Wittig-Type Olefination Catalyzed by PEG-telluride

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Received February 4, 2002

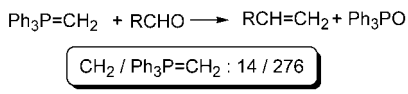
Soluble poly(ethylene glycol) (PEG)-supported telluride **2** was designed and synthesized for catalytic Wittig-type reactions. It was found that the catalytic loading could be reduced from 20 to 2 mol % by the introduction of PEG (even to 0.5 mol % when some telluride salts were used as the catalyst). Under the catalytic reaction conditions, a wide variety of aldehydes with different structures could react with bromoacetate to afford *β*-substitutited or α,*β*-disubstituted unsaturated esters in high yields with excellent *E*-stereoselectivity. The modified process, by using sodium bisulfite instead of triphenyl phosphite, represented a very simple product isolation procedure. The roles of PEG for promoting the ylide formation and stabilizing the catalytic species were disclosed. The mechanism was also studied.

Introduction

In 1953, Wittig and his co-worker discovered the ylide olefination reaction between diphenyl ketone and phosphonium ylide.[1] To date, modifications of this reaction are the most powerful approaches in constructing carbon−carbon double bonds due to its unambiguous positioning and good stereoselectivity of the double bond.[2] From the view of atom economy, however, it is not a perfect reaction.[3] For example, only the methylene group is used, and a large amount of triphenylphosphine oxide is produced as waste in the reaction of methylene triphenylphosphine with aldehyde (Scheme 1). Because triphenylphosphine oxide is hard to reduce, this drawback also limits its further applications in organic synthesis. Thus, chemists are interested in developing catalytic process of this reaction, but few examples have been successful. The first example of catalytic Wittig-type reactions appeared in 1989, in which Huang et al. found tributylarsine could be used as the catalyst in the presence of triphenyl phosphite.[4] Later, they described the catalytic ylide olefination, epoxidation, and cyclopropanation reactions mediated by *n*-butyl telluride or isobutyl telluride.[5]

Unfortunately, 20 mol % of the catalyst should be used for both reactions described above. Reduction of the amount of catalyst means low yield even if the reaction time was prolonged.[6] Compared to other catalytic reactions, needless to say, the low catalytic efficiency and the use of triphenyl phosphite are the two serious drawbacks. To develop catalytic ylide olefinations for practical use remains a challenge. In our continuing studies on the application of ylides in organic synthesis,[7] we focused on the catalytic efficiency of ylide olefinations and communicated a modified catalytic ylide process, in which only 2 mol % of PEG-telluride was used.[8] In this paper, we report the possible mechanism, modification, scope, and limitations of these reactions in detail.

Scheme 1



Results and Discussion

Catalyst Design and Synthesis. By analysis of the corresponding mechanism reported (Scheme 2), probably the formation of ylide is the rate-determining step in the catalytic ylide olefination.[6] Improving the rate of ylide generation may essentially speed up this catalytic cycle. Thus, we designed PEG-telluride as the catalyst for the following considerations. First, the PEG may interact with potassium ion, like crown ether,[9] by self-assembling

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10.1021/jo025586h CCC: $22.00
Published on Web 03/30/2002

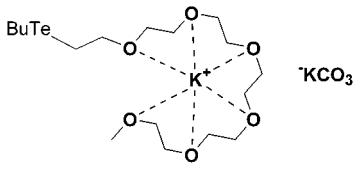
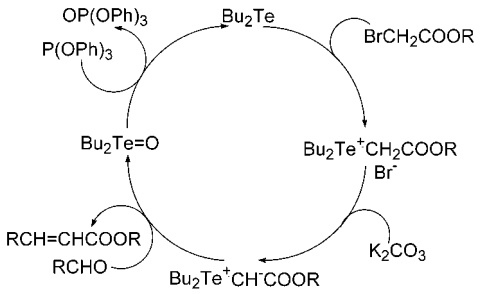
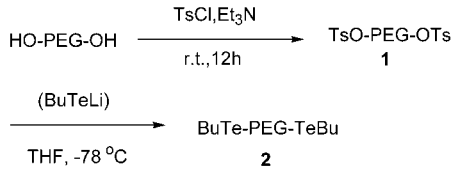


Figure 1.

Scheme 2



Scheme 3



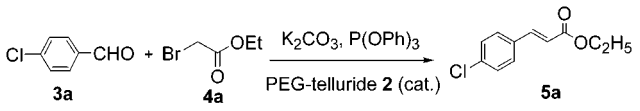
to form a half-open crown ether as shown in Figure 1. PEG would be proposed not only to play a role as a phase-transfer catalyst but also to increase the basicity of potassium carbonate in the reaction system. And thus, it is expected to accelerate the reaction of ylide formation and to enhance the catalytic activity. Second, soluble PEG is being developed as an alternative matrice for organic synthesis owing to the advantages of homogeneous solution chemistry with those of solid-phase methods.[10] The soluble PEG-supported telluride catalyst could be recoverable easily and be reusable.

The PEG-supported telluride **2** was readily available from poly(ethylene glycol) in two steps as shown in Scheme 3. Tosylation[11] of PEG (#4000) in anhydrous CH_2Cl_2 in the presence of Et_3N at room temperature for 12 h afforded compound **1** in 99% yield. Treatment of compound **1** with BuTeLi, generated in situ in anhydrous THF at −78 °C, followed by precipitation with diethyl ether, afforded PEG-supported telluride **2** in 83% yield.

Effects of Reaction Conditions. We first tried the olefination of *p*-chlorobenzaldehyde and ethyl bromoacetate in the presence of 10 mol % of PEG-telluride **2** under the optimized reaction condition mediated by $^nBu_2Te$.[5] It was disappointing that this reaction gave the product in 58% yield (entry 1, Table 1). It was found that, as shown in Table 1, the reaction could be carried out in a wide variety of solvents such as THF, hexane, and ethyl ether, etc. The best ones were THF, CH_2Cl_2, and toluene probably due to good solubility of the PEG-supported telluride **2** in these solvents (entries 2, 3, and 6, Table 1).

Several kinds of base, including weak organic base (entry 9, Table 1), were examined in the reactions when toluene was employed as the solvent. Although $KHCO_3$, KOH, and Na_2CO_3 could be used as the bases (entries 10, 11, and 12, Table 1), the best ones were K_2CO_3 and Cs_2CO_3 (entries 13 and 14, Table 1). Further studies showed that the reaction temperature strongly influenced the yield of olefin. As shown in Table 1, an almost quantitative yield of olefin **5a** was obtained at 110 °C while 35% yield was isolated at 50 °C (entries 15 and 16, Table 1).

Table 1. Effects of Reaction Conditions on the Catalytic Ylide Olefination of *p*-Chlorobenzaldehyde with Ethyl Bromoacetate[a]

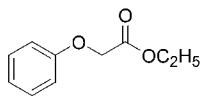


3a 4a 5a

entry	catalyst loading[b]	solvent	base	*T* (°C)	method[c]	yield (%)
1[d]	10	THF/H_2O	K_2CO_3	80	1	58
2	10	THF	K_2CO_3	80	1	66
3	10	CH_2Cl_2	K_2CO_3	80	1	58
4	10	ethyl ether	K_2CO_3	80	1	31
5	10	butyl ether	K_2CO_3	80	1	32
6	10	toluene	K_2CO_3	80	1	70
7	10	petroleum ether	K_2CO_3	80	1	39
8	10	hexane	K_2CO_3	80	1	47
9	10	toluene	DBU	80	1	0
10	10	toluene	$KHCO_3$	80	1	22
11	10	toluene	KOH	80	1	22
12	10	toluene	Na_2CO_3	80	1	59
13	10	toluene	K_2CO_3	80	1	70
14	10	toluene	Cs_2CO_3	80	1	76
15	10	toluene	K_2CO_3	110	1	96
16	10	toluene	K_2CO_3	50	1	35
17	10	toluene	K_2CO_3	80	1	70
18	10	toluene	K_2CO_3	80	2	100
19	5	toluene	K_2CO_3	80	2	92
20	2.5	toluene	K_2CO_3	80	2	80
21	1.3	toluene	K_2CO_3	80	2	73
22	1.3	toluene	K_2CO_3	80	3	83
23	1.3	toluene	K_2CO_3	80	4	94
24	1	toluene	K_2CO_3	80	5	88
25	2	toluene	K_2CO_3	80	5	97
26	2	toluene	K_2CO_3	80	6	98

[a] Please see the Experimental Section. [b] Catalytic loading (mol %). [c] Isolated yields.

Surprisingly, we found that the addition sequence of reactants affected the yields dramatically. Only 70% yield of compound **5a** was isolated when *p*-chlorobenzaldehyde was added before the addition of PEG-telluride (entry 17, Table 1). However, quantitative yield was obtained if the aldehyde was added after PEG-telluride (entry 18, Table 1) at the same reaction conditions. It is worthy to note that, by the using of method 2, this reaction also gave 73% yield even if the amount of PEG-telluride **2** was reduced from 10 mol % to 1.3 mol % (entry 21, Table 1). In this reaction, interestingly, we got a byproduct **6**,[12] which may be formed from ethyl bromoacetate and $P(OPh)_3$. This finding meant that the side reaction consumed the bromide **4a**.



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Thus, we tried to add ethyl bromoacetate or the aldehyde or the mixture of these two starting materials in portions to reduce their decomposition. It is pleasant

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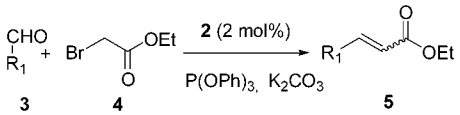
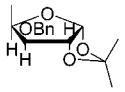
Table 2. Olefination of Aldehydes Catalyzed by PEG-Supported Telluride



3 4 5

Entry	R_1	Yield [a] (%)	E/Z [b]
1	*p*-ClC_6H_4	98(**5a**)	>99:1
2	C_6H_5	98(**5b**)	>99:1
3	*p*-$CF_3C_6H_4$	74(**5c**)	>99:1
4	*p*-$CH_3C_6H_4$	93(**5d**)	90:10
5	*p*-$CH_3OC_6H_4$ [c]	94(**5e**)	>99:1
6	2-furyl	96(**5f**)	>99:1
7	$C_6H_4CH\overset{E}{=}CH$-[c]	74(**5g**)	>99:1
8	cyclohexyl	70(**5h**)	>99:1
9	n-C_9H_{19}	74(**5i**)	86:14
10		79(**5j**)	58:42
11[d]	*p*-ClC_6H_4	94(**5a**)	> 99:1

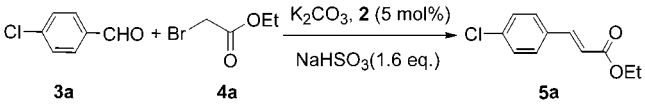
[a] Isolated yields. [b] The ratio of *E*/*Z* isomers was determined by ^{1}H NMR. [c] 5 mol % catalyst used. [d] 0.5 mol % of the salt **16** ($[C_2H_5O_2C(Bu)Te-PEG-Te(Bu)CO_2C_2H_5]^{2+}2Br^-$) was used.

to find that the side reaction could be inhibited more or less (entries 22, 23, and 24, Table 1) by this method. Even in the presence of 1 mol % of PEG-telluride **2**, 88% yield of compound **5a** was isolated (entry 24, Table 1). Further studies showed that method 6 was the best one and was easily reproducible. In this method, the mixture of PEG-telluride **2**, ethyl bromoacetate (0.45 mmol), and $P(OPh)_3$ was stirred in toluene at 80 °C for 5 min, and then the K_2CO_3, the mixture of *p*-chlorobenzaldehyde (1.0 mmol), and the rest bromide were added (entry 26, Table 1).

Ylide Olefination of Aldehydes with Ethyl Bromoacetate Catalyzed by PEG-Supported Telluride in the Presence of $P(OPh)_3$. To determine the generality of this reaction, a variety of structurally different aldehydes were employed. Some results are summarized in Table 2, with the optimized condition of Table 1.

It was found that both aliphatic and aromatic aldehydes worked well with high stereoselectivity in reasonable yields. In most cases, traditional *E*-stereoselectivity was maintained compared with typical Wittig reactions of stable ylides. Aromatic aldehydes with an electron-withdrawing group (entries 1 and 3, Table 2) or a weak electron-donating group (entry 4, Table 2) in the para positon as well as the heteroaromatic aldehyde (entry 6, Table 2) were the most suitable substrates. All of them can afford the desired products in excellent yields with high stereoselectivity. Although aromatic aldehyde with a strong electron-donor group such as *p*-methoxybezaldehyde (entry 5, Table 2) was less active, it still worked well when 5 mol % of catalyst **2** was employed. Functionalized and unfunctionalized aliphatic aldehydes with different structures were also available in this reaction to give the corresponding olefins in moderate yields with high stereoselectivity except entry 10 (entries 7−10, Table 2). Importantly, when only 0.5% mol of the corresponding salt was taken as the catalyst instead of PEG-telluride, this olefination reaction could also give 94% yield (entry 11, Table 2).

Table 3. Effects of Reaction Conditions on the Catalytic Ylide Olefination of *p*-Chlorobenzaldehyde with Bromoacetate Using $NaHSO_3$ as the Reducing Agent[a]



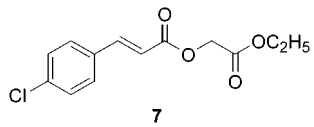
3a 4a 5a

entry	base (equiv)	solvent	*T* (°C)	yield (%)
1	K_2CO_3 (2)	THF/H_2O (4/0.1)	80	82
2	K_2CO_3 (2)	THF/H_2O (4/0.1)	80	66[b]
3	Na_2CO_3 (2)	THF/H_2O (4/0.1)	80	25
4	$KHCO_3$ (2)	THF/H_2O (4/0.1)	80	33
5	K_2CO_3 (2)	THF/H_2O (4/0.07)	80	80
6	K_2CO_3 (2)	THF/H_2O (4/0.04)	80	73
7	K_2CO_3 (2)	THF	80	7[c]
8	K_2CO_3 (1.6)	THF/H_2O (4/0.1)	80	77
9	K_2CO_3 (1.2)	THF/H_2O (4/0.07)	80	47
10	K_2CO_3 (2)	THF/H_2O (4:0.1)	50	50
11	K_2CO_3 (2)	THF/toluene/H_2O (3:1:0.1)	80	75
12	K_2CO_3 (2)	THF/H_2O (8:0.1)	80	70

[a] 5 mol % of the catalyst was used except as noted. [b] 2 mol % of the catalyst was used in this reaction. [c] Bu_4NBr was added.

Ylide Olefination Catalyzed by PEG-Supported Telluride in the Presence of $NaHSO_3$. To make this reaction practical, we took our efforts to use inorganic reducing reagents instead of $P(OPh)_3$. First, we tried $NaHSO_3$ as the reducing agent, and it was found that only trace product **5a** was detected when this reaction was carried out in toluene, whether in the presence of a trace of water or not. Fortunately, 82% yield could be achieved in THF/trace H_2O in the reaction of *p*-chlorobenzaldehyde with ethyl bromoacetate in the presence of $NaHSO_3$ when 5 mol % of PEG-telluride **2** was used. Reduction of the catalyst loading resulted in low yield (entry 2, Table 3).

In these reactions, unexpectedly, trace of compound **7** was isolated and was characterized as the following structure.



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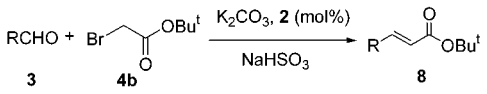
This result suggested that the product **5a** was hydrolyzed under these reaction conditions and thus lowered the yield.

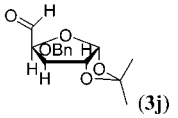
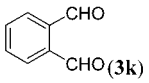
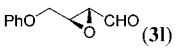
To inhibit this side reaction and improve the yield, we tried to use weaker bases (entries 3 and 4, Table 3) or reduce the amount of potassium carbonate (entries 8 and 9, Table 3) and water (entries 5 and 6, Table 3), but no good results were obtained. Attempts to use TBAB instead of water as the phase-transfer catalyst (entry 7, Table 3) or to lower the reaction temperature and so on (entries 10, 11, and 12, Table 3) failed too. Finally, we

(12) The reaction afforded compound **6** in 15% yield. ^{1}H NMR (300 MHz, $CDCl_3$/TMS): δ 7.33−7.26 (m, 2H), 7.02−6.97 (m, 1H), 6.93−6.90 (m, 2H), 4.62 (s, 2H), 4.28 (q, J = 7.1 Hz, 2H), 1.30 (t, J = 7.1 Hz, 3H). IR (film): ν = 2900, 1760, 1601, 1199, 1089, 755, 691 cm^{-1}. GC/MS (*m*/*e*): 180 (M^+), 77 (100).

Table 4. Olefination of Aldehydes Catalyzed by PEG-Supported Telluride in the Presence of $NaHSO_3$[a]



3 **4b** **8**

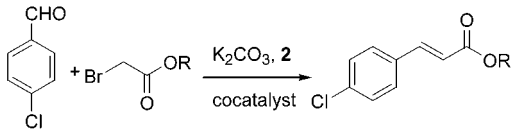
Entry	R	Catalyst loading (mol%)	Yield (%) [b]	E / Z[c]
1	*p*-ClC_6H_4 (**3a**)	5	99(**8a**)	99:1
2	*p*-ClC_6H_4 (**3a**)	2	93(**8a**)	99:1
3	*p*-ClC_6H_4 (**3a**)	1	81(**8a**)	99:1
4	C_6H_5 (**3b**)	2	92(**8b**)	99:1
5	*p*-$NO_3C_6H_4$ (**3c**)	2	77(**8c**)	99:1
6	*p*-$CH_3C_6H_4$ (**3d**)	2	96(**8d**)	94:6
7	*p*-$CH_3OC_6H_4$(**3e**)	5	87(**8e**)	99:1
8	2-furyl (**3f**)	2	88(**8f**)	99:1
9	$C_6H_4CH\overset{E}{=}CH$- (**3g**)	5	89(**8g**)	99:1
10	cyclohexyl (**3h**)	2	76(**8h**)	99:1
11	n-C_9H_{19} (**3i**)	2	84(**8i**)	95:5
12	 (**3j**)	2	65(**8j**)	99:1
13	 (**3k**)	1	73(**8k**)	99:1
14	 (**3l**)	2	69(**8l**)	99:1

[a] Other reaction conditions: K_2CO_3 (2.0 mmol); $NaHSO_3$ (1.6 mmol); PEG-telluride; THF/H_2O = 4:0.07; reflux, aldehyde (1.0 mmol); *tert*-butyl bromoacetate (1.2 mmol). [b] Isolated yield. [c] *E*/*Z* ratio was determined by 300 MHz ^1H NMR.

chose *tert*-butyl bromoacetate, which is difficult to hydrolyze under these conditions, instead of ethyl ester and found 99% yield of olefin **8a** was reached. Even if 1 mol % of catalyst was used, the yield was still 81% (entries 1, 2, and 3, Table 4). A variety of structurally different aldehydes including some functionalized aldehydes such as epoxy aldehyde (entry 14, Table 4) could react with *tert*-butyl bromoacetate in the presence of 2 mol % of PEG-telluride **2** when using $NaHSO_3$ as the cocatalyst. As shown in Table 4, $NaHSO_3$ turned out to be another effective reducing reagent in this catalytic Wittig-type reaction. It is interesting that the use of $NaHSO_3$ improved the stereoselectivity of the reaction of aldehyde **3j** greatly. The ratio (*E*/*Z*) of the product was enhanced from 58/42 (entry 10, Table 3) to 99/1 (entry 12, Table 4). The *E*/*Z* selectivity of aldehyde **3i** was also improved. It is noteworthy that the product isolation procedure was very simple by this modification. After the reaction was complete, almost pure product could be obtained just by filtering off the inorganic salts, followed by precipitating PEG-Telluride **2** in ether.

Further studies showed that the catalyst could be recovered quantitatively but lost its activity partially through multiple cycles. We found 2-furaldehyde (10.85 mmol) reacted with *tert*-butyl bromoacetate in the presence of sodium bisulfite to afford the desired product in 90% yield when 2 mol % of PEG-telluride was used. The

Table 5. Comparisons between PEG-Te and $^nBu_2Te$[a]



Cocatalyst: $P(OPh)_3$, R=C_2H_5; $NaHSO_3$, R=$^tC_4H_9$

entry	cat. (mol %)	solvent	co-catalyst	other reagent[b]	yield of **6** (%)	yield[c] (%)
1	Bu_2Te (4)	toluene	$P(OPh)_3$		trace	69
2	Bu_2Te (4)	toluene	$P(OPh)_3$	18-crown-6	69	(68)[d]
3	2 (2)	toluene	$P(OPh)_3$		54	98
4	Bu_2Te (2)	THF/H_2O (4/0.03)	$NaHSO_3$			(12)[d]
5	2 (1)	THF/H_2O (4/0.03)	$NaHSO_3$			81

[a] The other reaction conditions: when R = C_2H_5, K_2CO_3 (1.3 mmol), $P(OPh)_3$ (1.4 mmol), toluene (4 mL), 80 °C, aldehyde (1.0 mmol), ethyl bromoacetate (1.6 mmol); when R = $^tC_4H_9$, K_2CO_3 (2 mmol), $NaHSO_3$ (1.6 mmol),THF/H_2O (4/0.07), aldehyde (1.0 mmol); *tert*-butyl bromoacetate (1.2 mmol). [b] 0.6 equiv of 18-crown-6 was used. [c] Isolated yield. [d] Determined by GC.

catalyst could be recovered in 100% yield by filtering off the solid of the reaction mixture, followed by addition of ether and collection of the precipitate. The recovered catalyst could be used in the second run but only 69% yield was obtained probably due to the decomposition of PEG-telluride during the catalytic olefination.[13]

The Roles of PEG. By the introduction of the PEG-chain, we successfully reduced the amount of telluride from 20 into 2 mol % in the catalytic ylide olefination. To understand the role of PEG-chain in this reaction, we compared Bu_2Te-catalyzed with PEG-telluride **2** catalyzed olefination reaction in the presence of $P(OPh)_3$ in detail. It was found that only a trace of compound **6** was formed when Bu_2Te was used. Under the same conditions, however, 69% yield of compound **6** was isolated in the presence of 18-crown-6 (entry 2, Table 5). When PEG-telluride was used instead of Bu_2Te and 18-crown-6, 54% yield of compound **6** was afforded. These results suggested that PEG, like crown ether, could enhance the basicity of potassium carbonate probably due to the self-asembling with potassium ion. This interaction improved the rate of ylide formation and speeded up the catalytic cycle.

Further study showed that only 12% conversion was detected when the amount of *n*-butyl telluride was reduced from 4 to 2 mol % in the presence of $NaHSO_3$. However, the corresponding product was obtained in 81% yield when 1 mol % of PEG-telluride **2** was used. So, we proposed that PEG-chain probably also stabilized the telluronium salt due to the interaction of PEG-oxygen and tellurium. This may slow the rate of catalyst deactivation and enhance the catalytic efficiency. To get further details, we synthesized PEG-like compound **11** as shown in Scheme 4.[16]

(13) (a) Detty, M. D. *J. Org. Chem.* **1980**, *45*, 274. (b) Drew, H. D. K. *J. Chem. Soc.* **1929**, 560.

(14) (a) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University: Ithaca, NY, 1960; p 260. (b) Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1981**, *20*, 3071.

(15) Petragnani, N.; Comasseto, J. V. *Synthesis* **1991**, 897.

(16) (a) Morishita, S.; Saito, T.; Hirai, Y.; Shoji, M.; Mishima, Y.; Kawakami, M. *J. Med. Chem.* **1988**, *31*, 1205. (b). The procedure is similar to the synthesis of compound **2**. The product was purified by distillation under the reduced pressure

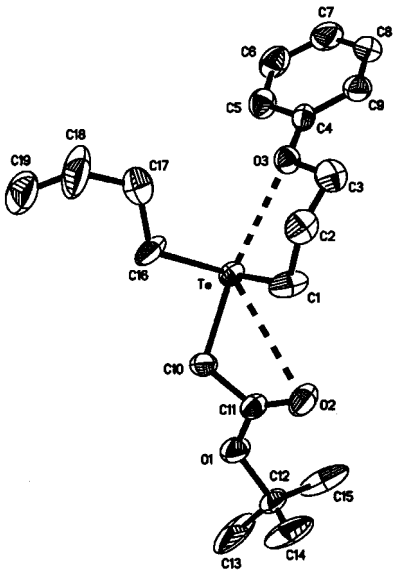
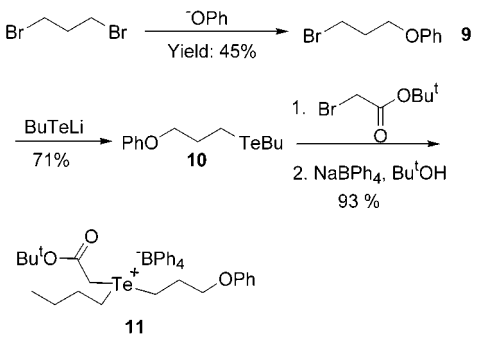


Figure 2. View of the structure of compound **11**. Selected the bond lengths (Å): Te−C(1), 2.098(6); Te−C(10), 2.148(6); Te−C(16), 2.205(7); O(1)−C(11), 1.292(7); O(1)−C(12), 1.502(8); O(2)−C(11), 1.190(8); O(3)−C(4), 1.361(7); O(3)−C(3), 1.447-(8); O(2)−Te, 3.282; O(3)−Te, 2.926.

Scheme 4



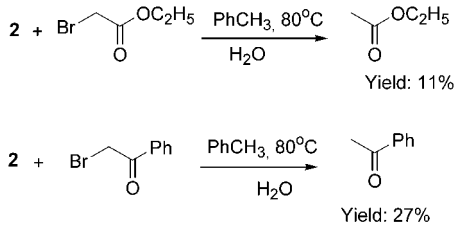
The ORTEP diagram of its X-ray structure analysis was shown in Figure 2. The distance of Te−O3 is 2.926 Å, which is shorter than the van der Waals sum of 3.60 Å.[14] This result indicated the existence of bonding interaction between the tellurium and the side-chain oxygen to make Te atom pseudo six-coordinated. This interaction of course could make the tellurium compound stable.

According to our speculation, compound **10** should be better catalyst for ylide olefination than dibutyltelluride. Actually, the conversion was improved from 12% to 19% when 2 mol % of compound **10** was used instead of *n*-butyl telluride.

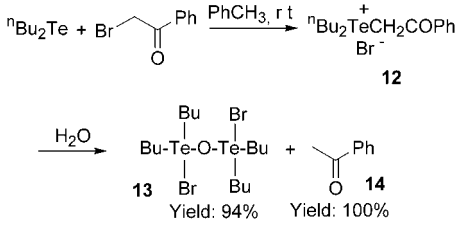
Mechanism. In an initial study, we proposed that this reaction was a typical ylide reaction. In the reaction of 4-chlorobenzaldehyde with *ω*-bromoacetophenone, however, we detected a trace of acetophenone. Further study showed that the telluride **2** could react with ethyl bromoacetate or bromoacetophenone directly to afford ethyl acetate and acetophenone separately in the presence of a trace of water (Scheme 5). They may be produced from the dehalogenation of the corresponding bromides by telluride.[15]

To make it clear, we synthesized compound **12**, which was characterized by X-ray analysis. It was found that this salt could react with water to give acetophenone in

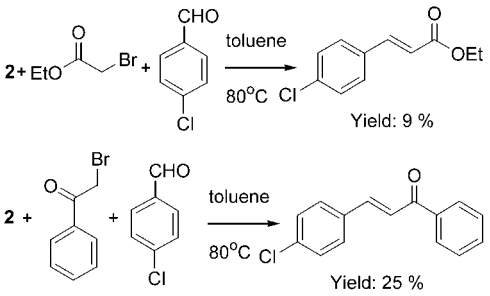
Scheme 5



Scheme 6



Scheme 7



quantitative yield and compound **13** in 94% yield even at room temperature (Scheme 6). The structure of compound **13** was determined by NMR, elemental analysis, and X-ray crystal analysis. These results showed that the trace of acetophenone came from the decomposition of the corresponding salt, which gave a reasonable explanation for the recovery PEG-telluride **2** partially losing the activation as described above.

These results also suggested that there may exist reaction pathways other than ylide olefination. To demonstrate it, the best way is to inhibit the formation of ylide as far as possible in this reaction. So, we first examined the reaction of *p*-chlorobezenaldehyde with ethyl bromoacetate or bromoacetophenone in the presence of stoichiometric PEG-telluride **2** without using potassium carbonate, separately (Scheme 7).

To our surprise, both reactions gave the desired products although the yields were much lower when compared with those carried out in the presence of K_2CO_3.

In the literature, Huang et al.[17] reported that carbethoxydibutyltelluronium bromide could directly react with aromatic aldehydes to afford a,*β*-unsaturated esters. They proposed a six-membered ring transition state to elucidate the reaction pathway (Figure 3).

According to the above results, in our reaction, we proposed that both reaction pathways are compatible as shown in Scheme 8. The major product was obtained via ylide route while the trace one was formed via path II.

In mechanism I, the olefination proceeded via a ylide route. The PEG-supported telluride **2** reacted with bro-

(17) Huang, X.; Xie, L.; Wu, H. *Tetrahedron Lett.* **1987**, *28*, 801.

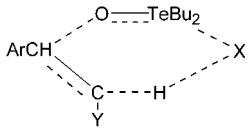
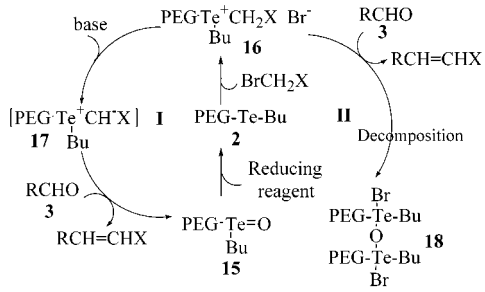


Figure 3.

Scheme 8



moacetate to form the corresponding telluronium salt **16**. After deprotonation of salt **16** by K_2CO_3, followed by the reaction with aldehyde, the desired alkene was formed. And the PEG-supported telluride **2** was regenerated by the reduction of telluride oxide with triphenyl phosphite or sodium bisulfite. This is also the main pathway in this reaction. Besides, in mechanism II, the salt **16** could react with aldehyde directly to afford the desired product but this way led the decomposition of catalytic telluride species.

Conclusion

In the past decades, highly efficient catalysis has become one of the most important frontiers in exploratory organic synthetic research.[18] Any catalytic process usually contains multistep reactions. One of the key points to improve the turnover number, we think, is to find out and speed up the rate-determining step. Another key factor is to stabilize the catalytic species in the catalytic cycle in case of deactivation of catalyst. Following these concepts, in this paper, an effective catalytic ylide olefination were successfully developed by the introduction of PEG. In which, it involves in simple procedure, mild reaction conditions, in particular, the use of sodium bisulfite as cocatalyst. The highly catalytic efficiency, together with the ability to easily purify the product, demonstrates our method to be practical for the synthesis of α,β-unsaturated esters. The extension of our method to epoxidation, cyclopropanation, and aziridination is in progress in our laboratory.

Experimental Section

General Methods. All reaction flasks and equipment were dried for several hours prior to use, and all reactions were carried out under nitrogen. Solvents and aldehydes were purified according to standard method. Chemical shifts are given in ppm relative to internal TMS. The reagents were purchased from commercial sources and used directly.

(18) (a) Jacobsen, E. N.; Pfaltz, A.; Yamamoto, H. *Comprehensive Asymmetric Catalysis*; Springer: Berlin, 1999. (b) Burke, S. D.; Danheiser, R. L. *Oxidizing and Reducing Agents* in *Handbook of Reagents for Organic Synthesis*; Paquette, L. A., Ed.; John Wiley & Son, New York, 1999; Vol. 2. (c) Ojima, I. *Asymmetric Synthesis*; VCH: New York, 1993. (d) Santelli, M. Pons, J.-M. *Lewis Acid and Selectivity in Organic Synthesis*; CRC Press: Boca RAton, 1995.

Preparation of Polymer-Supported Catalyst: Preparation of Compound 1. To a stirred and chilled solution of PEG#4000 (30 g, 10 mmol) and triethylamine (50 mL, 360 mmol) in dichloromethane (80 mL) was added *p*-toluenesulfonyl chloride (25 g, 120 mmol) at 0 °C in portions. The resulting light red slurry was stirred at room temperature for 24 h. The reaction mixture was filtered and washed with CH_2Cl_2. The combined filtrate was concentrated to about 10 mL and triturated with Et_2O (1600 mL). The resulting white solid was filtered, washed with 2-propanol, and dried in vacuo to provide compound **1**. Yield: 33.0 g (99%). ^{1}H NMR (300 MHz, $CDCl_3$/TMS): 7.81 (d, J = 8.0 Hz, 4H), 7.35 (d, J = 8.0 Hz, 4H), 4.16 (t, J = 4.8 Hz, 4H), 3.88−3.41 (m, ∼280H), 2.45 (s, 6H). IR (KBr): 2887, 1600 cm^{-1}.

Preparation of Compound 2. To a suspension of Te (0.1250 g, 48.0 mmol) in THF (250 mL) was added BuLi (43.5 mL in hexane, c = 1.33 mol/ L) dropwise at 0 °C. After addition, the light yellow solution was cooled to −78 °C and the solution of compound **1** (10.03 g, 3.0 mmol) in THF (120 mL) was added. The resulting light green slurry was stirred for an additional 8 h and then warmed to room temperature. The reaction mixture was concentrated. The residue was dissolved in CH_2Cl_2, filtered through a glass funnel with a thin layer of Celite, and washed with CH_2Cl_2. The combined filtrates were concentrated (∼10 mL) and triturated with Et_2O (2000 mL). The resulting white solid was collected, washed with ether, and dried in vacuo to afford compound **2**. Yield: 8.4 g (83%). ^{1}H NMR (300 MHz, $CDCl_3$/TMS): δ 3.90−3.40 (m, ∼280H), 2.80 (t, J = 7.6 Hz, 4H), 2.66 (t, J = 7.4 Hz, 4H), 1.75−1.70 (m, 4H), 1.39−1.36 (m, 4H), 0.92 (t, J = 7.2 Hz, 6H). IR (KBr): 2888, 1113, 529 cm^{-1}. ^{125}Te ($CDCl_3$/Me_2Te): δ 200.203.

Effect of the Addition Sequence of Reactants. Method 1. The reactants were combined in the following order: *p*-chlorobenzaldehyde (1.0 mmol), K_2CO_3 (1.3 mmol), toluene, ethyl bromoacetate (1.6 mmol), telluride **2**, and $P(OPh)_3$. The mixture was heated at 80 °C for several hours. **Method 2.** Method 2 was similar to method 1 but the addition sequence was changed as follows: telluride **2**, toluene, ethyl bromoacetate (1.6 mmol), $P(OPh)_3$, K_2CO_3 (1.3 mmol). and *p*-chlorobenzaldehyde (1.0 mmol). **Method 3.** Method 3 was similar to method 2, but the ethyl bromoacetate was added in portions in 4−6 h. **Method 4.** Method 4 was similar to method 2, but *p*-chlorobenzaldehyde was added in portions in 4−6 h. **Method 5.** Method 5 was similar to method 2, but the mixture of *p*-chlorobenzaldehyde and ethyl bromoacetate was added in portions in 4−6 h. **Method 6.** Method 6 was similar to method 5, but the mixture of telluride **2**, toluene, ethyl bromoacetate, and $P(OPh)_3$ was stirred at 80 °C for 5 min before the K_2CO_3 and the mixture of *p*-chlorobenzaldehyde and ethyl bromoacetate was added.

Typical Procedure A. $P(OPh)_3$ as the Cocatalyst. A mixture of catalyst **2** (0.0680 g, 2 mol %), ethyl bromoacetate (0.06 mL, 0.5 mmol), and $P(OPh)_3$ (0.36 mL, 1.4 mmol) in toluene (3.0 mL) was stirred at 80 °C for 10 min, and then K_2CO_3 (0.1796 g, 1.3 mmol) was added. The resulting suspension was stirred for 1 min, followed by addition of a mixture of aldehyde (1.0 mmol) and ethyl bromoacetate (0.12 mL, 1.1 mmol) in toluene (1.0 mL) in portions in 3.5 h. After the reaction was completed (monitored by TLC), the mixture was filtered rapidly through a glass funnel with a thin layer of silica gel, washed with ethyl acetate. The filtrate was concentrated, and the residue was purified by flash column chromatography to afford the desired product.

Ethyl (*E*)-3-(4-Chlorophenyl)acrylate (R = *p*-ClC$_6$H$_4$, 5a). Procedure A. Yield: 206.8 mg (98%). E/Z > 99:1.^{1}H NMR (300 MHz, $CDCl_3$/TMS): δ 7.64 (d, J = 16.0 Hz, 1H), 7.46 (dd, J = 1.8, 6.7 Hz, 2H),7.36 (dd, J = 1.8,6.7 Hz, 2H), 6.41 (d, J = 16.0 Hz, 1H), 4.27 (q, J = 7.1 Hz, 2H), 1.34 (t, J = 7.1 Hz, 3H).

Ethyl (*E*)-3-Phenylacrylate (R = C$_6$H$_5$, 5b). Procedure A. Yield: 171.0 mg (98%). E/Z > 99:1. ^{1}H NMR (300 MHz, $CDCl_3$/TMS): δ 7.70 (d, J = 15.9 Hz, 1H), 7.55−7.52 (m, 2H), 7.40−7.38 (m, 3H), 6.45 (d, J = 15.9 Hz, 1H), 4.27 (q, J = 7.1 Hz, 2H), 1.35 (t, J = 7.1 Hz, 3H).

Ethyl (*E*)-3-(4-Trifluoromethylphenyl)acrylate (R = *p*-$CF_3C_6H_4$, 5c). Procedure A. Yield: 181.3 mg (74%). *E*/*Z* > 99:1. ^{1}H NMR (300 MHz, $CDCl_3$/TMS): δ 7.70 (d, J = 16.1 Hz, 1H), 7.64 (s, 4H), 6.51 (d, J = 16.1 Hz, 1H), 4.27 (q, J = 7.1 Hz, 2H), 1.35 (t, J = 7.1 Hz, 3H). ^{19}F NMR (56.4 MHz, CCl_4/CF_3COOH): δ −15.0.

Ethyl (*E*)-3-(*p*-Tolyl)acrylate (R = *p*-$CH_3C_6H_4$, 5d). Procedure A Yield: 177.5 mg (93%). *E*/*Z* = 90:10. ^{1}H NMR (300 MHz, $CDCl_3$/TMS) (for trans isomer): δ 7.59 (d, J = 15.9 Hz, 1H), 7.41 (d, J = 7.9 Hz, 2H), 7.18 (d, J = 7.9 Hz, 2H), 6.32 (d, J = 15.9 Hz, 1H), 3.50 (q, J = 7.0 Hz, 2H), 2.37 (s, 3H), 1.33 (t, J = 7.0 Hz, 3H).

Ethyl (*E*)-3-(*p*-Anisyl)acrylate (R = *p*-$CH_3OC_6H_4$, 5e). Procedure A. Yield: 208.4 mg (94%). *E*/*Z* > 99:1. 5 mol % catalyst was used. ^{1}H NMR (300 MHz, $CDCl_3$/TMS): δ 7.64 (d, J = 16.0 Hz, 1H), 7.47 (d, J = 6.8 Hz, 2H), 6.90 (d, J = 6.8 Hz, 2H), 6.31 (d, J = 16.0 Hz, 1H), 4.25 (q, J = 7.2 Hz, 2H), 3.83 (s, 3H), 1.33 (t, J = 7.2 Hz, 3H).

Ethyl (*E*)-3-(2-Furyl)acrylate (R = C_4H_3O, 5f). Procedure A. Yield: 160.0 mg (96%). *E*/*Z* > 99:1. ^{1}H NMR (300 MHz, $CDCl_3$/TMS): δ 7.48 (d, J = 1.4 Hz, 1H), 7.43 (d, J = 15.7 Hz, 1H), 6.60 (d, J = 3.3 Hz, 1H), 6.47 (dd, J = 1.7,3.3 Hz, 1H), 6.32 (d, J = 15.7 Hz, 1H), 4.25 (q, J = 7.1 Hz, 2H), 1.32 (t, J = 7.1 Hz, 3H).

Ethyl (*E*,*E*)-5-Phenylpenta-2,4-dienoate (R = C_6H_5CH=CH_2, 5g). Procedure A. Yield: 150.4 mg (74%). 5 mol % catalyst was used. *E*/*Z* > 99:1. ^{1}H NMR (300 MHz, $CDCl_3$/TMS): δ 7.49−7.38 (m, 3H), 7.38−7.30 (m, 3H), 6.90−6.87 (m, 2H), 5.99 (d, J = 15.2 Hz, 1H), 4.23 (q, J = 7.1 Hz, 2H), 1.32 (t, J = 7.1 Hz, 3H).

Ethyl (*E*)-3-Cyclohexylacrylate (R = C_6H_{11}, 5h). Procedure A. Yield: 128.0 mg (70%). *E*/*Z* > 99:1. ^{1}H NMR (300 MHz, $CDCl_3$/TMS): δ 6.92 (dd, J = 6.9, 15.8 Hz, 1H), 5.77 (dd, J = 15.8, 1.0 Hz, 1H), 4.19 (q, J = 7.1 Hz, 2H), 2.20−2.15 (m, 1H), 1.78−1.64 (m, 4H), 1.36−1.12 (m, 9H).

Ethyl (*E*)-dodec-2-enoate (R = $CH_3(CH_2)_8$, 5i). Procedure A. Yield: 168.9 mg (74%). *E*/*Z* = 88:12. ^{1}H NMR (300 MHz, $CDCl_3$/TMS) (for trans isomer): δ 6.97 (dt, J = 15.7, 6.9 Hz, 1H), 5.81 (dt, J = 15.7, 1.4 Hz, 1H), 4.18 (q, J = 7.1 Hz, 2H), 2.23−2.15 (m, 2H), 1.47−1.27 (m, 17H), 0.88 (t, J = 6.7 Hz, 3H).

Ethyl 3-(6-Benzyloxy-2,2-dimethyltetrahydrofuro[2,3-*d*][1,3]dioxol-5-yl)acrylate (5j). Procedure A. A 0.5 mmol portion of the corresponding aldehyde was employed. Yield: 137.9 mg (79%). *E*/*Z* = 58:42. ^{1}H NMR (300 MHz, $CDCl_3$/TMS) (for trans isomer): δ 7.36−7.26 (m, 5H), 6.96 (dd, J = 15.9, 5.1 Hz, 1H), 6.17 (dd, J = 15.8, 1.7 Hz, 1H), 6.00 (d, J = 3.6 Hz, 1H), 4.81−4.79 (m, 1H), 4.65−4.48 (m, 3H), 4.22 (q, J = 7.1 Hz, 2H), 3.71 (d, J = 3.0 Hz, 1H), 1.49 (s, 3H), 1.33 (s, 3H), 1.30 (t, J = 7.2 Hz, 3H). ^{1}H NMR (300 MHz, $CDCl_3$/TMS) (for cis isomer): δ 7.38−7.21 (m, 5H), 6.39 (dd, J = 11.9, 6.8 Hz, 1H), 6.01 (d, J = 3.6 Hz, 1H), 5.91 (dd, J = 11.6, 1.2 Hz, 1H), 5.63−5.60 (m, 1H), 4.65−4.44 (m, 3H), 4.28 (d, J = 3.3 Hz, 1H), 4.11 (q, J = 7.2 Hz, 2H), 1.51 (s, 3H), 1.33 (s, 3H), 1.26 (t, J = 6.9 Hz, 3H).

Preparation of Ethyl (*E*)-3-(4-chlorophenyl)acrylate (R = *p*-ClC_6H_4) in the Presence of $NaHSO_3$. A mixture of catalyst **2** (0.1680 g, 5 mol %), bromoacetate (0.06 mL, 0.5 mmol), and $NaHSO_3$ (0.1664 g, 1.6 mmol) and in THF (3.0 mL) was refluxed for 10 min, and then H_2O (0.04 mL) was added. The resulting mixture was stirred for 10 min, followed by addition of K_2CO_3 (0.2760 g, 2.0 mmol). After being stirred for 1 min, to this suspension was added a mixture of *p*-chlorobenzaldehyde (1.0 mmol), ethyl bromoacetate (0.12 mL, 1.1 mmol), and water (0.03 mL) in THF (1.0 mL) in portions in 3.5 h. The reaction was quenched by anhydrous $MgSO_4$ after the reaction was complete (monitored by TLC). The resulting mixture was filtered rapidly through a glass funnel with a thin layer of silica gel, washed with ethyl acetate. The combined filtrate was concentrated and the residue was purified by flash column chromatography to afford the desired product. Yield for ethyl (*E*)-3-(4-chlorophenyl)acrylate: 172.6 mg (82%). *E*/*Z* > 99:1. Yield for compound **7**: 8.5 mg (3%). *E*/*Z* > 99:1. The product was recrystallized with ethyl acetate/petroleum ether. Mp: 69−70 °C. Compound **7**. ^{1}H NMR (300 MHz, $CDCl_3$/TMS): δ 7.73 (d, J = 16.1 Hz, 1H), 7.48 (d, J = 7.7 Hz, 2H), 7.38 (d, J = 7.7 Hz, 2H), 6.50 (d, J = 16.1 Hz, 1H), 4.74 (s, 2H), 4.26 (q, J = 7.1 Hz, 2H), 1.31 (t, J = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): 167.868, 165.937, 144.758, 136.558, 132.695, 129.402, 129.256, 117.448, 61.513, 60.945, 14.141 ppm. IR (KBr): ν = 2984, 1743, 1714, 1633, 1591, 1493, 825 cm^{-1}. MS (*m*/*e*): 270 (M^+(^{37}Cl), 12.25), 268 (M^+(^{35}Cl), 34.53), 167 (M^+(^{37}Cl), 36.68), 165 (M^+(^{35}Cl), 100%). HRMS: calcd for $C_{13}H_{13}ClO_4$ 268.050 24, found 268.048 09.

Typical Procedure B: $NaHSO_3$ as the Cocatalyst. A mixture of catalyst **2** (0.0680 g, 2 mol %), *tert*-butyl bromoacetate (0.06 mL, 0.4 mmol), and $NaHSO_3$ (0.1664 g, 1.6 mmol) in THF (3.0 mL) was refluxed for 10 min, and then H_2O (0.04 mL) was added. The resulting mixture was stirring for 10 min, followed by addition of K_2CO_3 (0.2760 g, 2.0 mmol). After being stirred for 1 min, to this suspension was added a mixture of aldehyde (1.0 mmol), *tert*-butyl bromoacetate (0.12 mL, 0.8 mmol), and water (0.03 mL) in THF (1.0 mL) in portions in 3.5 h. This reaction was quenched by anhydrous $MgSO_4$ after it was complete (monitored by TLC). The resulting mixture was filtered rapidly through a glass funnel with a thin layer of silica gel, washed with ethyl acetate. The combined filtrate was concentrated, and the residue was purified by flash column chromatography to afford the desired product.

***tert*-Butyl (*E*)-3-(4-Chlorophenyl)acrylate (R = *p*-ClC_6H_4, 8a).** Procedure B. Yield: 237.5 mg (93%). *E*/*Z* > 99:1. ^{1}H NMR (300 MHz, $CDCl_3$/TMS): δ 7.53 (d, J = 16.0 Hz, 1H), 7.44 (d, J = 7.0 Hz, 2H), 7.34 (d, J = 7.0 Hz, 2H), 6.34 (d, J = 16.0 Hz, 1H), 1.53 (s, 9H).

***tert*-Butyl (*E*)-3-Phenylacrylate (R = C_6H_5, 8b).** Procedure B. Yield: 189.0 mg (92%). *E*/*Z* > 99:1. ^{1}H NMR (300 MHz, $CDCl_3$/TMS): δ 7.60 (d, J = 16.0 Hz, 1H), 7.53−7.50 (m, 2H), 7.38−7.36 (m, 3H), 6.38 (d, J = 16.0 Hz, 1H), 1.53 (s, 9H).

***tert*-Butyl (*E*)-3-(4-Nitrophenyl)acrylate (R = *p*-$NO_3C_6H_4$, 8c).** Procedure B. Yield: 191.3 mg (77%). *E*/*Z* > 99:1.^{1}H NMR (300 MHz, $CDCl_3$/TMS): δ 8.24 (d, J = 20.6 Hz, 2H), 7.67−7.58 (m, 3H), 6.50 (d, J = 15.9 Hz, 1H), 1.55 (s, 9H).

***tert*-Butyl (*E*)-3-(*p*-Tolyl)acrylate (R = *p*-$CH_3C_6H_4$, 8d).** Procedure B. Yield: 209.9 mg (96%). *E*/*Z* = 94:6. ^{1}H NMR (300 MHz, $CDCl_3$/TMS) (for trans isomer): δ 7.57 (d, J = 15.9 Hz, 1H), 7.41 (d, J = 8.1 Hz, 2H), 7.18 (d, J = 8.1 Hz, 2H), 6.32 (d, J = 15.9 Hz, 1H), 2.37 (s, 3H), 1.53 (s, 9H).

***tert*-Butyl (*E*)-3-(*p*-Anisyl)acrylate (R = *p*-$CH_3OC_6H_4$, 8e).** Procedure B. Yield: 203.9 mg (87%). *E*/*Z* > 99:1. 5 mol % catalyst was used. ^{1}H NMR (300 MHz, $CDCl_3$/TMS): δ 7.55 (d, J = 16.0 Hz, 1H), 7.46 (d, J = 8.7 Hz, 2H), 6.89 (d, J = 8.7 Hz, 2H), 6.24 (d, J = 16.0 Hz, 1H), 3.83 (s, 3H), 1.53 (s, 9H).

***tert*-Butyl (*E*)-3-(2-Furyl)acrylate (R = C_4H_3O, 8f).** Procedure B. Yield: 171.1 mg (88%). *E*/*Z* > 99:1. ^{1}H NMR (300 MHz, $CDCl_3$/TMS): δ 7.45 (s, 1H), 7.33 (d, J = 15.8 Hz, 1H), 6.57 (d, J = 3.4 Hz, 1H), 6.44 (dd, J = 3.4, 1.9 Hz, 1H), 6.25 (d, J = 15.8 Hz, 1H), 1.52 (s, 9H).

***tert*-Butyl (*E*,*E*)-5-Phenylpent-2,4-dienoate (R = C_6H_5-CH=CH_2, 8g).** Procedure B. Yield: 205.3 mg (89%). *E*/*Z* > 99:1. 5 mol % catalyst was used. ^{1}H NMR (300 MHz, $CDCl_3$/TMS): δ 7.48−7.20 (m, 6H), 6.87−6.85 (m, 2H), 5.92 (d, J = 15.3 Hz, 1H), 1.51 (s, 9H).

***tert*-Butyl (*E*)-3-Cyclohexylacrylate (R = C_6H_{11}, 8h).** Procedure B. Yield: 161.2 mg (76%). *E*/*Z* > 99:1. ^{1}H NMR (300 MHz, $CDCl_3$/TMS): δ 6.81 (dd, J = 15.8, 6.8 Hz, 1H), 5.68 (dd, J = 15.8, 1.3 Hz, 1H), 2.11−2.09 (m, 1H), 1.81−1.61 (m, 4H), 1.48 (s, 9H), 1.43−1.07 (m, 6H).

***tert*-Butyl (*E*)-Dodec-2-enoate (R = $CH_3(CH_2)_8$, 8i).** Procedure B. Yield: 214.3 mg (84%). *E*/*Z* = 95:5. Bp: 90 °C/2 mmHg. ^{1}H NMR (300 MHz, $CDCl_3$/TMS) (for trans isomer): δ 6.86 (dt, J = 15.5, 7.0 Hz, 1H), 5.74 (d, J = 15.5 Hz, 1H), 2.16 (q, J = 7.2 Hz, 2H), 1.49 (s, 9H), 1.47−1.27 (m, 14H), 0.89 (t, J = 6.5 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): 166.220, 148.195, 122.930, 79.940, 32.077, 31.895, 29.503, 29.426, 29.308, 29.200, 28.188, 28.123, 22.682, 14.100 ppm. IR (film): ν = 2928, 1718, 1368 cm^{-1}. MS (*m*/*e*): 255 (0.65), 199 (100). Anal. Calcd for $C_{16}H_{30}O_2$: C, 75.53; H, 11.89. Found: C, 75.75; H, 11.74.

***tert*-Butyl (*E*)-3-(6-Benzyloxy-2,2-dimethyltetrahydrofuro[2,3-*d*][1,3]dioxol-5-yl)acrylate (8j).** Procedure B. A 0.5

mmol portion of the corresponding aldehyde was employed. Yield: 121.9 mg (65%). *E*/*Z* > 99:1. The product was recrystallized from ethyl acetate/petroleum. Mp: 92−94 °C. ^{1}H NMR (300 MHz, $CDCl_3$/TMS): δ 7.37−7.27 (m, 5H), 6.88 (dd, J = 15.7, 5.3 Hz, 1H), 6.09 (dd, J = 15.8, 1.3 Hz, 1H), 6.00 (m, 1H), 4.78 (s, 1H), 4.66−4.62 (m, 2H), 4.50 (d, J = 12.1 Hz, 1H), 3.96 (d, J = 3.2 Hz, 1H), 1.50 (s, 9H), 1.33 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): 165.275, 140.132, 137.247, 128.654, 128.535, 128.214, 128.065, 127.812, 125.370, 111.921, 105.104, 83.134, 82.923, 80.448, 79.594, 72.295. 28.188, 26.880, 26.288 ppm. IR (KBr): ν = 2981, 2935, 1714, 1662, 1028, 699 cm^{-1}. MS (*m*/*e*): 361 (M − 15), 91 (100). Anal. Calcd for $C_{21}H_{28}O_6$: C, 67.00; H, 7.50. Found: C, 66.92; H, 7.39.

***tert*-Butyl (*E*,*E*)-3-[2-(2-*tert*-Butoxycarbonylvinyl)phenyl]acrylate (8k).** Procedure B. A 0.5 mmol portion of the corresponding aldehyde was used. Other conditions: *tert*-butyl acetate (0.18 mL, 1.2 mmol), $NaHSO_3$ (0.1664 g, 1.6 mmol), K_2CO_3 (0.2764 g, 2.0 mmol), PEG-supported telluride **2** (0.0337 g, 0.01 mmol), THF/H_2O (2 mL/0.04 mL). Yield: 120.8 mg (73%). ^{1}H NMR (300 MHz, $CDCl_3$/TMS): δ 7.94 (d, J = 15.8 Hz, 2H), 7.92−7.54 (m, 2H), 7.38−7.35 (m, 2H), 6.27 (d, J = 15.8 Hz, 2H), 1.55(s, 18H).

***tert*-Butyl 7-Benzyloxy-(4*S*,5*S*)-epoxy-2(*E*)-heptenoate (8l).** Procedure B. The aldehyde was synthesized from 2,3-epoxy-5-benzyloxypentan-1-ol (0.16 mmol) by Swern oxidation. After the oxidation was complete, the mixture was concentrated. The residue was used directly without further purification. Yield based on 2,3-epoxy-5-benzyloxypentan-1-ol: 33.7 mg (69%). *E*/*Z* > 99:1. ^{1}H NMR (300 MHz, $CDCl_3$/TMS): δ 7.37−7.26 (m, 5H), 6.55 (dd, J = 15.7, 7.2 Hz, 1H), 6.04 (d, J = 15.7 Hz, 1H), 4.52 (s, 2H), 3.61 (t, J = 6.1 Hz, 2H), 3.25 (d, J = 7.1 Hz, 1H), 3.06−3.02 (m, 1H), 1.94−1.88 (m, 2H), 1.48 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): 164.952, 143.294, 138.192, 128.444, 127.702, 127.638, 125.804, 80.731, 73.147, 66.624, 59.018, 56.442, 32.458, 28.108 ppm. IR (film): ν = 2927, 1714, 1640, 1162 cm^{-1}. MS (*m*/*e*): 247 (M − 57), 91(100).

The Roles of PEG. Preparation of 11. A solution of butyl 3-phenoxylpropyl telluride[16] and *tert*-butyl bromoacetate (0.40 mL, 2.80 mmol) in THF (0.5 mL) was stirred at 0 °C for 2.5 h. The reaction mixture was concentrated and dried in vacuo. The resulting colorless oil was dissolved in tertiary butyl alcohol (1 mL), and then a solution of sodium tetraphenylborate (0.6844 g, 2.0 mmol) in tertiary butyl alcohol (10 mL) was added at room temperature. The suspension was filtered and washed twice with methanol. The white solid was collected as the desired product. Yield: 93% (1.4011 g). The product was recrystallized with CH_2Cl_2/ethyl acetate/ether at −20 °C. Mp: 127−129 °C. ^{1}H NMR (300 MHz, $CDCl_3$/TMS): δ 7.52 (s, 8H), 7.34−7.28 (m, 2H), 7.08−7.01 (m, 9H), 6.90 (t, J = 7.1 Hz, 4H), 6.75 (dd, J = 8.7, 0.9 Hz, 2H), 3.75 (t, J = 4.1 Hz, 2H), 2.51 (s, 2H), 2.10−2.08 (m, 4H), 1.48 (s, 2H), 1.44 (s, 9H), 1.26−1.22 (m, 4H), 0.83 (t, J = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 165.922, 164.223 (q, J = 48.9 Hz), 156.686, 136.111, 129.765, 125.986, 125.957, 122.077, 114.269, 84.630, 67.068, 27.853, 27.362, 26.064, 25.457, 24.597, 24.226, 22.230, 13.138 ppm. IR (KBr): ν = 1719, 1601, 1589, 1579, 1236, 709, 604 cm^{-1}. Anal. Calcd. for $C_{43}H_{51}BO_3Te$: C, 68.47; H, 6.82. Found: C, 68.32; H, 6.80.

Mechanism Research. Dehalogenation of ω-Bromoacetophenone and Ethyl Bromoacetate with PEG-Supported Telluride Compound 2. The solution of PEG-supported telluride **2** (0.1684 g, 0.05 mmol), water (0.003 g, 0.16 mmol), and ω-bromoacetophenone (0.03185 g, 0.16 mmol) or ethyl bromoacetate (0.018 mL, 0.16 mmol) in toluene (1 mL) was stirred at 80 °C for 2 h. Mesitylene (0.0120 g, 0.1 mmol) was added to the reaction mixture as the interal standard. The reaction mixture was filtered, and the filtrate was analyzed by GC to afford the yield.

Dehalogenation of ω-Bromoacetophenone with Dibutyl Telluride. The solution of *n*-butyl telluride (0.4548 g, 1.88 mmol) and ω-bromoacetophenone (0.4310 g, 2.16 mmol) was stirred at room temperature for 5 h. The resulting white solid was washed with ether to afford the desired product **12**. Yield: 823.0 mg (99.5%). The product **12** was recrystallized from THF. ^{1}H NMR (300 MHz, $CDCl_3$/TMS): δ 8.21 (d, J = 7.2 Hz, 2H), 7.65 (t, J = 7.4 Hz, 1H), 7.52 (t, J = 7.7 Hz, 2H), 4.48 (s, 2H), 3.22−3.07 (m, 4H), 1.89−1.79 (m, 4H), 1.47−1.35 (m, 4H), 0.92 (t, J = 1.7 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 194.918, 135.119, 134.128, 128.994, 128.745, 34.199, 27.765, 27.617, 24.457, 13.148 ppm. ^{125}Te ($CDCl_3$/Me_2Te): δ 551.191. MS (ESI): 363.1 [M^+(^{130}Te)], 361.1 [M^+(^{128}Te)], 359.1 [M^+(^{126}Te)]. IR (KBr): ν = 2962, 1662, 742, 690, 588 cm^{-1}. Anal. Calcd for $C_{16}H_{25}BrOTe$: C, 43.59; H, 5.72; Br, 18.12. Found: C, 43.38; H, 5.57; Br, 17.50.

A mixture of compound **12** (0.1881 g, 0.4 mmol) and water (0.02 mL) in CH_2Cl_2/THF (0.5 mL/0.5 mL) was stirred at room temperature overnight. The yield of aceophenone was determined by GC (mesitylene as interal standard). Yield: 100%. The reaction mixture was filtered, and the filtrate was concentrated. The residue was washed with ether to give compound **13** as a white solid. Yield: 117.5 mg (94%). ^{1}H NMR (300 MHz, $CDCl_3$/TMS): δ 3.48 (br, 4H), 3.10 (br, 4H), 2.02−2.00 (m, 8H), 1.57 (q, J = 7.4 Hz, 8H), 1.00 (t, J = 1.3 Hz, 12H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 43.2917, 27.2311, 24.5575, 13.6348 ppm. MS (ESI): 261.1 [M^+(^{130}Te)], 259.1 [M^+(^{128}Te)], 257.1 [M^+(^{126}Te)]. IR (KBr): ν = 2961, 1464, 632, 439 cm^{-1}. Anal. Calcd for $C_{16}H_{36}Br_2OTe_2$: C, 29.14; H, 5.50; Br, 24.23. Found: C, 29.31; H, 5.75; Br, 24.27.

One-Pot Reaction of *p*-Chlorobenzaldehyde, PEG-Supported Telluride 2, ω-Bromoacetophenone or Ethyl Bromoacetate. A solution of PEG-supported telluride **2** (0.1684 g, 0.05 mmol), *p*-chlorobenzaldehyde (0.014 g, 0.1 mmol), and ω-bromoacetophenone (0.0320 g, 0.16 mmol) or ethyl bromoacetate (0.018 mL, 0.16 mmol) in toluene (1 mL) was stirred at 80 °C for 2 h. After the reaction was complete, the reaction mixture was filtered, and the filtrate was analyzed by GC to give the yields (mesitylene was used as internal reference).

Acknowledgment. We are grateful for the financial support from the National Natural Sciences Foundation of China, the State Key Project of Basic Research (PROJECT 973, No.2000 48007), and the "Hundred Scientist Program" from the Chinese Academy of Sciences.

Supporting Information Available: Crystal structure data of compounds **11**−**13**. This material is available free of charge via the Internet at http://pubs.acs.org.

JO025586H