Synthesis and Characterization of Pentaerythritol-Derived Oligoglycol and Their Application to Catalytic Wittig-Type Reactions

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Abstract: Several pentaerythritol-derived oligoglycols **1** with free hydroxyl groups are readily prepared by a convergent approach. Quantitative ^{13}C NMR proves to be an efficient tool for the characterization of oligoglycols. The corresponding telluride of oligoglycol **17** is synthesized and used as a good catalyst for Wittig-type reactions in preparing both disubstituted and trisubstituted *o*lefins in good to high yields.

Wittig reaction[1] and its variants have been developed as one of the most powerful approaches in constructing carbon–carbon double bonds due to its unambiguous positioning and good stereoselectivity of the double bond.[2] Recent developments mainly focused on the catalytic reactions,[3] the control of stereoselectivity,[4,5] and new techniques.[6] The transition metal-based catalytic approach provided a new method of ylide generation under

SCHEME 1
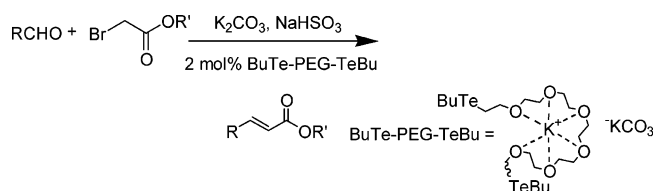
neutral conditions from the easily accessible diazo compounds.[3] Reaction conditions[4] and substituents[5] on phosphorus proved to influence the stereoselectivity. Thus the selectivity could be improved and even be switched by the change of these factors in certain cases.[7] Despite their wide success in numerous applications, the need for improvement in several aspects of Wittig-type reactions remains evident. In particular, a large amount of triphenylphosphine oxide is produced as a waste, resulting in the purification problem of the desired product and polluting environment. A catalytic process of this reaction, developed first by Huang et al. using 20 mol % of tributylarsine or 20 mol % of dibutyl telluride as the catalyst in the presence of stoichiometric triphenyl phosphite,[8] provided a potential way to solve this problem. In a previous study on ylide chemistry,[9] we designed soluble poly(ethyleneglycol) (PEG)-supported telluride as the catalyst for ylide olefination and found that the catalytic loading could be reduced to 2 mol % (Scheme 1).[10] Furthermore, an investigation of other reducing agents shows that sodium bisulfite is better than triphenyl phosphite. This modification, using sodium bisulfite instead of triphenyl phosphite, provided a very simple procedure for the product purification. In this case, almost pure product can be obtained just by filtering off the inorganic salts, followed by precipitating the catalyst in ethyl ether after the reaction is complete.

Mechanism studies show that the PEG chain promotes the ylide formation and stabilizes the catalytic species, suggesting that the PEG chain plays important roles in improving the catalytic efficiency. To further investigate the role of PEG units in more detail and to further improve the efficiency of catalytic ylide olefination as well as to increase the telluronium loading in the PEG carrier,[11] we designed several pentaerythritol-derived oligoglycols **1** as a new type of carrier. In this paper, we wish to report the synthesis and the characterization of

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(11) One of the major drawbacks with PEG-telluride as the catalyst is that the telluronium loading in PEG is low due to the unfavorable stoichiometry between PEG and Te.
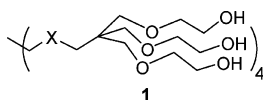
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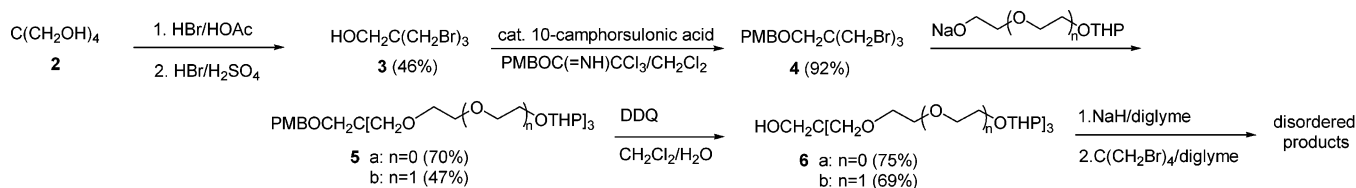
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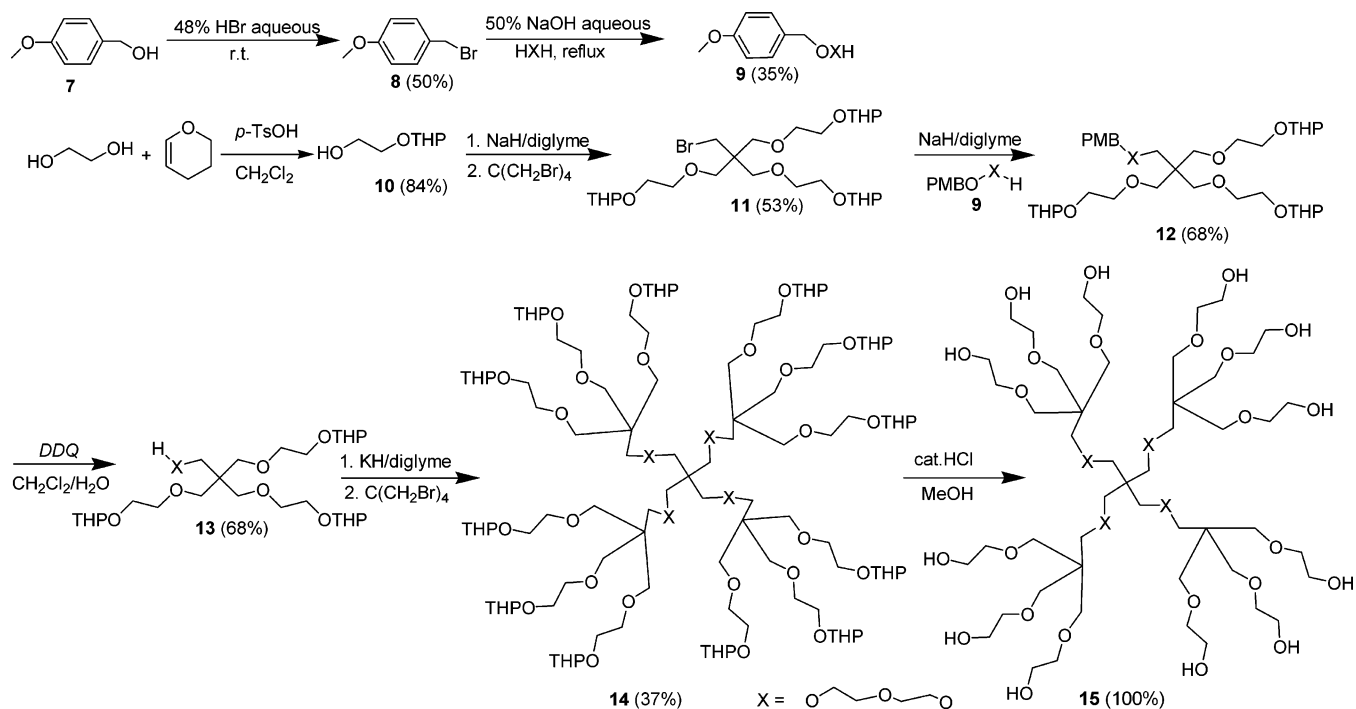
the oligoglycols with hydroxyl groups at the surface, as well as their application as the catalyst carrier in catalytic Wittig olefination.

Synthesis and Characterization of the Oligoglycols. The most important requirement for the synthesis of pentaerythritol-derived oligoglycols **1** is the efficient formation of ether linkages. To prevent elimination during the formation of ether under Williamson conditions, we designed tribromide **4** and pentaerythritol-derived alcohol **6** with the oligoglycol skeleton as new monomers and chose pentaerythrityl tetrabromide as the core for our synthesis. The initial synthetic route is outlined in Scheme 2.

The monomer **6** was readily prepared from pentaerythritol **2** in four steps. The tribromide **3** was obtained by treating pentaerythritol **2** with 40% HBr (aq) (1:5, v/v) in HOAc, followed by 40% HBr (aq)/concentrated H_2SO_4.[12] Compound **4,** prepared from compound **3** by protecting **it** with *p*-methoxybenzyl (PMB),[13] reacted with THP-

masked sodium diglycolate or glycolate to afford compound **5**, which was deprotected to give the key intermediate **6**. It is noteworthy that the choice of the protecting group is fundamental to the success of this synthesis, as it must be readily removed under mild conditions without affecting the oligoether. First, we chose the benzyl group as the masking group but found that it was difficult to deprotect completely by hydrogenation in the presence of 10% Pd/C. As the tetrahydropyranyl (THP) has been proved useful in hydroxyl group protection,[14] it was selected for use in our construction of the target molecules. Compound **6b**, after being treated with NaH, reacted with pentaerythrityl tetrabromide to give disordered products in a variety of conditions and no desired tetrasubstituted product was detected. Changing diglycol derivative **6b** ($n = 1$) into glycol derivative **6a** ($n = 0$), the result was still negative, presumably because the attached long oligo(ethyleneglycol) chain blocked the reactive site and prevented further substitution.

Thus, when modifying the monomer **6** into **13** by lengthening the chain of the reactive site, the etherification reaction to form the symmetric oligoglycol worked well (Scheme 3). Glycol was protected by THP, followed by the reaction with pentaerythrityl tetrabromide to afford compound **11** in 53% yield in one step just by

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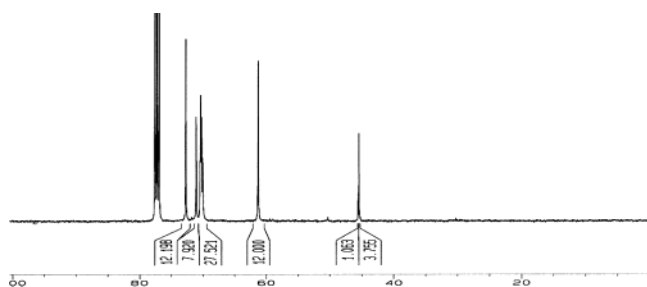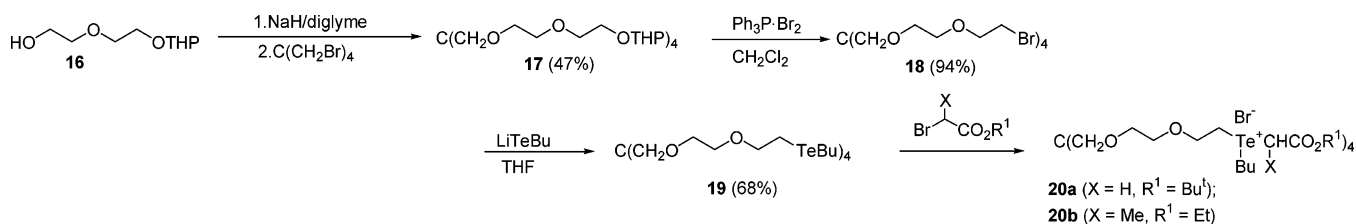
FIGURE 1. Quantitative ^{13}C NMR of compound **15** from a Bruker DR × 400 NMR spectrometer. The inverse gated decoupling pulse sequence (Bruker standard pulse program: 2 gig) was used with a relaxation delay of 60 s and a pulse of 45° flip angle.

TABLE 1. Reaction of Aldehyde with Bromoacetate

$$RCHO + Br\text{-}CH_2CO\text{-}OBu^t \xrightarrow[\text{THF-H}_2\text{O/reflux}]{\text{cat., NaHSO}_3\text{ /K}_2\text{CO}_3} R\text{-}CH=CH\text{-}CO\text{-}OBu^t$$

21   **22**   **23**

entry	cat.	cat. loading, mol %[a]	23	R	reaction time (h)	E/Z	yield (%)
1	**20a**	5	**23a**	4-ClC$_6$H$_4$	24	>99:1	98
2	**20a**	5	**23b**	Ph	24	>99:1	80
3	**20a**	5	**23c**	2-ClC$_6$H$_4$	24	>99:1	87
4	**20a**	5	**23d**	4-CH$_3$C$_6$H$_4$	24	>99:1	93
5	**20a**	5	**23e**	2-CH$_3$OC$_6$H$_4$	48	>99:1	82
6	**20a**	5	**23f**	furanyl	48	>99:1	94
7	**20a**	5	**23g**	cinnanyl	48	90:10	85
8	**20a**	5	**23h**	n-C$_9$H$_{19}$	48	97:3	68
9	**20a**	2	**23a**	4-ClC$_6$H$_4$	24	>99:1	90
10	**24a**[b]	5	**23a**	4-ClC$_6$H$_4$	24	>99:1	65
11	**24a**[b]	2	**23a**	4-ClC$_6$H$_4$	24	>99:1	35
12	**24b**[c]	5	**23a**	4-ClC$_6$H$_4$	24	>99:1	99

[a] Calculated by telluride. [b] **24a** = Bu$^n_2$Te$^+$CH$_2$CO$_2$Bu^t·Br$^-$. [c] **24b** = BuTe-PEG-TeBu.

controlling the ratio of the reactants. Noticeably, the material adding sequence was crucial to this reaction. When the solution of the corresponding sodium salt of monoalcohol **10** was added dropwise into pentaerythrityl tertrabromide in refluxing diglyme, the desired product **11** was given in a reasonable yield. But almost nothing was obtained when the reverse adding sequence was employed. The Williamson etherification reaction of compound **11** with diglycol monomasked by the 4-methoxybenzyl group gave oligoether **12** in 68% yield, which was easily deprotected by DDQ in dichloromethane in the presence of water to produce compound **13** in 68% yield. Reaction of alcohol **13** with pentaerythrityl tetrabromide in diglyme afforded oligoglycol **14** in 37% yield. The peripheral ketal of compound **14** was easily removed in the presence of hydrogen chloride in dioxane when using methanol as the solvent to give the desired oligoglycol **15**, having hydroxyl groups at the surface, in quantitative yield (Scheme 3).
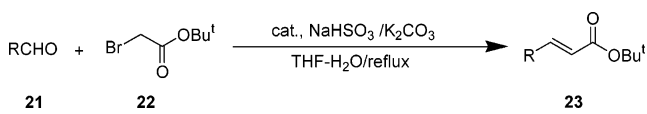
Both **14** and **15** could be purified with precise molecular weight and structure. The purity and structure of both **14** and **15** were determined by elemental analysis, ^{1}H NMR, ESI-MS, and quantitative ^{13}C NMR. In the ESI-MS spectra of these two compounds, peaks corresponding to the mass of the oligoglycol plus sodium and/or potassium are observed. Quantitative ^{13}C NMR of compound **15** showed that there are 5 tertiary carbons and 60 carbons related to $-OCH_2-$ units (Figure 1). These data demonstrate the structure of the desired oligoglycol.

Synthesis of the Telluride. With oligoglycol **15** at hand, we tried to synthesize the corresponding telluride for our study but failed. The reason is that the hydroxyl groups of oligoglycol **15** could not be full-transformed into the corresponding tosylates or bromides under a variety of conditions. In all conditions, disordered compounds were obtained and no pure product could be isolated. Thus, we synthesized a simple telluride **19** with the oligo-

(ethyleneglycol) skeleton (Scheme 4) for our study and tested its catalytic activity for Wittig-type olefination.

The telluronium salt **20** was easily made from THP-masked diglycol **16** as follows: Alcohol **16** reacted with NaH, followed by C(CH$_2$Br)$_4$ to afford compound **17**, which was readily transformed into corresponding bromide **18** in the presence of Ph$_3$P·Br$_2$.[15] Bromide **18** reacted with LiTeBu, followed by the bromo compounds to give the desired telluronium salts **20a** and **20b**. It was found that salt **20a** was a comparable catalyst to PEG-telluride for the Wittig-type reaction of aldehydes with bromoacetate.[10] The results are shown in Table 1. In the presence of NaHSO$_3$, both aromatic aldehydes and alphatic aldehydes worked well when 1.25 mol % of catalyst **20a** was employed. All reactions gave E-isomers with excellent stereoselectivity and in good to high yields.[16] Noticeably, compared with the known dibutyltelluronium salt **24a**, the new synthesized tellurium salt **20a** was more efficient and is comparable to the PEG-telluride **24b**. Even when the loading is reduced to 2 mol %, the isolated yield was still 90% (entries 1, 9, 10, and 11).

Although several catalytic Wittig reactions have been developed, few involved the olefination of aldehydes with α-bromopropionate. It was found that moderate to good yields could be obtained when using the newly designed **20b** as the catalyst for the Wittig-type reaction of α-bromopropionate, although higher reaction temperature is necessary, compared with the corresponding olefination of bromoacetate. For instance, the yield decreased from 72% to 32% when p-chlorobenzylaldehyde was used when the temperature was lowered to 80 °C. As shown in Table 2, both aromatic and aliphatic alde-

SCHEME 4

TABLE 2. Reaction of Aldehyde with α-bromopropionate

entry	reaction time (h)	25	R	E/Z[a]	isolated yield (%)
1	24	25a	4-ClC$_6$H$_4$	96:4	72
2	24	25b	Ph	97:3	69
3	24	25c	4-NO$_2$C$_6$H$_4$	96:4	68
4	40	25d	2-CH$_3$OC$_6$H$_4$	99:1	67
5	24	25e	Cy	70:30	63

[a] Determined by ^{1}H NMR.

hydes were good substrates for this reaction. Aromatic aldehydes gave high stereoselectivity (entries 1−4) and poor selectivity was afforded when cyclohexylaldehyde was used.

In conclusion, we have developed a convergent way to prepare a symmetric oligoglycol having hydroxyl groups at the surface, which is potentially useful as a catalyst carrier. Quantitative ^{13}C NMR proved to be an efficient tool for the characterization of such compounds. The simple oligo(ethyleneglycol)-derived telluride **19** was synthesized and the corresponding telluronium salt **20** proved to be a good catalyst in Wittig-type reactions. Noticeably, salt **20** can also catalyze the olefination of aldehydes with α-bromopropionate to provide trisubstituted olefin.

Experimental Section

All reactions were carried out with use of standard Schlenk techniques under an atmosphere of dry, oxygen-free nitrogen unless otherwise stated. Solvents were dried and purified by standard method. Reagents were purchased from commercial sources. Aromatic aldehydes were distilled before use. Compound **10** was prepared according to the literature.[17] Chemical shifts were given in ppm relative to internal tetramethylsilane.

Oligoglycol 14. To a suspension of potassium hydride (124 mg, 3.1 mmol) in diglyme (fresh-distilled over sodium, 10 mL) at 0 °C in a three-neck flask, equipped with a reflux condenser and a dropping funnel, was added dropwise a solution of compound **13** (1.82 g, 3 mmol) in diglyme (5 mL) under argon atmosphere. The resulting mixture was stirred at 0 °C for 1 h, then at room temperature for a further 2 h, followed by heating to reflux. To this refluxing suspension was added dropwise a solution of pentaerythrityl tetrabromide (194 mg, 0.5 mmol) in diglyme (10 mL) within 0.5 h. The resulting mixture was refluxed for another 5 h, cooled to room temperature, and filtered through a Celite pad. The filtrate was concentrated. The residue was purified by Flash-chromatography to afford oligoglycol **14** (440 mg, 37%) as a colorless oil. ^{1}H NMR (300 MHz, CDCl$_3$/TMS): δ 1.43−1.65 (m, 72H), 3.37−3.81 (m, 144H), 4.65 (t, J = 3.5 Hz, 12H); ^{13}C NMR (75 MHz, CDCl$_3$/TMS) 19.4 (12C), 25.6 (12C), 30.7 (12C), 45.7 (1C), 45.8 (4C), 61.9 (12C), 66.5 (12C), 70.2−70.9 (28C), 71.1−71.1 (20C), 98.8 (12C); IR ν/cm^{-1} 1124; MS (ESI, *m/z*, rel intensity) 2537.4 ([M + K]$^+$, 10%), 1288.7 ([M + 2K]$^{2+}$, 75%), 872.1 ([M + 3K]$^{3+}$, 90%). Anal. Calcd for C$_{125}$H$_{228}$O$_{48}$: C, 60.09; H, 9.13. Found: C, 60.74; H, 9.47.

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(16) For a proposed mechanism, please see the Supporting Information.

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Oligoglycol 15. To a stirred solution of oligoglycol **14** (265 mg, 0.1 mmol) in 5 mL of methanol was added HCl (0.05 mL, 4 M in dioxane) and after 1 h, the solvent was evaporated out. The above operation was repeated two times to give the oligoglycol **15** in quantitative yield. No further purification was employed. ^{1}H NMR (300 MHz, CDCl$_3$/TMS) δ 3.58 (br s); ^{13}C NMR (100 MHz, CDCl$_3$/TMS) δ 45.4 (4C), 45.5 (1C), 61.3 (12C), 70.0, 70.2, 70.3 and 70.4 (28C), 71.0 (8C), 72.7 (12C); IR (net) ν/cm$^-$ 13403, 1101; ESI-HRMS calcd for C$_{65}$H$_{132}$O$_{36}$Na 1511.83905, found 1511.83505.

Telluride 19. To a stirred suspension of tellurium power (254 mg, 1.98 mmol) in 5 mL of dry THF was added dropwise 1.23 mL of butyllithium (1.6 M, 1.98 mmol) at 0 °C. After being stirred for half an hour at room temperature, the mixture was cooled to −78 °C and oligoglycol **18** (244 mg, 0.33 mmol) in 5 mL of dry THF was added. The resulting mixture was stirred at this temperature for 6 h, warmed to room temperature, and filtered. The filtrate was concentrated. The residue (hexane/ethyl acetate, 5:1) was purified by chromatography on silica gel to afford compound **19** as a pale yellow oil. Yield: 251 mg (68%). ^{1}H NMR (300 MHz, CDCl$_3$/TMS) δ 0.91 (t, J = 7.2 Hz, 12H), 1.39 (m, 8H), 1.72 (m, 8H), 2.63 (t, J = 7.5 Hz, 8H), 2.77 (t, J = 7.5 Hz, 8H), 3.45 (s, 8H), 3.57 (m, 16H), 3.75 (t, J = 7.8 Hz, 8H); ^{13}C NMR (75 MHz, CDCl$_3$/TMS) δ 1.8, 2.7, 13.3, 24.9, 34.2, 45.4, 69.5, 69.9, 70.8, 73.1; IR ν/cm^{-1} 2955, 2924, 2870, 1102. Anal. Calcd for C$_{37}$H$_{76}$O$_8$Te$_4$: C, 38.34; H, 6.53. Found: C, 38.58; H, 6.47.

Telluronium Salt 20a. To a stirred solution of oligoglycol **19** (251 mg, 0.22 mmol) was added *tert*-butyl bromoacetate (172 mg, 0.88 mmol) in 5 mL of dry THF at room temperature and the mixture was stirred overnight. The solvent was removed to give salt **20a** in quantitative yield. ^{1}H NMR (300 MHz, CDCl$_3$/TMS) δ 1.04 (t, J = 6.9 Hz, 12H), 1.56 (m, 44H), 2.02 (m, 8H), 3.25 (m, 8H), 3.42−3.87 (m, 40H), 4.21 (m, 8H); ^{13}C NMR (75 MHz, CDCl$_3$/TMS) δ 13.5, 24.8, 27.2, 27.8, 27.9, 28.2, 30.8, 45.5, 66.2, 70.1, 70.6, 70.7, 83.0, 167.8. Anal. Calcd for C$_{61}$H$_{120}$Br$_4$O$_{16}$-Te$_4$: C, 37.78; H, 6.19. Found: C, 37.97; H, 6.63.

General Procedure for the Catalytic Wittig-Type Reaction of Bromoacetate. To a Schlenk tube was added a 1 mL of solution of telluronium salt **20a** (1.25 × 10^{-2} M in THF) and NaHSO$_3$ (90 mg, 0.66 mmol). After the mixture was refluxed for 10 min, 0.04 mL of water and 138 mg of K$_2$CO$_3$ (1.0 mmol), followed by 0.5 mmol of aldehyde and 118 mg of *tert*-butyl bromoacetate (0.6 mmol), were added. The resulting suspension was refluxed for several hours. After the reaction was complete, the mixture was filtered rapidly through a glass funnel with a thin layer of silica gel (ethyl acetate as the elution). The filtrate was concentrated and the residue was purified by chromatography (hexane/ethyl acetate, 200:1) to afford the desired product.

General Procedure for the Catalytic Wittig-Type Reaction of α-Bromopropionate. To a Schlenk tube was added a 0.5-mL solution of telluronium salt **20b** (2.5 × 10^{-2} M in THF, prepared from the telluride **19** and ethyl α-bromopropionate at rt for 3 days in solvent-free condition) and THF was removed under vacuum at room temperature. Then the ethyl α-bromopropionate (136 mg, 0.75 mmol), triphenyl phosphite (105 mg, 0.5 mmol), aldehyde (0.5 mmol), potassium carbonate (104 mg, 0.75 mmol), potassium iodide (8 mg, 0.05 mmol), and 1 mL of dried toluene were added and the resulting suspension was refluxed. After the reaction was complete, the mixture was filtered rapidly through a glass funnel with a thin layer of silica gel (ethyl acetate as the elution). The filtrate was concentrated and the residue was purified by chromatography (hexane/ethyl acetate, 200:1) to afford the desired product.

Supporting Information Available: Detailed experimental procedures and characterization data for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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