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A Convenient Method for the Synthesis of Dialkyl Ethers by Alkylation of Alcohols Using Phosphinimidates in the Presence of a Catalytic Amount of Trimethylsilyl Triflate

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An alkylation reaction of alcohols with alkyl *N*-(methylsulfonyl)diphenylphosphinimidates proceeded smoothly in the presence of a catalytic amount of trimethylsilyl triflate (Me_3SiOTf) in DME at room temperature and the corresponding ethers were afforded in good to high yields. An alkyl *N*-(methylsulfonyl)diphenylphosphinimidate can be prepared easily from an alkyl diphenylphosphinite and methanesulfonyl azide, and is isolated without tedious operation. Moreover, it is easy to handle and can be stored for several months at room temperature because of its air- and moisture-resistant character. Also, one-pot tertiary alkylations of alcohols by using *t*-alkyl diphenylphosphinites and diphenoxyphosphoryl azide proceeded efficiently in the presence of a catalytic amount of Me_3SiOTf in cyclohexane/CH_2Cl_2 at 0 °C or −10 °C, and gave the corresponding tertiary alkyl ethers in good yields. By following these methods, various ethers having alkali-sensitive functional groups can be prepared easily.

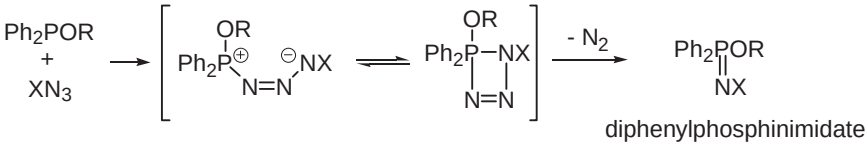
The preparation of ethers is considered one of the most fundamental and frequently used reactions important in synthetic organic chemistry. In 1850, the first ether synthesis was reported by Williamson using alkyl halide and metal alkoxide, which has been employed up to date by many resarchers.[1] The attack of alkoxides on alkyl halides, however, was synthetically effective only when the primary alkyl halide was used. When a secondary or tertiary alkyl halide was used, the desired ethers were obtained in low yields along with the corresponding olefins that were simultaneously formed by elimination reactions. Moreover, this method is not applicable to the substrates having alkali-sensitive functional groups because their reaction conditions are strongly basic. Then, a number of studies so as to prepare ethers under non-basic and milder conditions have been reported:[2] for example, Schmidt and Michel reported glycosyl trichloroacetimidate employed for glycoside synthesis in the presence of a catalytic amount of trifluoromethanesulfonic acid in 1980.[3] The method to use alkyl tricholoroacetimidate has been applied to various alkylation reactions of alcohols such as benzylation,[4a,b] allylation,[4c] and *t*-butylation[4d] since then. Very recently, new methods for the preparation of ethers via the coupling of two alcohols using oxidation–reduction condensation with tetrafluoro-1,4-benzoquinone[5] and for the alkylation of an alkoxysilane with an alkyl diphenylphosphinate ($Ph_2P(=O)OR$) and Me_3SiOTf[6] were also reported from our laboratory. In spite of these efforts, studies to prepare ethers under mild conditions still remain challenging.

It was reported from our laboratory that an alkyl diphenylphosphinite (Ph_2POR) could work as an alkylating agent if activated by an oxidant such as a quinone.[7] On the other hand, an alkyl diphenylphosphinite itself reacted with an azide compound (XN_3) as shown in the Staudinger reaction,[8] and formed a diphenylphosphinimidate ($Ph_2P(=NX)OR$) along with a loss of nitrogen (Scheme 1).[9] A diphenylphosphinimidate was expected to work as a good alkylating agent under acidic conditions like the above-mentioned alkyl diphenylphosphinate did because of having a similar structure. However, few reports have been done concerning the alkylation of alcohols with a diphenylphosphinimidate except for the glycosylation reaction in carbohydrate chemistry.[10]

In this paper, we would like to show good to high-yielding preparation of ethers by using alcohols and stable alkyl *N*-(methylsulfonyl)diphenylphosphinimidates in the presence of Me_3SiOTf. A one-pot tertiary alkylation reaction using a *t*-alkyl *N*-(diphenoxyphosphoryl)diphenyphosphinimidate in situ generated from a *t*-alkyl diphenylphosphinite and diphenoxyphosphoryl azide is also described (Scheme 2).

Results and Discussion

An Efficient Method for Alkylation of Alcohols with Alkyl *N*-(Methylsulfonyl)diphenylphosphinimidates.[11] At first, preparation of benzyl *N*-(diphenoxyphosphoryl)diphenyl-



Scheme 1.

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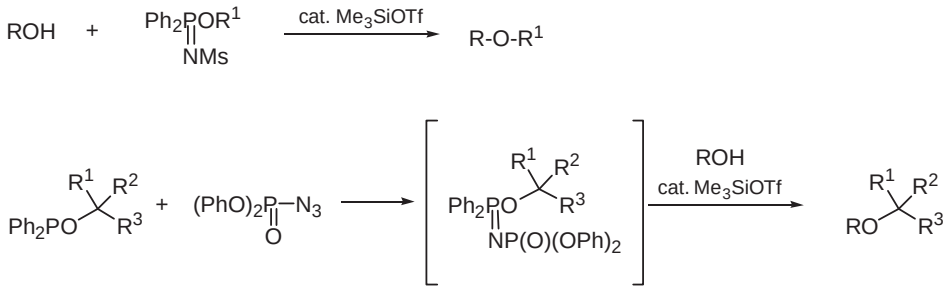
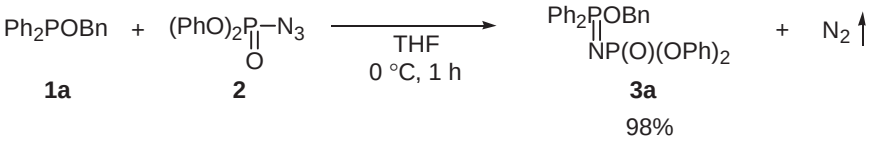
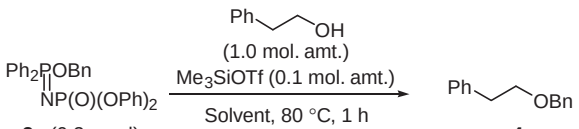


Scheme 2.



Scheme 3.

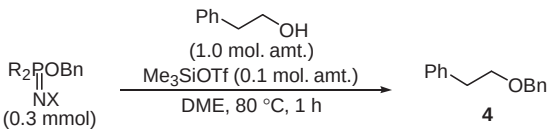
Table 1. Effect of Solvent on Benzylation of 2-Phenylethanol



Entry	Solvent	Yield/%	Entry	Solvent	Yield/%
1[a)]	EDC[b)]	N.R.	5	1,4-Dioxane	54
2	EDC	16	6	DME[c)]	55
3	Toluene	27	7	Acetonitrile	7
4	THF	33			

a) The reaction was carried out without Me_3SiOTf. b) 1,2-Dichloroethane. c) 1,2-Dimethoxyethane.

Table 2. Effect of Substituents on Phosphinimidate



Entry	R	X		Yield/%
1	Ph	$(PhO)_2P(O)$	**3a**	55
2	*i*-Pr	$(PhO)_2P(O)$	**3b**	38
3	Ph	Bz	**3c**	77
4	Ph	Ts	**3d**	89
5	Ph	Ms	**3e**	93

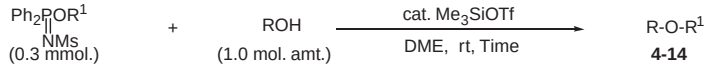
phosphinimidate (**3a**) by the reaction of a 1.0 molar amount of benzyl diphenylphosphinite (**1a**), formed from BnOH and Ph_2PCl, with a 1.1 molar amount of commercially available diphenoxyphosphoryl azide (**2**) was tried in THF at 0 °C, and **3a** was then obtained in 98% yield within 1 h (Scheme 3).

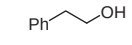
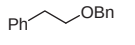
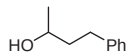
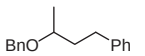
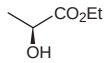
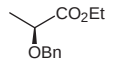
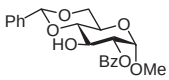
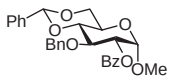
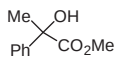
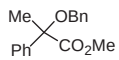
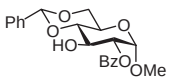
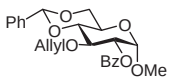
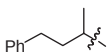
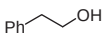
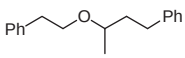
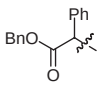
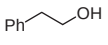
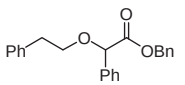
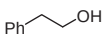
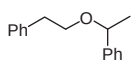
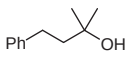
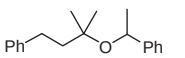
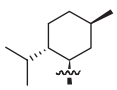
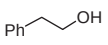
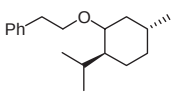
Next, the benzylation reaction of 2-phenylethanol was tried by using an equimolar amount of **3a** in 1,2-dichloroethane at 80 °C. However, the expected product **4** was not obtained within 1 h and both **3a** and the alcohol were recovered quantitatively (Table 1, Entry 1). The same result was obtained even when the reaction time was elongated to 12 h. Then, the reaction proceeded slightly and **4** was obtained in 16% yield in 1 h when a 0.10 molar amount of Me_3SiOTf was used as an activator of **3a** (Entry 2). In order to improve the yield, various solvents such as toluene, THF, 1,4-dioxane, 1,2-dimethoxyethane, and acetonitrile were tried next. As a result, 1,2-dimethoxyethane showed the most appropriate effect for this alkylation reaction and **4** was obtained in 55% yield in 1 h (Entries 3–7).

Next, the effect of the substituents on phosphinimidate was examined. When two phenyl groups on the phosphorus atom of **3a** were replaced by two isopropyl groups, the yield decreased, whereas it increased up to 77% when the diphenoxyphosphoryl group on the nitrogen atom was replaced by the benzoyl group (Table 2, Entris 1–3). Fortunately, the phosphinimidate having a methylsulfonyl group was found to afford a better result and **4** was obtained in 93% yield (Entry 5).

In order to carry out the reaction under milder conditions, reactions at lower temperatures were attempted. Then, the reaction proceeded even at room temperature and afforded **4** in 95% yield within 1 h (Table 3, Entry 1). The scope of the reaction with the optimized procedure was investigated (Entries 2–11). Then, benzylation of 4-phenyl-2-butanol, a secondary alcohol, proceeded smoothly and the desired ether **5** was obtained in 94% yield (Entry 2). In the case when ethyl (*S*)-(−)-lactate was used, the corresponding benzyl ether **6** was obtained exclusively without any accompanying epimerization (Entry 3). Under these reaction conditions, an alkali-sensitive ester group was tolerated. Benzylation of a secondary alcohol[12] having both acetal and ester groups or the tertiary alcohol having an ester group also took place and gave the corresponding ethers in good yields (Entries 4 and 5). In addition, allylation of the secondary alcohol took place and gave the corresponding allyl protected sugar **9** in 72% in 24 h (Entry 6). Next, a similar alkylation with 2-phenylethanol and **3g**, **3h**, or **3i** was tried (Entries 7–9). In the cases of **3g** and **3h**, the desired ethers were obtained in moderate yields in the presence of a 0.20 molar amount of Me_3SiOTf in 24 h, while it was consumed within 0.5 h when **3i** was used in the presence of only a 0.01 molar amount of catalyst and the corresponding ether with lost chirality was obtained alternatively in 85% yield.

Table 3. Primary or Secondary Alkylation of Alcohols with Alkyl *N*-(Methylsulfonyl)diphenylphosphinimidates and Me_3SiOTf

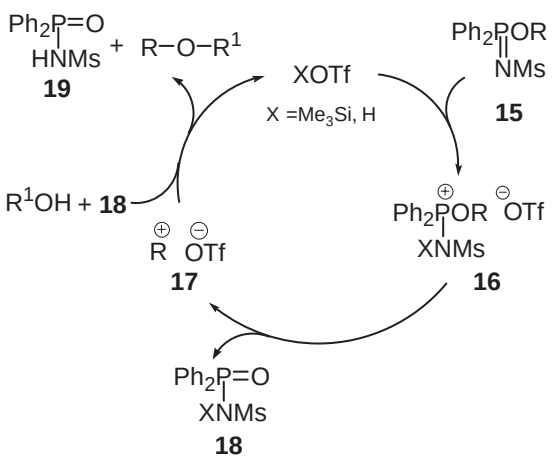


Entry	R^1		ROH	Me_3SiOTf /10^{-2} mol. amt.	Time /h	Product		Yield /%
1[a]	Bn	**3e**		10	1		**4**	95
2	Bn	**3e**		10	3		**5**	94
3	Bn	**3e**		10	3		**6**	88
4	Bn	**3e**		10	3		**7**	77
5	Bn	**3e**		10	3		**8**	73
6	Allyl	**3f**		10	24		**9**	72[b]
7		**3g**		20	24		**10**	55
8		**3h**		20	24		**11**	57
9		**3i**		1	0.5		**12**	85[c]
10		**3i**		1	0.5		**13**	83[c]
11		**3j**		30	24		**14**	N.D.

a) The desired ether was obtained in 91% yield when TfOH was used instead of Me_3SiOTf. b) 1.2 molar amount of the phosphinimidate was used. c) Racemic product was obtained.

Likewise, reaction of **3i** and tertiary alcohols also took place to give the corresponding tertiary ether with lost chirality in 83% yield (Entry 10). Unfortunately, the desired ether was not obtained when the less reactive (1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl *N*-(methylsulfonyl)diphenylphosphinimidate (**3j**) was used (Entry 11).

As shown in Table 3, racemic products were obtained when (*S*)-1-phenylethyl *N*-(methylsulfonyl)diphenylphosphinimidate was used. These results indicate that a phosphinimidate reacts with an alcohol via the S_N1 mechanism. In the first step, alkyl *N*-(methylsulfonyl)diphenylphosphinimidate (**15**) is silylated or protonated to yield the very reactive electrophilic alkyl cation **17**, which in turn reacts rapidly with alcohols to form ethers along with *N*-methylsulfonyl diphenylphosphinamide (**19**). The proton liberated in this step is subsequently involved in the catalytic cycle (Scheme 4).

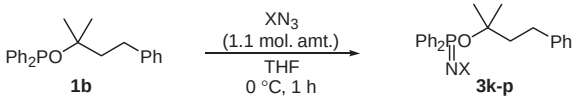


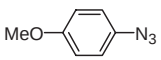
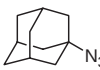
Scheme 4.

The Preparation of *t*-Alkyl Ethers by Using Alcohols and *t*-Alkyl Diphenylphosphinites. In order to extend the scope of this etherification, our attention was next focused on the tertiary alkylation of alcohols.

At first, preparation of 1,1-dimethyl-3-phenylpropyl *N*-(methylsulfonyl)diphenylphosphinimidate (**3k**) was tried according to the above mentioned method; however, **3k** was not successfully obtained due to its instability (Table 4, Entry 1). The cause for the result was thought to be the electron-withdrawing Ms group. Then, reactions of 1,1-dimethyl-3-phenylpropyl diphenylphosphinite (**1b**) and other azide compounds were further tried (Entries 2–6). Interestingly, the correspond-

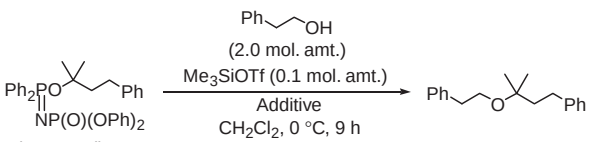
Table 4. Reactions of 1,1-Dimethyl-3-phenylpropyl Diphenylphosphinite with Azide Compounds



Entry	XN_3	Product	Yield/%
1	MsN_3	**3k**	Dec.
2	BzN_3	**3l**	(60)[a]
3	$(PhO)_2P(=O)-N_3$	**3m**	96
4		**3n**	Dec.
5	$Me_3SiCH_2N_3$	**3o**	Dec.
6		**3p**	Dec.

a) A mixture of **3l** and its decomposed products.

Table 5. Effect of Additives



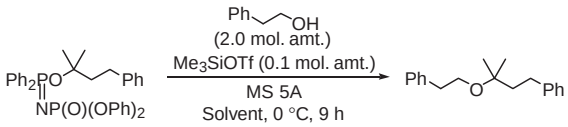
Entry	Additive	Yield/%	Entry	Additive	Yield/%
1	None	9	4	MS 4A	N.D.
2	Drierite	41	5	MS 5A	44
3	MS 3A	N.D.			

ing phosphinimidate **3m** was isolated as a stable compound only when diphenoxyphosphoryl azide was used (Entry 3).

Next, the *O*-alkylation reaction of a 2.0 molar amount of 2-phenylethanol in CH_2Cl_2 with a 1.0 molar amount of **3m** in the presence of a 0.1 molar amount of Me_3SiOTf was tried. However, the yield of the desired ether **20** was only 9% and a part of **3m** was recovered (Table 5, Entry 1). Even when the reaction time was elongated, the result remained the same. Then, the effect of an additive was investigated (Entries 2–5). After several additives were examined, **3m** was found consumed and the desired ether was obtained in 44% yield when MS 5A was used (Entry 5). The role of MS 5A has not yet been elucidated, but a similar effect of MS 5A was observed in protic acid catalyzed glcosylation using glycosyl fluoride.[13]

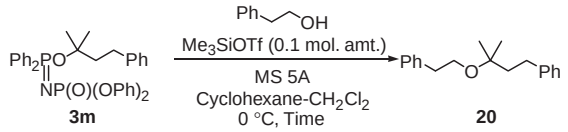
The solvent effect was next examined and the mixture of an equivalent amount of cyclohexane and CH_2Cl_2 gave a better result compared with that when only CH_2Cl_2 was used (Table 6, Entry 2). Further, the yield improved when the ratio of cyclohexane to CH_2Cl_2 was quadrupled, whereas the yield decreased as the ratio of cyclohexane to CH_2Cl_2 increased (Entries 3 and 4). Next, other solvents such as $CHCl_3$, DME, CH_3CN, and toluene were used in place of CH_2Cl_2 and the reaction in cyclohexane/$CHCl_3$ gave nearly the same result as the case in cyclohexane/CH_2Cl_2 (Entry 5). On the other hand, the reactions in other solvents did not give better results than that of cyclohexane/CH_2Cl_2 (Entries 6–8). Also, the yields decreased slightly when hexane was used instead of cyclohexane (Entry 9). Thus, it is concluded that cyclohexane/CH_2Cl_2 (4/1) is the most suitable solvent for this reaction.

Table 6. Effect of Solvent



Entry	Solvent	Yield/%
1	CH_2Cl_2	41
2	Cyclohexane/CH_2Cl_2 (1/1)	59
3	Cyclohexane/CH_2Cl_2 (4/1)	64
4	Cyclohexane/CH_2Cl_2 (9/1)	32
5	Cyclohexane/$CHCl_3$ (4/1)	62
6	Cyclohexane/DME (4/1)	49
7	Cyclohexane/CH_3CN (4/1)	14
8	Cyclohexane/Toluene (4/1)	48
9	Hexane/CH_2Cl_2 (4/1)	55

Table 7. Optimization of Reaction Conditions

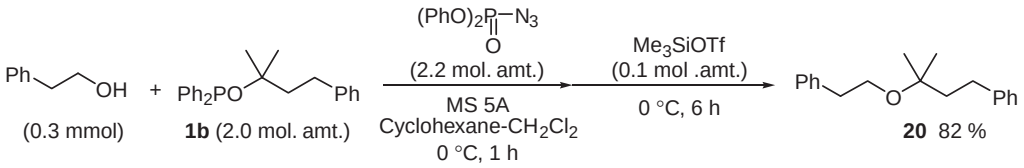


Entry	Phosphinimidate /mol. amt.	$Ph(CH_2)_2OH$ /mol. amt.	Time /h	Yield/%
1	1.0	1.0	9	50
2	1.0	2.0	9	64
3	1.5	1.0	9	66
4	1.7	1.0	9	77
5	2.0	1.0	9	80
6	2.0	1.0	6	81
7	2.0	1.0	3	65

Optimization of the molar ratio of the alcohol and **3m** was further tried and the yield increased up to 81% yield when a 2.0 molar amount of **3m** was used (Table 7, Entry 6).

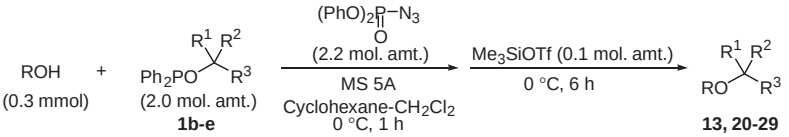
Next, it was thought that the present reaction would afford the ether from 2-phenylethanol, **1b**, and diphenoxyphosphoryl azide in a one-pot procedure without isolating **3m** because the only co-product generated is nitrogen gas in **3m** preparation. The experiment was conducted by the following procedure. To a stirred solution of a 2.0 molar amount of **1b**, a 1.0 molar amount of 2-phenylethanol, and MS 5A in cyclohexane/CH_2Cl_2 was added a 2.2 molar amount of diphenoxyphosphoryl azide at 0 °C. The reaction mixture was stirred for 1 h at 0 °C, and then was added Me_3SiOTf. After stirring the solution for 6 h at 0 °C and work up, the corresponding ether was obtained in 82% yield (Scheme 5). Thus, this one-pot procedure gave almost the same result as that carried out by the method using the isolated **3m**.

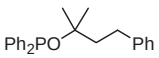
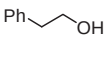
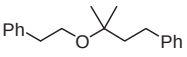
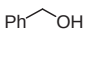
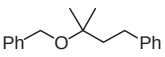
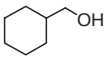
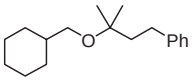
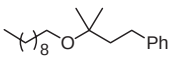
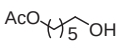
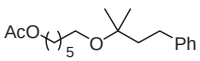
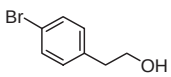
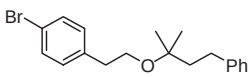
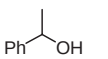
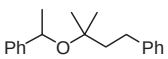
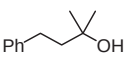
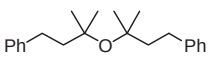
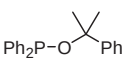
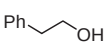
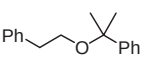
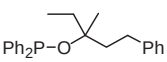
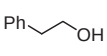
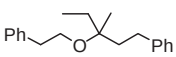
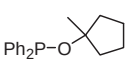
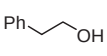
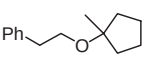
Various *O*-alkylation reactions that use an alcohol and a phosphinimidate in situ formed from a *t*-alkyl diphenylphosphinite and diphenoxyphosphoryl azide were next tried (Table 8). When tertiary alkylations of various primary alcohols by using **1b** were tried, the corresponding *t*-alkyl ethers were obtained in good yields (Entries 1–6). On the other hand, the desired ether was obtained in moderate yield when tertiary



Scheme 5.

Table 8. *tert*-Alkylations of Alcohols Using *t*-Alkyl Diphenylphosphinite and Diphenoxyphosphoryl Azide



Entry	Phosphinite		ROH	Product		Yield/%
1		**1b**			**20**	82
2					**21**	76
3					**22**	72
4					**23**	68
5					**24**	72[a]
6					**25**	74[a]
7					**13**	54
8					**26**	N.D.
9		**1c**			**27**	74
10		**1d**			**28**	63[b]
11		**1e**			**29**	36

a) The reaction was carried out at −10 °C for 24 h. b) 0.05 molar amount of Me_3SiOTf was used.

alkylation of a secondary alcohol like 1-phenylethanol was carried out (Entry 7). The tertiary alkylation of 2-methyl-4-phenyl-2-butanol did not take place as expected (Entry 8). Etherifications of 2-phenylethanol with several *t*-alkyl diphenylphosphinites were also tried and tertiary alkylation reactions using 1-methyl-1-phenylethyl diphenylphosphinite or 1-ethyl-1-methy-3-phenylpropyl diphenylphosphinite proceeded affording the corresponding ether in good yield (Entries 9 and 10). On the other hand, the yield decreased slightly when cyclic *t*-alkyl diphenylphosphinite was used (Entry 11).

Conclusion

A new and efficient method for the preparation of ethers from alcohols and phosphinimidates has been established. Benzyl, allyl, and secondary alkyl ethers were afforded in good to high yields by treating the corresponding alkyl *N*-(methylsulfonyl)diphenylphosphinimidates with alcohols and a catalytic amount of Me_3SiOTf.[14] An alkyl *N*-(methylsulfonyl)diphenylphosphinimidate prepared from an alkyl diphenylphosphinite and methanesulfonyl azide was easy to handle and could be stored for several months because of its inertness to air and moisture. Further, *t*-alkyl ethers were also afforded in good yields by using *t*-alkyl *N*-(diphenoxyphosphoryl)diphenylphosphinimidates in situ formed from *t*-alkyl diphenylphosphinites and diphenoxyphosphoryl azide, alcohols, and a catalytic amount of Me_3SiOTf. This method is considered very practical in the syntheses of ethers having alkali-sensitive functional groups because the reaction conditions are mild.

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 an 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 ($CDCl_3$; δ 77.0 ppm, DMSO; δ 39.5 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 a JASCO P-1020. 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. Chlorodiphenylphosphine and diphenoxyphosphoryl azide were purchased from Tokyo Kasei Kogyo and used without further purification. Powdered and pre-dried (at 260 °C/133 Pa, 6 h) molecular sieves 3A, 4A, and 5A were used in the etherifications. Sufficiently crushed and pre-dried (at 260 °C/133 Pa, 6 h) Drierite from W. A. Hammond Drierite Company was used in the etherifications. All reagents were purchased from Tokyo Kasei Kogyo, Wako Pure Chemical Industries, or Aldrich Chemical and used without further purification. Alcohols (Table 3, Entries 4 and 6[12] and Table 8, Entry 5[15]) were prepared following the literature procedures.

Typical Experimental Procedure for Preparation of Alkyl Diphenylphosphinite (1a–1e). To a stirred solution of alcohol (10 mmol) and DMAP (3 mmol) in dry THF (20 mL) were added Et_3N (12 mmol) followed by $ClPPh_2$ (11 mmol) under an Ar atmosphere. After stirring at rt for 2 h, TLC showed complete consumption of the alcohol, and the resulting white slurry was concentrated by a rotatory evaporator. After dilution of the residue with hexane/ethyl acetate (v/v = 9/1, 100 mL), the mixture was filtered through a pad of alumina (activated, 300 mesh; purchased from Wako Pure Chemical Industries, Ltd.) and Celite. The filtrate was concentrated under reduced pressure to give the desired phosphinites.

Benzyl Diphenylphosphinite (1a):[16] Isolated as a colorless oil (yield 94%); IR (ATR, cm^{-1}) 982, 735; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.54–7.47 (m, 4H), 7.37–7.27 (m, 11H), 4.89 (d, J = 9.2 Hz, 2H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 141.5 (d, J = 17.9 Hz), 138.6 (d, J = 8.4 Hz), 130.3 (d, J = 21.8 Hz), 129.2, 128.2, 128.2 (d, J = 6.7 Hz), 127.6, 127.3, 71.5 (d, J = 20.1 Hz); MS (APCI$^+$) m/z 293 $[M + H]^+$.

1,1-Dimethyl-3-phenylpropyl Diphenylphosphinite (1b): Isolated as a colorless oil (yield 91%); IR (ATR, cm^{-1}) 3055, 2969, 1602, 1434, 927, 911, 740, 693, 526; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.55–7.49 (m, 4H), 7.29–7.03 (m, 11H), 3.94–3.89 (m, 2H), 3.01–2.95 (m, 2H), 1.40 (s, 6H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 143.6 (d, J = 16.2 Hz), 142.3, 129.9 (d, J = 22.3 Hz), 128.6, 128.2, 128.2, 128.0 (d, J = 6.7 Hz), 125.5, 78.3 (d, J = 11.7 Hz), 45.1 (d, J = 6.1 Hz), 30.7, 28.1 (d, J = 9.5 Hz); HRMS (APCI$^+$) calcd for $C_{23}H_{26}OP$ $[M + H]^+$ 349.1721, found m/z 349.1712.

1-Methyl-1-phenylethyl Diphenylphosphinite (1c):[7a] Isolated as a white solid (yield 99%); mp 87–88 °C; IR (ATR, cm^{-1}) 946, 886, 745; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.54–7.44 (m, 6H), 7.34–7.22 (m, 9H), 1.73 (s, 6H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 147.3 (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), 128.0, 126.8, 125.3, 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-Ethyl-1-methyl-3-phenylpropyl Diphenylphosphinite (1d): Isolated as a colorless oil (yield 92%); IR (ATR, cm^{-1}) 3054, 3025, 2967, 2935, 1454, 1434, 1374, 932, 907, 737, 692, 512, 482; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.56–7.50 (m, 4H), 7.29–7.04 (m, 11H), 2.64–2.58 (m, 2H), 2.00–1.94 (m, 2H), 1.85–1.77 (m, 2H), 1.38 (s, 3H), 0.93–0.88 (m, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 143.7 (d, J = 16.2 Hz), 143.7 (d, J = 16.2 Hz), 142.3, 130.0 (d, J = 22.9 Hz), 129.9 (d, J = 22.4 Hz), 128.6, 128.5, 128.1, 128.1, 128.0, 127.9, 125.5, 80.9 (d, J = 10.6 Hz), 42.1 (d, J = 6.1 Hz), 33.3 (d, J = 7.3 Hz), 30.4, 25.3 (d, J = 11.2 Hz), 8.7; HRMS (APCI$^+$) calcd for $C_{24}H_{28}OP$ $[M + H]^+$ 363.1878, found m/z 363.1877.

1-Methylcyclopentyl Diphenylphosphinite (1e): Isolated as a white solid (yield 98%); mp 48–49 °C; IR (ATR, cm^{-1}) 922, 735; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.50–7.45 (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, $CDCl_3$) δ 143.6 (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.

Benzyl *N*-(Diphenoxyphosphoryl)diphenylphosphinimidate (3a). To a stirred solution of **1a** (146.2 mg, 0.50 mmol) in THF (0.5 mL) under an argon atmosphere was added diphenoxyphosphoryl azide (151.4 mg, 0.55 mmol) at 0 °C. After the reaction mixture was stirred at 0 °C for 1 h, it was concentrated in vacuo and purified by column chromatography (hexane/ethyl acetate = 1/2) to afford the title compound **3a** (263.3 mg, 98%) as a colorless oil; IR (ATR, cm^{-1}) 3061, 1591, 1487, 1307, 1247, 1196, 1162, 1126, 991, 911, 688, 495; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.75–7.68 (m, 4H), 7.65–7.20 (m, 19H), 7.10–7.01 (m, 2H), 4.97 (d, J = 7.1 Hz, 2H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 152.0 (d, J = 7.8 Hz), 135.4 (d, J = 8.4 Hz), 132.5 (d, J = 2.8 Hz), 131.7 (d, J = 11.2 Hz), 130.1, 130.0, 129.1, 128.5, 128.3, 128.2, 128.0, 127.9, 127.8, 120.5 (d, J = 5.0 Hz), 67.4 (d, J = 6.7 Hz); HRMS (APCI$^+$) calcd for $C_{31}H_{28}NO_4P_2$ $[M + H]^+$ 540.1494, found m/z 540.1475.

Benzyl *N*-(Diphenoxyphosphoryl)diisopropylphosphinimidate (3b). To a stirred solution of benzyl alcohol (1.2 g, 11.4 mmol) in THF (11 mL) was added a hexane solution of ^{n}BuLi (11.4 mmol) at room temperature under an argon atmosphere. After the solution was stirred at room temperature for 1 h, chlorodiisopropylphosphine (1.9 g, 12.6 mmol) was added at 0 °C. The reaction mixture was stirred for 1 h at room temperature and then diphenoxyphosphoryl azide (3.5 g, 12.6 mmol) was added at 0 °C. After the reaction mixture was stirred for 1 h at 0 °C, it was concentrated in vacuo and purified by column chromatography (hexane/ethyl acetate = 1/2) to afford the title compound **3b** (4.4 g, 83%) as a colorless oil; IR (ATR, cm^{-1}) 2969, 1592, 1488, 1323, 1244, 1196, 1162, 1004, 909, 690, 519; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.33–7.23 (m, 13H), 7.09–7.03 (m, 2H), 4.97 (d, J = 8.1 Hz, 2H), 2.24–2.07 (m, 2H), 1.17–1.06 (m, 12H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 152.2 (d, J = 7.8 Hz), 136.2 (d, J = 5.6 Hz), 129.0, 128.2, 128.0, 127.7, 123.5, 120.4 (d, J = 5.0 Hz), 67.9 (d, J = 8.3 Hz), 26.5 (d, J = 85.6 Hz), 26.5 (d, J = 87.2 Hz), 15.4, 15.4, 15.4, 15.3; HRMS (APCI$^+$) calcd for $C_{25}H_{32}NO_4P_2$ $[M + H]^+$ 472.1807, found m/z 472.1791.

Benzyl *N*-(Benzoyl)diphenylphosphinimidate (3c). Benzoyl chloride (140.6 mg, 1.0 mmol) was dissolved in DMF (1 mL) at 0 °C and was stirred for 1 h at 0 °C. Then, sodium azide (71.5 mg, 1.1 mmol) was added to the mixture at 0 °C and stirred for 2 h at 0 °C. After warming the reaction mixture to room temperature, a solution of **1a** (292.3 mg, 1.0 mmol) in dichloromethane (1 mL) was added dropwise, and the solution continued to be stirred for 1 h at room temperature and chloroform was added. Then, the mixture was washed successively with water and brine, and 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 **3c** (356.0 mg, 87%) as a colorless oil; IR (ATR, cm^{-1}) 3060, 1600, 1565, 1438, 1321, 1297, 1174, 1124, 1007, 992, 957, 726, 712, 689, 670, 538, 516; ^{1}H NMR (270 MHz, $CDCl_3$) δ 8.40–8.36 (m, 2H), 7.96–7.87 (m, 4H), 7.50–7.18 (m, 14H), 5.27 (d, J = 6.8 Hz, 2H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 175.4 (d, J = 7.3 Hz), 137.9, 137.6, 135.9 (d, J = 8.4 Hz), 132.3 (d, J = 2.8 Hz), 131.9, 131.8, 130.9, 129.8, 129.4, 129.4, 128.5, 128.3, 128.3, 128.1, 127.8, 127.8, 127.6, 68.6 (d, J = 6.2 Hz); HRMS (APCI$^+$) calcd for $C_{26}H_{23}NO_2P$ $[M+H]^+$ 412.1466, found m/z 412.1457.

Benzyl *N*-(*p*-Tolylsulfonyl)diphenylphosphinimidate (3d). *p*-Toluenesulfonyl chloride (190.7 mg, 1.0 mmol) was dissolved in DMF (1 mL) at 0 °C and was stirred for 1 h at 0 °C. Then, sodium azide (71.5 mg, 1.1 mmol) was added to the mixture at 0 °C, followed by stirring for 2 h at 0 °C. After warming up the reaction mixture to room temperature, a solution of **1a** (292.3 mg, 1.0 mmol) in dichloromethane (1 mL) was added dropwise and the solution continued to be stirred for 1 h at room temperature and chloroform was added. Then, the mixture was washed successively with water and brine, and 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 **3d** (392.0 mg, 85%) as a colorless oil; IR (ATR, cm^{-1}) 3034, 1592, 1440, 1276, 1142, 1119, 1088, 966, 746, 689, 664, 555, 517, 491; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.77–7.62 (m, 6H), 7.55–7.48 (m, 2H), 7.41–7.31 (m, 9H), 7.06–7.02 (m, 2H), 5.15 (d, J = 6.8 Hz, 2H), 2.30 (s, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 142.3 (d, J = 2.2 Hz), 140.9, 135.1 (d, J = 8.3 Hz), 132.8 (d, J = 3.3 Hz), 132.1 (d, J = 11.2 Hz), 128.6, 128.6, 128.4, 128.4, 128.4, 128.1, 126.9 (d, J = 138.4 Hz), 125.7, 68.4 (d, J = 6.1 Hz), 21.3; HRMS (APCI$^+$) calcd for $C_{26}H_{25}NO_3PS$ $[M+H]^+$ 462.1293, found m/z 462.1280.

Typical Experimental Procedure for Preparation of Alkyl *N*-(Methylsulfonyl)diphenylphosphinimidates (3e–3j). Methanesulfonyl chloride (10 mmol) was dissolved in DMF (10 mL) at 0 °C and was stirred for 1 h at 0 °C. Then, sodium azide (11 mmol) was added to the mixture at 0 °C, followed by stirring for 2 h at 0 °C. After warming the reaction mixture to room temperature, a solution of alkyl diphenylphosphinite (10 mmol) in dichloromethane (10 mL) was added dropwise and the solution continued to be stirred for 1 h at room temperature and chloroform was added. Then, the mixture was washed successively with water and brine, and the organic layer was dried over anhydrous sodium sulfate. After filtration and evaporation, the resulting crude solid was washed by diethyl ether to afford the desired product.

Benzyl *N*-(Methylsulfonyl)diphenylphosphinimidate (3e): Isolated as a white solid (yield 87%); mp 146–147 °C; IR (ATR, cm^{-1}) 1590, 1439, 1377, 1274, 1150, 1125, 1012, 964, 802, 752, 692, 540, 502, 486; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.88–7.80 (m, 4H), 7.62–7.31 (m, 11H), 5.24 (d, J = 6.9 Hz, 2H), 2.87 (d, J = 1.5 Hz, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 135.1 (d, J = 8.4 Hz), 133.1 (d, J = 3.4 Hz), 132.1 (d, J = 11.2 Hz), 128.7 (d, J = 14.0 Hz), 128.5, 128.5, 128.2, 127.1 (d, J = 139.2 Hz), 68.6 (d, J = 6.1 Hz), 43.9 (d, J = 3.9 Hz); HRMS (APCI$^+$) calcd for $C_{20}H_{21}NO_3PS$ $[M+H]^+$ 386.0980, found m/z 386.0974.

Allyl *N*-(Methylsulfonyl)diphenylphosphinimidate (3f): Isolated as a white solid (yield 74%); mp 80–81 °C; IR (ATR, cm^{-1}) 3067, 1590, 1484, 1439, 1270, 1160, 1123, 1013, 991, 961, 736, 688, 538, 497; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.90–7.82 (m, 4H), 7.64–7.46 (m, 6H), 6.05–5.91 (m, 1H), 5.42–5.34 (m, 1H), 5.29–5.25 (m, 1H), 4.75–4.69 (m, 2H), 2.87 (d, J = 1.6 Hz, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 133.1 (d, J = 3.4 Hz), 132.1 (d, J = 11.2 Hz), 131.9 (d, J = 7.8 Hz), 128.7 (d, J = 14.0 Hz), 127.2 (d, J = 139.2 Hz), 118.9, 67.6 (d, J = 6.1 Hz), 43.9 (d, J = 3.9 Hz); HRMS (APCI$^+$) calcd for $C_{16}H_{19}NO_3PS$ $[M+H]^+$ 336.0823, found m/z 336.0818.

1-Methyl-3-phenylpropyl *N*-(Methylsulfonyl)diphenylphosphinimidate (3g): Isolated as a white solid (yield 92%); mp 87–89 °C; IR (ATR, cm^{-1}) 2937, 1590, 1485, 1438, 1273, 1168, 1157, 1125, 981, 959, 727, 694, 549, 496; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.90–7.75 (m, 4H), 7.64–7.44 (m, 6H), 7.27–7.07 (m, 5H), 5.00–4.85 (m, 1H), 2.79 (d, J = 1.5 Hz, 3H), 2.70–2.64 (m, 2H), 2.12–1.87 (m, 2H), 1.40 (d, J = 6.3 Hz, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 141.1, 132.9 (d, J = 2.8 Hz), 132.2 (d, J = 11.2 Hz), 128.6 (d, J = 14.0 Hz), 128.6 (d, J = 14.0 Hz), 128.3, 128.3 (d, J = 138.6 Hz), 128.2 (d, J = 139.2 Hz), 128.1, 125.8, 76.3 (d, J = 7.3 Hz), 43.9 (d, J = 3.9 Hz), 39.0 (d, J = 5.0 Hz), 31.1, 21.4 (d, J = 2.8 Hz); HRMS (APCI$^+$) calcd for $C_{23}H_{27}NO_3PS$ $[M+H]^+$ 428.1449, found m/z 428.1431.

Benzyloxycarbonyl(phenyl)methyl *N*-(Methylsulfonyl)diphenylphosphinimidate (3h): Isolated as a white solid (yield 70%); mp 123–124 °C; IR (ATR, cm^{-1}) 1748, 1439, 1275, 1208, 1180, 1157, 1123, 1027, 805, 750, 738, 693, 543, 500; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.95–7.85 (m, 4H), 7.79–7.70 (m, 4H), 7.62–7.13 (m, 12H), 6.15 (d, J = 10.7 Hz, 1H), 5.14 (d, J = 12.2 Hz, 1H), 5.08 (d, J = 12.2 Hz, 1H), 2.70 (d, J = 1.5 Hz, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 168.2 (d, J = 5.6 Hz), 134.2 (d, J = 3.9 Hz), 133.2 (d, J = 2.8 Hz), 133.1 (d, J = 2.8 Hz), 132.2 (d, J = 11.7 Hz), 129.3, 128.8, 128.6, 128.6, 128.6, 128.4, 128.3, 128.2, 127.9, 127.6, 127.1 (d, J = 139.5 Hz), 76.4, 67.4, 43.7 (d, J = 3.9 Hz); HRMS (APCI$^+$) calcd for $C_{28}H_{27}NO_5PS$ $[M+H]^+$ 520.1348, found m/z 520.1336.

(*S*)-1-Phenylethyl *N*-(Methylsulfonyl)diphenylphosphinimidate (3i): Isolated as a white solid (yield, 83%); mp 121–122 °C; $[\alpha]_D^{23}$ −15.8 (c 0.99, $CHCl_3$); IR (ATR, cm^{-1}) 1589.3, 1439, 1269, 1178, 1123, 952, 693, 498; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.90–7.80 (m, 2H), 7.64–7.41 (m, 6H), 7.32–7.19 (m, 7H), 5.83–5.72 (m, 1H), 2.75 (d, J = 1.5 Hz, 3H), 1.75 (d, J = 6.4 Hz, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 140.7 (d, J = 3.4 Hz), 132.9 (d, J = 2.8 Hz), 132.7 (d, J = 2.8 Hz), 132.3 (d, J = 11.2 Hz), 131.9 (d, J = 11.2 Hz), 129.2, 128.7, 128.5, 128.3, 128.3, 128.2, 128.1, 128.1, 127.1, 126.2, 77.4 (d, J = 6.7 Hz), 43.8 (d, J = 3.4 Hz), 24.3 (d, J = 5.0 Hz); HRMS (APCI$^+$) calcd for $C_{21}H_{22}NNaO_3PS$ $[M+Na]^+$ 422.0956, found m/z 422.0944.

(1*R*,2*S*,5*R*)-2-Isopropyl-5-methylcyclohexyl *N*-(Methylsulfonyl)diphenylphosphinimidate (3j): Isolated as a colorless oil (yield 89%); $[\alpha]_D^{25}$ −6.1 (c 0.73, $CHCl_3$); IR (ATR, cm^{-1}) 2953, 2868, 1439, 1273, 1171, 1123, 1007, 986, 959, 795, 723, 692, 541, 499; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.89–7.72 (m, 4H), 7.62–7.43 (m, 6H), 4.60–4.48 (m, 1H), 2.79 (d, J = 1.3 Hz, 3H), 2.30–2.26 (m, 1H), 2.14–2.07 (m, 1H), 1.70–1.37 (m, 4H), 1.27–

0.76 (m, 9H), 0.65 (d, $J = 6.9$ Hz, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 132.7 (d, $J = 3.4$ Hz), 132.6 (d, $J = 2.8$ Hz), 132.1 (d, $J = 11.2$ Hz), 131.9 (d, $J = 11.2$ Hz), 129.0 (d, $J = 137.5$ Hz), 128.4 (d, $J = 139.7$ Hz), 128.4 (d, $J = 14.0$ Hz), 128.3 (d, $J = 14.0$ Hz), 81.0 (d, $J = 8.9$ Hz), 48.8 (d, $J = 7.3$ Hz), 43.8 (d, $J = 1.1$ Hz), 33.8, 31.5, 25.6, 22.6, 21.9, 21.1, 15.4; HRMS (APCI$^+$) calcd for $C_{23}H_{33}NO_3PS$ $[M + H]^+$ 434.1919, found m/z 434.1907.

Typical Experimental Procedure for Preparation of Ethers by the Alkylation of Alcohols Using Alkyl *N*-(Methylsulfonyl)-diphenylphosphinimidate (Table 3). To a stirred solution of alkyl *N*-(methylsulfonyl)diphenylphosphinimidate (0.3 mmol) and alcohol (0.3 mmol) in 1,2-dimethoxyethane (0.48 mL) under an argon atmosphere was added a solution of Me_3SiOTf (0.03 mmol) in 1,2-dimethoxyethane (0.02 mL) at 0 °C. The reaction mixture was stirred at room temperature. After completion of the reaction (detected by TLC), the mixture was quenched with saturated $NaHCO_3$ and was extracted with ethyl ether. The organic layers were dried over anhydrous sodium sulfate, then filtered and concentrated. The crude product thus obtained was purified by preparative TLC to give the corresponding ether.

Benzyl Phenethyl Ether (4):[17] Colorless oil; IR (ATR, cm^{-1}) 2856, 1098, 734; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.31–7.20 (m, 10H), 4.52 (s, 2H), 3.69 (t, $J = 7.2$ Hz, 2H), 2.93 (t, $J = 7.2$ Hz, 2H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 138.8, 138.2, 128.8, 128.2, 128.2, 127.5, 127.4, 126.1, 72.9, 71.2, 36.4; HRMS (GC-EI$^+$) calcd for $C_{15}H_{16}O$ $[M]^+$ 212.1296, found m/z 212.1194.

Benzyl 1-Methyl-3-phenyl Ether (5):[18] Colorless oil; IR (ATR, cm^{-1}) 3062, 3026, 2967, 2927, 2860, 1495, 1453, 1373, 1133, 1090, 1064, 1028, 732, 695; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.35–7.14 (m, 10H), 4.57 (d, $J = 12.0$ Hz, 1H), 4.43 (d, $J = 12.0$ Hz, 1H), 3.58–3.47 (m, 1H), 2.82–2.60 (m, 2H), 2.00–1.67 (m, 2H), 1.22 (d, $J = 6.1$ Hz, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 142.2, 138.9, 128.3, 128.2, 128.2, 127.5, 127.3, 125.6, 74.1, 70.3, 38.5, 31.9, 19.7; HRMS (APCI$^+$) calcd for $C_{17}H_{21}O$ $[M + H]^+$ 241.1592, found m/z 241.1596.

Ethyl (*S*)-2-Benzyloxypropanoate (6):[19] Colorless oil; $[\alpha]_D^{26}$ −83.0 (*c* 0.99, $CHCl_3$), [lit.[19] $[\alpha]_D^{20}$ −80.9 (*c* 7.15, AcOEt)]; IR (ATR, cm^{-1}) 2984, 2938, 1743, 1453, 1372, 1269, 1197, 1139, 1115, 1064, 1023, 738, 697; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.36–7.25 (m, 5H), 4.70 (d, $J = 11.6$ Hz, 1H), 4.45 (d, $J = 11.3$ Hz, 1H), 4.27–4.15 (m, 2H), 4.05 (q, $J = 6.8$ Hz, 1H), 1.44 (d, $J = 6.8$ Hz, 3H), 1.29 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 173.0, 137.4, 128.3, 127.8, 127.7, 74.0, 71.9, 60.8, 18.8, 14.3; HRMS (APCI$^+$) calcd for $C_{12}H_{17}O_3$ $[M + H]^+$ 209.1178, found m/z 209.1175.

Methyl 2-*O*-Benzoyl-3-*O*-benzyl-4,6-di-*O*-benzylidene-α-D-glucopyranoside (7):[20] Colorless oil; $[\alpha]_D^{20}$ +130.1 (*c* 1.05, $CHCl_3$), [lit.[20] $[\alpha]_D$ +135 (*c* 1.0, $CHCl_3$)]; IR (ATR, cm^{-1}) 2931, 2859, 1727, 1453, 1368, 1268, 1090, 1043, 998, 713, 699; ^{1}H NMR (270 MHz, $CDCl_3$) δ 8.06–8.03 (m, 2H), 7.62–7.38 (m, 8H), 7.26–7.17 (m, 5H), 5.62 (s, 1H), 5.14–5.06 (m, 2H), 4.88 (d, $J = 11.9$ Hz, 1H), 4.77 (d, $J = 11.9$ Hz, 1H), 4.34 (dd, $J = 4.1$ Hz, $J = 9.7$ Hz, 1H), 4.20 (t, $J = 9.4$ Hz, 1H), 3.97–3.76 (m, 3H), 3.37 (s, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 165.8, 138.1, 137.2, 133.2, 129.8, 129.5, 128.9, 128.3, 128.2, 128.1, 127.8, 127.5, 125.9, 101.3, 97.8, 82.2, 75.7, 74.7, 73.5, 69.0, 62.3, 55.4; HRMS (APCI$^+$) calcd for $C_{28}H_{29}O_7$ $[M + H]^+$ 477.1913, found m/z 477.1924.

Methyl 2-Benzyloxy-2-phenylpropanoate (8):[21] Colorless oil; IR (ATR, cm^{-1}) 3029, 2949, 1732, 1449, 1253, 1113, 1074, 1027, 732, 696; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.55–7.24 (m, 10H), 4.56 (d, $J = 11.2$ Hz, 1H), 4.41 (d, $J = 11.2$ Hz, 1H), 3.74 (s, 3H), 1.88 (s, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 173.4, 141.0, 138.3, 128.3, 128.2, 127.9, 127.3 (×2), 125.7, 81.9, 66.8, 52.5, 23.6; HRMS (GC-EI$^+$) calcd for $C_{17}H_{19}O_3$ $[M + H]^+$ 271.1334, found m/z 271.1320.

Methyl 3-*O*-Allyl-2-*O*-benzoyl-4,6-di-*O*-benzylidene-α-D-glucopyranoside (9): Colorless oil; $[\alpha]_D^{20}$ +124.4 (*c* 0.35, $CHCl_3$); IR (ATR, cm^{-1}) 2933, 1720, 1452, 1375, 1269, 1092, 1048, 991, 922, 710, 699; ^{1}H NMR (270 MHz, $CDCl_3$) δ 8.10 (d, $J = 7.1$ Hz, 2H), 7.62–7.36 (m, 8H), 5.91–5.77 (m, 1H), 5.60 (s, 1H), 5.21 (d, $J = 15.7$ Hz, 1H), 5.10–5.05 (m, 3H), 4.38–4.07 (m, 4H), 3.98–3.61 (m, 3H), 3.38 (s, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 165.8, 137.2, 134.7, 133.1, 129.7, 129.6, 128.8, 128.3, 128.1, 125.9, 116.9, 101.2, 97.8, 81.9, 75.6, 73.8, 73.5, 68.9, 62.3, 55.4; HRMS (APCI$^+$) calcd for $C_{24}H_{27}O_7$ $[M + H]^+$ 427.1757, found m/z 427.1753.

1-Methyl-3-phenylpropyl Phenethyl Ether (10): Colorless oil; IR (ATR, cm^{-1}) 3026, 2927, 2864, 1603, 1494, 1453, 1373, 1341, 1135, 1095, 1078, 1030, 906, 745, 696, 574, 476; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.32–7.09 (m, 10H), 3.77–3.69 (m, 1H), 3.55–3.47 (m, 1H), 3.42–3.31 (m, 1H), 2.88 (t, $J = 7.3$ Hz, 2H), 2.72–2.52 (m, 2H), 1.90–1.59 (m, 2H), 1.15 (d, $J = 6.2$ Hz, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 142.2, 139.1, 128.9, 128.3, 128.2, 128.1, 126.0, 125.5, 74.6, 69.5, 38.5, 36.9, 31.8, 19.7; HRMS (APCI$^+$) calcd for $C_{18}H_{23}O$ $[M + H]^+$ 255.1749, found m/z 255.1756.

Benzyl Phenethyloxy-2-phenylacetate (11): Colorless oil; IR (ATR, cm^{-1}) 3030, 2869, 1747, 1453, 1166, 1115, 730, 695; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.43–7.14 (m, 15H), 5.15 (d, $J = 12.4$ Hz, 1H), 5.09 (d, $J = 12.4$ Hz, 1H), 4.91 (s, 1H), 3.79–3.58 (m, 2H), 3.05–2.88 (m, 2H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 170.4, 138.2, 136.2, 135.3, 128.8, 128.5, 128.4, 128.3, 128.2, 128.1, 127.8, 127.0, 126.1, 81.1, 70.7, 66.7, 36.2; HRMS (APCI$^+$) calcd for $C_{23}H_{23}O_3$ $[M + H]^+$ 347.1647, found m/z 347.1639.

Phenethyl 1-Phenylethyl Ether (12): Colorless oil; IR (ATR, cm^{-1}) 2860, 1495, 1452, 1101, 752; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.31–7.16 (m, 10H), 4.40 (q, $J = 6.5$ Hz, 1H), 3.51 (t, $J = 7.4$ Hz, 2H), 2.91 (dt, $J = 7.4$ Hz, $J = 13.7$ Hz, 1H), 2.84 (dt, $J = 7.4$ Hz, $J = 13.7$ Hz, 1H), 1.43 (t, $J = 6.5$ Hz, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 143.8, 138.9, 128.8, 128.3, 128.3, 128.1, 127.2, 126.0, 78.1, 69.6, 36.6, 24.2; HRMS (GC-EI$^+$) calcd for $C_{16}H_{18}O$ $[M]^+$ 226.1358, found m/z 226.1352.

1,1-Dimethyl-3-phenylpropyl 1-Phenethyl Ether (13): Colorless oil; IR (ATR, cm^{-1}) 3026, 2971, 2927, 1603, 1493, 1452, 1382, 1366, 1203, 1080, 1027, 957, 759, 739, 697; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.38–7.05 (m, 10H), 4.66 (q, $J = 6.5$ Hz, 1H), 2.75–2.52 (m, 2H), 1.87–1.66 (m, 2H), 1.39 (d, $J = 6.5$ Hz, 3H), 1.17 (s, 3H), 1.14 (s, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 147.3, 142.8, 128.2, 128.1, 128.0, 126.4, 125.5, 125.4, 75.8, 69.7, 43.5, 30.6, 26.9, 26.5; Anal. calcd for $C_{19}H_{24}O$: C, 85.03; H, 9.01%; Found: C, 84.81; H, 9.21%.

***N*-(Methylsulfonyl)diphenylphosphinamide (19):** Isolated as a white solid; mp 249–250 °C; IR (ATR, cm^{-1}) 2886, 2742, 2610, 1385, 1314, 1182, 1152, 902, 692, 534, 504, 439; ^{1}H NMR (270 MHz, DMSO) δ 7.86–7.73 (m, 4H), 7.62–7.48 (m, 6H), 3.18 (s, 3H); ^{13}C NMR (68 MHz, DMSO) δ 132.0 (d, $J = 2.8$ Hz), 131.9 (d, $J = 127.4$ Hz), 131.2 (d, $J = 10.6$ Hz), 128.4 (d, $J = 12.9$ Hz), 44.4; HRMS (APCI$^+$) calcd for $C_{13}H_{15}NO_3PS$ $[M + H]^+$ 296.0510, found m/z 296.0507.

1,1-Dimethyl-3-phenypropyl *N*-(Diphenoxyphosphoryl)diphenylphosphinimidate (3m). To a stirred solution of **1b** (348.4 mg, 1.00 mmol) in THF (1.0 mL) under an argon atmo-

sphere was added diphenoxyphosphoryl azide (302.7 mg, 1.10 mmol) at 0 °C. After the reaction mixture had been stirred at 0 °C for 1 h, it was concentrated in vacuo and purified by column chromatography (hexane/ethyl acetate = 1/1) to afford the title compound **3m** (571.1 mg, 96%) as a colorless oil; IR (ATR, cm^{-1}) 3059, 2979, 1592, 1488, 1307, 1198, 988, 911, 748, 726, 689; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.75–7.67 (m, 4H), 7.52–7.33 (m, 6H), 7.27–6.98 (m, 15H), 2.74–2.68 (m, 2H), 2.04–1.98 (m, 2H), 1.48 (s, 6H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 152.1 (d, J = 7.9 Hz), 141.4, 133.1 (d, J = 5.1 Hz), 132.0, 131.9, 131.6, 129.0, 128.2, 128.0, 127.7, 123.5, 120.4 (d, J = 5.0 Hz), 87.9 (d, J = 10.0 Hz), 45.5 (d, J = 5.0 Hz), 30.7, 28.1 (d, J = 3.4 Hz); HRMS (ESI^+) calcd for $C_{35}H_{36}NO_4P_2$ $[M + H]^+$ 596.2120, found m/z 596.2121.

Procedure for the Preparation of 1,1-Dimethyl-3-phenylpropyl Phenethyl Ether (20) by Using 3m and 2-Phenylethanol (Table 7, Entry 6). To a stirred solution of **3m** (0.6 mmol), 2-phenylethanol (0.3 mmol), MS 5A (300 mg) in cyclohexane (0.80 mL) and CH_2Cl_2 (0.18 mL) under an argon atmosphere was added Me_3SiOTf (0.03 mmol) in CH_2Cl_2 (0.02 mL) at 0 °C. The reaction mixture was stirred for 6 h at 0 °C. After completion of the reaction (detected by TLC), the mixture was quenched with triethylamine. The mixture was filtered through a pad of Celite, and the filtrate was concentrated under reduced pressure. The crude product thus obtained was purified by preparative TLC to give the corresponding ether **20**. Colorless oil; IR (ATR, cm^{-1}) 3026, 2970, 2936, 2863, 1603, 1495, 1453, 1382, 1362, 1209, 1076, 739, 696; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.31–7.12 (m, 10H), 3.55 (t, J = 7.3 Hz, 2H), 2.85 (t, J = 7.3 Hz, 2H), 2.60–2.55 (m, 2H), 1.77–1.71 (m, 2H), 1.19 (s, 6H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 142.8, 139.3, 129.0, 128.2 (×2), 128.1, 126.0, 125.5, 74.4, 62.7, 42.2, 37.4, 30.3, 25.7; HRMS ($APCI^+$) calcd for $C_{19}H_{25}O$ $[M + H]^+$ 269.1905, found m/z 269.1916.

Typical Experimental Procedure for the Preparation of *t*-Alkyl Ethers by the Alkylation of Alcohols Using *t*-Alkyl Diphenylphosphinites and Diphenoxyphosphoryl Azide (Table 8). To a stirred solution of alkyl diphenylphosphinite (0.6 mmol), alcohol (0.3 mmol), and MS 5A (300 mg) in cyclohexane (0.80 mL) and CH_2Cl_2 (0.18 mL) was added diphenoxyphosphoryl azide (6.6 mmol) at 0 °C. The reaction mixture was stirred for 1 h at 0 °C and then Me_3SiOTf (0.03 mmol) in CH_2Cl_2 (0.02 mL) was added. The reaction mixture was stirred for 6 h at 0 °C (24 h at −10 °C). After completion of the reaction (detected by TLC), the mixture was quenched with triethylamine. The mixture was filtered through a pad of Celite and the filtrate was concentrated under reduced pressure. The crude product thus obtained was purified by preparative TLC to give the corresponding ether.

Benzyl 1,1-Dimethyl-3-phenylpropyl Ether (21): Colorless oil; IR (ATR, cm^{-1}) 3062, 3026, 2970, 2933, 2863, 1495, 1453, 1382, 1363, 1207, 1088, 1060, 1028, 731, 694; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.34–7.13 (m, 10H), 4.46 (s, 2H), 2.75–2.69 (m, 2H), 1.91–1.84 (m, 2H), 1.31 (s, 6H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 142.8, 139.7, 128.2, 128.2, 128.2, 127.2, 127.0, 125.5, 74.9, 63.7, 42.5, 30.5, 25.8; HRMS ($APCI^+$) calcd for $C_{18}H_{23}O$ $[M + H]^+$ 255.1749, found m/z 255.1744.

Cyclohexylmethyl 1,1-Dimethyl-3-phenylpropyl Ether (22): Colorless oil; IR (ATR, cm^{-1}) 3025, 2969, 2920, 2850, 1449, 1362, 1084, 1067, 738, 696; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.29–7.15 (m, 5H), 3.13 (d, J = 6.4 Hz, 2H), 2.67–2.61 (m, 2H), 1.82–1.41 (m, 8H), 1.28–1.13 (m, 9H), 0.98–0.84 (m, 2H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 143.0, 128.2 (×2), 125.5, 73.7, 67.1, 42.4, 38.7, 30.6, 30.5, 26.9, 26.1, 25.8; HRMS ($APCI^+$) calcd for $C_{18}H_{29}O$ $[M + H]^+$ 261.2218, found m/z 261.2215.

Decyl 1,1-Dimethyl-3-phenylpropyl Ether (23): Colorless oil; IR (ATR, cm^{-1}) 3026, 2923, 2853, 1455, 1362, 1079, 738, 697; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.18–7.02 (m, 5H), 3.22 (t, J = 6.6 Hz, 2H), 2.56–2.50 (m, 2H), 1.69–1.62 (m, 2H), 1.49–1.36 (m, 2H), 1.21–1.10 (m, 20H), 0.78 (t, J = 7.1 Hz, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 142.9, 128.2, 128.2, 125.5, 73.9, 61.2, 42.2, 32.0, 30.8, 30.4, 29.7, 29.7, 29.7, 29.4, 26.5, 25.8, 22.8, 14.2; HRMS ($APCI^+$) calcd for $C_{21}H_{37}O$ $[M + H]^+$ 305.2844, found m/z 305.2838.

6-(1,1-Dimethyl-3-phenylpropoxy)hexyl Acetate (24): Colorless oil; IR (ATR, cm^{-1}) 3026, 2934, 2861, 1737, 1363, 1233, 1076, 1032, 739, 698; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.19–7.02 (m, 5H), 3.95 (t, J = 6.6 Hz, 2H), 3.23 (t, J = 6.6 Hz, 2H), 2.56–2.49 (m, 2H), 1.92 (s, 3H), 1.69–1.62 (m, 2H), 1.58–1.40 (m, 4H), 1.32–1.24 (m, 4H), 1.10 (s, 6H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 171.0, 142.8, 128.2, 128.1, 125.5, 73.9, 64.5, 61.0, 42.2, 30.5, 30.3, 28.6, 26.1, 25.9, 25.7, 21.0; HRMS ($APCI^+$) calcd for $C_{19}H_{31}O_3$ $[M + H]^+$ 307.2273, found m/z 307.2270.

4-Bromophenethyl 1,1-Dimethyl-3-phenyl Ether (25): Colorless oil; IR (ATR, cm^{-1}) 3025, 2969, 2933, 2864, 1488, 1070, 1011, 697; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.40–7.37 (m, 2H), 7.29–7.09 (m, 7H), 3.51 (t, J = 6.8 Hz, 2H), 2.78 (t, J = 6.8 Hz, 2H), 2.59–2.53 (m, 2H), 1.76–1.69 (m, 2H), 1.17 (s, 6H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 142.7, 138.5, 131.1, 130.7, 128.2, 128.1, 125.5, 119.8, 74.4, 62.2, 42.2, 36.7, 30.3, 25.6; HRMS ($APCI^+$) calcd for $C_{19}H_{24}BrO$ $[M + H]^+$ 347.1011, found m/z 347.1020.

1-Methyl-1-phenylethyl Phenethyl Ether (27):[5] Colorless oil; IR (ATR, cm^{-1}) 2866, 1158, 1069, 763, 749; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.30–7.13 (m, 10H), 3.36 (t, J = 7.4 Hz, 2H), 2.84 (t, J = 7.4 Hz, 2H), 1.52 (s, 6H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 146.2, 139.1, 128.9, 128.1, 128.0, 126.6, 126.0, 125.6, 76.7, 64.1, 37.2, 28.4; HRMS (GC-EI^+) calcd for $C_{17}H_{20}O$ $[M]^+$ 240.1509, found m/z 240.1496.

1-Ethyl-1-methyl-3-phenylpropyl Phenethyl Ether (28): Colorless oil; IR (ATR, cm^{-1}) 3025, 2966, 2936, 2864, 1495, 1453, 1079, 749, 696; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.24–7.06 (m, 10H), 3.45 (t, J = 7.3 Hz, 2H), 2.75 (t, J = 7.3 Hz, 2H), 2.48 (t, J = 8.2 Hz, 2H), 1.69–1.58 (m, 2H), 1.55–1.35 (m, 2H), 1.06 (s, 3H), 0.78 (t, J = 7.6 Hz, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 142.9, 139.4, 129.0, 128.2, 128.2, 128.1, 126.0, 125.5, 76.5, 62.2, 39.6, 37.4, 30.6, 30.0, 22.7, 8.1; HRMS ($APCI^+$) calcd for $C_{20}H_{27}O$ $[M + H]^+$ 283.2062, found m/z 283.2054.

1-Methylcyclopentyl Phenethyl Ether (29): Colorless oil; IR (ATR, cm^{-1}) 3027, 2961, 2867, 1495, 1452, 1075, 748, 697; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.31–7.16 (m, 5H), 3.52 (t, J = 7.3 Hz, 2H), 2.82 (t, J = 7.3 Hz, 2H), 1.81–1.35 (m, 8H), 1.23 (s, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 139.4, 128.9, 128.1, 125.9, 84.3, 63.7, 38.1, 37.5, 23.9, 23.6; HRMS ($APCI^+$) calcd for $C_{14}H_{21}O$ $[M + H]^+$ 205.1592, found m/z 205.1595.

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