75.7, 44.2 (d, $J = 8.9$ Hz), 36.2, 31.0 (d, $J = 1.2$ Hz); HRMS (APCI$^+$) calcd for $C_{22}H_{26}OP$ $[M + H]^+$ 337.1717, found m/z 337.1714.

(1-Methylcyclohexyloxy)diphenylphosphine (20e). Colorless oil; IR (ATR, cm^{-1}) 2930, 908, 738; ^{1}H NMR (270 MHz, $CDCl_3$) δ7.74–7.66 (m, 1H), 7.57–7.46 (m, 5H), 7.34–7.24 (m, 4H), 1.96–1.94 (m, 3H), 1.63–1.44 (m, 7H), 1.32 (s, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ143.8 (d, $J = 16.3$ Hz), 132.5 (d, $J = 3.3$ Hz), 130.6 (d, $J = 11.2$ Hz), 129.9 (d, $J = 22.4$ Hz),

128.8 (d, $J = 13.0$ Hz), 128.3 (d, $J = 32.4$ Hz), 127.9, 121.0, 77.9 (d, $J = 10.7$ Hz), 38.6 (d, $J = 7.3$ Hz), 30.0, 25.5 (d, $J = 17.3$ Hz), 24.0, 23.0, 22.5 (d, $J = 8.4$ Hz); HRMS (APCI$^+$) calcd for $C_{19}H_{24}OP$ $[M + H]^+$ 299.1501, found m/z 299.1498.

(1-Methylcyclopentyloxy)diphenylphosphine (20f). White solid; mp 48–49 °C; IR (ATR, cm^{-1}) 922, 735; ^{1}H NMR (270 MHz, $CDCl_3$) δ7.50–7.45 (m, 4H), 7.34–7.23 (m, 6H), 2.14–2.08 (m, 2H), 1.75–1.53 (m, 6H), 1.46 (s, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ143.6 (d, $J = 15.6$ Hz), 129.9 (d, $J = 22.4$ Hz), 128.5, 128.1 (d, $J = 6.7$ Hz), 87.7 (d, $J = 11.7$ Hz), 40.3 (d, $J = 7.1$ Hz), 26.6 (d, $J = 10.7$ Hz), 23.9; HRMS (APCI$^+$) calcd for $C_{18}H_{22}OP$ $[M + H]^+$ 285.1404, found m/z 285.1467.

(1,1-Dimethyl-2-phenylethoxy)diphenylphosphine (20g). Colorless oil; IR (ATR, cm^{-1}) 917, 740; ^{1}H NMR (270 MHz, $CDCl_3$) δ7.47–7.41 (m, 4H), 7.29–7.19 (m, 11H), 2.98 (s, 2H), 1.36 (s, 6H); ^{13}C NMR (68 MHz, $CDCl_3$) δ143.3 (d, $J = 15.6$ Hz), 137.7, 130.8, 129.9 (d, $J = 22.4$ Hz), 128.6, 128.0 (d, $J = 6.7$ Hz), 127.6, 126.1, 78.9 (d, $J = 12.3$ Hz), 49.7 (d, $J = 5.0$ Hz), 27.8, 27.6; HRMS (APCI$^+$) calcd for $C_{22}H_{24}OP$ $[M + H]^+$ 335.1561, found m/z 335.1562.

1-Methyl-1-phenylethyl Benzoate (21a).[55] Colorless oil; IR (ATR, cm^{-1}) 1716, 1278, 1096, 763; ^{1}H NMR (270 MHz, $CDCl_3$) δ8.06–8.03 (m, 2H), 7.57–7.51 (m, 1H), 7.45–7.22 (m, 7H), 1.91 (s, 6H); ^{13}C NMR (68 MHz, $CDCl_3$) δ164.9, 145.6, 132.5, 131.3, 129.4, 128.2 (×2), 126.9, 124.2, 82.1, 28.8; HRMS (APCI$^+$) calcd for $C_{16}H_{17}O_2$ $[M + H]^+$ 241.1229, found m/z 241.1231.

1,1-Diethylpropyl Benzoate (21c).[56] White solid; mp 64–65 °C; IR (ATR, cm^{-1}) 2971, 1709, 1274, 1113; ^{1}H NMR (270 MHz, $CDCl_3$) δ8.02–7.98 (m, 2H), 7.56–7.49 (m, 1H), 7.44–7.38 (m, 2H), 1.98 (q, $J = 7.5$ Hz, 6H), 0.88 (t, $J = 7.5$ Hz, 9H); ^{13}C NMR (68 MHz, $CDCl_3$) δ165.2, 132.3, 131.7, 129.2, 128.1, 88.9, 27.0, 7.9; MS (FAB$^+$) m/z 191 $[M - Et]^+$.

Adamantyl Benzoate (21d).[57] White solid; mp 85–87 °C (lit.[57] mp 66.5–67.0 °C); IR (ATR, cm^{-1}) 2907, 2848, 1704, 1270, 1048; ^{1}H NMR (270 MHz, $CDCl_3$) δ8.01–7.97 (m, 2H), 7.55–7.49 (m, 1H), 7.44–7.37 (m, 2H), 2.26–2.22 (m, 9H), 1.72–1.65 (m, 6H); ^{13}C NMR (68 MHz, $CDCl_3$) δ165.3, 132.2, 131.9, 129.3, 128.0, 81.0, 41.4, 36.3, 30.9; HRMS (APCI$^+$) calcd for $C_{17}H_{21}O_2$ $[M + H]^+$ 257.1542, found m/z 257.1539.

1-Methylcyclohexyl Benzoate (21e).[31c] Colorless oil; IR (ATR, cm^{-1}) 2932, 1709, 1244, 1112; ^{1}H NMR (270 MHz, $CDCl_3$) δ8.04–8.01 (m, 2H), 7.53–7.40 (m, 3H), 2.37–2.32 (m, 2H), 1.61–1.49 (m, 11H); ^{13}C NMR (68 MHz, $CDCl_3$) δ165.4, 132.3, 131.9, 129.3, 128.1, 82.4, 36.8, 25.9, 25.5, 22.2; MS (FAB$^+$) m/z 219 $[M]^+$.

1-Methylcyclopentyl Benzoate (21f). Colorless oil; IR (ATR, cm^{-1}) 2965, 1709, 1280, 1112; ^{1}H NMR (270 MHz, $CDCl_3$) δ7.99 (d, $J = 7.3$ Hz, 2H), 7.54–7.38 (m, 3H), 2.34–2.23 (m, 2H), 1.85–1.69 (m, 9H); ^{13}C NMR (68 MHz, $CDCl_3$) δ165.7, 132.3, 131.7, 129.2, 128.0, 90.5, 39.2, 24.4, 23.9; HRMS (APCI$^+$) calcd for $C_{13}H_{17}O_2$ $[M + H]^+$ 205.1229, found m/z 205.1297.

1,1-Dimethyl-2-phenylethyl 3-Phenylpropionate (22a). Colorless oil; IR (ATR, cm^{-1}) 1724, 1115, 730; ^{1}H NMR (270 MHz, $CDCl_3$) δ7.30–7.12 (m, 10H), 3.02 (s, 2H), 2.90 (t, $J = 7.8$ Hz, 2H), 2.54 (dt, $J = 7.2$, 1.4 Hz, 2H), 1.42 (s, 6H); ^{13}C NMR (68 MHz, $CDCl_3$) δ172.2, 140.5, 137.1, 130.4, 128.3, 128.2, 127.8, 126.3, 126.0, 82.1, 46.5, 37.2, 31.0, 26.0; HRMS (APCI$^+$) calcd for $C_{19}H_{23}O_2$ $[M + H]^+$ 283.1694, found m/z 283.1689.

1,1-Diethylpropyl 3-Phenylpropionate (22b). Colorless oil; IR (ATR, cm^{-1}) 1724, 1131; ^{1}H NMR (270 MHz, $CDCl_3$) δ7.31–7.15 (m, 5H), 2.92 (t, $J = 7.8$ Hz, 2H), 2.58 (dt, $J = 7.2$, 1.6 Hz, 2H), 1.80 (q, $J = 7.5$ Hz, 6H), 0.76 (t, $J = 7.5$ Hz, 9H); ^{13}C NMR (68 MHz, $CDCl_3$) δ171.8, 140.6, 128.3, 128.2, 126.0, 88.3, 36.9, 31.2, 26.8, 7.7; HRMS (APCI$^+$) calcd for $C_{16}H_{25}O_2$ $[M + H]^+$ 249.1850, found m/z 249.1844.

1-Methyl-1-phenylethyl Pentanoate (22c). Colorless oil; IR (ATR, cm^{-1}) 1734, 1138, 763; ^{1}H NMR (270 MHz, $CDCl_3$) δ7.37–7.23 (m, 5H), 2.29 (t, $J = 7.4$ Hz, 2H), 1.76 (s, 6H), 1.63–1.52 (m, 2H), 1.40–1.23 (m, 2H), 0.91 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ172.3, 145.8, 128.1, 126.8, 124.1, 81.1, 35.2, 28.7, 27.1, 22.3, 13.9; HRMS (APCI$^+$) calcd for $C_{14}H_{21}O_2$ $[M + H]^+$ 221.1537, found m/z 221.1529.

1,1-Dimethyl-2-phenylethyl Trimethylacetate (22d).[58] Colorless oil; IR (ATR, cm^{-1}) 1720, 1159, 1116, 729; ^{1}H NMR (270 MHz, $CDCl_3$) δ7.30–7.18 (m, 5H), 3.05 (s, 2H), 1.44 (s, 6H), 1.13 (s, 9H); ^{13}C NMR (68 MHz, $CDCl_3$) δ177.7, 137.0, 130.5, 127.6, 126.2, 81.3, 46.7, 39.2, 27.1, 25.8; HRMS (APCI$^+$) calcd for $C_{15}H_{23}O_2$ $[M + H]^+$ 235.1694, found m/z 235.1690.

1-Methylcyclopentyl (*E*)-3-Phenyl-2-propenoate (22e). Colorless oil; IR (ATR, cm^{-1}) 1703, 1161, 767; ^{1}H NMR (270 MHz, $CDCl_3$) δ7.59 (d, $J = 15.9$ Hz, 1H), 7.53–7.49 (m, 2H), 7.38–7.36 (m, 3H), 6.38 (d, $J = 15.9$ Hz, 1H), 2.25–2.13 (m, 2H), 1.81–1.68 (m, 6H), 1.63 (s, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ166.3, 143.4, 134.5, 129.9, 128.7, 127.8, 119.9, 90.0, 39.2, 24.5, 23.9; HRMS (APCI$^+$) calcd for $C_{15}H_{19}O_2$ $[M + H]^+$ 231.1381, found m/z 231.1378.

Adamantyl 2-Chloroacetate (22f). White solid; mp 77–78 °C; IR (ATR, cm^{-1}) 1783, 1177, 1054; ^{1}H NMR (270 MHz, $CDCl_3$) δ3.97 (s, 2H), 2.19–2.12 (m, 9H), 1.66 (d, $J = 3.5$ Hz, 6H); ^{13}C NMR (68 MHz, $CDCl_3$) δ165.7, 83.1, 42.1, 41.2, 36.0, 30.9; HRMS (APCI$^+$) calcd for $C_{12}H_{18}ClO_2$ $[M + H]^+$ 229.0991, found m/z 229.0989.

Adamantyl 2-Phenylbutyrate (22g). Colorless oil; IR (ATR, cm^{-1}) 1724, 1165, 1055; ^{1}H NMR (270 MHz, $CDCl_3$) δ7.31–7.20 (m, 5H), 3.33 (t, $J = 7.7$ Hz, 1H), 2.12–1.99 (m, 10H), 1.78–1.59 (m, 7H), 0.90 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ172.9, 139.7, 128.2, 127.8, 126.7, 80.5, 54.6, 41.2, 36.2, 30.8, 27.0, 12.3; HRMS (APCI$^+$) calcd for $C_{20}H_{27}O_2$ $[M + H]^+$ 299.2011, found m/z 299.2015.

1-Methylcyclopentyl Triphenylacetate (22h). White solid; mp 73–74 °C; IR (ATR, cm^{-1}) 1716, 1173, 751; ^{1}H NMR (270 MHz, $CDCl_3$) δ7.27–7.23 (m, 15H), 2.02–2.00 (m, 2H), 1.60–1.42 (m, 9H); ^{13}C NMR (68 MHz, $CDCl_3$) δ172.3, 143.2, 130.2, 127.4, 126.5, 91.7, 67.9, 38.9, 23.8, 23.7; HRMS (APCI$^+$) calcd for $C_{26}H_{27}O_2$ $[M + H]^+$ 371.2011, found m/z 371.2006.

1-Phenylethyl 4-Nitrophenyl Ether (23a).[59] Red oil; IR (ATR, cm^{-1}) 1494, 1334, 1250; ^{1}H NMR (270 MHz, $CDCl_3$) δ8.07 (dd, $J = 5.1$, 2.0 Hz, 2H), 7.35–7.25 (m, 5H), 6.89 (dd, $J = 4.9$, 2.2 Hz, 2H), 5.39 (q, $J = 6.4$ Hz, 1H), 1.67 (d, $J = 6.4$ Hz, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ162.8, 141.5, 141.0, 128.7, 127.8, 125.6, 125.2, 115.5, 76.9, 24.5; HRMS (APCI$^+$) calcd for $C_{14}H_{14}NO_3$ $[M + H]^+$ 244.0969, found m/z 244.0985.

1-Methyl-1-phenylethyl 4-Nitrophenyl Ether (23b).[60] Red oil; IR (ATR, cm^{-1}) 1509, 1337, 1251, 1100; ^{1}H NMR (270 MHz, $CDCl_3$) δ7.918 (d, $J = 9.2$ Hz, 2H), 7.38–7.25 (m, 5H), 6.66 (d, $J = 9.2$ Hz, 2H), 1.80 (s, 6H); ^{13}C NMR (68 MHz, $CDCl_3$) δ161.6, 144.5, 140.9, 128.8, 127.5, 125.1, 124.8, 118.2, 81.9, 29.5; HRMS (APCI$^+$) calcd for $C_{15}H_{16}NO_3$ $[M + H]^+$ 257.1052, found m/z 257.1050.

Benzyldiphenylphosphine Oxide (24).[18b] Into a methoxydiphenylphosphine (1.1 g, 5.0 mmol) under argon atmosphere was dropped a benzyl chloride (0.63 g, 5.0 mmol) at room temperature. After the reaction mixture was stirred at 100 °C for 1 h, the reaction mixture was cooled. Crystallization of the

crude product from ethanol (2 mL) gave the title compound (**24**) (0.60 g, 41%) as a white needles: mp 188–189 °C (lit.[50b] mp 189–190 °C); IR (ATR, cm^{-1}) 1180; ^1H NMR (270 MHz, $CDCl_3$) δ7.87–7.79 (m, 4H), 7.54–7.40 (m, 6H), 7.37–7.32 (m, 5H), 5.06 (d, $J = 6.8$ Hz, 2H); ^{13}C NMR (68 MHz, $CDCl_3$) δ136.2 (d, $J = 7.3$ Hz), 132.1 (d, $J = 2.2$ Hz), 132.1, 131.6 (d, $J = 10.6$ Hz), 130.1, 128.5 (d, $J = 7.8$ Hz), 128.2 (d, $J = 12.9$ Hz), 127.7, 66.3 (d, $J = 5.8$ Hz); HRMS ($APCI^+$) calcd for $C_{19}H_{18}OP$ $[M + H]^+$ 293.1091, found m/z 293.1128.

Benzyloxydiphenylphosphine Oxide (25).[61] Into a stirred solution of benzyl alcohol (0.54 g, 5.0 mmol) and triethylamine (0.51 g, 5.0 mmol) in dichloromethane (5 mL) under argon atmosphere was dropped a dichloromethane (5 mL) solution of diphenylphosphinic chloride (1.2 g, 5.0 mmol) at 0 °C. After the reaction mixture was stirred at room temperature for 0.5 h, diethyl ether was added. The solution was washed with 1 mol dm^{-3} HCl (20 mL), water (20 mL) and brine. The organic layer was dried over anhydrous sodium sulfate. After filtration and evaporation, the resulting residue was purified by column chromatography (hexane/ethyl acetate = 2/1) to afford the title compound (**25**) (1.4 g, 94%) as a white solid: mp 77–78 °C (lit.[61b] mp 75–76 °C); IR (ATR, cm^{-1}) 1217, 1015, 860, 729; ^1H NMR (270 MHz, $CDCl_3$) δ7.73–7.65 (m, 4H), 7.54–7.40 (m, 6H), 7.19–7.08 (m, 5H), 3.66 (d, $J = 13.8$ Hz, 2H); ^{13}C NMR (68 MHz, $CDCl_3$) δ132.8, 131.7 (d, $J = 2.8$ Hz), 131.3 (d, $J = 19.0$ Hz), 131.0 (d, $J = 2.8$ Hz), 130.0 (d, $J = 5.0$ Hz), 128.4, 128.3 (d, $J = 2.8$ Hz), 126.7 (d, $J = 3.3$ Hz), 38.1 (d, $J = 3.3$ Hz); HRMS ($APCI^+$) calcd for $C_{19}H_{18}O_2P$ $[M + H]^+$ 309.1040, found m/z 309.1035.

Diphenylphosphinic Acid 4-Hydroxy-3,5-dimethylphenyl Ester (26). Isolated as white solid; mp 144–146 °C; IR (ATR, cm^{-1}) 3309, 1182, 1133, 1017, 877, 849, 733; ^1H NMR (270 MHz, $CDCl_3$) δ7.90–7.83 (m, 4H), 7.55–7.41 (m, 6H), 6.71 (s, 2H), 5.66 (br, 1H), 2.06 (s, 6H); ^{13}C NMR (68 MHz, $CDCl_3$) δ149.3, 132.2 (d, $J = 2.8$ Hz), 132.1, 131.7 (d, $J = 10.7$ Hz), 130.0, 128.4 (d, $J = 13.4$ Hz), 124.8, 120.1 (d, $J = 4.5$ Hz), 16.3; HRMS ($APCI^+$) calcd for $C_{20}H_{20}O_3P$ $[M + H]^+$ 339.1146, found m/z 339.1164.

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References

1 a) E. Haslam, *Tetrahedron*, **36**, 2409 (1980). b) J. Otera, *Chem. Rev.*, **93**, 1449 (1993). c) W. G. Theodora and G. M. W. Peter, in "Protective Groups in Organic Synthesis," John Wiley & Sons, New York (1991), 2nd ed, p. 143 and p. 224. d) K. Takahashi, M. Shibagaki, and H. Matsushita, *Bull. Chem. Soc. Jpn.*, **62**, 2353 (1989). e) R. O. Clinton and S. C. Laskowski, *J. Am. Chem. Soc.*, **70**, 3135 (1948). f) G. A. Olah, T. Keumi, and D. Meidar, *Synthesis*, **1978**, 929. g) M. Hino and K. Arata, *Chem. Lett.*, **1981**, 1671. h) T. Mukaiyama, M. Usui, E. Shimada, and K. Saigo, *Chem. Lett.*, **1975**, 1045. i) B. Neises and W. Steglich, *Angew. Chem., Int. Ed. Engl.*, **17**, 522 (1978). j) A. Hassner and V. Alexanian, *Tetrahedron Lett.*, **19**, 4475 (1978). k) J. Inanaga, K. Hirata, H. Saeki, T. Katsuki, and M. Yamaguchi, *Bull. Chem. Soc. Jpn.*, **52**, 1989 (1979). l) I. Shiina, R. Ibuka, and M. Kubota, *Chem. Lett.*, **2002**, 286.

2 T. Mukaiyama, I. Kuwajima, and Z. Suzuki, *J. Org. Chem.*, **28**, 2024 (1963).

3 I. Kuwajima and T. Mukaiyama, *J. Org. Chem.*, **29**, 1385 (1964).

4 T. Mukaiyama, R. Matsueda, and M. Suzuki, *Tetrahedron Lett.*, **22**, 1901 (1970).

5 O. Mitsunobu, M. Yamada, and T. Mukaiyama, *Bull. Chem. Soc. Jpn.*, **40**, 935 (1967).

6 a) O. Mitsunobu and M. Yamada, *Bull. Chem. Soc. Jpn.*, **40**, 2380 (1967). b) O. Mitsunobu and M. Eguchi, *Bull. Chem. Soc. Jpn.*, **44**, 3427 (1971). c) O. Mitsunobu, *Synthesis*, **1981**, 1. d) D. L. Hughs, in "Organic Reactions," ed by L. A. Paquette, John Wiley & Sons, New York (1992), Vol. 42, p. 335. e) R. A. Amos, R. W. Emblidge, and N. Havens, *J. Org. Chem.*, **48**, 3598 (1983). f) L. D. Arnold, H. I. Assil, and J. C. Vederas, *J. Am. Chem. Soc.*, **111**, 3973 (1989). g) A. R. Tunoori, D. Dutta, and G. I. Georg, *Tetrahedron Lett.*, **39**, 8751 (1998). h) A. P. Dobbs and C. M. Johnson, *Tetrahedron Lett.*, **43**, 2807 (2002). i) J. A. Dodge, J. I. Trujillo, and M. Presnell, *J. Org. Chem.*, **59**, 234 (1994). j) S. F. Martin and J. A. Dodge, *Tetrahedron Lett.*, **32**, 3017 (1991).

7 a) T. Tsunoda, Y. Yamamiya, and S. Ito, *Tetrahedron Lett.*, **34**, 1639 (1993). b) T. Tsunoda, F. Ozaki, and S. Ito, *Tetrahedron Lett.*, **35**, 5081 (1994). c) T. Tsunoda, Y. Yamamiya, Y. Kawamura, and S. Ito, *Tetrahedron Lett.*, **36**, 2529 (1995). d) S. Ito, *Yakugaku Zasshi*, **121**, 567 (2001).

8 T. Mukaiyama, T. Shintou, and W. Kikuchi, *Chem. Lett.*, **2002**, 1126.

9 T. Shintou, W. Kikuchi, and T. Mukaiyama, *Chem. Lett.*, **32**, 22 (2003).

10 T. Mukaiyama, W. Kikuchi, and T. Shintou, *Chem. Lett.*, **32**, 300 (2003).

11 J. Zaloom, M. Calandra, and D. C. Roberts, *J. Org. Chem.*, **50**, 2601 (1985).

12 a) H. J. Cristau, A. Chene, and H. Christol, *Synthesis*, **1980**, 551. b) F. Jakle, M. Mattner, T. Priermeir, and M. Wagner, *J. Organomet. Chem.*, **502**, 123 (1995). c) W. Walker, *J. Chem. Soc., Perkin Trans. 1*, **1975**, 1309.

13 A. B. Ouryupin, I. A. Rakhov, V. A. Kolesova, P. V. Petrovskii, T. A. Mastryukova, and M. I. Kabachnik, *Russian Chem. Bull.*, **44**(11), 2157 (1995).

14 W. Voksuil and J. F. Arens, *Org. Synth.*, Coll. Vol. V, 211 (1973).

15 G. M. Kosolapoff and L. Maier, in "Organic Phosphorus Compounds," John Wiley & Sons, New York (1973), Vol. 4, p. 504.

16 P. Denis, A. Mortreux, F. Petit, G. Buono, and G. Peiffer, *J. Org. Chem.*, **49**, 5274 (1984).

17 D. A. Evans, K. R. Campos, J. S. Tedrow, F. E. Michael, and M. R. Gagne, *J. Am. Chem. Soc.*, **122**, 7905 (2000).

18 a) B. A. Arbouzov and N. P. Grechkin, *Zh. Obshch. Khim.*, **20**, 107 (1950). b) N. Zhao and D. C. Neckers, *J. Org. Chem.*, **65**, 2145 (2000).

19 S. Yasui, K. Shioji, M. Yoshihara, T. Maeshima, and A. Ohno, *Bull. Chem. Soc. Jpn.*, **66**, 2077 (1993).

20 R. Engel, T. Santo, D. Liotta, and Donald Freed, *J. Chem. Soc., Chem. Commun.*, **1970**, 646.

21 a) K. Diemert, G. Hein, A. Janssen, and W. Kuchen, *Phosphorus, Sulfur, and Silicon*, **53**, 339 (1990). b) L. Maier, *Helv. Chim. Acta*, **46**, 2667 (1963).

22 a) J. J. Hans, R. W. Driver, and S. D. Burke, *J. Org. Chem.*, **65**, 2114 (2000). b) T. Oriyama, Y. Hori, K. Imai, and R. Sasaki,

Tetrahedron Lett., **37**, 8543 (1996).
23 P. Strazzolini, A. G. Giumanini, and G. Verardo, *Tetrahedron*, **50**, 217 (1994).
24 a) Y. Kita, S. Akai, M. Yamamoto, M. Taniguchi, and Y. Tamura, *Synthesis*, **1989**, 334. b) T. Shono, O. Ishige, H. Uyama, and S. Kashimura, *J. Org. Chem.*, **51**, 546 (1986).
25 Y. Hu, W. Pa, W. Cui, and J. Wang, *Synth. Commun.*, **22**, 2763 (1992).
26 a) I. Shibata, T. Suwa, K. Ryu, and A. Baba, *J. Org. Chem.*, **66**, 8690 (2001). b) D. H. R. Barton, G. Bringmann, and W. B. Motherwell, *Synthesis*, **1980**, 68.
27 K. Saigo, M. Usui, K. Kikuchi, E. Shimada, and T. Mukaiyama, *Bull. Chem. Soc. Jpn.*, **50**, 1863 (1977).
28 P. Ilankumaran and J. G. Verkade, *J. Org. Chem.*, **64**, 3086 (1999).
29 E. R. Marinelli, T. Arunachalam, G. Diamantidis, J. Emswiler, H. Fan, R. Neubeck, K. M. R. Pillai, T. R. Wagler, C. K. Chen, K. Natalie, N. Soundararajan, and R. S. Ranganathan, *Tetrahedron*, **52**, 11177 (1996).
30 a) C. Zeggaf, J. Poncet, P. Jouin, M. N. Dufour, and B. Castro, *Tetrahedron*, **45**, 5039 (1989). b) M. K. Dhaon, R. K. Olsen, and K. Ramasamy, *J. Org. Chem.*, **47**, 1962 (1982).
31 a) J. Barluenga, L. Alonso-Cires, P. J. Campos, and G. Asensio, *Synthesis*, **1983**, 649. b) K. Takeda, K. Tsuboyama, H. Takayanagi, and H. Ogura, *Synthesis*, **1987**, 560. c) M. Ochiai, T. Ito, H. Takahashi, A. Nakanishi, M. Toyonari, T. Sueda, S. Goto, and M. Shiro, *J. Am. Chem. Soc.*, **118**, 7716 (1996).
32 M. Node, K. Nishide, Y. Shigeta, H. Shiraki, and K. Obata, *J. Am. Chem. Soc.*, **122**, 1927 (2000).
33 a) S. W. Pelletier, Z. Djarmati, and C. Pape, *Tetrahedron*, **32**, 995 (1976). b) R. Adams, E. K. Rideal, W. B. Burnett, R. L. Jenkins, and E. E. Dreger, *J. Am. Chem. Soc.*, **48**, 1758 (1926).
34 M. P. Cooke, *J. Org. Chem.*, **51**, 951 (1986).
35 a) J. Forrester, R. V. H. Jones, L. Newton, and P. N. Preston, *Tetrahedron*, **57**, 2871 (2001). b) D. Bogdal, J. Pielichowski, and A. Boron, *Synth. Commun.*, **28**, 3029 (1998). c) A. R. Tunoori, D. Dutta, and G. I. Georg, *Tetrahedron Lett.*, **39**, 8751 (1998). d) L. Testaferri, M. Tiecco, M. Tingori, D. Chianelli, and M. Montanucci, *Tetrahedron*, **38**, 3687 (1982).
36 A. Ryokawa and H. Togo, *Tetrahedron*, **57**, 5915 (2001).
37 P. Maslak and R. D. Guthrie, *J. Am. Chem. Soc.*, **108**, 2628 (1986).
38 B. Miller, M. P. Mclaughlin, and V. C. Marhevka, *J. Org. Chem.*, **47**, 710 (1982).
39 a) P. Maslak and R. D. Guthrie, *J. Am. Chem. Soc.*, **108**, 2637 (1986). b) Y. Hamada, N. Kato, Y. Kakamu, and T. Shioiri, *Chem. Pharm. Bull.*, **29**, 2246 (1981).
40 M. A. Keegstra, T. H. A. Peters, and L. Brandsma, *Tetrahedron*, **48**, 3633 (1992).
41 T. F. Woiwode, C. Rose, and T. J. Wandless, *J. Org. Chem.*, **63**, 9594 (1998).
42 T. Ohishi, J. Yamada, Y. Inui, T. Sakaguchi, and M. Yamashita, *J. Org. Chem.*, **59**, 7521 (1994).
43 Y. Yukawa, Y. Tsuno, and M. Sawada, *Bull. Chem. Soc. Jpn.*, **45**, 1198 (1972).
44 A. R. Katritzky, S. Rachwal, and B. Rachwal, *Synthesis*, **1991**, 69.
45 R. M. Carlson and L. J. Heinis, *J. Org. Chem.*, **44**, 2530 (1979).
46 R. J. Aromstrong and L. Weiler, *Can. J. Chem.*, **61**, 2530 (1983).
47 P. Kumar, R. K. Pandey, M. S. Bodas, and M. K. Dongare, *Synlett*, **2001**, 206.
48 W. Adam, Z. Lukacs, K. Viebach, H. U. Humpf, C. R. Saha-Moller, and P. Schreier, *J. Org. Chem.*, **65**, 186 (2000).
49 R. Paredes, F. Agudelo, and G. Taborda, *Tetrahedron Lett.*, **37**, 1965 (1996).
50 a) K. Kabuto, M. Imuta, E. S. Kempner, and H. Ziffer, *J. Org. Chem.*, **43**, 2357 (1978). b) A. M. Barrett, D. C. Braddock, R. A. James, N. Koike, and P. A. Procopiou, *J. Org. Chem.*, **63**, 6273 (1998).
51 M. Node, K. Nishide, Y. Shigeta, H. Shiraki, and K. Obata, *J. Am. Chem. Soc.*, **122**, 1927 (2000).
52 J. E. Kaminska, Z. J. Kaminski, and J. Gora, *Synthesis*, **1999**, 593.
53 a) S. A. Said, A. Fiksdahl, and P. H. J. Carlsen, *Tetrahedron Lett.*, **41**, 5593 (2000). b) S. A. Said and A. Fiksdahl, *Tetrahedron: Asymmetry*, **12**, 893 (2001).
54 A. G. Schultz, J. P. Dittami, F. P. Lavieri, C. Salowey, P. Sundararaman, and M. B. Szymula, *J. Org. Chem.*, **49**, 4429 (1984).
55 K. T. Liu, J. K. Lee, and H. I. Chen, *J. Org. Chem.*, **55**, 3662 (1990).
56 E. M. Kaiser and R. A. Woodruff, *J. Org. Chem.*, **35**, 1198 (1970).
57 L. Brown and M. Koreeda, *J. Org. Chem.*, **49**, 3875 (1984).
58 Y. Kita, H. Maeda, K. Omori, T. Okuno, and Y. Tamura, *J. Chem. Soc., Perkin Trans. 1*, **1993**, 2999.
59 a) P. Maslak and R. D. Guthrie, *J. Am. Chem. Soc.*, **108**, 2628 (1986). b) K. Bansho and K. Shibayama, *Jpn. Kokai Tokkyo Koho*, Jp 2002-255905.
60 E. N. Peters, *J. Polym. Sci., Polym. Lett. Ed.*, **13**, 479 (1975).
61 a) J. J. G. S. Van Es, A. Ten Wollde, and A. Van der Gen, *J. Org. Chem.*, **55**, 4069 (1990). b) Z. E. Golubski, *Synth. Commun.*, **8**, 632 (1980).