Supporting Information for

Synthesis, Characterization of Pentaerythritol-derived Oligoglycol and Their Application to Catalytic Wittig-type Reaction

*Kai Li, Li Ran,[#] Yi-Hua Yu, Yong Tang **

State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry,

354 Fenglin Lu, Shanghai 200032, China

SUPPORTING INFORMATION

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General. 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. ^{1}H NMR spectra were recorded at Bruker AM-300 and the chemical shifts are given in ppm relative to internal TMS. IR spectra were recorded with a Perkin-Elmer 983 spectrometer and MS spectra were recorded at Finnigan GC-MS-4021 (CI, 70ev). HRMS were performed on Finnigan MAT8430. The reagents were purchased from commercial sources and used directly. GC was performed on a SPB^{TM}-5 Capillary Column (30 m × 0.32 mm × 0.25 μm) and a VARIAN Chrompack CP 3800 gas chromatograph.

Preparation of Oligoglycol

Bromide **4**. ^{1}H NMR (300 MHz, $CDCl_3$/TMS): δ 3.51 (s, 2H), 3.56 (s, 6H), 3.82 (s, 3H), 4.49 (s, 2H), 6.90 (d, J = 8.4 Hz, 2H), 7.28 (d, J = 8.4 Hz, 2H); IR ν/cm^{-1} 1612 (s), 1513 (s), 1247 (s), 1098 (s); MS (EI, m/z, rel. intensity): 442 ([M]$^+$, Br = 79, 1.46%), 444 ([M]$^+$, 2×Br = 2×79, Br = 81, 4.27%), 446 ([M]$^+$, Br = 79, 2×Br = 2×81, 4.14%), 448 ([M]$^+$, Br = 81, 1.36%), 121 ([PMB]$^+$, 100%); HRMS (EI) for $C_{13}H_{17}O_2Br$ Calcd : 441.87786; Found: 441.87362.

Oligoglycol 5a. ^{1}H NMR (300 MHz, $CDCl_3$/TMS): δ 1.60 (m, 18H), 3.56–3.82 (m, 29H), 4.41 (s, 2H), 4.62 (m, 3H), 6.83 (d, J = 6.8 Hz, 2H), 7.22 (d, J = 6.8 Hz, 2H); IR ν/cm^{-1} 2940 (s), 2870 (s), 1613 (w), 1514 (m), 1124 (s), 1036 (s); MS (ESI, m/z, rel. intensity): 663.4 [M + Na]$^+$; HRMS (ESI) for $C_{40}H_{68}O_{14}Na$ Calcd.: 795.4501280; Found: 795.4489140.

Oligoglycol 5b ^{1}H NMR (300 MHz, $CDCl_3$/TMS): δ 1.52 (m, 18H), 3.45-3.85 (m, 41H), 4.4 (s, 2H), 4.62 (t, *J* = 3.0 Hz, 3H), 6.58 (d, *J* = 6.6 Hz, 2H), 7.22 (d, *J* = 6.6 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$/TMS): δ 19.37, 25.34, 30.46, 55.11, 62.04, 66.60, 68.97, 69.96, 70.26, 70.41, 70.96, 72.80, 98.78, 113.48, 128.79, 130.98, 158.83. IR *v*/cm^{-1} 2940 (s), 2870 (s), 1613 (w), 1514 (m), 1124 (s), 1036 (s); MS (ESI, m/z, rel. intensity): 795.5 $[M+Na]^+$.HRMS (ESI) for $C_{34}H_{56}O_{11}Na$ Calcd: 66.3714837; Found: 663.3723120.

Oligoglycol 6a ^{1}H NMR (300 MHz, $CDCl_3$/TMS): δ 1.50–1.82 (m, 18H), 3.20 (brs, 1H), 3.47– 3.90 m, 26H), 4.64 (t, *J* = 3.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$/TMS): δ 19.42, 25.57, 30.65, 45.31, 62.04, 65.54, 66.41, 70.95, 71.50, 98.83; IR *v*/cm^{-1} 3461 (m), 2941 (s), 2871 (s), 1124 (s), 1035 (s); MS (ESI, m/z, rel intensity): 543.4 $[M + Na]^+$; Anal. for $C_{26}H_{48}O_{10}$ Calcd: C, 60.00; H, 9.23; Found: C, 60.15; H, 9.33.

Oligoglycol 6b ^{1}H NMR (300 MHz, $CDCl_3$/TMS): δ 1.50-1.80 (m, 18H), 3.18 (brs, 1H), 3.47-3.93 (m, 38H), 4.46 (t, *J* = 3.9 Hz, 3H); IR *v*/cm^{-1} 3489 (m), 2940 (s), 2870 (s), 1123 (s), 1035 (s); MS (ESI, m/z, rel. intensity): 675.3 $[M + Na]^+$; HRMS (ESI) for $C_{32}H_{60}O_{13}Na$ Calcd.: 675.3926131; Found: 675.3913160.

Compound 9. To 25 g (180 mmol) of 4-methoxybenzyl alcohol was added 20 mL of 48% HBr, and the mixture was stirred at ambient temperature for 30 minutes. The resulting mixture was diluted with 100 mL of diethyl ether, and the organic layer was collected, dried over K_2CO_3. After concentration under reduced pressure, the

residue was distilled under high vacuum to afford 4-methoxybenzyl bromide as colorless oil (30 g) that was used directly in the following reaction.

To a three-necked round flask equipped with a condenser, was added 105 g (496 mmol) of diglycol, followed by 4-methoxybenzyl bromide (25 g, 124 mmol) and 5 equivalents of aqueous sodium hydroxide solution (50%). The resulting mixture was refluxed for 24 hours with stirring. The reaction mixture was cooled and diluted with water. Extraction was carried out with ether and the organic layer was collected, dried over anhydrous sodium sulfate. The solution was concentrated under reduced pressure. The pure product was obtained by chromatography on silica gel as colorless oil. Yield: 9.7 g (35%). ^{1}H NMR (300 MHz, $CDCl_3$/TMS): δ 2.63 (t, J = 6.1 Hz, 1H), 3.60 (m, 4H), 3.65 (m, 4H), 3.82 (s, 3H), 4.51 (s, 2H), 6.87 (d, J = 7.3 Hz, 2H), 7.28 (d, J = 7.3 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$/TMS): δ 55.18, 61.56, 69.06, 70.29, 72.55, 72.86, 113.72, 129.43, 129.97, 159.23; IR ν /cm^{-1} 3442, 1613, 1514, 1248; MS (EI, m/z, rel. intensity); 226 $[M]^+$; Anal. Calcd for $C_{12}H_{18}O_4$: C, 63.72; H, 7.96; Found: C, 63.85; H, 7.87.

Compound 11. To a suspension of sodium hydride (2.4 g, 60 mmol, 60% suspension in oil) in 140 mL of dry diglyme at 0°C in a 250 mL of three-necked flask, equipped with magnetic stirrer and a 60 mL of addition funnel, a solution of mono-protected glycol **10** (8.76 g, 60 mmol) in 30 mL dry diglyme was added dropwise under nitrogen atmosphere. The resulting mixture was stirred at 0°C for 1 h and then at room temperature for another 2 hrs to give the solution of sodium

alcoholate. This alcoholate was added dropwise to the refluxing solution of pentaerythrityl tetrabromide (6.6 g, 17.1 mmol) in 100 mL of diglyme under nitrogen atmosphere. After the addition, the mixture was heated for further 3 hrs and then cooled to room temperature. The mixture was passed through a celite pad and the filtrate was concentrated. Flash-chromatography on silica gel (hexane/ethyl acetate, 5:1) afforded compound **11** as colorless oil Yield: 10 g (53%). ^{1}H NMR (300 MHz, $CDCl_3$/TMS): δ 1.57-1.87 (m, 18H), 3.54-3.67 (m, 20H), 3.84-3.95 (m, 6H), 4.70 (t, J = 3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$/TMS): δ 19.24, 25.43, 30.51, 35.62, 44.95, 61.77, 66.29, 69.84, 70.80, 98.57; IR (film) ν /cm^{-1} 1123; MS (ESI, m/z, rel. intensity): 621 $[M + K]^+$ ESI-HRMS Calcd for $C_{26}H_{47}O_9BrK$: 621.20536; Found: 621.20350.

Compound 12. To a suspension of sodium hydride (1.24 g, 31 mmol, 60% suspension in oil) in 100 mL of dry diglyme at 0°C in a three-necked flask (250 mL), equipped with magnetic stirrer and a addition funnel (60 mL), was added dropwise a solution of PMB mono-protected diglycol **9** (7.02 g, 31 mmol) in 50 mL of dry diglyme under nitrogen atmosphere. The resulting mixture was stirred at 0°C for 1h and then at room temperature for another 2 hrs to give the solution of sodium alcoholate. This solution was added dropwise to a refluxing solution of compound **11** (9.04 g, 15.5 mmol) in 50 mL of diglyme under nitrogen atmosphere. After the addition, the mixture was heated for further 2 hrs and then cooled to room temperature. The mixture was filtered through a celite pad and the filtrate was concentrated. The residue was purified by chromatography on silica gel (hexane/ethyl

acetate, 2:1) to afford compound **12** as coreless oil. Yield: 7.67 g (68%). ^{1}H NMR (300 MHz, $CDCl_3$/TMS): δ 1.47-1.59 (m, 18H), 3.44-3.64 (m, 29H), 3.76-3.85 (m, 8H), 4.48 (s, 2H), 4.62 (t, *J* = 3.3 Hz, 3H), 6.84 (d, *J* = 8.7 Hz, 2H), 7.26 (d, *J* = 8.7 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$/TMS): δ : 19.30, 25.43, 30.53, 45.60, 55.21, 61.89, 66.35, 69.08, 69.90, 69.96, 70.32, 70.63, 70.78, 71.01, 72.85, 98.67, 113.68, 129.36, 130.28, 159.10; IR *v* /cm^{-1} 1613, 1123; MS (ESI, m/z, rel. intensity): 767.5 $[M + K]^+$. ESI-HRMS Calcd. for $C_{38}H_{64}O_{13}K$: 767.39897, Found: 767.39785.

Compound 13. To a stirred solution of PMB ether **12** (9.34 g, 12.8 mmol) in CH_2Cl_2/H_2O (130 mL/6.5mL), was added DDQ (2.90 g, 12.8 mmol) at 0°C. After the reaction was complete, saturated aqueous $NaHCO_3$ (10 mL) was added. The resulting solution was extracted with CH_2Cl_2. The extraction was washed with saturated brine, and dried over Na_2SO_4, and concentrated. The residue was purified by chromatography on silica gel to give pure **13** as a coreless oil. Yield: 5.29 g (68%). ^{1}H NMR (300 MHz, $CDCl_3$/TMS): δ 1.47-1.66 (m, 18H), 3.00 (t, *J* = 6.1 Hz, 1H), 3.42-3.82 (m, 34H), 4.61 (t, *J* = 3.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$/TMS): δ : 19.30, 25.46, 30.54, 45.64, 61.81, 61.91, 66.37, 69.76, 69.94, 70.37, 70.81, 71.06, 72.50, 98.68; IR *v* /cm^{-1} 3470, 1124; MS (ESI, m/z) 631.36 $[M + Na]^+$. ESI-HRMS Calcd for $C_{30}H_{56}O_{12}Na$: 631.36640; Found: 631.36601.

Oligoglycol 17. To a suspension of sodium hydride (400 mg, 10 mmol, 60% suspension in oil) in 30 mL of dry diglyme at 0°C, in a three-necked flask (100 mL) equipped with a addition funnel of 60 mL, was added dropwise a solution of THP

mono-protected diglycol **16** (1.90g, 10 mmol) in 10 mL of dry diglyme under nitrogen atmosphere. The resulting mixture was stirred at 0 ℃ for 1h and then at room temperature for another 2 hrs to give the solution of sodium alcoholate. To this solution was added pentearythrityl tetrabromide (970 mg, 2.5 mmol) and the resulting mixture was refluxed for 24 hours. After cooling to room temperature, the mixture was filtered through a celite pad. The filtrate was concentrated and the residue was purified by flash-chromatography (hexane/ethyl acetate, v/v, 1/2) to afford oligoglycol **17** (732 mg, 47%) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$/TMS): δ 1.49-1.83 (m, 24H), 3.44-3.68 (m, 40H), 3.83-3.88 (m, 8H), 4.64 (t, J = 3.1 Hz, 4H); ^{13}C NMR (75 MHz, $CDCl_3$/TMS): δ 19.66, 25.62, 30.74, 45.72, 62.34, 66.88, 70.16, 70.53, 70.68, 71.23, 99.07; IR ν/cm^{-1} 2940, 2869, 1125; MS (ESI, m/z) 847.6 [M + Na]$^{+}$; Anal. Calcd for $C_{41}H_{76}O_{16}$: C, 59.71; H, 9.22; Found: C, 60.27; H, 8.76.

Oligoglycol 18. To a stirred solution of oligoglycol **17** (206 mg, 0.25mmol) in 2 mL of dry CH_2Cl_2, was added $Ph_3P{\cdot}Br_2$ (464 mg, 1.1 mmol) at 0 °C. The resulting mixture was stirred at room temperature for 1 h. After the reaction was complete, the mixture was diluted with 20 mL of CH_2Cl_2, and washed with 2 mL of water. The CH_2Cl_2 layer was separated, dried over Na_2SO_4 and concentrated. The residue was purified by chromatography on silica gel to give oligoglycol **18** (170 mg, 94%). ^{1}H NMR (300 MHz, $CDCl_3$/TMS): δ 3.45-3.50 (m, 16H), 3.57-3.67 (m, 16H), 3.82 (t, J = 6.3 Hz, 8H); ^{13}C NMR (75 MHz, $CDCl_3$/TMS): δ 30.55, 45.58, 69.95, 70.38, 71.05, 71.16; IR ν/cm^{-1} 2870, 1107, 572; MS (ESI, m/z, rel intensity) 754 ([M +

$H_2O]^+$, 16%), 756 ([M + $H_2O]^+$, 69%), 758 ([M + $H_2O]^+$, 100%), 760 ([M + $H_2O]^+$, 74%), 760 ([M + $H_2O]^+$, 17%); Anal. Calcd. for $C_{21}H_{40}O_8Br_4$: C, 34.07; H, 5.40; Found: C, 34.49; H, 5.10.

Preparation of Telluronium Salts

Dibutyl Telluride Salt 24.[1] To a stirred solution of dibutyl telluride (242 mg, 1 mmol) in 1 mL of dry THF was added *ter*-butyl bromoacetate (195 mg, 1 mmol) at room temperature. And the mixture was stirred overnight. After the solvent was removed, salt **24** was given in quantitative yield. ^{1}H NMR (300 MHz, $CDCl_3$/TMS): δ 1.00 (m, 6H), 1.50 (m, 13H), 1.95 (m, 4H), 3.27 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$/TMS): δ 13.73, 24.99, 26.59, 28.17, 28.31, 28.63, 83.54, 168.05.

Catalytic Olefination

***tert*-Butyl (E)-3-(4-Chlorophenyl) acrylate (23a, R = 4-ClC$_6$H$_4$).**[2] Yield: 116 mg (98%).

***tert*-Butyl (E)-3-Phenylacrylate (23b, R = C$_6$H$_5$).**[2] Yield: 81 mg (80%).

***tert*-Butyl (E)-3-(2-Chlorophenyl)acrylate (23c, R = 2-ClC$_6$H$_4$).** Yield: 103 mg (87%). ^{1}H NMR (300 MHz, $CDCl_3$/TMS): δ 1.56 (s, 9H), 6.38 (d, J = 16.2 Hz, 1H), 7.28 (m, 2H), 7.41 (m, 1H), 7.61 (m, 1H), 8.02 (d, J = 16.2 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$/TMS): δ 28.09, 80.71, 122.67, 126.93, 127.47, 130.03, 130.68, 132.80, 134.73, 139.27, 165.75; IR ν/cm^{-1} 3067, 1709, 1636, 1321, 1150, 979, 757; MS (EI, m/z, rel intensity) 238 (M^+, 6%), 147 (100%); Anal. Calcd for $C_{13}H_{15}O_2Cl$: C, 65.40; H, 6.28; Found: C, 65.45; H, 6.56.

***tert*-Butyl (E)-3-(*p*-Toyl) acrylate (23d, R=4-$CH_3C_6H_4$)**.[2] Yield: 101 mg (93%).

***tert*-Butyl (E)-3-(*p*-Anisyl)acrylate (23e, R=2-$CH_3OC_6H_4$).**[2] Yield: 96 mg (82%).

***tert*-Butyl (E)-3-(2-Furyl)acrylate (23f, R=furanyl).**[2] Yield: 87 mg (94%).

***tert*-Butyl (E,E)-5-Phenylpent-2,4-dienoate (23g, R=cinmanyl)**.[10] Yield: 98 mg (85%).

***tert*-Butyl (E)-Dodec-2-enoate (23h, R= n-C_9H_{19})**.[2] Yeld: 86 mg (68%).

Ethyl-3-(4-chlorobenzyl)-2-methyl-2-propenoate (25a, R = 4-chlorobenzyl).[3] Yield: 81 mg (72%).

^{1}H NMR (300 MHz, $CDCl_3$/TMS): δ 1.35 (t, J = 7.0 Hz, 3H), 2.10 (s, 3H), 4.26 (q, J = 7.0 Hz, 2H), 7.15 (d, J = 7.0 Hz, 1H), 7.33 (m, 3H), 7.62 (s, 1H)

Ethyl-3-benzyl-2-methyl-2-propenoate (25b, R = benzyl). [3] Yield: 66 mg (69%).

^{1}H NMR (300 MHz, $CDCl_3$/TMS): δ 1.36 (t, J = 7.2 Hz, 3H), 2.13 (s, 3H), 4.28 (q, J = 7.2 Hz, 2H), 7.40 (m, 5H), 7.70 (s, 1H).

Ethyl-3-(4-nitrobenzyl)-2-methyl-2-propenoate (25c, R = 4-nitrobenzyl). [4] Yield: 80 mg, (68%).

^{1}H NMR (300 MHz, $CDCl_3$/TMS): δ 1.37 (t, J = 6.9 Hz, 3H), 2.12 (s, 3H), 4.29 (q, J = 7.2 Hz, 2H), 7.53 (d, J = 8.7 Hz, 2H), 7.69 (s, 1H), 8.26 (d, J = 8.1 Hz, 2H).

Ethyl-3-(4-methoxybenzyl)-2-methyl-2-propenoate (25d, R = 4-methoxybenzyl). [4] Yield: 82 mg, (74%).

^{1}H NMR (300 MHz, $CDCl_3$/TMS): δ 1.37 (t, J = 6.9 Hz, 3H), 2.12 (s, 3H), 3.89 (s, 3H), 4.29 (q, *J* = 7.2 Hz, 2H), 7.53 (d, *J* = 8.7 Hz, 2H), 7.69 (s, 1H), 8.26 (d, *J* = 8.1 Hz, 2H).

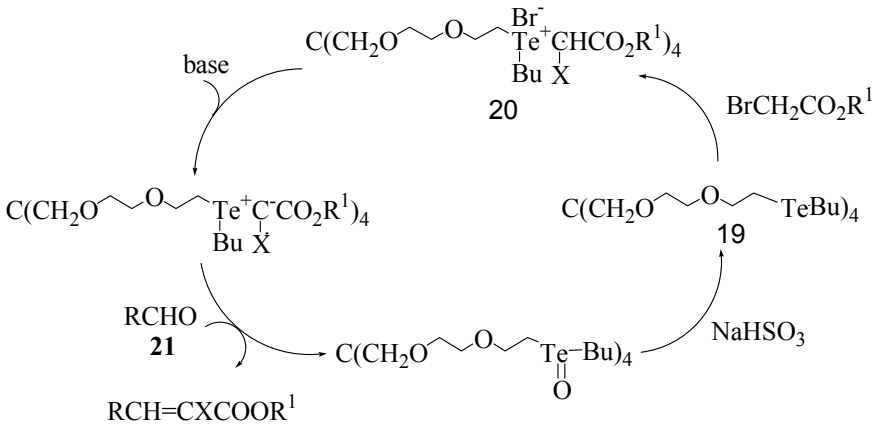
Ethyl-3-cyclohexyl-2-methyl-2-propenoate (25e, R = cyclohexyl). [5] Yield: 62 mg, (63%).

^{1}H NMR (300 MHz, $CDCl_3$/TMS) for cis/trans mixture: δ 0.84-1.80 (m, 15H), 2.25 and 2.89 (m, 1H), 4.19 (m, 3H), 5.73 and 6.58 (d, *J* = 9.6 Hz and d, *J* = 9.4 Hz, 1H).

Proposed Mechanism for catalytic ylide olefination

A proposed mechanism is describes in Scheme 1. The oefination proceeds via a ylide route. The telluride **19** reacted with bromoacetate to form the corresponding telluronium salt **20**. After deprotonation of salt by K_2CO_3, followed by the reaction with aldehyde, the desired alkene was formed. And the telluride **19** was regenerated by the reduction of telluride oxide with sodium bisulfite.

Scheme 1



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