Pergamon

TETRAHEDRON

Tetrahedron 57 (2001) 5991–6001

Acetonyltriphenylphosphonium bromide and its polymer-supported analogues as catalysts in protection and deprotection of alcohols as alkyl vinyl ethers

Yung-Son Hon,* Chia-Fu Lee, Rong-Jiunn Chen and Ping-Hui Szu

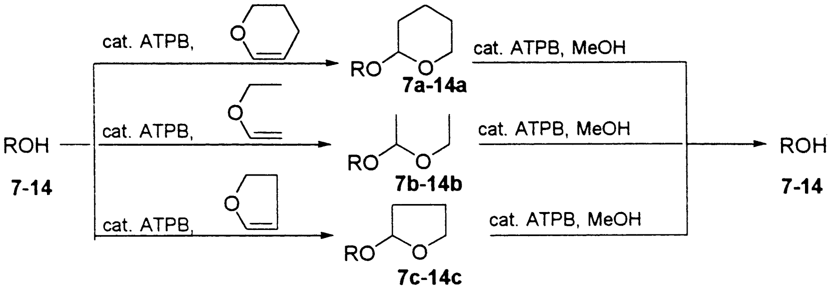
Department of Chemistry, National Chung Cheng University, Chia-Yi, Taiwan 621, Taiwan, R.O.C.

Received 30 March 2001; accepted 16 May 2001

Abstract—Both acetonyltriphenylphosphonium bromide (ATPB, **1**) and poly-*p*-styryldiphenylacetonylphosphonium bromide (**A**) were effective catalysts in the protection of alcohols as THP, THF, and EE ethers as well as the cleavage of THP, THF, and EE ethers to the corresponding alcohols. They could be applied to 1°, 2° and 3° alcohols, phenol and acid-labile alcohols. Both ATPB and catalyst **A** are excellent catalysts in the present study. It needed only 1×10^{-2}–1.25×10^{-2} mol equiv. of the polymer-supported catalyst **A** in the reactions.

1. Introduction

The 2-tetrahydropyranyl ether (OTHP) and 1-ethoxyethyl ether (OEE) are two of the most versatile protecting groups for the alcohols in organic syntheses because of their low cost, ease of installation, general stability to most nonacidic reagents, and the ease with which they can be removed.[1] Sometimes, the tetrahydrofuranyl ether (ROTHF) has also been used as a protecting group for alcohols. A variety of reagents have been developed for these protections which include mainly protic acids,[2] Lewis acids,[3] basic conditions,[4] neutral conditions,[5] transition metal catalysts,[6] and heterogeneous catalysts.[7] On the other hand, the deprotection of these ethers were carried out under acidic,[1,2d,7b,8] neutral,[9] and reductive conditions.[10] In our earlier communication, we discovered the catalytic activity of ATPB (acetonyltriphenylphosphonium bromide) in the protection of alcohols with alkyl vinyl ethers and their deprotection (Scheme 1).[11] Acetonyltriphenylphosphonium bromide is a precursor in the preparation of 1-(triphenylphosphoranylidene)-2-propanone used in a Wittig reaction. There was no reports on the use of ATPB in organic synthesis other than in ylide formation.[12] There are two possible functionalites responsible to the catalytic activity of ATPB. One is the acidic proton α to the carbonyl group. The other one is the phosphonium center of ATPB. Intrigued by this curiosity, we tried to prepare a series of the phosphonium and sulfonium salts in order to find out which is the best catalyst in the protection and deprotection reactions among them. The immobilization of reagents on polymeric supports has been investigated extensively.[13] Polymer-supported phosphines have been widely used as ligands for the binding of metal complexes, as stoichiometric reagents in their own right, and as phase transfer catalysts when converted to an appropriate phosphonium salt.[14] To the best of our knowledge, there is no report to use



Scheme 1.

Keywords: acetonyltriphenylphosphonium bromide; polymer-supported reagent; protection; deprotection.

* Corresponding author. Tel.: +886-5-2720411 ext. 66412; fax: +886-5-2721040; e-mail: cheysh@ccunix.ccu.edu.tw

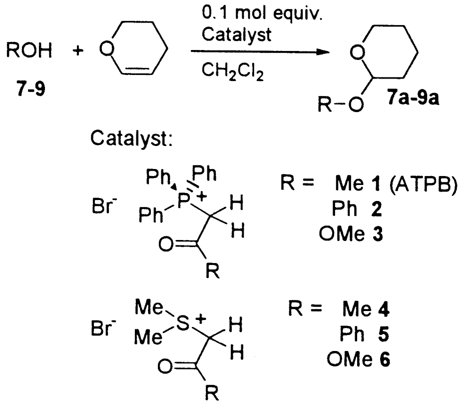
0040–4020/01/$ - see front matter © 2001 Elsevier Science Ltd. All rights reserved.
PII: S0040-4020(01)00558-0

polymer-support phosphonium salts as catalyst in organic reaction other than phase transfer catalysis. Therefore, once we find the best catalyst from our pool, we try to anchor the catalyst on polymeric backbone for practical purpose.

2. Results and discussion

2.1. Comparison of the catalytic activity of the onium salts in the protection and deprotection of alcohols as alkyl vinyl ethers

Acetonyltriphenylphosphonium bromide (ATPB) (**1**) (mp 221–223°C) can be easily prepared from triphenylphosphine and bromoacetone in benzene at room temperature in excellent yield.[15,16] It is soluble in CH_2Cl_2, $CHCl_3$, MeOH, EtOH, CH_3CN but not in THF, Et_2O, benzene and EtOAc. ATPB (**1**) is crystalline and nonhydroscopic. Phenacyltriphenylphosphonium bromide (**2**),[15] carbomethoxymethyltriphenylphosphonium bromide (**3**),[17] acetonyldimethylsulfonium bromide (**4**),[18] phenacyldimethylsulfonium bromide (**5**),[19] and carbomethoxymethyldimethylsulfonium bromide (**6**)[19] were also prepared according to the literature procedure. All the phosphonium bromides **1**–**3** and the sulfonium bromide **5** are white solid. Acetonyldimethylsulfonium bromide (**4**) is a pale yellow viscous liquid.



(1)

We tried to use the onium salts (**1**–**6**) as catalysts in the protection of benzyl alcohol (**7**) with 3,4-dihydro-2*H*-pyran and their results were shown in Table 1. The typical procedure was described as follows. To a solution of benzyl alcohol (**7**) (1 mol equiv.) and 3,4-dihydro-2*H*-pyran (1.2 mol equiv.) in CH_2Cl_2, the onium salt (0.1 mol equiv.) was added and the solution was stirred at rt. The reaction was monitored by thin layer chromatography. The solution was then concentrated and chromatographed on silica gel to give the desired product. Among the triphenylphosphonium salts, the order of the catalytic reactivity for Eq. (1) is arranged in the following order: compound **1**>compound **3**>compound **2**, based on the reaction time and the percentage of the conversion of the reaction (entries 1–3, Table 1). On the other hand, the order of the catalytic reactivity for the dimethylsulfonium salts is arranged in the following order: compound **4**>compound **5**>compound **6** (entries 4–6, Table 1). Both ATPB (**1**) and acetonyldimethylsulfonium bromide (**4**), having acetyl group on the P and S respectively, are two of the best catalysts for the protection of benzyl alcohol (entries 1–6, Table 1). These results indicate that the substituents on the heteroatom affect their reactivities. Both of them are also very effective to protect the secondary alcohols such as menthol (**8**) and cholesterol (**9**). However, ATPB usually gives better yields than that of sulfonium bromide **3** (entries 7, 9 vs 8 and 10). Furthermore, the disadvantage to use the sulfonium bromide **3** is its viscous and hydroscopic property. Therefore, ATPB is the choice in the present study and its results were shown in Table 2.

Table 1. Comparison of the catalytic activity of the phosphonium and sulfonium salts in the protection reaction

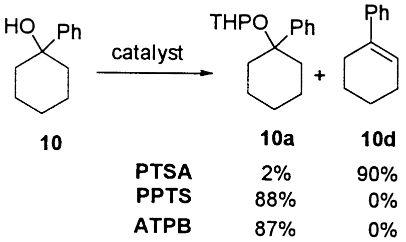
Entry	Alcohol	Catalyst[a]	Time (h)	Yield (%)	
1	Benzyl alcohol **7**	**1**	1/12	**7a**	97
2	Benzyl alcohol **7**	**2**	24	**7a**	91[b]
3	Benzyl alcohol **7**	**3**	5/6	**7a**	96
4	Benzyl alcohol **7**	**4**	1/12	**7a**	97
5	Benzyl alcohol **7**	**5**	24	**7a**	50[c]
6	Benzyl alcohol **7**	**6**	24	**7a**	89[d]
7	Menthol **8**	**1**	1/12	**8a**	98
8	Cholesterol **9**	**1**	1/12	**9a**	90
9	Menthol **8**	**4**	1/3	**8a**	94
10	Cholesterol **9**	**4**	1/2	**9a**	83

[a] 0.1 mol equiv. of the catalyst was used.
[b] Recovered 7% of **7**.
[c] Recovered 44% of **7**.
[d] Recovered 6% of **7**.

2.2. ATPB is the catalyst in the protection and deprotection of alcohols as alkyl vinyl ethers

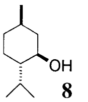
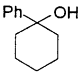
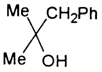
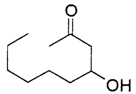
Benzyl alcohol (**7**) reacted with 3,4-dihydro-2*H*-pyran in the presence of 0.1 mol equiv. of ATPB to give the protected product **7a** in 97% yield in 5 min (entry 1, Table 2 and Scheme 1). Under similar condition, secondary and tertiary alcohols also gave THP ethers in excellent yields (entries 4, 7, 10 and 13, Table 2). All the reactions mentioned above were complete in a short time at rt. In the case of phenol, the reaction was incomplete and only 65% yield of the THP ether was formed by the similar condition. It needed 4 mol equiv. of 3,4-dihydro-2*H*-pyran in order to give the product **12a** in excellent yield (entry 16, Table 2).

Under stronger acidic conditions such as PTSA, tertiary alcohols **10** underwent dehydration predominately (Eq. (2)). Similarly, the yield of the protection of β-hydroxyketone **13** or **14** was low due to the dehydration occurred (Eq. (3)). Fortunately, ATPB could be applied to catalyze the protection of these three compounds perfectly (entries 10, 13 and 19, Table 2). The results in Eqs. (2) and (3) indicate that ATPB and PPTS are comparable catalysts for the protection of the acid-labile alcohols.

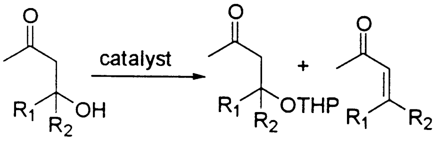


(2)

Table 2. Protection of alcohols with alkyl ether and its deprotection catalyzed by ATPB (**1**)

Entry	ROH	Catalyst	Time (min)	Protected ROH, yield (%)			Time (min)	Deprotection yield (%)	
1	$PhCH_2OH$ **7**	ATPB	<5	–OTHP	**7a**	97	60	91	**7**
2	$PhCH_2OH$ **7**	ATPB	<5	–OTHF	**7b**	94	15	90	**7**
3	$PhCH_2OH$ **7**	ATPB	<5	–OEE	**7c**	95	10	95	**7**
4	 **8**	ATPB	<5	–OTHP	**8a**	98	70	91	**8**
5		ATPB	<5	–OEE	**8b**	92	10	90	**8**
6		ATPB	<5	–OEE	**8c**	99	15	95	**8**
7	Cholesterol **9**	ATPB	<5	–OTHP	**9a**	90	50	84	**9**
8	Cholesterol **9**	ATPB	<5	–OTHF	**9b**	97	30	95	**9**
9	Cholesterol **9**	ATPB	<5	–OEE	**9c**	97	30	98	**9**
10	 **10**	ATPB	20	–OTHP	**10a**	86	10	94	**10**
11		ATPB	10	–OTHF	**10b**	83	10	93	**10**
12		ATPB	10	–OEE	**10c**	80	10	96	**10**
13	 **11**	ATPB	30	–OTHP	**11a**	88	30	94	**11**
14		ATPB	20	–OTHF	**11b**	83	20	94	**11**
15		ATPB	30	–OEE	**11c**	84	20	98	**11**
16	PhOH **12**	ATPB	<5	–OTHP	**12a**	92[a]	10	91	**12**
17	PhOH **12**	ATPB	<5	–OTHF	**12b**	88[a]	10	91	**12**
18	PhOH **12**	ATPB	<5	–OEE	**12c**	87[a]	10	92	**12**
19	 **13**	ATPB	25	–OTHP	**13a**	84	50	92	**13**

[a] 4 mol equiv. of the protecting reagent were needed.



R_1=H, R_2=C_6H_{13} **13**		**13a**	**13d**
	PTSA	59%	23%
	PPTS	94%	0%
	ATPB	96%	0%
R_1=Me, R_2=Me **14**		**14a**	**14d**
	PTSA	16%	84%
	PPTS	86%	0%
	ATPB	84%	0%

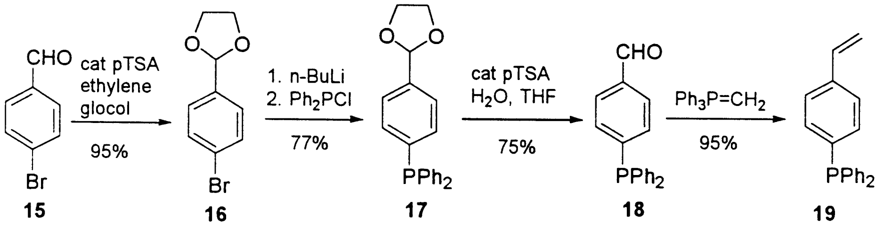
(3)

2-Chlorotetrahydrofuran instead of 2,3-dihydrofuran was frequently used in the protection of alcohols because either a laborious workup procedure[20] or low yield[21]occurred when 2,3-dihydrofuran was used. Interestingly, by using 0.1 mol equiv. of ATPB as a catalyst, alcohols of different types (i.e. 1°, 2°, 3°, and phenolic alcohols) could react with 2,3-dihydrofuran (1.2 mol equiv.) to give THF ethers in excellent yields (entries 2, 5, 8, 11, 14 and 17, Table 2). It also needed 4 mol equiv. of 2,3-dihydrofuran in order to give the product **12b** in excellent yield.

Similar conditions could be applied to the preparation of 1-ethoxyethyl ethers (ROEE, entries 3, 6, 9, 12 and 15, Table 2) in excellent yields from different kinds of alcohols with ethyl vinyl ether. However, in the protection of phenol, it needed 4 mol equiv. of the ethyl vinyl ether in order to give the product **12c** in excellent yield (entry 18).

The THP ethers (**7a**–**13a**), tetrahydrofuranyl ether (ROTHF, **7b**–**13b**), and 1-ethoxyethyl ethers (ROEE, **7c**–**13c**) could also be deprotected under the catalysis of ATPB in MeOH at rt to afford the corresponding alcohols in excellent yields (Table 2 and Scheme 1). Typical procedure for the deprotection reaction catalyzed by ATPB is described as follows. To a solution of OTHP-protected compound **7a** (1.4 mmol) in 2.8 mL of MeOH, ATPB (0.14 mmol) was added and the solution was stirred at rt for 60 min. The solution was concentrated and chromatographed on silica gel to give the desired product **7** in 91% yield (entry 1, Table 2). In other words, ATPB is an excellent catalyst in both protection and deprotection reactions.

Since the solubility of ATPB in THF, Et_2O, benzene or EtOAc is very low, we are able to recover the catalyst by using this property. The reaction mixture was concentrated and the ether was added to crude residue so that ATPB was precipitated out. By simple filtration, we are able to recover at least 95% of the catalyst. We found that the recovered catalyst either from protection or deprotection reaction can be reused at least four times to give high product yield.



Scheme 2.

2.3. Preparation of poly-*p*-styryldiphenylacetonylphosphonium bromide

ATPB has been proved to be the excellent catalyst in the present study, we tried to anchor ATPB moiety on the polymer backbone. For general purpose, 4-bromobenzaldehyde (**15**) was used as the starting material to react with ethylene glycol in the presence of a catalytic amount of PTSA to give bromoacetal **16** in 95% yield.[22] Bromoacetal **16** was then treated with *n*-butyllithium in anhydrous tetrahydrofuran under nitrogen to give the lithiated intermediate, which was immediately treated with freshly distilled chlorodiphenylphosphine to give triphenylphosphine-acetal **17** in 77% yield.[23] The acetal group of compound **17** underwent acidic hydrolysis to give *p*-diphenylphosphinobenzaldehyde (**18**),[24] which was then used to carry out the Wittig reaction to give *p*-styryldiphenylphosphine (**19**) in excellent yield (Scheme 2). The spectral data of compound **19** is identical to those reported in the literature.[25,26] *p*-Diphenylphosphinobenzaldehyde (**18**) should be a suitable precursor to make polyacrylate (Type **B**) (Fig. 1). In this paper, we only emphasize the chemistry to attach ATPB on the polystyrene backbone (Type **A**).

Polymer **22** employed in this paper was a copolymer of styrene and *p*-styryldiphenylphosphine (**19**) in a ratio of 5:1 in the presence of 2 mol% divinylbenzene (**21**) as cross-linking agent. The suspension copolymerization used gelatin as dispersant and azoisobutyronitrile (AIBN) as radical source to afford white opaque solid beads **22**.[27] The white beads was thoroughly washed with water and benzene, and dried over P_2O_5 under high vacuum (Scheme 3). Each gram of copolymer **22** contained approximately 2.39 mmol of diphenylphosphine moiety, which was estimated by its elemental analysis (C, 85.25%; H, 7.35%). A suspension of **22** in THF was reacted with excess bromoacetone to give polymeric phosphonium salts **A** in high yield. The resulting polymeric phosphonium salt was removed by filtration and washed thoroughly with THF. Each gram of the polymeric catalyst **A** contained approximately 1.46 mmol of phosphonium bromide moiety, which was estimated by its elemental analysis (C, 75.55%; H, 5.95%). Our elemental analysis data indicated that only 61% of the phosphines on the polymer were converted to the corresponding phosphonium salts. It is probably because some embedded triphenylphosphines are not attachable by bromoacetone due to the steric effect.

2.4. Catalytic activity of polymer-supported phosphonium bromides

Based on our estimation described above, each gram of the

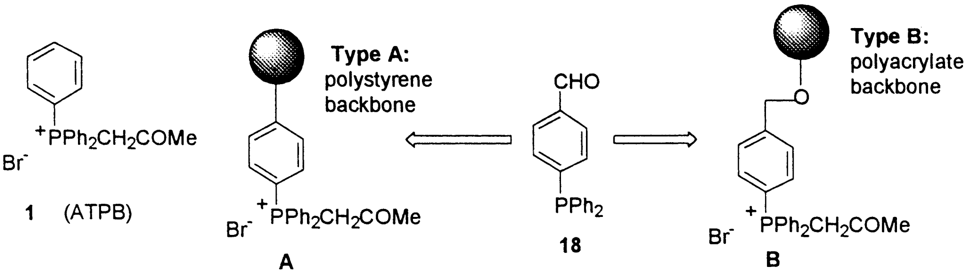
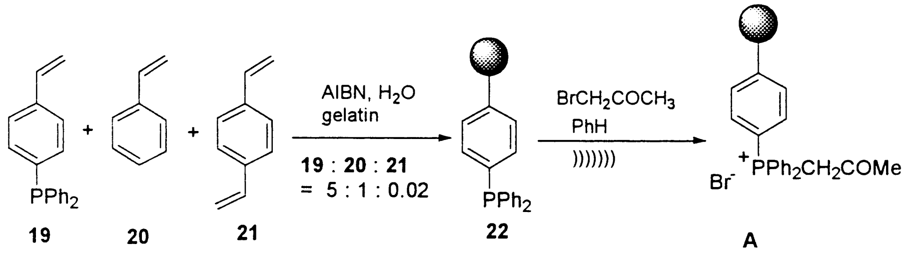
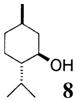
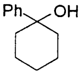
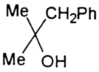
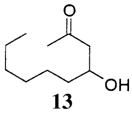
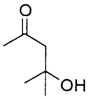


Figure 1.



Scheme 3.

Table 3. Protection of alcohols with alkyl vinyl ether and its deprotection catalyzed by catalyst **A**

Entry	ROH	Mole ratio[a]	Time (h)	Protected ROH, yield (%)			Protected ROH	Mole ratio	Time (h)	ROH, yield (%)	
1	$PhCH_2OH$ **7**	1:30	0.2	–OTHP	**7a**	95	–	–	–	–	–
2	$PhCH_2OH$ **7**	1:50	0.5	–OTHP	**7a**	96	–	–	–	–	–
3	$PhCH_2OH$ **7**	1:70	1.3	–OTHP	**7a**	97	–	–	–	–	–
4	$PhCH_2OH$ **7**	1:110	4	–OTHP	**7a**	95[b]	–	–	–	–	–
5	$PhCH_2OH$ **7**	1:100	2	–OTHP	**7a**	98	**7a**	1:80	6	91	**7**
6	$PhCH_2OH$ **7**	1:100	0.5	–OTHF	**7b**	99	**7b**	1:80	6	90	**7**
7	$PhCH_2OH$ **7**	1:100	0.5	–OEE	**7c**	93	**7c**	1:80	5.5	95	**7**
8	 **8**	1:100	3	–OTHP	**8a**	95	**8a**	1:80	6	91	**8**
9		1:100	3	–OTHF	**8b**	97	**8b**	1:80	6	90	**8**
10		1:100	1	–OEE	**8c**	87	**8c**	1:80	5.5	95	**8**
11	Cholesterol **9**	1:100	3	–OTHP	**9a**	99	**9d**	1:80	60	84	**9**
12	Cholesterol **9**	1:100	5	–OTHF	**9b**	97	**9e**	1:70	26	95	**9**
13	Cholesterol **9**	1:100	2	–OEE	**9c**	99	**9c**	1:70	26	98	**9**
14	 **10**	1:90	40	–OTHP	**10a**	98	**10a**	1:80	15	94	**10**
15		1:90	36	–OTHF	**10b**	84	**10b**	1:80	15	94	**10**
16		1:90	24	–OEE	**10c**	97	**10c**	1:80	10	98	**10**
17	 **11**	1:90	36	–OTHP	**11a**	98	**11a**	1:80	18	94	**11**
18		1:90	36	–OTHF	**11b**	93	**11b**	1:80	10	95	**11**
19		1:90	16	–OEE	**11c**	91	**11c**	1:80	16	93	**11**
20	PhOH **12**	1:100	3	–OTHP	**12a**	99	**12a**	1:80	5.5	91	**12**
21	PhOH **12**	1:100	5	–OTHF	**12b**	97	**12b**	1:80	5.5	91	**12**
22	PhOH **12**	1:100	2	–OEE	**12c**	99	**12c**	1:80	5	92	**12**
23	 **13**	1:100	5	–OTHP	**13a**	96	**13a**	1:80	24	90	**13**
24		1:100	5	–OTHF	**13b**	92	**13b**	1:80	24	96	**13**
25		1:100	5	–OEE	**13c**	97	**13c**	1:80	18	96	**13**
26	 **14**	1:90	15	–OTHP	**14a**	96	**14a**	1:70	12	74	**14**
27		1:90	15	–OTHF	**14b**	95	**14b**	1:70	12	70	**14**
28		1:90	15	–OEE	**14c**	90	**14c**	1:70	10	70	**14**

[a] 1.46 mmol of the catalytic centers in 1 g of resin was proposed according to its elemental analysis data.

[b] 2% of the benzyl alcohol was recovered.

polymeric catalyst **A** contained approximately 1.46 mmol of phosphonium bromide moiety. We tried to find out the optimal condition between the mol equiv. ratio of the alcohol and the catalyst. The mol equiv. ratio of the benzyl alcohol (**7**) to the catalyst was studied from 1:30 (i.e. 3.3% mol equiv.) to 1:110 (i.e. 0.91% mol equiv.) for the reaction with 3,4-dihydro-2*H*-pyran (entries 1–5, Table 3). All these protection reactions were completed in 2 h and their chemical yields were excellent (entries 1–3 and 5). When the mol equiv. ratio was 1:110, we can isolate the desired product in 96% yield and recovered 2% of the starting alcohol after 4 h stirring (entry 4). These results indicate that the polymer-supported catalyst **A** is an effective catalyst for the protection of primary alcohol. The reaction condition specified in entry 5 (i.e. mol equiv. ratio of the catalyst and alcohol is 1:100) was used as a standard protocol for the following studies and the typical procedure is described as follows. To a solution of benzyl alcohol (**7**) (508.3 mg, 4.7 mmol) and 3,4-dihydro-2*H*-pyran (486.8 mg, 5.6 mmol) in 1 mL of CH_2Cl_2 was added 32.2 mg of catalyst **A** (which is approximately equivalent to 4.7×10^{-2} mmol equiv. of ATPB moiety). The suspension solution was stirred at rt for 2 h. The polymer can be recovered by simple filtration. The filtrate was concentrated in vacuo to give the desired product in the pure form. In some cases, the simple filtration through the short path silica gel column chromatography is used to purify the product.

By using this protocol, primary, secondary or phenolic alcohols could react with 3,4-dihydro-2*H*-pyran in the presence catalyst **A** in CH_2Cl_2 at rt to give THP ethers in excellent yields (entries 5, 8, 11, 10, 13 and 20, Table 3). It is noteworthy that all the reactions mentioned above were completed in less than 5 h at rt. For the tertiary alcohols, the protection reactions were incomplete by using the above condition. When we raise the mol equiv. ratio of the tertiary alcohol to the catalyst as 1:90, the reactions were completed within 40 h and the chemical yields were excellent (entries 14 and 17). Similarly, the chemical yields of the protection of acid-labile hydroxy compounds **13** (2°-ol) and **14** (3°-ol) by the catalysis of polymer **A** were also excellent (entries 23 and 26, Table 3). Neither dehydration nor retro-aldol products was observed in these reactions.

Similar conditions could be applied to the preparation of 2-tetrahydrofuran ethers (ROTHF, entries 6, 9, 12, 15, 18, 21, 24 and 17) and 1-ethoxyethyl ethers (ROEE, entries 7, 10, 13, 16, 19, 22, 25 and 28, Table 3) in excellent yields from different kinds of alcohols.

The THP ethers (**7a**–**13a**) could also be deprotected under the catalysis of polymer **A** in MeOH at rt to afford the corresponding alcohols in excellent yields (entries 5, 8, 11, 14, 17, 20 and 23, Table 3). Typical procedure for the deprotection reaction catalyzed by catalyst **A** is described as follows. To a solution of OTHP-protected compound **7a** (1.4 mmol) in 2.8 mL of MeOH was added polymer **A** (12 mg, which is approximately equivalent to 1.75×10^{-2} mmol equiv. of ATPB moiety, i.e. alcohol/catalyst=80:1) and the solution was stirred at rt. When the reactions completed, the solution was filtered to recover the catalyst **A** (recover>95%). The filtrate was concentrated to give the desired product **7** in a pure form. The tetrahydrofuranyl ether (ROTHF) and 1-ethoxyethyl ethers (ROEE) could also be deprotected under the catalysis of polymer **A** in MeOH at rt to afford the corresponding alcohols in excellent yields (Table 3). By simple filtration, we are able to recover at least 95% of the catalyst. To test the reactivity of the recovered catalyst **A**, either from protection or deprotection reaction, we found that it can be reused at least four times to give high product yield. However, we did observe its catalytic activity was slightly decreasing each time. So far, we don't know the real reason why the catalyst **A** losses its reactivity after using several times. In the literature, the debromination of α-bromo ketones using polymer-supported triphenylphosphine in refluxing methanol has been reported.[28] Presumably, the corresponding phosphonium bromide might react with refluxing methanol to give the corresponding debrominated ketone. Our deprotection reactions were carried out in methanol at room temperature. This possible side reaction might occur only in small portion. Therefore, the possible reason of the decreasing reactivity of the catalyst **A** after reused several times might be due to the decomposition of the polymer-supported ATPB moiety by methanol.

3. Conclusions

The triphenylphosphonium bromides and dimethylsulfonium bromides are suitable to be the catalyst in the protection reaction. Among them, ATPB is a useful and economic catalyst to prepare THP, THF, and EE ethers as well as the cleavage of THP, THF, and EE ethers to the corresponding alcohols. The advantages of this methodology are mild conditions, fast reaction rate, excellent yields and tolerance to acid-sensitive functionalities. Interestingly, ATPB is much less hydroscopic than that of pyridinium *p*-toluenesulfonate (PPTS). The poly-*p*-styryldiphenylacetonylphosphonium bromide (**A**) is also a very efficient and excellent catalyst for the above mentioned reactions. It has the advantage of the polymer-supported reagent and need only about 1% mol equiv. of the catalyst for the reaction.

4. Experimental

4.1. General

All reactions were carried out under nitrogen. Unless otherwise noted, materials were obtained from commercial suppliers and used without further purification. Melting points were determined by using a Thomas–Hoover melting point apparatus and were uncorrected. The ^{1}H- and ^{13}C NMR spectra were recorded on a Bruker Avance DPX400 spectrometer, and chemical shifts were given in ppm downfield from tetramethylsilane (TMS). IR spectra were taken with a Perkin–Elmer 682 spectrophotometer and only noteworthy absorptions were listed. Mass spectra were measured on a VG Trio-2000GC/MS spectrometer by electronic impact at 70 eV (unless otherwise indicated). High Resolution Mass Spectroscopy (HRMS) was measured on a JEOL JMS-HX 110 (National Hsing-Hua University) or VG-11-250J (Academia Sinica) Mass Spectrometer. The acetonyltriphenylphosphonium bromide (**1**),[15,16] phenacyltriphenylphosphonium bromide (**2**),[15] carbomethoxymethyltriphenylphosphonium bromide (**3**),[17] acetonyldimethylsulfonium bromide (**4**),[18] phenacyldimethylsulfonium bromide (**5**),[19] and carbomethoxymethyldimethylsulfonium bromide (**6**)[19] were prepared according to the literature procedure.

4.1.1. 2-(4-Bromophenyl)-1,3-dioxolane (16).[22] To a stirring solution of the 4-bromobenzaldehyde (**15**) (5.0 g, 27.0 mmol) in 30 mL of anhydrous toluene was added *p*-toluenesulfonic acid (22 mg, 0.1 mmol) and ethylene glycol (2.5 g, 40.3 mmol) at rt under nitrogen. The reaction mixture was refluxed in the Dean–Stark apparatus for 24 h. The reaction mixture was cooled to rt and extracted with 10 mL of saturated $NaHCO_3$ and then 10 mL of brine. The organic layer was dried over $MgSO_4$ and concentrated in vacuo to give the crude product. The desired product was purified by vacuum distillation (106–107°C at 2 Torr) to give 5.86 g of the product **16** in 95% yield as colorless oil. R_f=0.44 (Hexane/EtOAc=10:1); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.02–4.11 (m, 4H, RO–CH_2CH_2–OR), 5.77 (s, 1H, –OPhC*H*O–), 7.34–7.52 (m, 4H, Ar–H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 65.3 (2°), 103.0 (3°, –OPh*C*HO–), 123.2 (4°), 128.2 (3°), 131.5 (3°), 137.0 (4°); IR (CH_2Cl_2, cm^{-1}): 2976 (s), 2884 (s), 1590 (s), 1484 (s), 1382 (m). Mass (*m*/*z*): 229 (M^+, 99), 227 (M^+-2, 100), 183 (38), 149 (53), 89 (40), 73 (48).

4.1.2. [4-(1,3-Dioxolan-2-yl)phenyl]diphenylphosphine (17).[23] To a stirring solution of the 2-(4-bromophenyl)-1,3-dioxolane (**16**) (4.74 g, 20.7 mmol) in 30 mL of anhydrous THF was added *n*-BuLi (1.6 M in hexane, 16 mL, 25.6 mmol) dropwise at −78°C. The reaction was stirred at this temperature for 40 min. To the resulted solution was added a solution of chlorodiphenylphosphine (freshly distilled; 5.02 g, 23 mmol) in 25 mL of THF at −78°C. The reaction was warmed slowly to rt and stirred at rt for 3 h. The reaction was quenched with 15 mL of saturated NH_4Cl. The organic layer was extracted with 15 mL of brine. The organic layer was dried over $MgSO_4$ and concentrated in vacuo to give the crude product. The desired product was purified by recrystallization in EtOH to give 5.32 g of the product **17** in 77% yield as white solid;

R_f=0.22 (Hexane/EtOAc=10:1) mp 88–89°C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.63–3.78 (m, 4H, –O–CH_2CH_2–O–), 5.63 (s, 1H, –OPhC*H*O–), 7.29–7.40 (m, 12H, Ar–H), 7.48 (d, *J*=7.8 Hz, 2H, Ar–H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 63.4 (2°), 103.5 (3°, OPhCHO–), 126.5 (3°, d, $^3J_{p-c}$=6.9 Hz), 128.5 (3°, d, $^3J_{p-c}$=7.0 Hz), 128.7 (3°), 133.7 (3°, d, $^2J_{p-c}$=19.4 Hz), 137.0 (4°, d, $^1J_{p-c}$=10.7 Hz), 138.4 (4°), 138.6 (4°, d, $^1J_{p-c}$=11.5 Hz); IR (CH_2Cl_2, cm^{-1}): 3050 (s), 2985 (s), 2884 (s), 1484 (s), 1438 (s). Mass (*m/z*): 183 (M^+-151, 51), 108 (90), 89 (29), 77 (32), 73 (100).

4.1.3. 4-(Diphenylphosphino)benzaldehyde (18).[24] To a stirring solution of the [4-(1,3-Dioxolan-2-yl)phenyl]-diphenylphosphine (**17**) (2.5 g, 7.5 mmol) in 45 mL of THF and 5 mL of water was added *p*-toluenesulfonic acid (47 mg, 0.2 mmol) at rt under nitrogen. The reaction mixture was refluxed for 7 h. Subsequently, the reaction mixture was cooled to rt, diluted with 10 mL of water and extracted with 100 mL of ether twice. The organic layer was dried over $MgSO_4$, concentrated and chromatographed to give the desired product. The product was further purified by recrystallization in a mixed solvent of dichloromethane and methanol to give 1.63 g of the product **18** in 75% yield as pale yellow solid; mp 65–68°C; R_f=0.33 (Hexane/EtOAc=10:1); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.35–7.41 (m, 12H, Ar–H), 7.80 (t, *J*=6.4 Hz, 2H, Ar–H), 10.01 (s, 1H, RCHO); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 128.7 (3°, d, $^3J_{p-c}$=7.4 Hz), 129.2 (3°, d, $^3J_{p-c}$=5.4 Hz), 129.3 (3°), 133.5 (3°, d, $^2J_{p-c}$=18.3 Hz), 134.0 (3°, d, $^2J_{p-c}$=20.1 Hz), 135.8 (4°, d, $^1J_{p-c}$=11.1 Hz), 136.0 (4°), 146.5 (4°, d, $^1J_{p-c}$=15.6 Hz); IR (CH_2Cl_2, cm^{-1}): 3059 (s), 2801 (s), 1705 (s), 1599 (s), 1438 (s). Mass (*m/z*): 290 (M^+, 29), 183 (32), 91 (100).

4.1.4. *p*-Styryldiphenylphosphine (19).[25,26] Methylenetriphenylphosphorane ($Ph_3P{=}CH_2$) was prepared from the reaction of methyltriphenylphosphonium bromide (3.45 g, 9.7 mmol) and *n*-BuLi (6.1 mL, 1.6 M in hexane, 9.7 mmol) in 20 mL of THF at 0°C for 0.5 h. To the resulted solution a solution of 4-(diphenylphosphino)benzaldehyde (**18**) (2.0 g, 6.9 mmol) in 10 mL of THF was added at −78°C and the reaction was warmed slowly to ambient temperature. After 5 h, the reaction was quenched with 30 mL of saturated NH_4Cl. The organic layer was extracted with 15 mL of brine. The aqueous layer was extracted with 20 mL of ether twice. The combined organic layer was dried over $MgSO_4$ and concentrated in vacuo to give the crude product. The reaction mixture was concentrated and chromatographed on a silica gel by elution with hexane to give the desired product. The product was further purified by recrystallization in a mixture of dichloromethane and hexane to give 1.91 g of the product **19** in 96% yield as a white solid. R_f=0.62 (Hexane/EtOAc=10:1); mp 77–78°C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.27 (dd, *J*=11.2, 0.5 Hz, 1H), 5.76 (dd, *J*=17.6, 0.8 Hz, 1H), 6.69 (dd, *J*=17.6, 10.9 Hz, 1H), 7.23–7.37 (m, 14H, Ar–H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 114.6 (2°, PhCH=*C*H$_2$), 126.3 (3°, d, $^3J_{p-c}$=7.1 Hz), 128.5 (3°, d, $^3J_{p-c}$=6.9 Hz), 128.7 (3°), 133.7 (3°, d, $^2J_{p-c}$=19.4 Hz), 133.9 (3°, d, $^2J_{p-c}$=22.6 Hz), 136.4 (3°, Ph*C*H=CH$_2$), 136.8 (4°, d, $^1J_{p-c}$=10.7 Hz), 137.2 (4°, d, $^1J_{p-c}$=10.8 Hz), 137.9 (4°); IR (CH_2Cl_2, cm^{-1}): 3050 (s), 1631 (s), 1438 (s), 1267 (s), 1092 (s). Mass (*m/z*): 288 (M^+, 100), 183 (53), 108 (20).

4.2. Procedure of the copolymerization of *p*-styryldiphenlyphosphine and styrene

Gelatin (0.45 g) was dissolved 10 mL of deionized water at 80°C with magnetic stirring. The homogeneous solution was then cooled to 40°C. To the resulted solution, a mixture of styrene (1.1 g, 10.5 mmol), *p*-styryldiphenlyphosphine (0.61 g, 2.1 mmol), *p*-divinylbenzene and AIBN (0.04 g, 0.25 mmol; freshly recrystallized from MeOH) was added under nitrogen. The reaction mixture was heated to reflux for 24 h. The mixture was cooled and filtered through a fine-porosity Corning glass frit (4–5.5 μm) under vacuum. The filtered polymer was washed with water, methanol. The washed polymer was dried at 60°C for 10 h to give a pale yellow solid **22** (1.00 g).

4.3. Procedure for the preparation of poly-*p*-styryldiphenylacetonylphosphonium bromide (A)

To a suspension solution of polymer **22** (1.05 g) in 20 mL of benzene was added bromoacetone (0.22 g, 1.88 mmol) and then under ultrasound irradiation for 3 h. The reaction mixture was filtered and then washed with anhydrous benzene through a fine-porosity Corning glass frit (4–5.5 μm) under vacuum. The washed polymer was dried at 60°C for 10 h to give a brown solid **A** (1.11 g).

4.4. General procedure for the protection reaction catalyzed by ATPB

To a solution of cholesterol (**9**) (288.1 mg, 0.75 mmol) and 3,4-dihydro-2*H*-pyran (75.1 mg, 0.89 mmol) in 1.5 mL of dichloromethane was added ATPB (29.7 mg, 0.07 mmol) and the solution was stirred at rt. The reaction was completed in 5 min. The solution was concentrated and chromatographed on silica gel to give the desired product **9a** (321.0 mg, 0.68 mmol) in 90% yield.

4.5. General procedure for the deprotection reaction catalyzed by ATPB

To a solution of OTHP-protected compound **9a** (66.5 mg, 0.14 mmol) in a mixture of dichloromethane/methanol (2.8 mL; 1:1 by volume) was added ATPB (56 mg, 0.14 mmol) and the solution was stirred at rt for 50 min. (Note: Compound **9a** was not quite soluble in methanol so that dichloromethane was used as a cosolvent. Only methanol was used in the other cases.) The solution was concentrated and chromatographed on silica gel to give the desired product **9** (46 mg, 0.12 mmol) in 84% yield.

4.6. General procedure for the protection reaction catalyzed by dimethylsulfonium salt 4

To a solution of benzyl alcohol (**7**) (80.0 mg, 0.74 mmol) and 3,4-dihydro-2*H*-pyran (74.7 mg, 0.89 mmol) in 1.5 mL of dichloromethane was added dimethylsulfonium salt **4** (14.7 mg, 0.07 mmol) and the solution was stirred at rt. The reaction was completed in 5 min. The solution was concentrated and chromatographed on silica gel to give the desired product **7a** (137.1 mg, 0.71 mmol) in 97% yield.

4.7. General procedure for the protection reaction catalyzed by polymer-supported catalyst A

To a solution of benzyl alcohol (**7**) (80.0 mg, 0.74 mmol) and 3,4-dihydro-2*H*-pyran (74.7 mg, 0.89 mmol) in 1.5 mL of dichloromethane was added catalyst **A** (5.1 mg, 0.07 mmol) and the heterogeneous solution was stirred at rt. The reaction was complete in 5 h. The reaction mixture was filtered through sintered glass and the filtrate was concentrated and chromatographed on silica gel to give the desired product **7a** (139.1 mg, 0.73 mmol) in 98% yield.

4.8. General procedure for the deprotection reaction catalyzed by polymer-supported catalyst A

To a solution of OTHP-protected compound **7a** (192 mg, 0.1 mmol) in a 2.8 mL of methanol was added **A** (8.6 mg, 1.25×10^{-2} mmol) and the heterogeneous solution was stirred at rt for 50 h. The solution was filtered through sintered glass and the filtrate was concentrated and chromatographed on silica gel to give the desired product **7** (98.4 mg, 0.91 mmol) in 91% yield.

4.8.1. 2-Benzyloxytetrahydropyran (7a). ^{1}H NMR ($\mathrm{CDCl_3}$, 400 MHz) δ 1.51–1.74 (m, 6H, $\mathrm{OCH_2(C}H_2)_3$–), 3.53–3.56 (m, 1H, $\mathrm{OC}H_2\mathrm{CH_2}$–), 3.89–3.94 (m, 1H, $\mathrm{OC}H_2\mathrm{CH_2}$–), 4.50 (d, J=12.0 Hz, 1H, $\mathrm{PhC}H_2$), 4.71 (t, J=3.3 Hz, 1H, BnOCH(R)OR′), 4.79 (d, J=12.0 Hz, 1H, $\mathrm{PhC}H_2$), 7.27–7.38 (m, 5H, Ar–H); ^{13}C NMR ($\mathrm{CDCl_3}$, 100 MHz) δ 19.3 (2°), 25.4 (2°), 30.5 (2°), 62.0 (2°, BnOCH(R)OCH$_2$–), 68.7 (2°, PhCH$_2$O–), 97.7 (3°, BnOCH(R)OR′), 127.4 (3°, Ar), 127.7 (3°, Ar), 128.3 (3°, Ar), 138.3 (4°, Ar); IR ($\mathrm{CH_2Cl_2}$, cm^{-1}): 3041, 2930, 1452, 1351; Mass (*m/z*): 192 (M$^+$, 1), 108 (M$^+$−THP, 17), 91 (100, $\mathrm{PhCH_2}$); Anal. Calcd for $\mathrm{C_{12}H_{16}O_2}$: C, 74.97; H, 8.39. Found: C, 74.89; H, 8.40.

4.8.2. 2-Benzyloxytetrahydrofuran (7b). ^{1}H NMR ($\mathrm{CDCl_3}$, 400 MHz) δ 1.84–2.04 (m, 4H, $\mathrm{C}H_2\mathrm{C}H_2\mathrm{CH_2O}$–), 3.86–3.95 (m, 2H, $-\mathrm{OC}H_2\mathrm{CH_2}$–), 4.47 (d, J=11.6 Hz, 1H, $\mathrm{PhC}H_2\mathrm{O}$–), 4.71 (d, J=11.6 Hz, 1H, $\mathrm{PhC}H_2\mathrm{O}$–), 5.21 (dd, J=4.0, 2.4 Hz, 1H, OCHR′(OR)), 7.25–7.34 (m, 5H, Ar–H); ^{13}C NMR ($\mathrm{CDCl_3}$, 100 MHz) δ 23.4 (2°), 32.2 (2°), 66.9 (2°, −OCH$_2$CH$_2$–), 68.6 (2°, PhCH$_2$O–), 103.0 (3°, BnOCHR′(OR)), 127.3 (3°, Ar), 127.7 (3°, Ar), 128.2 (3°, Ar), 138.3 (4°, Ar); IR ($\mathrm{CH_2Cl_2}$, cm^{-1}): 3068, 2949, 1461, 1355; Mass (*m/z*): 178 (M$^+$, 10), 108 (80), 92 (70), 91 (100), 71 (82); Anal. Calcd for $\mathrm{C_{11}H_{14}O_2}$: C, 74.13; H, 7.92. Found: C, 73.96; H, 8.22.

4.8.3. Acetaldehyde ethyl benzyl acetal (7c). ^{1}H NMR ($\mathrm{CDCl_3}$, 400 MHz) δ 1.23 (t, J=7.0 Hz, 3H, $-\mathrm{OCH_2C}H_3$), 1.37 (d, J=5.4 Hz, 3H, $-\mathrm{CHC}H_3$), 3.50–3.55 (m, 1H, $\mathrm{OC}H_2\mathrm{CH_3}$), 3.66–3.70 (m, 1H, $\mathrm{OC}H_2\mathrm{CH_3}$), 4.52 (d, J=11.8 Hz, 1H, $\mathrm{PhC}H_2$–), 4.64 (d, J=11.8 Hz, 1H, $\mathrm{PhC}H_2$–), 4.82 (q, J=5.3 Hz, 1H, BnOCH($\mathrm{CH_3}$)OEt), 7.27–7.35 (m, 5H, Ar–H); ^{13}C NMR ($\mathrm{CDCl_3}$, 100 MHz) δ 15.3 (1°), 19.8 (1°), 60.6 (2°, −OCH$_2$CH$_3$), 66.9 (2°, PhCH$_2$O–), 99.1 (3°, BnOCH($\mathrm{CH_3}$)OEt), 127.4 (3°, Ar), 127.7 (3°, Ar), 128.3 (3°, Ar), 138.5 (4°, Ar); IR ($\mathrm{CH_2Cl_2}$, cm^{-1}): 2986, 2865, 1456, 1387; Mass (*m/z*): 91 (M$^+$−94, 92), 79 (66), 77 (100), 73 (45), 65 (89).

4.8.4. 2-((1*R*,2*S*,5*R*)-Menthyl)tetrahydropyran (8a). A mixture of two diastereomers; ^{1}H NMR ($\mathrm{CDCl_3}$, 400 MHz) δ 0.76–1.10 (m, 12H), 1.20–1.83 (m, 10H), 2.05–2.37 (m, 2H), 3.28–3.50 (m, 2H, $-\mathrm{OC}H_2\mathrm{CH_2}$–), 3.86–4.00 (m, 1H, RR″CHOR′), 4.58–4.80 (m, 1H, (RO)CH(OR′)$\mathrm{CH_2}$–); ^{13}C NMR ($\mathrm{CDCl_3}$, 100 MHz) δ 15.6 (1°), 16.3 (1°), 19.7 (2°), 20.2 (2°), 21.1 (1°), 21.2 (1°), 22.2 (2°), 22.3 (2°), 23.1 (1°), 23.3 (1°), 25.2 (3°), 25.5 (3°), 25.6 (2°), 31.2 (2°), 31.3 (2°), 31.4 (3°), 31.8 (3°), 34.4 (2°), 34.6 (2°), 40.1 (2°), 43.6 (2°), 48.2 (3°), 48.9 (3°), 62.4 (2°), 63.0 (2°), 74.1 (3°), 79.9 (3°), 94.4 (3°), 101.2 (3°); IR ($\mathrm{CH_2Cl_2}$, cm^{-1}): 2949, 1452, 1374; Mass (*m/z*): 139 (M$^+$−101, 10), 85 (100), 69 (70), 57 (80); HRMS Calcd for $\mathrm{C_{15}H_{28}O_2}$: 240.2090. Found: 240.2086. Anal. Calcd for $\mathrm{C_{15}H_{28}O_2}$: C, 74.95; H, 11.74. Found: C, 75.04; H, 11.91.

4.8.5. 2-((1*R*,2*S*,5*R*)-Menthyl)tetrahydrofuran (8b). A mixture of two diastereomers; ^{1}H NMR ($\mathrm{CDCl_3}$, 400 MHz) δ 0.84–1.16 (m, 12H), 1.28–1.35 (m, 1H), 1.51–1.58 (m, 1H), 1.77–1.87 (m, 2H), 2.00–2.43 (m, 6H), 3.64–3.90 (m, 1H), 4.26–4.42 (m, 2H), 5.81–5.96 (m, 1H, (RO)CH(OR′)$\mathrm{CH_3}$); ^{13}C NMR ($\mathrm{CDCl_3}$, 100 MHz) δ 15.5 (1°), 16.3 (1°), 21.0 (2°), 21.1 (2°), 22.2 (1°), 22.3 (1°), 23.2 (2°), 23.3 (2°), 23.5 (1°), 23.6 (1°), 25.4 (3°), 25.6 (3°), 31.4 (2°), 31.7 (2°), 32.5 (3°), 32.6 (3°), 34.4 (2°), 34.6 (2°), 40.0 (2°), 43.5 (2°), 48.1 (3°), 48.7 (3°), 66.5 (2°), 66.7 (2°), 73.6 (3°), 78.7 (3°), 99.4 (3°), 105.3 (3°); IR ($\mathrm{CH_2Cl_2}$, cm^{-1}): 2940, 1457, 1360, 1236; Mass (*m/z*): 226 (M$^+$, 1), 185 (4), 91 (13), 71 (100); Anal. Calcd for $\mathrm{C_{14}H_{26}O_2}$: C, 74.29; H, 11.58. Found: C, 74.25; H, 11.64.

4.8.6. Acetaldehyde ethyl menthyl acetal (8c). A mixture of two diastereomers; ^{1}H NMR ($\mathrm{CDCl_3}$, 400 MHz) δ 0.75–1.04 (m, 12H), 1.17–1.36 (m, 8H), 1.62–1.67 (m, 2H), 2.02–2.33 (m, 2H), 3.20–3.40 (m, 1H), 3.42–3.65 (m, 2H), 4.69– 4.84 (m, 1H, (RO)CH(OR′)$\mathrm{CH_3}$); ^{13}C NMR ($\mathrm{CDCl_3}$, 100 MHz) δ 15.2 (1°), 15.3 (1°), 15.7 (1°), 16.0 (1°), 20.3 (1°), 20.9 (1°), 21.2 (1°), 22.3 (1°), 22.9 (2°), 23.1 (2°), 24.9 (3°), 25.2 (3°), 31.4 (3°), 31.7 (3°), 34.35 (2°), 34.42 (2°), 41.1 (2°), 42.7 (2°), 48.2 (3°), 48.6 (3°), 59.5 (2°), 59.7 (2°), 74.8 (3°), 77.9 (3°), 96.8 (3°), 100.4 (3°); IR ($\mathrm{CH_2Cl_2}$, cm^{-1}): 2940, 1457, 1374; Mass (*m/z*): 228 (M$^+$, 1), 183 (12), 139 (73), 73 (100); Anal. Calcd for $\mathrm{C_{14}H_{28}O_2}$: C, 73.63; H, 12.36. Found: C, 73.60; H, 12.49.

4.8.7. Cholesteryl-2-tetrahydropyran (9a). A mixture of two diastereomers; ^{1}H NMR ($\mathrm{CDCl_3}$, 400 MHz) δ 0.67 (br t, 3H, $-\mathrm{CH_3}$), 0.85–1.61 (m, 35H), 1.78–2.18 (m, 9H), 2.25–2.36 (m, 2H), 3.42–3.48 (m, 1H, $-\mathrm{OC}H_2\mathrm{CH_2}$–), 3.80–3.93 (m, 2H, $-\mathrm{OC}H_2\mathrm{CH_2}$– and −OC$H$RR′), 5.29 (br t, J=2.4 Hz, 1H, OCHR″(OR′)), 5.34 (br t, J=5.2 Hz, 1H, olefinic-H); ^{13}C NMR ($\mathrm{CDCl_3}$, 100 MHz) δ 11.8 (1°), 18.7 (1°), 19.4 (1°), 21.0 (2°), 22.5 (1°), 22.8 (1°), 23.5 (2°), 23.8 (2°), 24.3 (2°), 28.0 (3°), 28.2 (2°), 29.9 (2°), 31.90 (3°), 31.92 (2°), 32.6 (2°), 35.8 (3°), 36.2 (2°), 36.70 (2°), 36.77 (2°), 37.26 (2°), 37.39 (2°), 39.0 (2°), 39.5 (2°), 39.8 (2°), 40.4 (2°), 42.3 (4°), 50.2 (3°), 56.2 (3°), 56.8 (3°), 66.6 (2°), 76.18 (3°), 76.23 (3°), 101.97 (3°), 102.00 (3°), 121.4 (3°), 121.5 (3°), 140.9 (4°), 141.0 (4°); IR ($\mathrm{CH_2Cl_2}$, cm^{-1}): 2930, 1466, 1378; Mass (*m/z*): 470 (M$^+$, 1), 368 (100), 91 (13), 71 (90); Anal. Calcd for $\mathrm{C_{32}H_{54}O_2}$: C, 81.64; H, 11.56. Found: C, 81.60; H, 11.58.

4.8.8. Cholesteryl-2-tetrahydrofuran (9b). A mixture of two diastereomers; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.67 (br t, 3H, $-CH_3$), 0.85–1.65 (m, 33H), 1.75–2.07 (m, 9H), 2.12–2.38 (m, 2H), 3.39–3.50 (m, 1H, $-OCH_2-$), 3.80–3.97 (m, 2H, $-OCH_2-$ and $-OCHRR'$), 5.28 (br t, J=2.0 Hz, 1H, $OCHR''(OR')$), 5.34 (br t, J=5.6 Hz, 1H, olefinic-H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 11.8 (1°), 18.7 (1°), 19.3 (1°), 21.0 (2°), 22.5 (1°), 22.8 (1°), 23.5 (2°), 23.8 (2°), 24.3 (2°), 28.0 (3°), 28.2 (2°), 29.9 (2°), 31.89 (3°), 31.91 (2°), 32.6 (2°), 35.8 (3°), 36.2 (2°), 36.7 (2°), 36.8 (2°), 37.3 (2°), 37.4 (2°), 38.9 (2°), 39.5 (2°), 39.8 (2°), 40.4 (2°), 42.3 (4°), 50.2 (3°), 56.2 (3°), 56.7 (3°), 66.6 (2°), 76.17 (3°), 76.21 (3°), 101.96 (3°), 101.99 (3°), 121.4 (3°), 121.5 (3°), 140.9 (4°), 141.0 (4°); IR (CH_2Cl_2, cm^{-1}): 2940, 1470, 1374; Mass (*m/z*): 456 (M^+, 2), 368 (98), 91 (24), 71 (100); Anal. Calcd for $C_{31}H_{52}O_2$: C, 81.52; H, 11.47. Found: C, 81.43; H, 11.55.

4.8.9. Acetaldehyde cholesteryl ethyl acetal (9c). A mixture of two diastereomers; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.68 (br t, 3H, $-CH_3$), 0.80–1.68 (m, 38H), 1.78–2.05 (m, 6H), 2.20–2.35 (m, 2H), 3.41–3.50 (m, 2H, $-OCH_2CH_3$), 3.60–3.70 (m, 1H, $RR''CH(OR')$), 4.72–4.80 (m, 1H, $OCHMe(OR')$), 5.34 (br, 1H, olefinic-H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 11.8 (1°), 15.3 (1°), 18.7 (1°), 19.3 (1°), 20.96 (1°), 20.99 (1°), 21.02 (2°), 22.5 (1°), 22.8 (1°), 23.8 (2°), 24.3 (2°), 28.0 (3°), 28.2 (2°), 29.0 (2°), 29.4 (2°), 31.9 (3°), 35.8 (3°), 36.2 (2°), 36.7 (2°), 37.2 (2°), 37.4 (2°), 39.5 (2°), 39.7 (2°), 39.8 (2°), 40.1 (2°), 42.3 (4°), 50.2 (3°), 50.2 (3°), 56.2 (3°), 56.8 (3°), 60.1 (2°), 75.68 (3°), 75.71 (3°), 98.16 (3°), 98.2 (3°), 121.4 (3°), 121.5 (3°), 140.8 (4°), 142.0 (4°); IR (CH_2Cl_2, cm^{-1}): 2940, 1475, 1378; Mass (*m/z*): 458 (M^+, 1), 369 (100), 91 (51), 71 (98); Anal. Calcd for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92. Found: C, 73.96; H, 8.22.

4.8.10. 2-(1-Phenyl-1-cyclohexyloxy)tetrahydropyran (10a). A mixture of two diastereomers; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.26–2.14 (m, 16H), 3.30–3.35 (m, 1H, 1H, $ROCH_2R'$), 3.93–3.97 (m, 1H, $ROCH_2R'$), 4.22 (br t, J=4.7 Hz, 1H, $(RO)CH(OR')CH_3$), 7.20–7.34 (m, 3H, Ar–H), 7.45–7.47 (m, 2H, Ar–H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 20.5 (2°), 22.3 (2°), 22.4 (2°), 25.4 (2°), 25.6 (2°), 32.1 (2°), 33.7 (2°), 39.8 (2°), 63.7 (2°), 78.8 (4°, $Ph(RO)C(CH_2R')_2$), 95.4 (3°, $(RO)CH(OR')CH_2-$), 126.6 (3°, Ar), 126.9 (3°, Ar), 127.9 (3°, Ar), 145.8 (4°, Ar); IR (CH_2Cl_2, cm^{-1}): 3050, 2940, 1452, 1355; Mass (*m/z*): 260 (M^+, 9), 159 (100), 91 (86), 85 (89); HRMS *m/z* Calcd for $C_{17}H_{24}O_2$: 260.1777. Found: 260.1772.

4.8.11. 1-(1-Phenyl-1-cyclohexyloxy)tetrahydrofuran (10b). A mixture of two diastereomers; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.23–1.26 (m, 1H), 1.46–2.04 (m, 12H), 2.20–2.24 (m, 1H), 3.70–3.76 (m, 1H, $ROCH_2R'$), 3.89–3.94 (m, 1H, $ROCH_2R'$), 4.90–4.91 (m, 1H, $(RO)CH(OR')CH_2-$), 7.21–7.44 (m, 5H, Ar–H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 22.1 (2°), 22.4 (2°), 23.9 (2°), 25.7 (2°), 33.4 (2°), 34.4 (2°), 40.0 (2°), 67.0 (2°), 78.2 (4°, $Ph(RO)C(CH_2R')_2$), 99.9 (3°, $(RO)CH(OR')\ CH_3$), 126.4 (3°, Ar), 126.8 (3°, Ar), 128.1 (3°, Ar), 146.7 (4°, Ar); IR (CH_2Cl_2, cm^{-1}): 3059, 2948, 1498, 1456; Mass (*m/z*): 246 (M^+, 2), 159 (28), 71 (100); Anal. Calcd for $C_{16}H_{22}O_2$: C, 78.00; H, 9.00. Found: C, 77.95; H, 9.04.

4.8.12. 1-Phenylcyclohexyl 1-(1-ethoxyethyl) ether (10c). A mixture of two diastereomers; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.03 (t, J=7.0 Hz, 3H, $-CH_2CH_3$), 1.14 (d, J=5.4 Hz, 3H, $-CHCH_3$), 1.28–2.12 (m, 10H), 3.22–3.31 (m, 2H, $-OCH_2CH_3$), 4.36–4.40 (m, 1H, $(RO)CH(OR')CH_3$), 7.23–7.35 (m, 3H, Ar–H), 7.45–7.48 (m, 2H, Ar–H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 15.2 (1°, $-CH_2Ci_3$), 21.3 (1°, $-CHCH_3$), 22.4 (2°), 22.5 (2°), 25.7 (2°), 34.8 (2°), 38.6 (2°), 59.4 (2°), 78.0 (4°, $Ph(RO)C(CH_2R'_2)$, 95.4 (3°, $(RO)CH(OR')CH_3$), 126.7 (3°, Ar), 127.0 (3°, Ar), 127.9 (3°, Ar), 145.2 (4°, Ar); IR (CH_2Cl_2, cm^{-1}): 3068, 2940, 1452, 1378; Mass (*m/z*): 248 (M^+, 0.2), 202 (26), 159 (72), 91 (95), 73 (100); Anal. Calcd for $C_{16}H_{24}O_2$: C, 77.38; H, 9.74. Found: C, 77.33; H, 9.82.

4.8.13. 2-(1,1-Dimethylphenylethoxy)tetrahydropyran (11a). A mixture of two diastereomers; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.16 (s, 3H, $-CH_3$), 1.24 (s, 3H, $-CH_3$), 1.49–1.65 (m, 5H), 1.86–1.87 (m, 1H), 2.76 (d, J=13.2 Hz, 1H, $PhCH_2-$), 2.84 (d, J=13.2 Hz, 2H, $PhCH_2-$), 3.40–3.43 (m, 1H), 3.83–3.93 (m, 1H), 4.79 (br t, J=4.4 Hz, 1H, $ROCHR''(OR')$), 7.17–7.27 (m, 5H, Ar–H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 20.4 (2°), 25.2 (1°, $-CH_3$), 25.4 (2°), 26.9 (1°, $-CH_3$), 32.2 (2°), 48.9 (2°), 62.7 (2°, $PhCH_2-$), 76.4 (4°, $RC(CH_3)_2OR'$), 93.6 (3°, $ROCHR''(OR')$), 125.9 (3°, Ar), 127.6 (3°, Ar), 130.7 (3°, Ar), 138.4 (4°, Ar); IR (CH_2Cl_2, cm^{-1}): 2958, 1604, 1457, 1383; Mass (*m/z*): 235 ($M^+ + 1$, 8), 133 (45), 117 (46), 91 (100), 85 (95); Anal. Calcd for $C_{15}H_{22}O_2$: C, 76.88; H, 9.45. Found: C, 76.81; H, 9.60.

4.8.14. 2-(1,1-Dimethylphenylethoxy)tetrahydrofuran (11b). A mixture of two diastereomers; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.19 (s, 3H, $-CH_3$), 1.22 (s, 3H, $-CH_3$), 1.79–2.02 (m, 4H, $-CH_2CH_2-$), 2.78 (s, 2H, $PhCH_2-$), 3.76–3.80 (m, 1H, $-OCH_2-$), 3.88–3.92 (m, 1H, $-OCH_2-$), 5.43 (br t, J=3.3 Hz, 1H, $ROCHR''(OR')$), 7.18–7.26 (m, 5H, Ar–H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 23.8 (2°), 25.6 (1°, $-CH_3$), 27.1 (1°, $-CH_3$), 33.4 (2°), 48.8 (2°), 66.5 (2°, $PhCH_2-$), 76.0 (4°, $RC(CH_3)_2OR'$), 98.5 (3°, $OCHR''(OR')$), 125.9 (3°, Ar), 127.6 (3°, Ar), 130.6 (3°, Ar), 138.5 (4°, Ar); IR (CH_2Cl_2, cm^{-1}): 2967, 1604, 1498, 1461, 1374; Mass (*m/z*): 219 ($M^+ - 1$, 6), 115 (45), 91 (100), 71 (85); Anal. Calcd for $C_{14}H_{20}O_2$: C, 76.32; H, 9.15. Found: C, 75.92; H, 9.30.

4.8.15. Acetaldehyde 1,1-dimethylphenylethyl ethyl acetal (11c). A mixture of two diastereomers; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.13–1.29 (m, 12H), 2.80 (s, 2H, $PhCH_2-$), 3.44–3.49 (m, 2H, $-OCH_2-$), 4.93 (q, J=5.2 Hz, 1H, $ROCHR''(OR')$), 7.21–7.25 (m, 5H, Ar–H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 15.4, 21.6, 25.6, 26.5, 49.0, 58.3, 76.0, 93.8, 126.0, 127.6, 130.7, 138.3; IR (CH_2Cl_2, cm^{-1}): 2986, 1613, 1498, 1452, 1386; Mass (*m/z*): 222 (M^+, 1), 133 (89), 118 (73), 91 (100).

4.8.16. 2-Phenoxytetrahydropyran (12a). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.50–1.69 (m, 3H), 1.83–1.87 (m, 2H), 1.90–2.01 (m, 1H), 3.57–3.61 (m, 1H, $-OCH_2CH_2-$), 3.88–3.94 (m, 1H, $-OCH_2CH_2-$), 5.41 (br t, J=3.3 Hz, 1H, $PhOCHR''(OR')$), 6.95–7.06 (m, 3H, Ar–H), 7.25–7.29 (m, 2H, Ar–H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 18.8 (2°), 25.2 (2°), 30.4 (2°), 62.0 (2°), 96.3 (3°, $PhOCH(OR)_2$), 116.4 (3°, Ar), 121.5 (3°, Ar), 129.3 (3°, Ar), 157.0 (4°, Ar); IR

(CH$_2$Cl$_2$, cm^{-1}): 3041, 2949, 1599, 1498, 1355; Mass (*m/z*): 178 (M$^+$, 19), 94 (45), 85 (100), 67 (38); HRMS *m/z* Calcd for C$_{11}$H$_{14}$O$_2$: 178.0994. Found: 178.0987.

4.8.17. 2-Phenoxytetrahydrofuran (12b). ^{1}H NMR (CDCl$_3$, 400 MHz) δ 1.94–1.97 (m, 1H), 2.12–2.22 (m, 3H), 3.96–4.00 (m, 1H, OC*H*$_2$CH$_2$–), 4.05–4.09 (m, 1H, –OC*H*$_2$CH$_2$–), 5.83 (br t, *J*=4.5 Hz, 1H, PhOC*H*R′(OR)), 6.98–7.08 (m, 3H, Ar–H), 7.28–7.32 (m, 2H, Ar–H); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 23.4 (2°), 32.7 (2°), 67.9 (2°), 102.2 (3°, PhOCH(OR)$_2$), 116.5 (3°, Ar), 121.4 (3°, Ar), 129.3 (3°, Ar), 157.1 (4°, Ar); IR (CH$_2$Cl$_2$, cm^{-1}): 3049, 2948, 1599, 1493, 1360; Mass (*m/z*): 164 (M$^+$, 1), 94 (100), 71 (95); HRMS *m/z* Calcd for C$_{10}$H$_{12}$O$_2$: 164.0838. Found: 164.0835.

4.8.18. Acetaldehyde ethyl phenyl acetal (12c). ^{1}H NMR (CDCl$_3$, 400 MHz) δ 1.20 (t, *J*=7.1 Hz, 3H, –OCH$_2$C*H*$_3$), 1.49 (d, *J*=5.2 Hz, 3H, PhOCHC*H*$_3$), 3.52–3.56 (m, 1H, –OC*H*$_2$CH$_3$), 3.77–3.81 (m, 1H, –OC*H*$_2$CH$_3$), 5.38 (q, *J*=5.4 Hz, 1H, PhOC*H*(CH$_3$)OR), 6.96–7.01 (m, 3H, Ar–H), 7.25–7.29 (m, 2H, Ar–H); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 15.1 (1°), 20.3 (1°), 61.4 (2°), 99.5 (3°, PhOCH(CH$_3$)OR), 117.3 (3°, Ar), 121.7 (3°, Ar), 129.4 (3°, Ar), 157.0 (4°, Ar); IR (CH$_2$Cl$_2$, cm^{-1}): 2976, 1595, 1489, 1378; Mass (*m/z*): 166 (M$^+$, 5), 121 (17), 94 (100), 73 (76); HRMS *m/z* Calcd for C$_{10}$H$_{14}$O$_2$: 166.0994. Found: 164.0988.

4.8.19. 4-(Tetrahydropyranyl-2-oxy)decane-2-one (13a). A mixture of two diastereomers; ^{1}H NMR (CDCl$_3$, 400 MHz) δ 0.88 (t, *J*=7.2 Hz, 3H, –CH$_2$C*H*$_3$), 1.28–1.79 (m, 16H), 2.16–2.22 (m, 3H), 2.45–2.85 (m, 1H), 3.40–3.50 (m, 1H), 3.80–3.89 (m, 1H), 4.07–4.12 (m, 1H), 4.57–4.68 (m, 1H); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 13.8 (1°), 19.8 (2°), 20.1 (2°), 22.4 (2°), 22.4 (2°), 24.9 (2°), 25.1 (2°), 25.2 (2°), 29.0 (2°), 29.1 (2°), 30.7 (1°), 30.9 (1°), 31.0 (2°), 31.6 (2°), 34.4 (2°), 35.5 (2°), 48.1 (2°), 49.5 (2°), 62.6 (2°, –O*C*H$_2$–), 62.9 (2°, –O*C*H$_2$–), 73.8 (3°, RR′*C*HOR″), 98.4 (3°, O*C*HR″(OR′)), 98.8 (3°, O*C*HR″(OR′)), 207.2 (4°, C=O), 207.4 (4°, C=O); IR (CH$_2$Cl$_2$, cm^{-1}): 2939, 1719 (C=O), 1461, 1359; Mass (*m/z*): 257 (M$^+$+1, 29), 173 (61), 155 (34), 85 (100); Anal. Calcd for C$_{15}$H$_{28}$O$_3$: C, 70.27; H, 11.01. Found: C, 70.01; H, 11.15.

4.8.20. 4-(Tetrahydrofuranyl-2-oxy)decane-2-one (13b). A mixture of two diastereomers; ^{1}H NMR (CDCl$_3$, 400 MHz) δ 0.80 (t, *J*=6.4 Hz, 3H, –CH$_2$C*H*$_3$), 1.12–1.50 (m, 10H), 1.63–1.95 (m, 4H), 2.07–2.15 (m, 3H), 2.34–2.43 (m, 1H), 2.52–2.63 (m, 1H), 3.66–3.81 (m, 2H), 3.90–4.00 (m, 1H), 5.09–5.17 (m, 1H); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 13.9 (1°), 22.4 (2°), 23.3 (2°), 23.4 (2°), 25.1 (2°), 29.1 (2°), 29.1 (2°), 30.1 (2°), 31.0 (1°), 31.6 (1°), 31.7 (2°), 32.4 (2°), 34.4 (2°), 35.5 (2°), 48.4 (2°), 49.6 (2°), 66.6 (2°, –O*C*H$_2$–), 66.7 (2°, –O*C*H$_2$–), 73.2 (3°, RR′*C*HOR″), 72.8 (3°, RR′*C*HOR″), 102.9 (3°, O*C*HR″ (OR′)), 103.0 (3°, O*C*HR″ (OR′)), 207.3 (4°, C=O); IR (CH$_2$Cl$_2$, cm^{-1}): 2921, 1719, 1456, 1359.

4.8.21. 4-(1-Ethoxyethoxy)decane-2-one (13c). A mixture of two diastereomers; ^{1}H NMR (CDCl$_3$, 400 MHz) δ 0.82 (t, *J*=4.2 Hz, 3H, –CH$_2$C*H*$_3$), 1.07–1.60 (m, 15H), 2.09–2.18 (m, 3H), 2.40–2.50 (m, 1H), 2.59–2.73 (m, 1H), 3.29–3.58 (m, 2H), 3.90–3.98 (m, 1H), 4.56–4.69 (m, 1H); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 13.9 (1°), 15.2 (1°), 15.2 (1°), 20.4 (1°), 20.6 (1°), 22.4 (2°), 22.5 (2°), 24.9 (2°), 25.1 (2°), 29.2 (2°), 31.1 (1°), 31.1 (1°), 31.5 (2°), 31.7 (2°), 34.8 (2°), 35.4 (2°), 48.6 (2°), 49.2 (2°), 60.3 (2°, –O*C*H$_2$–), 60.4 (2°, –O*C*H$_2$–), 72.9 (3°, RR′*C*HOR″), 73.0 (3°, RR′*C*HOR″), 99.4 (3°, O*C*HR″ (OR′)), 99.6 (3°, O*C*HR″(OR′)), 207.4 (4°, C=O); IR (CH$_2$Cl$_2$, cm^{-1}): 2930, 1723, 1452, 1378.

4.8.22. 4-(Tetrahydropyranyl-2-oxy)-4-methyl-2-pentanone (14a). ^{1}H NMR (CDCl$_3$, 400 MHz) δ 1.31 (s, 3H, CH$_3$), 1.35 (s, 3H, CH$_3$), 1.47–1.55 (m, 4H), 1.63–1.68 (m, 1H), 1.81–1.83 (m, 1H), 2.21 (s, 3H,CH$_3$CO–), 2.58 (d, *J*=13.9 Hz, 1H, –C*H*$_2$CO), 2.69 (d, *J*=13.8 Hz, 1H, –C*H*$_2$CO), 3.44–3.48 (m, 1H), 3.90–3.95 (m, 1H), 4.80 (dd, *J*=5.2, 2.5 Hz, 1H, –OC*H*RO–); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 20.5 (2°), 25.3 (2°), 26.0 (1°, CH$_3$), 26.9 (1°, CH$_3$), 32.1 (2°), 32.3 (1°, CO*C*H$_3$), 55.2 (2°), 63.0 (2°), 75.3 (4°), 93.8 (3°, –O*C*HRO–), 207.9 (4°, C=O); IR (CH$_2$Cl$_2$, cm^{-1}): 2940, 1715, 1443, 1365; Mass (*m/z*): 200 (M$^+$, 9), 99 (100, M$^+$–OTHP), 98 (73), 85 (95); HRMS Calcd for C$_{11}$H$_{20}$O$_3$: 200.1413; Found: 200.1413.

4.8.23. 4-(Tetrahydrofuranyl-2-oxy)-4-methyl-2-pentanone (14b). ^{1}H NMR (CDCl$_3$, 400 MHz) δ 1.26 (s, 3H, CH$_3$), 1.28 (s, 3H, CH$_3$), 1.70–1.80 (m, 2H), 1.80–2.00 (m, 2H), 2.12 (s, 3H, CH$_3$CO–), 2.51 (d, *J*=13.8 Hz, 1H, –C*H*$_2$CO), 2.61 (d, *J*=13.8 Hz, 1H, –C*H*$_2$CO), 3.70–3.79 (m, 1H), 3.80–3.89 (m, 1H), 5.38 (br d, *J*=2.5 Hz, 1H, –OC*H*RO–); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 23.7 (2°), 26.3 (1°, CH$_3$), 27.0 (1°, CH$_3$), 32.1 (1°, CO*C*H$_3$), 33.3 (2°), 55.3 (2°), 66.6 (2°), 74.7 (4°), 98.3 (3°, –O*C*HRO–), 207.8 (4°, C=O); IR (CH$_2$Cl$_2$, cm^{-1}): 2985, 1714, 1465, 1359; Mass (*m/z*): 83 (M$^+$–103, 20), 71 (100), 55 (43).

4.8.24. 4-(1-Ethoxyethoxy)-4-methyl-2-pentanone (14c). ^{1}H NMR (CDCl$_3$, 400 MHz) δ 1.22 (t, *J*=7.0 Hz, 3H, –CH$_2$C*H*$_3$), 0.21 (d, *J*=1.6 Hz, 3H, –CHC*H*$_3$), 1.24 (s, 3H, CH$_3$), 1.29 (s, 3H, CH$_3$), 2.15 (d, *J*=0.7 Hz, 3H, CH$_3$CO–), 2.53 (d, *J*=13.8 Hz, 1H, –C*H*$_2$CO), 2.61 (d, *J*=13.8 Hz, 1H, –C*H*$_2$CO), 3.32–3.48 (m, 2H), 4.87 (q, *J*=1.4 Hz, 1H, –OC*H*CH$_3$O–); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 15.3 (1°, –OCH$_2$*C*H$_3$), 21.4 (1°, –CH*C*H$_3$), 26.0 (1°, CH$_3$), 26.6 (1°, CH$_3$), 32.4 (1°, COiH$_3$), 55.4 (2°), 58.5 (2°), 74.8 (4°), 93.8 (3°, –O*C*HCH$_3$O–), 207.9 (4°, C=O); IR (CH$_2$Cl$_2$, cm^{-1}): 3059, 2976, 1714, 1382, 1267 (s); Mass (*m/z*): 97 (M$^+$–91, 55), 83 (63), 73 (94), 69 (65), 57 (98), 55 (100).

Acknowledgements

We are grateful to the National Science Council and National Chung Cheng University, Republic of China for the financial support.

References

1. (a) Greene, T. W.; Wuts, P. G. M. *Protective Groups in Organic Synthesis*, 2; Wiley: New York, 1991. (b) Kocienski, P. J. In *Protecting Groups*, Enders, D., Noyori, R., Trost, B. M., Eds.; Georg Thieme: Stuttgart, 1994.

2. (a) Ott, A. C.; Murray, M. F.; Pederson, R. L. *J. Am. Chem. Soc.* **1952**, *74*, 1239. (b) Jones, R. G.; Mann, M. J. *J. Am. Chem. Soc.* **1953**, *75*, 4048. (c) Creenhalgh, C. W.; Henbest, H. B.; Jones, E. R. H. *J. Chem. Soc.* **1951**, 1190. (d) Miyashita, M.; Yoshikoshi, A.; Grieco, P. A. *J. Org. Chem.* **1977**, *42*, 3772. (e) Torii, S.; Inokuchi, T.; Kondo, K.; Ito, H. *Bull. Chem. Soc. Jpn* **1985**, *58*, 1347. (f) Bolitt, V.; Mioskowski, C.; Shin, D. S.; Falck, J. R. *Tetrahedron Lett.* **1988**, *29*, 4583. (g) Yadav, J. S.; Srinivas, D.; Reddy, G. S. *Synth. Commun.* **1998**, *28*, 1399.
3. Alper, H.; Dinkes, L. *Synthesis* **1972**, 81.
4. Brown, D. S.; Ley, S. V.; Vile, S.; Thompson, M. *Tetrahedron* **1991**, *47*, 1329.
5. Tanemura, K.; Horaguchi, T.; Suzuki, T. *Bull. Chem. Soc. Jpn* **1992**, *65*, 304.
6. (a) Maity, G.; Roy, S. C. *Synth. Commun.* **1993**, *23*, 1667. (b) Iqbal, J.; Srivastava, R. R.; Gupta, K. B.; Khan, M. A. *Synth. Commun.* **1989**, *19*, 901. (c) Kantam, M. L.; Santhi, P. L. *Synth. Commun.* **1993**, *23*, 2225. (d) Bhuma, V.; Kantam, M. L. *Synth. Commun.* **1992**, *22*, 2941. (e) Ma, S.; Venanzi, L. M. *Tetrahedron Lett.* **1993**, *34*, 5269. (f) Molnar, A.; Beregszaszi, T. *Tetrahedron Lett.* **1996**, *37*, 8597.
7. (a) Bongini, A.; Cardillo, G.; Orena, M.; Sandri, S. *Synthesis* **1979**, 618. (b) Johnston, R. D.; Marston, C. R.; Krieger, P. E.; Goe, G. L. *Synthesis* **1988**, 393. (c) Olah, G. A.; Husain, A.; Singh, B. P. *Synthesis* **1983**, 892. (d) Menger, F. M.; Chu, C. H. *J. Org. Chem.* **1981**, *46*, 5044. (e) Hoyer, S.; Laszlo, P.; Orlovic, M.; Polla, E. *Synthesis* **1986**, 655. (f) Upadhya, T. T.; Daniel, T.; Sudalai, A.; Ravindranathan, T.; Sabu, K. R. *Synth. Commun.* **1996**, *26*, 4539. (g) Campelo, J. M.; Garcia, A.; Lafont, F.; Luna, D.; Marinas, J. M. *Synth. Commun.* **1994**, *24*, 1345. (h) Bandgar, B. P.; Jagtap, S. R.; Aghade, B. B.; Wadgaonkar, P. P. *Synth. Commun.* **1995**, *25*, 2211. (i) Kumar, P.; Dinesh, C. U.; Reddy, R. S.; Pandey, B. *Synthesis* **1993**, 1069. (j) Chavez, F.; Godinez, R. *Synth. Commun.* **1992**, *22*, 159. (k) Patney, H. K. *Synth. Commun.* **1991**, *21*, 2329. (l) Campelo, J. M.; Garcia, A.; Lafont, F.; Luna, D.; Marinas, J. M. *Synth. Commun.* **1992**, *22*, 2335.
8. (a) Kim, S.; Park, J. H. *Tetrahedron Lett.* **1987**, *28*, 439. (b) Ogawa, Y.; Shibasaki, M. *Tetrahedron Lett.* **1984**, *25*, 663. (c) Otera, J.; Nozaki, H. *Tetrahedron Lett.* **1986**, *27*, 5743. (d) Wagner, A.; Heitz, M. P.; Mioskowski, C. *J. Chem. Soc., Chem. Commun.* **1989**, 1619.
9. Raina, S.; Singh, V. K. *Synth. Commun.* **1995**, *25*, 2395.
10. Srikrishna, A.; Sattigeri, J. A.; Viswajanani, R.; Yelamaggad, C. V. *J. Org. Chem.* **1995**, *60*, 2260.
11. Hon, Y. S.; Lee, C. F. *Tetrahedron Lett.* **1999**, *40*, 2389.
12. (a) Maryanoff, B. E.; Reitz, A. B. *Chem. Rev.* **1989**, *89*, 863. (b) Maercker, A. *Org. React.* **1965**, *14*, 270. (c) Johnson, A. W. *Ylides and Imines of Phosphorus*, Wiley: New York, 1993.
13. (a) Ho, T. L. *Distinctive Techniques for Organic Synthesis: A Practical Guide*, World Scientific: Singapore, 1998 Chapter 2 and references cited therein. (b) Shuttleworth, S. J.; Allin, S. M.; Sharma, P. K. *Synthesis* **1997**, 1217. (c) Hodge, P. *Chem. Soc. Rev.* **1997**, *26*, 417.
14. (a) *Solid Supports and Catalysts in Organic Synthesis*, Smith, K., Ed.; Prentice-Hall: New York, 1992. (b) Mckenzie, W. M.; Sherrington, D. C. *J. Polym. Sci., Polym. Chem. Ed.* **1982**, *20*, 431. (c) In *Polymer-Supported Reactions in Organic Synthesis*, Hodge, P., Sherrington, D. C., Eds.; Wiley: Chichester, 1980. (d) Steven, L. R.; Dan, P. L. *J. Org. Chem.* **1975**, *40*, 1669. (e) Bernard, M.; Ford, W. T. *J. Org. Chem.* **1983**, *48*, 326. (f) Amos, R. A.; Fawcett, S. M. *J. Org. Chem.* **1984**, *49*, 2637. (g) Hughes, I. *Tetrahedron Lett.* **1996**, *37*, 7595. (h) Stanetty, P.; Kremslehner, M. *Tetrahedron Lett.* **1998**, *39*, 811. (i) Horiki, K. *Tetrahedron Lett.* **1976**, *17*, 4103.
15. Ramirez, F.; Dershowitz, S. *J. Org. Chem.* **1957**, *22*, 41.
16. Hon, Y. S.; Lee, C. F. *Tetrahedron* **2000**, *56*, 7893.
17. Isler, O.; Gutmann, H.; Montavon, M.; Ruegg, R.; Ryser, G.; Zeller, P. *Helv. Chim. Acta* **1957**, *40*, 1242.
18. (a) Bohme, H.; Krause, W. *Chem. Ber.* **1949**, *82*, 426. (b) Samet, A. V.; Shestopalov, A. M.; Nesterov, V. N.; Semenov, V. V. *Synthesis* **1997**, 623.
19. Johnson, A. W.; Amel, R. T. *J. Org. Chem.* **1969**, *34*, 1240.
20. Eliel, E. L.; Nowak, B. E.; Daignault, R. A.; Badding, V. G. *J. Org. Chem.* **1965**, *30*, 2441.
21. Ohtsuka, E.; Yamane, A.; Ikehara, M. *Chem. Pharm. Bull.* **1983**, *31*, 1534.
22. Hoffmann, A. K.; Thomas, W. M. *Synthesis* **1959**, 581.
23. Schiemenz, G. P.; Kaack, H. *Liebigs Ann. Chem.* **1973**, 1480.
24. Schiemenz, G. P.; Kaack, H. *Liebigs Ann. Chem.* **1973**, 1494.
25. Rabinowitz, R.; Marcus, R. *J. Org. Chem.* **1961**, *26*, 4157.
26. Naaktgeboren, A. J.; Nolte, R. J. M.; Drenth, W. *J. Am. Chem. Soc.* **1980**, *102*, 3350.
27. (a) Camps, F.; Castells, J.; Font, J.; Vela, F. *Tetrahedron Lett.* **1971**, 1715. (b) Balakrishnan, T.; Ford, W. T. *J. Appl. Polym. Sci.* **1982**, *27*, 133. (c) Borhan, B.; Wilson, J. A.; Gasch, M. J.; Ko, Y.; Kurth, D. M.; Kurth, M. J. *J. Org. Chem.* **1995**, *60*, 7375.
28. (a) Borowitz, I. J.; Grossmann, L. I. *Tetrahedron Lett.* **1962**, *11*, 471. (b) Borowitz, I. J.; Virhaus, R. *J. Am. Chem. Soc.* **1963**, *85*, 2183. (c) Chopard, P. A.; Hudson, R. F.; Klopman, G. *J. Chem. Soc.* **1965**, 1379. (d) Dhuru, S. P.; Padiya, K. J.; Salunkhe, M. M. *J. Chem. Res. (S)* **1998**, 56.