Supporting Information for:

Preparation of Titanated Alkoxyallenes from 3-Alkoxy-2-propyn-1-yl Carbonates and (η^2-Propene)Ti(O-*i*-Pr)$_2$ as an Efficient Ester Homoaldol Equivalent

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Preparation of 2b: The compounds **2a**-**c** were prepared according to the procedure reported by Porter [Porter, N. A.; Dussault, P.; Breyer, R. A.; Kaplan, J.; Morelli, J. *Chem. Res. Toxicol.* **1990**, *3*, 236] with modifications; To a suspension of potassium hydride (11.4 g, 35 wt% in oil, 100 mmol) and imidazole (10 mg) in THF (200 mL) was added slowly a solution of cyclohexanol (5.28 mL, 50 mmol) in THF (50 mL) at room temperature. After stirring for 0.5 h, the mixture was cooled to 0 ºC and to this was added dropwise trichloroethylene (4.49 mL, 50 mmol). After stirring for 0.5 h at room temperature, the mixture was cooled to –78 ºC and to this was added *n*-BuLi (83.3 mL, 1.50 M in hexanes, 125 mmol) and then the mixture was allowed to warm to –40 ºC over 1 h. After addition of paraformaldehyde (3.0 g, 100 mmol) at –40 ºC, the resulting mixture was allowed to warm to room temperature over 2 h. To the reaction mixture were slowly added methanol (10 mL) and then water (100 mL). The organic layer was separated and the aqueous layer was extracted with ether (3 x 50 mL). The combined organic layers were washed with brine (2 x 100 mL), dried over Na_2SO_4, concentrated, and chromatographed on silica gel (hexanes : ether = 9 : 1 with a trace amount of Et_3N) to provide 3-cyclohexyloxy-2-propyn-1-ol (6.2 g) as a colorless oil in 81% yield; ^{1}H NMR (300 MHz, $CDCl_3$[*1]) δ 4.24 (s, 2H), 3.92-4.05 (m, 1H), 2.21 (br s, 1H, OH), 1.88-1.96 (m, 2H), 1.62-1.76 (m, 2H), 1.40-1.61 (m, 3H), 1.18-1.38 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$[*1]) δ 93.2, 86.3, 50.8, 37.8, 30.9, 25.1, 23.1. To a solution of 3-cyclohexyloxy-2-propyn-1-ol thus prepared (1.54 g, 10.0 mmol) and pyridine (1.78 mL, 22 mmol) in THF (20 mL) was added dropwise ethyl chloroformate (1.44 mL, 15 mmol) at 0 ºC. The resulting mixture was allowed to warm to room temperature over 1.5 h. After addition of sat. $NaHCO_3$ aq. (20 mL), the mixture was extracted with ether (2 x 15 mL), dried over $MgSO_4$, concentrated, and purified by column chromatography on silica gel (hexanes : ether =19 : 1 with a trace amount of Et_3N) to afford **2b** (2.05 g) as a colorless oil in 91% yield; ^{1}H NMR (300 MHz, $CDCl_3$[*1]) δ 4.72 (s, 1H), 4.17 (q, J = 7.2 Hz, 2H), 4.00-4.08 (m, 1H), 1.88-195 (m, 2H), 1.66-1.76 (m, 2H), 1.42-1.63 (m, 3H), 1.27 (t, J = 7.2 Hz, 3H), 1.21-1.32 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$[*1]) δ 154.5, 94.5, 86.8, 63.9, 56.2, 33.6, 30.8, 25.0, 23.1, 14.2.

The reaction of Alkoxyallyltitanium (1) Derived from 2b and (η^2-Propene)Ti(O-*i*-Pr)$_2$ with Benzaldehyde: To a mixture of **2b** (180 mg, 0.80 mmol), Ti(O-*i*-Pr)$_4$ (234 μL, 0.80 mmol), and diethyl ether (2 mL) was added *i*-PrMgCl (1.41 mL, 1.125 M in ether, 1.59 mmol) at –50 ºC and the mixture was stirred for 1.5 h at –50 ºC ~ -40 ºC. To this was added a solution of benzaldehyde (59 mg, 0.56 mmol) in ether (1.2 mL) at –40 ºC. After stirring at –40 ºC for 2 h, the mixture was allowed to warm to 0 ºC over 4 h.

Quenching with 3N NaOH aq. affording 4-cyclohexyloxy-1-phenyl-3-propyn-1-ol: After addition of 3N NaOH aq. (a few drops) to the reaction mixture obtained above, the resulting mixture was stirred for 10 min at room temperature. NaF (0.5 g) and Celite (0.5 g) were added and the mixture was filtered through a pad of Celite. The filtrate was concentrated *in vacuo* to provide 4-cyclohexyloxy-1-phenyl-3-propyn-1-ol as a crude residue which was subjected to ^{1}H NMR analysis using an internal standard for determination of the yield; ^{1}H NMR (300 MHz, $CDCl_3$[*1]) δ 7.17-7.41 (m, 5H), 4.70-4.78 (m, 1H), 3.87-3.98 (m, 1H), 2.63 (dd, *J* = 5.7, 16.5 Hz, 1H), 2.55 (dd, *J* = 7.2, 16.5 Hz, 1H), 2.36 (s, 1H, OH), 1.10-2.10 (m, 10H); ^{13}C NMR (75 MHz, $CDCl_3$[*1]) δ 142.9, 128.2, 127.5, 125.8, 90.6, 85.9, 73.0, 34.2, 31.0, 28.9, 25.3, 23.3.

*Quenching with 1N HCl aq. and the following treatment with NaH affording **4***: After addition of a mixture of aq. 1N HCl (1.5 mL) and THF (1.5 mL) to the reaction mixture, the resulting mixture was stirred for 1 h at ambient temperature, extracted with ether (2 x 5 mL), washed with sat. $NaHCO_3$ aq., dried over $MgSO_4$, and concentrated to give a crude mixture of **3** (R'=Ph) and **4** (R'=Ph) in a ratio of 3 : 1, which was isolated as a mixture of **3** and **4** by short-column chromatography in 81% combined yield. The mixture of **3** and **4** thus obtained was further treated with NaH (70 mg, 55 wt% in oil, 1.6 mmol) in THF (5 mL) at 0 ºC and purified by column chromatography to give lactone **4** (66 mg) in 72% yield. The compound **3** (R' = Ph); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.20-7.42 (m, 5H), 4.75-4.78 (m, 2H), 2.41 (t, *J* = 6.9 Hz, 2H), 2.07 (dt, *J* = 5.7, 6.9 Hz, 2H), 1.15-1.95 (m, 10H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.6, 144.3, 128.6, 127.7, 125.8, 73.6, 72.8, 33.9, 31.5, 31.0, 25.3, 23.6. The compound **4** (R' = Ph); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.20-7.50 (m, 5H), 5.52 (dd, *J* = 6.0, 8.1 Hz, 1H), 2.50-2.72 (m, 2H), 2.12-2.28 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.5, 139.2, 128.6, 128.3, 125.1, 81.2, 31.0, 29.0.

[*1]$CDCl_3$ for NMR analyses was treated with K_2CO_3 to neutralize prior to use because commercial chloroform has sometimes a trace amount of HCl and water which causes partial decomposition by acidic hydration of alkoxyacetylene moiety.