

Selected Paper

Efficient Method for the Preparation of Inverted Alkyl Carboxylates and Phenyl Carboxylates via Oxidation–Reduction Condensation Using 2,6-Dimethyl-1,4-benzoquinone or Simple 1,4-Benzoquinone

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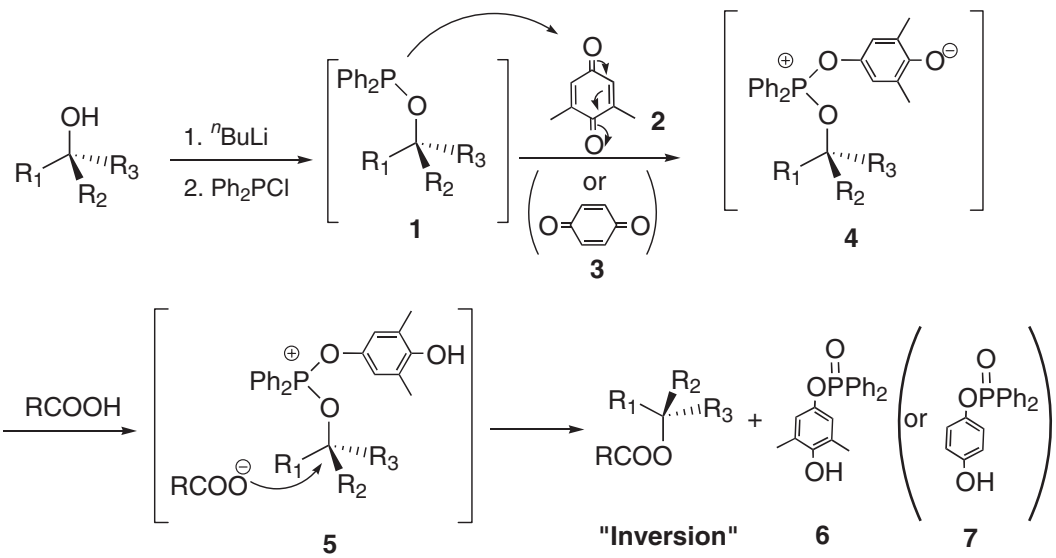
Oxidation–reduction condensation using in situ formed alkoxydiphenylphosphines, 2,6-dimethy-1,4-benzoquinone, and carboxylic acids provides a useful method for the preparation of inverted tertiary alkyl carboxylates from the corresponding chiral tertiary alcohols under mild and neutral conditions. Similarly, it has afforded alkyl carboxylates successfully in good-to-high yields by the combined use of alkoxydiphenylphosphines having primary, secondary, or tertiary alkoxy groups, carboxylic acids, and simple 1,4-benzoquinone. When chiral secondary or tertiary alcohols are used, the corresponding inverted secondary or tertiary alkyl carboxylates are also obtained in good-to-high yields. In addition, a convenient method for the preparation of phenyl carboxylates in high yields has been established by utilizing oxidation–reduction condensation in toluene at 110 °C using phenoxydiphenylphosphines in situ-formed from phenols and chlorodiphenylphosphine, 2,6-dimethyl-1,4-benzoquinone, and carboxylic acids.

Oxidation–reduction condensation using a combination of 2,6-dimethyl-1,4-benzoquinone and alkoxydiphenylphosphines formed in situ from alcohols and chrolodiphenylphosphine or *N*,*N*-(dimethylamiono)diphenylphosphine proceeded smoothly just from the corresponding alcohols and carboxylic acids in a one-pot procedure to afford alkyl carboxylates in high yields.[1] Esterification of various chiral secondary alcohols proceeded smoothly to afford the corresponding esters in high yields with a perfect inversion of the stereochemistry.[1] It was also shown that the reaction of various carboxylic acids with tertiary alkoxydiphenylphosphines formed in situ, e.g., 2,2-dimethylpropionic acid and 2-methyl-1-phenylpropan-2-ol, or 2-phenylbutyric acid and 1-adamantanol, afforded the corresponding *t*-alkyl carboxylates in 85 to 96% yields, respectively.[1] Thus, the possibility of the inversion of *t*-alkyl alcohol in this ester-forming reaction was further examined and the chiral tertiary alcohols were converted into their corresponding esters with almost complete inversion of the configuration by oxidation–reduction condensation (Scheme 1).[2] In addition, the olefins produced from tertiary alcohols, except for the case using (*S*)-2-(4-methoxypheny)-2-butanol, were not observed because they proceeded under "mild and neutral" conditions without having any assistance of acids or bases. In order to develop practical and convenient reactions, condensation using simple



Scheme 1.

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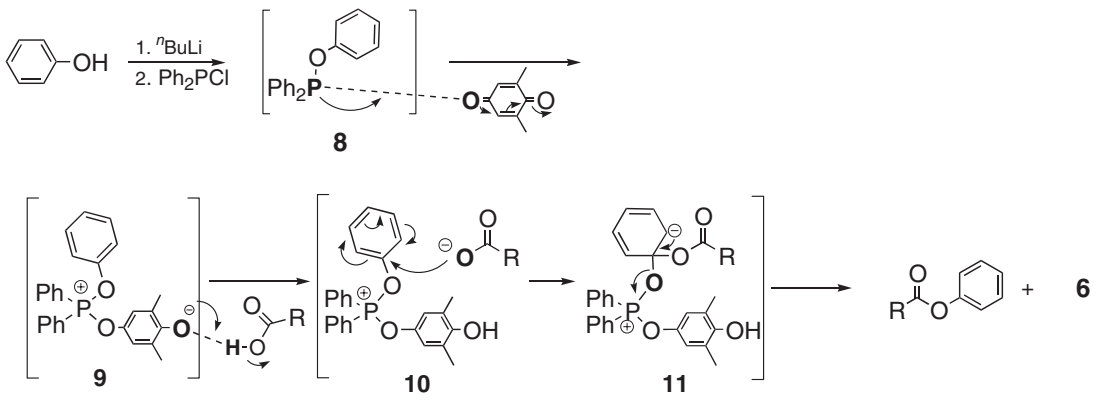


Scheme 2.

1,4-benzoquinone was tried instead of the above-mentioned 2,6-dimethyl-1,4-benzoquinone, and the desired reaction proceeded smoothly to afford alkyl carboxylates in good-to-high yields by using a combination of alkoxydiphenylphosphines having primary, bulky secondary or tertiary alkoxy groups, 1,4-benzoquinone, and carboxylic acids (Scheme 1).[3] In the case of chiral secondary or tertiary alcohols, the corresponding inverted carboxylates were also obtained in good-to-high yields.[3] In order to extend the scope of these reactions, the formation of phenyl carboxylates by condensation reactions of phenols with carboxylic acids was further studied by using in situ-formed phenoxydiphenylphosphines instead of the above-mentioned alkoxydiphenylphosphines, and the above condensation proceeded smoothly in toluene at 110 °C and afforded the corresponding phenyl carboxylates in high yields under neutral conditions (Scheme 2).

Results and Discussion

Preparation of Inverted *t*-Alkyl Carboxylates from Chiral *t*-Alcohols by a New Type of Oxidation–Reduction Condensation Using 2,6-Dimethy-1,4-benzoquinone. In the first place, alkylations of several carboxylic acids with 1.2 equivalents of chiral tertiary alkoxydiphenylphosphines formed in situ from chiral ^{n}BuLi treated tertiary alcohols and chlorodiphenylphosphine were tried by using 1.0 equivalent of 2,6-dimethyl-1,4-benzoquinone in dichloromethane at room temperature. Condensations of carboxylic acids with various chiral tertiary alcohols proceeded smoothly to afford the corresponding *t*-alkyl carboxylates in good yields with almost complete inversion of stereochemistries; the results are shown in Table 1. When a CH_2Cl_2 solution of 1-adamantanol and benzoic acid was refluxed for 15 h, the corresponding ester was obtained in 83% yield with the retention of stereochemistry because of its rigid structure (Table 1, entry 1). When benzoic acid or *p*-methoxybenzoic acid having an electron-donating group was used, esterifications using various chiral tertiary alcohols proceeded within 18 h at room temperature to afford the corresponding alkyl esters in good yields (81–90%) with almost complete inversion of the stereochemistries (98 to >99%) (Table 1, entries 4, 5, 8, 9, and 12–14). When hydrocinnamic acid (3-phenylpropionic acid) or *p*-chlorobenzoic acid was used, on the other hand, the desired esters were obtained in 76–86% yields with 70–84% inversion (Table 1, entries 6, 7, 10, and 11). When a CH_2Cl_2 solution of (−)-terpinen-4-ol and benzoic acid or hydrocinnamic acid was refluxed for 15 h, the desired esters were obtained in 78% chemical yield with 98% inversion or 76% chemical yield with 40% inversion, respectively (Table 1, entries 2 and 3), whereas the corresponding olefin was formed in 81% yield in the case of 2-(4-methoxyphenyl)-2-buthanol, and no desired esters were detected (Table 1, entry 15).

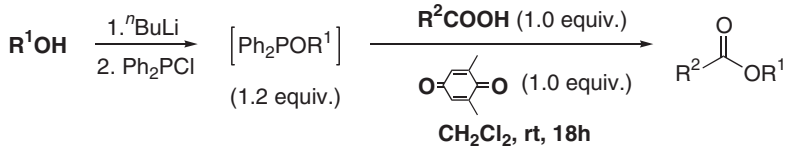
Next, the esterifications of (−)-linalool with benzoic acid having electron-donating or electron-withdrawing groups at the *o*-position or the *m*-position, such as *o*-nitrobenzoic acid, *m*-nitrobenzoic acid, or *m*-chlorobenzoic acid or *o*-methoxybenzoic acid, were tried and the corresponding esters were obtained in 75–79% chemical yields with 94–99% inversion after having been allowed to react for 18 h at room temperature (Table 2, entries 1–3, and 5).

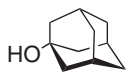
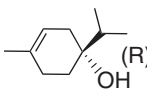
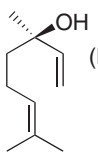
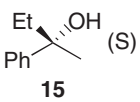
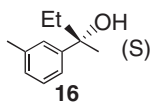
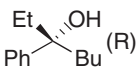
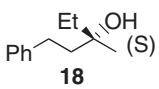
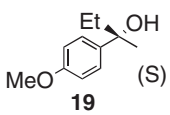
Thus, oxidation–reduction condensation using in situ-formed alkoxydiphenylphosphines, 2,6-dimethyl-1,4-benzoquinone, and carboxylic acids provided a new and efficient method for the preparation of inverted *t*-alkyl carboxylates from various chiral tertiary alcohols.

Efficient Method for the Preparation of Primary, Inverted Secondary, and Tertiary Alkyl Carboxylates from Alcohols and Carboxylic Acids by Oxidation–Reduction Condensation Using Simple 1,4-Benzoquinone. First, when benzyl alcohol and benzoic acid were treated with 1.0 equivalent of 1,4-benzoquinone in dichloromethane, benzyl benzoate was obtained in 75% yield within 3 h (Table 3, entry 1). When 1.0 equivalent each of 1,4-benzoquinone and benzoic acid were used, the yields of the desired ester were not influenced by the amount of benzyloxydiphenylphosphine (Table 3, entries 1–4). Next, the above effect was further investigated by using the same equivalents; each of benzyloxydiphenylphosphine and 1,4-benzoquinone were used (Table 3, entries 5–9). As a result, the ester was obtained in 98% yield when 1.7 equivalents each of the in situ-formed benzyloxydiphenylphosphine and 1,4-benzoquinone were treated with 1.0 equivalent of benzoic acid at room temperature for 1 h (Table 3, entry 8, and Fig. 1).

Next, esterifications of the in situ-formed alkoxydiphenylphosphines from alcohols and chlorodiphenylphosphine with various carboxylic acids were tried; the result are shown in Table 4. Benzylation of benzoic acids having electron-donating or electron-withdrawing groups and saturated or unsaturated aliphatic carboxylic acids proceeded smoothly to afford the corresponding benzyl carboxylates in high-to-excellent yields

Table 1. Esterification between Several Carboxylic Acids and Various Chiral Tertiary Alcohols

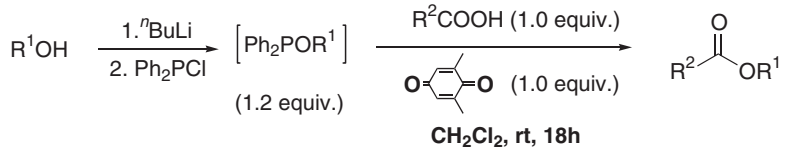


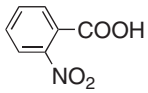
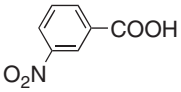
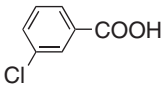
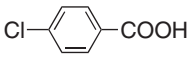
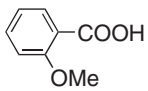
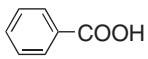
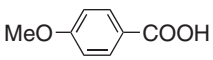
Entry	R^1OH[c]	R/S[d]	R^2	Product	Yield/%	R/S[e]	Inversion/%
1[a]	 **12**		Ph	**20**	83		0
2[a]	 **13**	86/14	Ph	**21**	78	16/84	98
3[a]			$PhCH_2CH_2$–	**22**	76	66/34	40
4	 **14**	95/5	Ph	**23**	85	7/93	98
5			*p*-MeO–C_6H_4–	**24**	86	5/95	>99
6			*p*-Cl–C_6H_4–	**25**	83	20/80	84
7			$PhCH_2CH_2$–	**26**	76	24/76	80
8	 **15**	2/98	Ph	**27**	90	98/2	>99
9			*p*-MeO–C_6H_4–	**28**	88	98/2	>99
10			*p*-Cl–C_6H_4–	**29**	86	70/30	71
11			$PhCH_2CH_2$–	**30**	86	69/31	70
12	 **16**	1/99	Ph	**31**	86	99/1	>99
13	 **17**	91/9	Ph	**32**	83	9/91	>99
14	 **18**	22/78	Ph	**33**	81	77/23	99
15[b]	 **19**		Ph	**34**	N.D.		

a) The reaction mixture was refluxed for 15 h. b) The corresponding olefin was obtained in 81% yield. c) Entries 2–7: Chiral alcohols of (−)-terpinen-4-ol (Acros Organics) and (−)-linalool (Fulka Chemika) were purchased. Entry 8–15: Chiral alcohols were prepared according to Walsh's procedure.[1] d) The enantiomeric ratios of *t*-alcohols were determined by preparing the corresponding esters with the carboxylic chlorides. e) The conditions of separating the corresponding esters were shown in Ref. 2.

under mild conditions (Table 4, entries 1–6). When 1-butanol or *p*-methoxybenzyl alcohol having an electron-donating group or secondary alcohol, such as benzhydrol, was used, the corresponding esters were obtained in high yields upon a treatment with benzoic acid for 1–3 h (Table 4, entries 7–9). Similarly, the reaction of alkoxydiphenylphosphine, in-situ formed from *t*-butyl alcohol and chlorodiphenylphosohine, with 1,4-benzoquinone and benzoic acid under the same conditions afforded the desired ester in 75% yield (Table 4, entry 12). Condensations of tertiary alcohol and carboxylic acid, such as 1-adamantanol and 2-phenylbutyric acid or 1-methylcyclopentanol and triphenylacetic acid, also proceeded smoothly to afford the corresponding alkyl carboxylates in excellent yields (Table 4, entries 13 and 14). It was also noted that the corresponding alkyl carboxylates were obtained in excellent yields with perfect inversion of the stereochemistry in the case when a chiral secondary alcohol, such as L-menthol, was used (Table 4, entries 10 and 11). In addition, in the case of using chiral tertiary alcohol

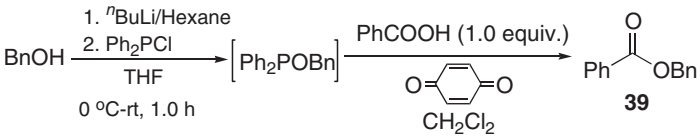
Table 2. Esterification between Several Carboxylic Acids and (−)-Linalool



Entry	R^1OH	R/S	R^2COOH	pK_a[a)]	Product	Yield/%	R/S	Inversion/%
1	 **14**			2.16	**35**	79	5/95	>99
2				3.47	**36**	76	11/84	94
3		95/5		3.82[b)]	**37**	75	6/94	99
4				4.00	**25**	83	20/80	84
5				4.09	**38**	77	7/93	98
6				4.19	**23**	85	7/93	98
7				4.47	**24**	86	5/95	>99

a) See Ref. 1. b) See Ref. 4.

Table 3. Esterification of Benzoic Acid Using ^{n}BuLi and Benzyl Alcohols



Entry	Ph_2POBn/equiv.	Benzoquinone/equiv.	Time/h	Yield/%
1	1.0	1.0	3.0	75
2	1.1	1.0	3.0	75
3	1.3	1.0	3.0	74
4	1.5	1.0	3.0	60
5	1.1	1.1	1.0	76
6	1.3	1.3	1.0	84
7	1.5	1.5	1.0	93
8	**1.7**	**1.7**	**1.0**	**98**
9	1.9	1.9	1.0	98
10	1.1	1.7	1.0	68

such as (*S*)-2-phenyl-2-butanol, the corresponding ester was obtained in 92% yield with 99% inversion.

Efficient Method for the Preparation of Phenyl Carboxylates from Phenols and Carboxylic Acids by Oxidation–Reduction Condensation Using 2,6-Dimethyl-1,4-benzoquinone. There are a number of reactions reported concerning aromatic substitution reactions via the addition–elimination mechanism.[5] These reactions generally proceed smoothly by using aromatic compounds having electron-withdrawing groups, such as a nitro or carbonyl group, and nucleophiles with the assistance of transition metals, such as copper or palladium.[5] Oxidation–reduction condensation using in situ-generated alkoxydiphenylphosphines, carboxylic acids, and 2,6-dimethyl-1,4-benzoquinone or 1,4-benzoquinone provides a new and efficient method for the preparation of primary, inverted secondary, and tertiary alkyl carboxylates from the corresponding alcohols under mild and neutral condition as described in our previous reports.[1–3] In order to extend the scope of these reactions, the formation of phenyl carboxylates by the condensation reaction of phenols with carboxylic acids was studied by using in situ-formed phenoxydiphenylphosphines instead of the abovementioned alkoxydiphenylphosphines. First, it was observed

that the phenyl 4-methoxybenzoate was formed in 22% yield within 3.0 h at room temperature when *p*-methoxybenzoic acid was allowed to react with 1.0 equivalent each of 2,6-dimethyl-1,4-benzoquinone and phenoxydiphenylphosphine formed in situ from ^{n}BuLi-treated phenol and chlorodiphenylphosphine in dichloromethane (Table 5, entry 1). This phenyl carboxylate was obtained in 51% yield when the reaction mixture was refluxed for 2.5 h. Yields of phenyl esters were intact regardless of the reaction time, which was 5.0 h, or the amounts of phenoxydiphenylphosphine and 2,6-dimethyl-1,4-benzoquinone, which was 1.5 equivalents each in that case (Table 5, entries 3 and 4). However, when 1.0 equivalent each of phenoxydiphenylphosphine and 2,6-dimethyl-1,4-bemzoquinone were treated with *p*-methoxybenzoic acid at 110 °C for 2.0 h, the desired ester was obtained in 64% yield (Table 5, entry 5). Then, the effect of the amounts of phenoxydiphenylphosphine and 2,6-dimethyl-1,4-benzoquinone (1:1) was further examined (Table 5, entries 6–10) and, as a consequence, the ester was obtained in 92% yield when 1.5 equivalents each of the in situ-formed phenoxydiphenylphosphine and 2,6-dimethyl-1,4-benzoquinone were treated with 1.0 equivalent of *p*-methoxybenzoic acid at 110 °C for 2.0 h (Table 5, entry 7).

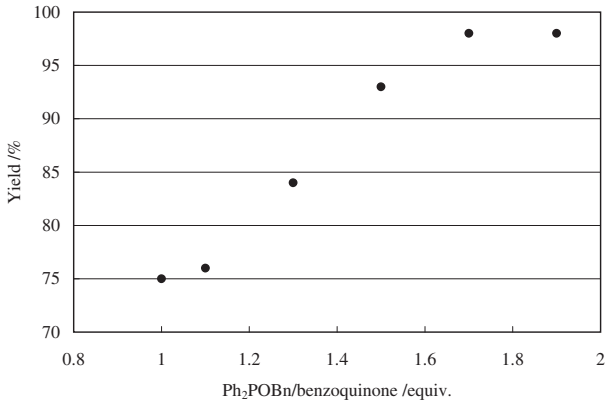
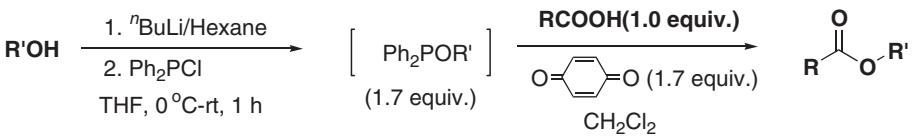
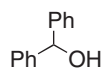
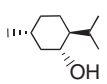
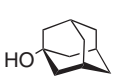
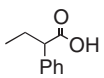
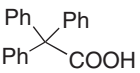
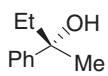


Fig. 1. Esterification of benzoic acid with ^{n}BuLi and benzyl alcohol.

Next, esterifications using in situ-formed phenoxydiphenylphosphines and various carboxylic acids were tried under the conditions shown in Table 6. Phenylation of benzoic acids having electron-donating or electron-withdrawing groups or saturated and unsaturated aliphatic carboxylic acids proceeded

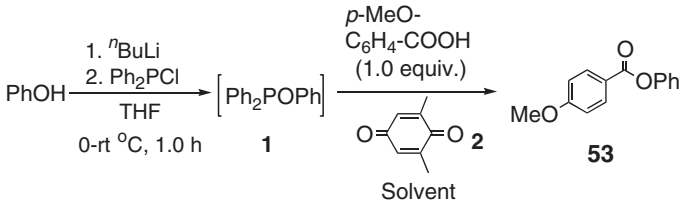
Table 4. Esterifications of Various Carboxylic Acids Using Several Alcohols



Entry	R′OH	RCOOH	Product	Time/h	Yield/%	Yield/%[a)]
1	BnOH	PhCOOH	**39**	1.0	98	98
2		*p*-MeO-C_6H_4COOH	**40**	1.0	95	95
3		*p*-NO_2-C_6H_4COOH	**41**	1.0	96	95
4		$PhCH_2CH_2COOH$	**42**	1.0	92	93
5		PhCH=CHCOOH	**43**	1.0	98	92
6		$CH_3(CH_2)_3COOH$	**44**	1.0	90	93
7	*p*-MeO-$C_6H_4CH_2OH$	PhCOOH	**45**	1.0	93	91
8	$CH_3(CH_2)_3OH$	PhCOOH	**46**	1.0	90	88
9		PhCOOH	**47**	3.0	90	94
10[b)]		PhCOOH	**48**	3.0	91 (>99.9%)	86 (>99.9%)
11[b)]		*p*-NO_2-C_6H_4COOH	**49**	3.0	96 (>99.9%)	95 (>99.9%)
12		PhCOOH	**50**	15.0	75	69
13			**51**	15.0	95	96
14			**52**	15.0	95	91
15[b)]		PhCOOH	**27**	15.0	95 (>99%)	96 (>99%)

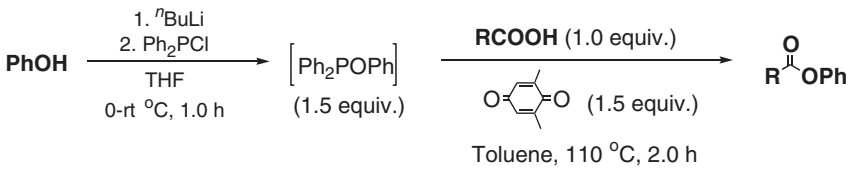
a) See Ref. 5d. Esterifications of various carboxylic acids with various alcohols by using of 2,6-dimethyl-1,4-benzoquinone [alcohols (1.1–1.2 equiv.), carboxylic acids (1.0 equiv.), 2,6-dimethyl-1,4-benzoquinone (1.0 equiv.)]. b) Yields in the parenthesis are inversion.

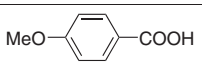
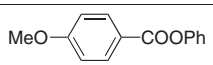
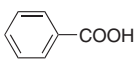
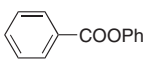
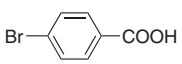
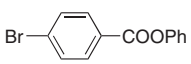
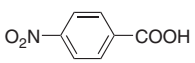
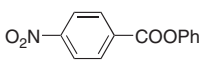
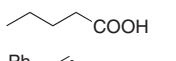
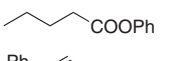
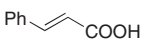
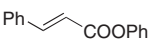
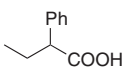
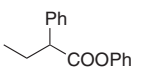
Table 5. Esterification of *p*-Methoxybenzoic Acid Using ^{n}BuLi and Phenol



Entry	**1**/equiv.	**2**/equiv.	Solvent	Condition	Yield/%
1	1.0	1.0	CH_2Cl_2	rt, 3.0 h	22
2	1.0	1.0	CH_2Cl_2	reflux, 2.5 h	51
3	1.0	1.0	CH_2Cl_2	reflux, 5.0 h	50
4	1.5	1.5	CH_2Cl_2	reflux, 5.0 h	52
5	1.0	1.0	Toluene	110 °C, 2.0 h	64
6	1.2	1.2	Toluene	110 °C, 2.0 h	77
7	**1.5**	**1.5**	**Toluene**	**110 °C, 2.0 h**	**92**
8	1.6	1.6	Toluene	110 °C, 2.0 h	91
9	1.8	1.8	Toluene	110 °C, 2.0 h	82
10	2.0	2.0	Toluene	110 °C, 2.0 h	32

Table 6. Esterifications of Various Carboxylic Acids with Phenol

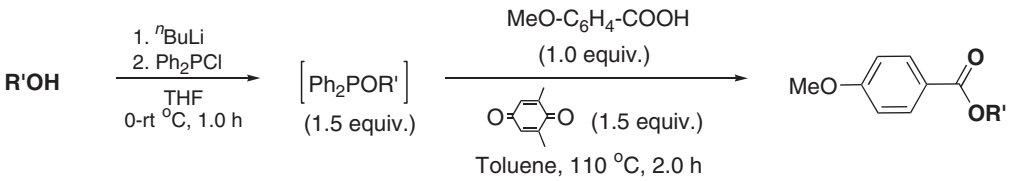


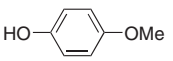
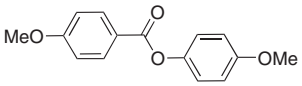
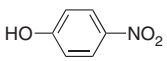
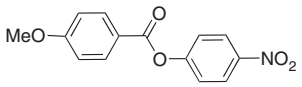
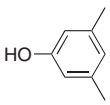
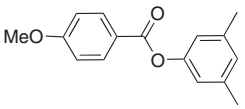
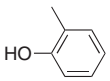
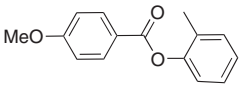
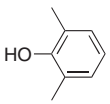
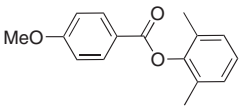
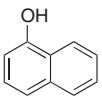
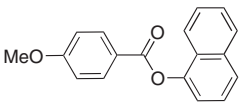
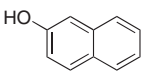
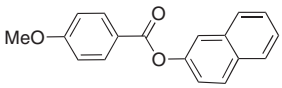
Entry	RCOOH	Product		Yield/%
1			**53**	92
2			**54**	88
3			**55**	90
4			**56**	90
5			**57**	90
6			**58**	92
7			**59**	93
8			**60**	95

smoothly to afford the corresponding phenyl carboxylates in high yields under neutral conditions (Table 6, entries 1–6). When bulky secondary or tertiary carboxylic acids, such as 2-phenylbutyric acid or trimethylacetic acid (2,2-dimethylpropionic acid), were used, the corresponding esters were also obtained in high yields by treating these acids with in situ-formed phenoxydiphenylphosphine for 2.0 h at 110 °C (Table 6, entries 7 and 8).

Phenyl carboxylates forming reactions by using 2,6-dimethyl-1,4-benzoquinone, *p*-methoxybenzoic acid, and various phenoxydiphenylphosphines formed in situ from various ^{n}BuLi-treated phenols and chlorodiphenylphosphine were further tried (Table 7). When phenols having electron-donating or electron-withdrawing groups were used, the corresponding phenyl carboxylates were obtained in 90 to 94% yields, respectively (Table 7, entries 1 and 2). Esterifications of *p*-methoxybenzoic acid and phenols having methyl groups at the *m*-positions, such as 3,5-dimethylphenol, or at the *o*-positions, such as 2-methylphenol, proceeded smoothly to afford the desired esters in 86–93% yields within 2.0 h (Table 7, entries 3 and 4). On the other hand, the corresponding phenyl ester was obtained in 23% yield when ortho-substituted phenol, such as 2,6-dimethylphenol, was allowed to react under the above conditions for 6.0 h at 110 °C (Table 7, entry 5). When the reaction was carried out for 2 h at 160 °C using a solvent, such as *p*-xylene, the desired product was then obtained in 76% yield (Table 7,

Table 7. Esterifications of Carboxylic Acid with Various Phenols



Entry	R′OH	Time/h	Product		Yield/%
1		2.0		**61**	90
2[a)]		2.0		**62**	94
3		2.0		**63**	93
4		2.0		**64**	86
5		6.0		**65**	23
6		2.0			76[b)]
7		2.0		**66**	86
8		2.0		**67**	92

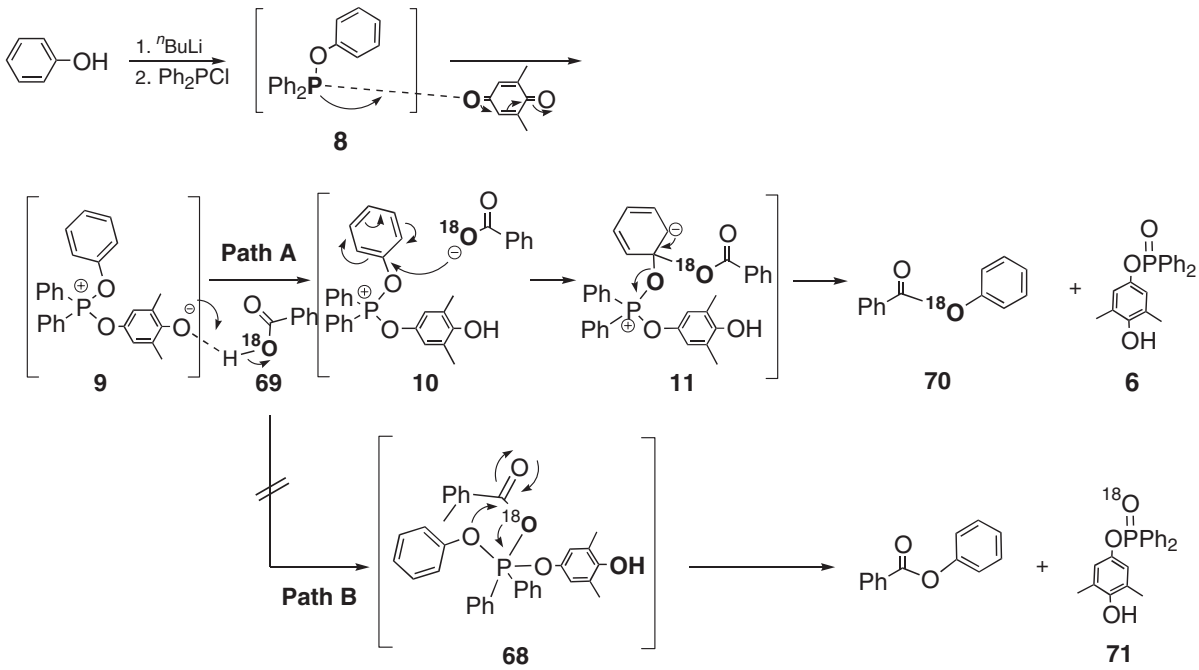
a) A corresponding diphenylphosphine was prepared from R′OH, Et_3N, and Ph_2PCl. b) The reaction mixture was stirred for 2.0 h in *p*-xylene at 160 °C.

entry 6). The corresponding esters were also obtained in good-to-high yields when 1-naphthol or 2-naphthol was used (Table 7, entries 7 and 8).

A proposed reaction mechanism of oxidation–reduction condensation by the combined use of benzoic acid, 2,6-dimethyl-1,4-benzoquinone, and phenoxydiphenylphosphine formed in situ from phenol and chlorodiphenylphosphine is shown in Scheme 3. Phenoxydiphenylphosphine (**8**) was assumed to react with 2,6-dimethyl-1,4-benzoquinone to form the intermediate phosphonium salt (**9**). The formed phosphonium salt (**9**) was, in turn, transformed to the phosphonium carboxylate (**10**) by catching one hydrogen atom from the carboxylic acids. Aromatic substitution took place via addition–elimination processes after a nucleophilic attack of carboxylate anion of the intermediate (**10**), and the corresponding phenyl carboxylate was formed (Scheme 3, Path A). On the other hand, an alternative pathway was considered in which the formed phosphonium salt (**9**) was in turn transformed to the penta-valent phosphorus compound (**68**) by catching one hydrogen atom from the carboxylic acids. A successive nucleophilic attack of oxygen of the phenol group might afford the phenyl carboxylate (Scheme 3, Path B). In order to examine the above-mentioned possible pathways, an ^{18}O-labeling study[6] was carried out by employing a $PhCO^{18}OH$ (**69**). $PhCO^{18}OH$ was prepared from PhCOCl and $H_2{}^{18}O$ in 93% yield, and the incorporation of ^{18}O was 45%.[7] As a result, $PhCO^{18}OPh$ (**70**) was obtained in 88% yield (45% ^{18}O-incorporation) along with diphenylphosphinic acid 4-hydroxy-3,5-dimethylphenyl ester **6** (^{18}O-incorporation was not detected). This result thus indicated that the reaction took place via addition–elimination processes of aromatic substitution, as shown in **Path A**, and that it proceeded smoothly to afford phenyl carboxylate.

Conclusion

A new and efficient method for the preparations of inverted alkyl carboxylates from *t*-alkoxydiphenylphosphines generated in situ from chiral tertiary alcohols, 2,6-dimethyl-1,4-benzoquionone, and carboxylic acids was established by way of oxidation–reduction condensation under a mild condition. It was also shown that the condensation proceeded successfully to afford alkyl carboxylates in good-to-high yields by the combined use of alkoxydiphenylphosphines formed in situ from primary, bulky secondary or tertiary alcohol, simple 1,4-benzoquinone, and various carboxylic acids. In the case of chiral secondary or tertiary alcohols, the corresponding inverted carboxylates were obtained similarly in good-to-high yields. Further, oxidation–reduction condensation using phenoxydiphenylphosphines formed in situ from various phenols and chlorodiphenyl-



Scheme 3.

phosphine, 2,6-dimethy-1,4-benzoquinone, and various carboxylic acids proceeded smoothly at 110 °C in toluene to afford the corresponding phenyl carboxylates in high yields under neutral conditions via addition–elimination processes of aromatic substitution.

Experimental

General Information. All of the melting points were determined on a Yanagimoto micro melting point apparatus (Yanaco MP-S3) and were not corrected. Infrared (IR) spectra were recorded on a Nicolet AVATAR360 (ATR) or a Horiba FT300 FT-IR spectrometer (neat). ^{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 teteramethylsilane. Splitting patterns are designated as s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad. ^{13}C NMR spectra were recorded on an EX270L (68 MHz) spectrometer with complete proton decoupling. The chemical shifts are reported in parts per million relative to tetramethylsilane with the solvent resonance as the internal standard ($CDCl_3$; δ 77.0). High-resolution mass spectra (HRMS) were reported on a JEOL LCmate. MS spectra were reported on a JEOL DX-303HF. The polarimeter was used 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 (ϕ4.6 × 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.

General Procedure for the Preparation of Chiral Tertiary Alcohols. Chiral tertiary alcohols were prepared according to Walsh's procedure.[2] The characterization of the products (**15**–**19**) were shown in Ref. 2.

General Procedure for the Preparation of Carboxylates with Retention of Stereochemistry.[2] Into a stirred solution of chiral *t*-alcohol (0.6 mmol) in Et_2O (2 mL) was dropped a hexane solution of ^{n}BuLi (0.6 mmol) at 0 °C under argon atmosphere. After the solution was stirred at room temperature for 1.0 h, a Et_2O (1 mL) solution of carboxylic acid chloride (0.6 mmol) was added at 0 °C. The reaction mixture was stirred for 2.0 h at room temperature. After completion of the reaction (detected by TLC), it was quenched with saturated aq NH_4Cl, and mixture was extracted with Et_2O. The organic layers were dried over anhydrous sodium sulfate, filtered, and concentrated. The crude product was purified by preparative TLC to afford the desired product.

General Procedure for the Preparation of Inverted Carboxylates.[2] Into a stirred solution of chiral *t*-alcohol (1.5 mmol) in THF (5 mL) was dropped a hexane solution of ^{n}BuLi (1.5 mmol) at 0 °C under argon atmosphere. After the solution was stirred at room temperature for 1.0 h, a THF (2 mL) solution of chlorodiphenylphosphine (1.5 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, 2,6-dimethyl-1,4-benzoquinone, and dichloromethane were added to the residue and the mixture was stirred for 18 h at room temperature. 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 (3 mL) and ethyl acetate (0.5 mL), lithium chloride was removed by filtration through celite (1.0 g) after passing it through alumina (activated, basic) (Wako Pure Chemical Industries, LTD) (7 g). The solvent was concentrated in vacuo, and crude alkoxydiphenylphosphine was obtained. To a mixture of carboxylic acid (0.60 mmol) and 2,6-dimethyl-1,4-benzoquinone (0.60 mmol) under argon atmosphere was added a dichloromethane (0.50 mL) solution of the above crude alkoxydiphenylphosphine under above condition. 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. The characterization of the products (**26–34**) were shown in Ref. 2.

1,5-Dimethyl-1-vinyl-4-hexenyl 2-Nitrobenzoate (35). Colorless oil; R/S = 5/95: $[\alpha]_D^{27} = +15.3$ (*c* 0.98, $CHCl_3$), R/S = 95/5: $[\alpha]_D^{26} = -14.2$ (*c* 1.04, $CHCl_3$); IR (ATR, cm^{-1}) 1727, 1534, 1292, 1128, 1072, 732; ^1H NMR (270 MHz, $CDCl_3$) δ 7.85 (d, $J = 7.3$ Hz, 1H), 7.73 (d, $J = 7.3$ Hz, 1H), 7.65–7.60 (m, 2H), 6.10 (dd, $J = 10.9$, 6.5 Hz, 1H), 5.26–5.08 (m, 3H), 2.02–1.86 (m, 4H), 1.69 (s, 3H), 1.66 (s, 3H), 1.58 (s, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 163.6, 140.5, 132.5, 131.9, 131.3, 129.9, 128.4, 123.6, 123.4, 114.0, 86.1, 40.0, 25.7, 22.8, 22.4, 17.7; HRMS (EI^+) calcd for $C_{17}H_{21}NO_4$ $[M]^+$ 303.1470, found *m/z* 303.1484; HPLC analysis: DAICEL CHIRALCEL OD (ϕ4.6 × 250 mm), hexane/isopropyl alcohol = 900/1, flow rate: 0.5 mL/min, Temp.: 25 °C, detector: 254 nm, S ($t_R = 34.2$ min), R ($t_R = 28.4$ min).

1,5-Dimethyl-1-vinyl-4-hexenyl 3-Nitrobenzoate (36). Colorless oil; R/S = 11/89: $[\alpha]_D^{27} = +15.5$ (*c* 1.04, $CHCl_3$), R/S = 95/5: $[\alpha]_D^{25} = -16.4$ (*c* 1.93, $CHCl_3$); IR (ATR, cm^{-1}) 1722, 1534, 1350, 1292, 1263, 1133; ^1H NMR (270 MHz, $CDCl_3$) δ 8.82 (d, $J = 1.6$ Hz, 1H), 8.42–8.31 (m, 2H), 7.67–7.61 (m, 1H), 6.10 (dd, $J = 10.9$, 6.5 Hz, 1H), 5.32–5.13 (m, 3H), 2.08–1.94 (m, 4H), 1.72 (s, 3H), 1.65 (s, 3H), 1.60 (s, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 162.8, 148.1, 140.9, 153.0, 133.2, 132.1, 129.4, 127.0, 124.3, 123.3, 113.9, 85.0, 39.9, 25.7, 23.6, 22.6, 17.7; HRMS (EI^+) calcd for $C_{17}H_{21}NO_4$ $[M]^+$ 303.1470, found *m/z* 303.1450; HPLC analysis: DAICEL CHIRALCEL OD (ϕ4.6 × 250 mm), hexane/isopropyl alcohol = 900/1, flow rate: 0.5 mL/min, Temp.: 25 °C, detector: 254 nm, S ($t_R = 21.8$ min), R ($t_R = 18.3$ min).

1,5-Dimethyl-1-vinyl-4-hexenyl 3-Chlorobenzoate (37). Colorless oil; R/S = 6/94: $[\alpha]_D^{25} = +16.8$ (*c* 1.02, $CHCl_3$), R/S = 95/5: $[\alpha]_D^{25} = -16.5$ (*c* 0.82, $CHCl_3$); IR (ATR, cm^{-1}) 1719, 1288, 1256, 1128, 1072, 746; ^1H NMR (270 MHz, $CDCl_3$) δ 7.97–7.96 (m, 1H), 7.91–7.87 (m, 1H), 7.52–7.49 (m, 1H), 7.39–7.34 (m, 1H), 6.08 (dd, $J = 11.1$, 6.5 Hz, 1H), 5.29–5.12 (m, 3H), 2.05–1.93 (m, 4H), 1.69 (s, 3H), 1.65 (s, 3H), 1.59 (s, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 141.3, 134.3, 132.5, 131.9, 129.5, 129.4, 127.5, 123.6, 113.6, 84.2, 77.2, 40.0, 25.7, 23.7, 22.6, 17.7; HRMS (EI^+) calcd for $C_{17}H_{21}ClO_2$ $[M]^+$ 292.1230, found *m/z* 292.1236; HPLC analysis: DAICEL CHIRALCEL OD (ϕ4.6 × 250 mm), hexane/isopropyl alcohol = 900/1, flow rate: 0.5 mL/min, Temp.: 25 °C, detector: 254 nm, S ($t_R = 15.0$ min), R ($t_R = 12.7$ min).

1,5-Dimethyl-1-vinyl-4-hexenyl 2-Methoxybenzoate (38). Colorless oil; R/S = 7/93: $[\alpha]_D^{26} = +16.8$ (*c* 1.00, $CHCl_3$), R/S = 95/5: $[\alpha]_D^{28} = -17.4$ (*c* 1.33, $CHCl_3$); IR (ATR, cm^{-1}) 1703, 1249, 1077, 754; ^1H NMR (270 MHz, $CDCl_3$) δ 7.78–7.76 (m, 1H), 7.44–7.41 (m, 1H), 6.97–6.94 (m, 2H), 6.08 (dd, $J = 10.9$, 6.5 Hz, 1H), 5.30–5.14 (m, 3H), 3.88 (s, 3H), 2.05–1.88 (m, 4H), 1.68 (s, 3H), 1.66 (s, 3H), 1.59 (s, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 164.7, 159.0, 141.9, 132.9, 131.6, 131.4, 123.8, 121.3, 119.9, 113.0, 111.9, 83.5, 55.8, 40.0, 25.7, 24.0, 22.5, 17.6; HRMS (EI^+) calcd for $C_{18}H_{24}O_3$ $[M]^+$ 288.1725, found *m/z* 288.1732; HPLC analysis: DAICEL CHIRALCEL OJ (ϕ4.6 × 250 mm), hexane/isopropyl alcohol = 1000/1, flow rate: 0.5 mL/min, Temp.: 25 °C, detector: 254 nm, S ($t_R = 22.9$ min), R ($t_R = 26.1$ min).

Diphenylphosphinic Acid 4-Hydroxy-3,5-dimethylphenyl Ester (6). The characterization of the title compound was shown in Ref. 1.

General Procedure for the Preparation of Carboxylates by Using 1,4-Benzoquinone. Into a mixture of carboxylic acid (0.30 mmol) and 1,4-benzoquinone (0.30 mmol) under argon atmosphere was added a dichloromethane (0.3 mL) solution of alkoxydiphenylphosphine (0.51 mmol) 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 organic layers were dried over anhydrous sodium sulfate. After filtration and evaporation, the resulting residue was purified by preparative TLC to afford the corresponding ether. The above reactions were also carried out by a one-pot procedure, and the same results were obtained even in the presence of lithium chloride. The characterization of the products (**39–52**) were shown in Ref. 1.

Diphenylphosphinic Acid 4-Hydroxyphenyl Ester (7). Isolated as a white solid; mp 169–171 °C; IR (ATR, cm^{-1}) 3188, 1505, 1435, 1186, 1129, 910, 730; ^1H NMR (270 MHz, $CDCl_3$) δ 7.88–7.81 (m, 2H), 7.66–7.41 (m, 8H), 6.92–6.80 (m, 2H), 6.58–6.46 (m, 2H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 132.5, 131.9 (d, $J = 10.6$ Hz), 131.6 (d, $J = 10.6$ Hz), 128.7 (d, $J = 1.1$ Hz), 128.6 (d, $J = 2.2$ Hz), 121.5 (d, $J = 4.5$ Hz), 119.4, 116.4 (d, $J = 1.1$ Hz); HRMS ($APCI^+$) calcd for $C_{18}H_{16}O_3P$ $[M + H]^+$ 311.0837, found *m/z* 311.0831.

General Procedure for the Preparation of Phenyl Carboxylates. Into a mixture of carboxylic acid (0.30 mmol) and 2,6-dimethyl-1,4-benzoquinone (0.45 mmol) under argon atmosphere was added a toluene (0.35 mL) solution of phenoxydiphenylphosphine (0.45 mmol) at room temperature. The reaction mixture was stirred for 2 h in toluene while keeping the temperature of the oil bath at 110 °C. After the reaction monitored by TLC was completed, the mixture was cooled down to room temperature. Water was then added to quench the mixture and the aqueous layer was extracted with dichloromethane. The dichloromethane solution was dried over anhydrous sodium sulfate. After filtration and evaporation, the resulting residue was purified by preparative TLC to afford the corresponding ester. The above reactions could also be carried out by a one-pot procedure, and the same results were obtained in the coexistence of lithium chloride.

Phenyl 4-Methoxybenzoate (53).[8] White solid; mp 67–69 °C (lit.[8a] mp 67–69 °C); IR (ATR, cm^{-1}) 1723, 1254, 1193, 1161, 1075, 743; ^1H NMR (270 MHz, $CDCl_3$) δ 8.16 (d, $J = 8.9$ Hz, 2H), 7.45–7.39 (m, 2H), 7.29–7.19 (m, 3H), 6.98 (d, $J = 8.9$ Hz, 2H), 3.90 (s, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 164.8, 163.7, 150.9, 132.2, 129.3, 125.6, 121.7 (×2), 113.7, 55.5; HRMS ($ACPI^+$) calcd for $C_{14}H_{13}O_3$ $[M]^+$ 229.0865, found *m/z* 229.0871.

Phenyl Benzoate (54).[8a,9] White solid; mp 71–72 °C (lit.[8a] mp 70–72 °C); IR (ATR, cm^{-1}) 1726, 1257, 1196, 1060, 749; ^1H NMR (270 MHz, $CDCl_3$) δ 8.22–8.19 (m, 2H), 7.64–7.61 (m, 2H), 7.54–7.40 (m, 4H), 7.30–7.20 (m, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 165.0, 150.8, 133.5, 130.1, 129.5, 129.4, 128.5, 125.8, 121.6; HRMS ($ACPI^+$) calcd for $C_{13}H_{11}O_2$ $[M + H]^+$ 199.0759, found *m/z* 199.0764.

Phenyl 4-Bromobenzoate (55).[8b,10] White solid; mp 117–118 °C (lit.[10] mp 116–117 °C); IR (ATR, cm^{-1}) 1729, 1265, 1075, 747; ^1H NMR (270 MHz, $CDCl_3$) δ 8.06 (d, $J = 8.5$ Hz, 2H), 7.66 (d, $J = 8.5$ Hz, 2H), 7.47–7.41 (m, 2H), 7.31–7.19 (m, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 164.3, 150.6, 131.8, 131.5, 129.4, 128.7, 128.3, 126.0, 121.5; HRMS ($ACPI^+$) calcd for $C_{13}H_{10}BrO_2$ $[M + H]^+$ 276.9864, found *m/z* 276.9871.

Phenyl 4-Nitrobenzoate (56).[8b,11] White solid; mp 128–129 °C (lit.[11] mp 128–129 °C); IR (ATR, cm^{-1}) 1739, 1520, 1265, 1180, 1075, 755; ^1H NMR (270 MHz, $CDCl_3$) δ 8.38–8.37 (m,

4H), 7.49–7.44 (m, 2H), 7.34–7.32 (m, 1H), 7.26–7.22 (m, 2H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 163.0, 150.6, 150.2, 134.7, 131.1, 129.5, 126.2, 123.5, 121.2; HRMS (ACPI$^-$) calcd for $C_{13}H_9NO_4$ $[M]^+$ 243.0532, found m/z 243.0524.

Phenyl Pentanoate (57).[12] Colorless oil; IR (ATR, cm^{-1}) 1756, 1195, 1140, 1099; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.40–7.34 (m, 2H), 7.24–7.18 (m, 1H), 7.09–7.05 (m, 2H), 2.56 (t, J = 7.4 Hz, 2H), 1.80–1.69 (m, 2H), 1.49–1.41 (m, 2H), 0.97 (t, J = 7.4 Hz, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 172.1, 150.6, 129.3, 125.6, 121.5, 34.2, 27.1, 22.3, 13.8; HRMS (ACPI$^+$) calcd for $C_{11}H_{15}O_2$ $[M + H]^+$ 179.1072, found m/z 179.1073.

Phenyl Cinnamate (58).[13] White solid; mp 76–78 °C (lit.[13b] mp 76–78 °C); IR (ATR, cm^{-1}) 1723, 1306, 1140, 762; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.87 (d, J = 15.9 Hz, 1H), 7.57 (m, 2H), 7.43–7.38 (m, 5H), 7.28–7.16 (m, 3H), 6.64 (d, J = 15.9 Hz, 1H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 165.2, 150.6, 146.4, 134.0, 130.6, 129.3, 128.9, 128.2, 125.7, 121.5, 117.2; HRMS (ACPI$^+$) calcd for $C_{15}H_{13}O_2$ $[M + H]^+$ 225.0916, found m/z 225.0921.

Phenyl 2-Phenylbutylate (59).[14] Colorless oil; IR (ATR, cm^{-1}) 1752, 1192, 1133, 727; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.41–7.29 (m, 7H), 7.20–7.15 (m, 1H), 6.99–6.96 (m, 2H), 3.69 (t, J = 7.7 Hz, 1H), 2.28–2.17 (m, 1H), 1.95–1.85 (m, 1H), 0.99 (t, J = 7.3 Hz, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 172.4, 150.6, 138.4, 129.2, 128.6, 127.9, 127.3, 125.6, 121.3, 53.5, 26.8, 12.2; HRMS (ACPI$^+$) calcd for $C_{16}H_{17}O_2$ $[M + H]^+$ 241.1229, found m/z 241.1227.

Phenyl 2,2-Dimethylpropionate (60).[15] Colorless oil; IR (ATR, cm^{-1}) 1748, 1194, 1110, 740; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.40–7.34 (m, 2H), 7.23–7.21 (m, 1H), 7.06–7.03 (m, 2H), 1.36 (s, 9H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 176.9, 150.9, 129.2, 125.5, 121.4, 39.1, 27.2; HRMS (ACPI$^+$) calcd for $C_{11}H_{15}O_2$ $[M + H]^+$ 179.1072, found m/z 179.1079.

4-Methoxyphenyl 4-Methoxybenzate (61).[16] White solid; mp 124–125 °C (lit.[16] mp 125 °C); IR (ATR, cm^{-1}) 1721, 1509, 1246, 1189, 1164, 1024, 763; ^{1}H NMR (270 MHz, $CDCl_3$) δ 8.14 (d, J = 8.9 Hz, 2H), 7.11 (d, J = 8.9 Hz, 2H), 6.98 (d, J = 8.9 Hz, 2H), 6.93 (d, J = 8.9 Hz, 2H), 3.89 (s, 3H), 3.82 (s, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 165.1, 163.6, 157.0, 144.3, 132.1, 122.4, 121.8, 114.4, 113.7, 55.7, 55.5; HRMS (ACPI$^+$) calcd for $C_{15}H_{15}O_4$ $[M + H]^+$ 259.0970, found m/z 259.0966.

4-Nitrophenyl 4-Methoxybenzoate (62).[11,17] White solid; mp 167–168 °C (lit.[11] mp 167 °C); IR (ATR, cm^{-1}) 1732, 1512, 1264, 1208, 1164, 1063, 1010, 838, 758; ^{1}H NMR (270 MHz, $CDCl_3$) δ 8.32 (d, J = 8.9 Hz, 2H), 8.15 (d, J = 8.9 Hz, 2H), 7.41 (d, J = 8.9 Hz, 2H), 7.01 (d, J = 8.9 Hz, 2H), 3.92 (s, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 168.0, 163.8, 161.2, 149.2, 132.4, 126.1, 125.1, 122.6, 114.0, 55.6; HRMS (ACPI$^+$) calcd for $C_{14}H_{12}NO_5$ $[M + H]^+$ 274.0715, found m/z 274.0714.

3,5-Dimethylphenyl 4-Methoxybenzoate (63). White solid; mp 51–52 °C; IR (ATR, cm^{-1}) 1717, 1248, 1138, 1077; ^{1}H NMR (270 MHz, $CDCl_3$) δ 8.13 (d, J = 8.8 Hz, 2H), 6.97 (d, J = 8.8 Hz, 2H), 6.89 (s, 1H), 6.81 (s, 2H), 3.88 (s, 3H), 2.33 (s, 6H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 165.0, 163.6, 150.7, 139.1, 132.1, 127.4, 121.9, 119.2, 113.7, 55.5, 21.3; HRMS (ACPI$^+$) calcd for $C_{16}H_{17}O_3$ $[M + H]^+$ 257.1178, found m/z 257.1175.

2-Methylphenyl 4-Methoxybenzoate (64).[18] Colorless oil; IR (ATR, cm^{-1}) 1722, 1260, 1163, 1067, 752; ^{1}H NMR (270 MHz, $CDCl_3$) δ 8.17 (d, J = 8.6 Hz, 2H), 7.27–7.11 (m, 4H), 6.98 (d, J = 8.6 Hz, 2H), 3.88 (s, 3H), 2.22 (s, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 164.3, 163.6, 149.3, 132.0, 130.9, 130.1, 126.7, 125.7, 121.9, 121.5, 113.6, 55.4, 16.2; HRMS (ACPI$^+$) calcd for $C_{15}H_{15}O_3$ $[M + H]^+$ 243.1021, found m/z 243.1017.

2,6-Dimethylphenyl 4-Methoxybenzoate (65).[19] Colorless oil; IR (ATR, cm^{-1}) 1725, 1604, 1252, 1156, 764; ^{1}H NMR (270 MHz, $CDCl_3$) δ 8.20 (d, J = 8.9 Hz, 2H), 2.96 (s, 3H), 7.00 (d, J = 8.9 Hz, 2H), 3.89 (s, 3H), 2.18 (s, 6H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 163.7, 148.2, 132.1, 130.3, 128.4, 125.6, 121.5, 120.0, 113.8, 55.5, 16.5; HRMS (ACPI$^+$) calcd for $C_{16}H_{17}O_3$ $[M + H]^+$ 257.1178, found m/z 257.1186.

Naphthalen-1-yl 4-Methoxybenzoate (66).[20] White solid; mp 108–109 °C; IR (ATR, cm^{-1}) 1723, 1600, 1253, 1079, 763; ^{1}H NMR (270 MHz, $CDCl_3$) δ 8.29 (d, J = 9.0 Hz, 2H), 7.95–7.87 (m, 2H), 7.79–7.76 (m, 1H), 7.54–7.47 (m, 3H), 7.37–7.34 (m, 1H), 7.04 (d, J = 9.0 Hz, 2H), 3.92 (s, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 163.9, 146.8, 134.6, 132.3, 127.9, 127.5, 127.0, 126.3, 125.8, 125.4, 121.5, 121.2, 118.2, 113.9, 108.4, 55.6; HRMS (ACPI$^+$) calcd for $C_{18}H_{15}O_3$ $[M + H]^+$ 279.1021, found m/z 279.1025.

Naphthalen-2-yl 4-Methoxybenzoate (67).[21] White solid; mp 113–114 °C (lit.[21] mp 113–114 °C); IR (ATR, cm^{-1}) 1720, 1260, 1153, 1060, 750; ^{1}H NMR (270 MHz, $CDCl_3$) δ 8.20 (d, J = 8.8 Hz, 2H), 7.91–7.80 (m, 3H), 7.68 (m, 1H), 7.49–7.47 (m, 2H), 7.37–7.24 (m, 1H), 7.00 (d, J = 8.8 Hz, 2H), 3.90 (s, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 164.9, 163.7, 148.5, 133.7, 132.2, 131.3, 129.3, 127.7, 127.5, 126.4, 125.5, 121.7, 121.3, 118.6, 113.8, 55.5; HRMS (ACPI$^+$) calcd for $C_{18}H_{15}O_3$ $[M + H]^+$ 279.1021, found m/z 279. 1014.

Benzoic Acid [PhCO^{18}OH] (69).[7] Into a stirred solution of benzoyl chrolide (56 mmol) in pyridine (20 mL) was dropped a $H_2{}^{18}O$ (56 mmol) at room temperature under argon atmosphere. After the solution was stirred at room temperature for 18 h, concentrated HCl was added (pH 1). The solution was extracted with Et_2O (20 mL × 5) and the combined organic layer was dried over anhydrous sodium sulfate. After filtration and evaporation, the resulting residue was purified by recrystallization (from EtOH) to afford the title compound (**69**) (6.4 g, 93%) as a white solid: mp 122–123 °C; IR (ATR, cm^{-1}) 3069–2539, 1662, 1276, 930; ^{1}H NMR (270 MHz, $CDCl_3$) δ 12.7 (br, 1H), 8.17–8.11 (m, 2H), 7.67–7.44 (m, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 172.4, 134.4, 133.7, 130.4, 130.1, 129.2, 128.8, 128.4; HRMS (ACPI$^-$) calcd for $C_7H_5O^{18}O$ $[M]^+$ 123.0333, found m/z 123.0332 (45% ^{18}O-incorporation), calcd for $C_7H_5O_2$ $[M]^+$ 121.0298, found m/z 121.0290.

Phenyl Benzoate [PhCO^{18}OPh] (70). White solid: mp 69–70 °C; IR (ATR, cm^{-1}) 1727, 1696, 1257, 1196, 1060, 749; ^{1}H NMR (270 MHz, $CDCl_3$) δ 8.22–8.19 (m, 2H), 7.63–7.40 (m, 6H), 7.29–7.20 (m, 2H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 150.8, 133.5, 130.1, 129.5, 129.4, 128.5, 125.8, 121.6; HRMS (ACPI$^+$) calcd for $C_{13}H_{10}O^{18}O$ $[M + H]^+$ 201.0804, found m/z 201.0802 (45% ^{18}O-incorporation), calcd for $C_{13}H_{10}O_2$ $[M + H]^+$ 199.0754, found m/z 199.0757.

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