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A New Protocol for the Enantioselective Synthesis of Methyl-Substituted Alkanols and Their Derivatives via Hydroalumination–Zirconium-Catalyzed Alkylalumination Tandem Process

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General. All manipulations were conducted under a dry argon atmosphere, unless otherwise noted. THF and ether were distilled from sodium benzophenone ketyl, and the other solvents were dried and distilled under argon prior to use. Melting points (m. p.) were obtained by using a Mel-Temp capillary apparatus and are uncorrected. Flash chromatographic separations were carried out on 230 - 400 mesh silica gel 60. Gas chromatography was performed on an HP 6890 Gas Chromatograph using HP-5 capillary column (30 m X 0.32 mm, 0.5 μm film) with appropriate hydrocarbons as internal standards. HPLC was carried out on a Waters Breeze System equipped with a Waters 1525 binary pump and a Waters 2487 dual λ absorbance detector. Peak size analysis was carried out using Waters Breeze System Software (3.2 version). ^{1}H and ^{13}C NMR spectra were recorded on a Varian Inova-300 or Bruker DRX-500 spectrometers. Optical rotations were measured on an Autopol III automatic polarimeter. Dichlorobis(1-neomenthylindenyl)zirconium (**1**),[a] 4-(tert-butyldimethylsiloxyl)but-1-ene,[b] 4-(tert-butyldiphenylsilyl)but-1-ene,[b] 5-(tert-butyldimethylsiloxyl)pent-1-ene,[c] and 6-(tert-butyldimethylsiloxyl)hex-1-ene[c] were synthesized according to the corresponding literature procedures.

Preparation of IBAO (isobutylaluminoxane): To a 10 mL solution of 1.98 g (10 mmol) of triisobutylalane in CH_2Cl_2 cooled to -30 to -40 ^oC was added dropwise 0.18 g (10 mmol) of water *via* a micro syringe. After the addition was complete, the mixture was warmed to room temperature and stirred for 2 h to give a clear solution (1.0 M) of isobutylaluminoxane (IBAO).

Zirconium-Catalyzed Enantioselective Alkylalumination of 1-Alkenes via Hydroalumination–Carboalumination Tandem Process: Preparation of (3*R*)-3-Methyl-undecan-1-ol: Representative Procedure. In a dry, round-bottomed flask equipped with a magnetic stirring bar and a mercury bubbler were placed CH_2Cl_2 (6 mL) and dichlorobis(1-neomenthylindienyl)zirconium (**1**) (67 mg, 0.1 mmol) and *n*-octyldiisobutylalane prepared in situ by reacting 337 mg (3 mmol) of 1-octene and 427 mg (3 mmol) of diisobutylaluminum hydride (DIBAH) at 60 ^oC over 10 h.[d] The mixture was stirred at 23 ^oC for 5 min. To this mixture was added 2 mL (2 mmol) of IBAO in CH_2Cl_2 under an argon atmosphere. After stirring at 23 ^oC for 5 min, the reaction mixture was cooled to 0 ^oC with an ice bath, and 0.37 g (2 mmol) of $H_2C{=}CH(CH_2)_2OTBS$ was added dropwise to the resultant orange solution with subsequent stirring at 0 ^oC for 1 h and then at 23 ^oC for 3h. The resultant mixture was treated with 3 N HCl, extracted with ether (3 x 15 mL), washed with $NaHCO_3$, water, and brine, dried over anhydrous $MgSO_4$, filtered, and concentrated. The residue was dissolved in 4 mL of THF and treated with 3 mL of TBAF in THF (1.0 M) at 23 ^oC for 3 h. After removal of the solvent, the residue was dissolved in a minimum amount of CH_2Cl_2 and subjected to column chromatography (silica gel, 8/1 hexanes-ethyl acetate). Evaporation provided 0.48 g (78%) of (3*R*)-3-methylundecan-1-ol[e] as colorless oil: $[\alpha]_D^{23}$ +3.1^o (c 2.1, $CHCl_3$) [Lit.[e] $[\alpha]_D^{25}$ +2.98^o (c 3.23, $CHCl_3$)]; ^1H NMR (300 MHz, $CDCl_3$, Me_4Si) δ 0.85-0.9 (m, 6 H), 1.1-1.7 (m, 18 H), 3.6-3.7 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.06, 19.60, 22.64, 26.93, 29.31, 29.47, 29.63, 29.92, 31.88, 37.12, 39.93, 61.13; MS (EI, 70 eV) *m/z* (%) 168 (1) [M^+ - H_2O]; IR (neat) 3339, 2925, 1456, 1056 cm^{-1}. **Determination of ee:** (3*R*)-3-Methylundecan-1-ol was treated successively with $COCl_2$ and (*R*)-

1-(1-naphthyl)ethylamine to produce the corresponding urethane. HPLC analysis of this urethane (Chiralcel-OD-H, 4.6 mm x 250 mm, 95:5 hexane-isopropyl alcohol, 1 mL/min) showed two peaks with t_R of 17.1 and 19.4 min and ratio of 95.4:4.6 assignable to the *R,R* and *R,S* diastereomers, respectively, 91% ee.

(3*R*)-3-Methyldecan-1-ol: Yield 74 %; 92% ee; $[\alpha]_D^{23}$ +3.3° (c 2.2, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$, Me_4Si) δ 0.8-0.9 (m, 6 H), 1.05-1.6 (m, 16 H), 3.6-3.75 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.09, 19.62, 22.67, 26.95, 29.35, 29.48, 29.88, 31.88, 37.12, 39.97, 61.25; MS (CI) *m/z* (%) 155 (100) [M^+ + 1]; IR (neat) 3339, 2926, 1464, 1056 cm^{-1}.

(3*R*)-3-Methyltridecan-1-ol:[f] Yield 75 %; 91% ee; $[\alpha]_D^{23}$ +2.65° (c 4.3, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$, Me_4Si) δ 0.85-0.9 (m, 6 H), 1.1-1.45 (m, 19 H), 1.5-1.6 (m, 2 H), 2.0 (bs, 1 H), 3.6-3.75 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si) δ 14.14, 19.66, 22.74, 27.02, 29.42, 29.55, 29.71, 29.75, 29.77, 30.02, 31.98, 37.22, 39.98, 61.13; MS (CI) *m/z* (%) 213 (24.8) (M^+-1); HRMS calcd for $C_{14}H_{30}O$ (M^+-1) 213.2218; Found 213.2214.

(3*R*)-3,7-Dimethyloctan-1-ol[g] (5): Yield 82 %; 93% ee; $[\alpha]_D^{23}$ +4.0° (c 3.15, $CHCl_3$) [Lit.[g] $[\alpha]_D^{25}$ +4.2° (c 5, $CHCl_3$)]; ^1H NMR (300 MHz, $CDCl_3$, Me_4Si) δ 0.8-0.9 (m, 9 H), 1.0-1.65 (m, 10 H), 2.65 (s, 1 H), 3.55-3.7 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.67, 22.63, 22.73, 24.74, 28.01, 29.62, 37.48, 39.35, 39.99, 60.95; MS (EI, 70 eV) *m/z* (%) 157 (1) [M^+ - 1]; IR (neat) 3339, 2927, 1464, 1053 cm^{-1}.

(3*R*)-3,9-Dimethyldecan-1-ol: Yield 66 %; 91% ee; $[\alpha]_D^{23}$ +3.0° (c 1, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$, Me_4Si) δ 0.8-1.0 (m, 9 H), 1.05-1.7 (m, 14 H), 1.85 (s, 1 H), 3.6-3.75 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.59, 22.59 (2 C), 26.95, 27.39, 27.92, 29.48, 30.16, 37.13, 39.00, 39.91, 61.07; MS (EI, 70 eV) *m/z* (%) 168 (2) [M^+ - H_2O]; HRMS calc for $C_{12}H_{24}$ [M^+ - H_2O] 168.1878; Found 168.1880; IR (neat) 3335, 2926, 1464, 1054 cm^{-1}.

(3*R*)-3-Methyl-5-cyclohexylpentan-1-ol:[h] Yield 81 %; 91% ee; $[\alpha]_D^{23}$ +1.5° (c 1.0, $CHCl_3$) [Lit.[h] for (*S*)-enantiomer: $[\alpha]_D^{27}$ –1.0°]; ^1H NMR (300 MHz, $CDCl_3$, Me_4Si) δ 0.8-0.95

(m, 5 H), 1.05-1.75 (m, 17 H), 3.6-3.75 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.61, 26.38, 26.70, 29.74, 33.33, 33.53, 34.28, 34.67, 37.93, 39.88, 61.07; MS (EI, 70 eV) *m/z* (%) 166 (4) [M^+ - H_2O]; IR (neat) 3338, 2922, 1449, 1057 cm^{-1}.

(3*R*)-3-Methyl-6-dimethylphenylsilylhexan-1-ol: Yield 85 %; 91% ee; $[\alpha]_D^{23}$ +5.1° (c 2.5, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.25 (s, 6 H), 0.65-0.8 (m, 2 H), 0.85 (d, *J* = 6.4 Hz, 3 H), 1.0-1.8 (m, 8 H), 3.55- 3.7 (m, 2 H), 7.3-7.4 (m, 3 H), 7.45-7.55 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ -3.04 (2 C), 15.80, 19.49, 21.14, 29.09, 39.89, 41.06, 61.10, 127.66 (2 C), 128.71, 133.49 (2 C), 139.60; MS (EI, 70 eV) m/z (%): 235 (3) [M^+-CH_3]; Anal. Calcd. for $C_{15}H_{26}OSi$: C, 71.93; H, 10.46; Si, 11.21. Found: C, 71.55; H, 10.74; Si, 11.00; IR (neat) 3396, 3069, 2923, 1427, 1113 cm^{-1}.

(4*R*)-4-Methyldodecan-1-ol[i]: Yield 83 %; 92% ee; $[\alpha]_D^{23}$ +1.67° (c 3.78, $CHCl_3$) [Lit.[i] $[\alpha]_D^{22}$ +1.88 (neat)]; ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si) δ 0.85-0.95 (m, 6 H), 1.05-1.7 (m, 19 H), 2.57 (bs, 1 H), 3.59 (t, *J* = 6.7 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si) δ 13.99, 19.53, 22.61, 26.99, 29.30, 29.62, 29.96, 30.21, 31.86, 32.59, 32.94, 36.96, 63.09.

(4*R*)-4,8-Dimethylnonan-1-ol[j]: Yield 78%; 91% ee; $[\alpha]_D^{23}$ +2.2° (c 3.0, $CHCl_3$) [Lit.[j] $[\alpha]_D^{20}$ +2.86° (neat)]; ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si) δ 0.8-0.9 (m, 9 H), 1.0-1.7 (m, 12 H), 2.05-2.25 (m, 1 H), 3.61 (t, *J* = 6.6 Hz, 2 H); ^{13}C NMR (75 mz, $CDCl_3$) δ 19.56, 22.56, 22.65, 24.71, 27.91, 30.28, 32.60, 32.93, 37.17, 39.28, 63.28; MS (EI, 70 eV) *m/z* (%) 154 (1) [M^+ - H_2O]; IR (neat) 3369, 2924, 1456, 1056 cm^{-1}.

(5*R*)-5-Methyltridecan-1-ol:[k] Yield 76%; ~90% ee; $[\alpha]_D^{23}$ +1.75° (c 1.2, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si) δ 0.85-0.9 (m, 6 H), 1.05-1.4 (m, 19 H), 1.45-1.6 (m, 2 H), 1.72 (bs, 1 H), 3.63 (t, *J* = 6.6 Hz, 2 H); ^{13}C NMR (75 mz, $CDCl_3$, Me_4Si) δ 14.14, 19.66, 22.72, 23.26, 27.12, 29.41, 29.73, 30.06, 31.96, 32.78, 33.16, 36.89, 37.06, 63.06; MS (CI) *m/z* (%) 213 (42) (M^+-1); HRMS calcd for $C_{14}H_{30}O$ (M^+-1) 213.2218; Found 213.2219.

Zirconium-Catalyzed Enantioselective Alkylalumination of 1-Alkenes via Transmetallation–Carboalumination Tandem Process: Preparation of (3*R*)-3-Methylnonan-1-ol: Representative Procedure. To an ice-water cooled solution of $ClAl(i\text{-}Bu)_2$ in hexanes (0.5 M, 8 mL) was added dropwise 4 mL of HexLi in hexanes (1.0 M). After stirring at 23 ^oC for 2 h, the solvents were removed by *vacuum* and 6 mL of CH_2Cl_2 was added to the remained mixture followed by 67 mg of (-)-$(NMI)_2ZrCl_2$ (**1**), 2 mL of IBAO in CH_2Cl_2 (1.0 M), and 0.37 g of $H_2C{=}CH(CH_2)_2OTBS$ (2.0 mmol). The mixture was stirred for 96 h at 0 ^oC, quenched with 3 N HCl, extracted with ether (3 x 15 mL), washed with $NaHCO_3$, water, and brine, dried over anhydrous MgSO4, filtered, and concentrated. The residue was dissolved in 4 mL of THF and treated with 3 mL of TBAF in THF (1.0 M) at 23 ^oC for 3 h. After removal of the solvent, the residue was dissolved in a minimum amount of CH_2Cl_2 and subjected to column chromatography (silica gel, 8/1 hexanes-ethyl acetate). Evaporation provided 187 mg (59%) of (3*R*)-3-methyl-nona-1-ol[l] as colorless oil: $[\alpha]_D^{23}$ +3.46^o (c 2.46, $CHCl_3$) [Lit.[1] $[\alpha]_D^{22}$ +3.4^o (c 5.1, $CHCl_3$)]; ^1H NMR (300 MHz, $CDCl_3$, Me_4Si) δ 0.8-0.95 (m, 6 H), 1.0-1.7 (m, 13 H), 2.57 (bs, 1 H), 3.55-3.7 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.97, 19.52, 22.58, 26.85, 29.46, 29.54, 31.85, 37.11, 39.82, 60.84. **Determination of ee:** (3*R*)-3-Methylnona-1-ol was converted to the corresponding carboxylic acid by Jone's oxidation and then to the amide by treating the acid with (*R*)-1-(1-naphthyl)ethylamine. HPLC analysis of this amide (Chiralcel-AD, 4.6 mm x 250 mm, 96:4 hexane-isopropyl alcohol, 0.5 mL/min) showed two peaks (t_R 26.7 and 24.7 min, 96.0:4.0 ratio) assignable to the *R,R* and *R,S* diastereomers, respectively, 92% ee.

(4*R*)-4-Methyldecan-1-ol[m]: Yield 74 %; 91% ee; $[\alpha]_D^{23}$ +1.52^o (c 2.7, $CHCl_3$) [Lit.[m] (*S*)-enantiomer: $[\alpha]_D^{20}$ -1.1 (c 5.33, $CHCl_3$)]; ^1H NMR (300 MHz, $CDCl_3$, Me_4Si) δ 0.75-0.85 (m, 6 H), 0.95-1.6 (m, 15 H), 2.76 (bs, 1 H), 3.51 (t, *J* = 6.7 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.96, 19.50, 22.59, 26.93, 29.58, 30.17, 31.85, 32.57, 32.92, 36.93, 62.99.

Synthesis of (3*R*, 7*R*)-3,7,11-Trimethyldodecan-1-ol (6) (a C_{15} Side Chain of Vitamin E). (3*R*)-3,7-Dimethyloctan-1-ol (**5**) (96% ee) was converted to the corresponding (3*R*)-3,7-dimethyloctanal in 91% yield according to the literature procedure.[n] $[\alpha]_D^{23}$ +14.5° (c 3, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si) δ 0.8-0.9 (m, 6 H), 0.96 (d, *J* = 6.6 Hz, 3 H), 1.1-1.35 (m, 6 H), 1.5-1.6 (m, 1 H), 1.95-2.5 (m, 3 H), 9.76 (t, *J* = 2.4 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.91, 22.49, 22.58, 24.62, 27.85, 28.10, 37.07, 38.93, 51.03, 203.14; MS (CI) *m/z* (%) 157 (100) [M^++1]; IR (neat): 2956, 1727, 1464 cm^{-1}.

(3*R*)-3,7-Dimethyloctanal was converted to (4*R*)-4,8-dimethylnon-1-ene in 84% yield by Wittig reaction.[o] $[\alpha]_D^{23}$ +6.7° (c 2.9, CH_2Cl_2); ^{1}H NMR (30 MHz, $CDCl_3$, Me_4Si) δ 0.8-0.9 (m, 9 H), 1.05-1.6 (m, 8 H), 1.8-2.15 (m, 2 H), 4.9-5.1 (m, 2 H), 5.6-5.9(m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.46, 22.61, 22.70, 24.83, 27.98, 32.82, 36.82, 39.30, 41.49, 115.37, 137.78; MS (EI, 70 eV): m/z 154 (1) [M^+]; HRMS calcd for $C_{11}H_{22}$: 154.1722. Found 154.1724; IR (neat) 3078, 2927, 1641, 1463 cm^{-1}.

(3*R*, 7*R*)-3,7,11-Trimethyldodecan-1-ol (6):[p] To a solution of (-)-$(NMI)_2ZrCl_2$ (**1**) (67 mg, 0.1 mmol) in CH_2Cl_2 (8 mL) were added (3*R*)-3,7-dimethyl-octyldiisobutylalane (2.0 mmol), *in situ* prepared by the hydroalumination of (4*R*)-4,8-dimethylnon-1-ene with DIBAH, and IBAO (3.0 mmol, 1 M solution in CH_2Cl_2) under an argon atmosphere. After the mixture was stirred at 23 °C for 5 min, the resultant orange solution was cooled to 0 °C and 372 mg (3 mmol) of H_2C=$CH(CH_2)_2OTBS$ was added, followed by triisobutylaluminum (396 mg, 2.0 mmol). The reaction mixture was stirred at 15 °C for 24 h. The resultant mixture was quenched by 1 mL of water at *ca.* –50 °C, treated with 3 N HCl, extracted with ether (3 x 15 mL), washed with $NaHCO_3$, water, and brine, dried over anhydrous $MgSO_4$, filtered, and concentrated. The residue was dissolved in 4 mL of THF and treated with 4 mL of TBAF (1.0 M, THF) at 23 °C for 3 h. After removal of the solvent, the residue was dissolved in a minimum amount of CH_2Cl_2 and subjected to column chromatography (silica gel, 10/1 hexanes-ethyl acetate) to give the alcohol **6**.

Yield 72%; 96% *R* at C-3; $[\alpha]_D^{23}$ +3.6° (c 2.0, $CHCl_3$) [Lit.[p] $[\alpha]_D^{25}$ +3.55° (c 1.075, $CHCl_3$)]; ^1H NMR (300 MHz, $CDCl_3$, Me_4Si) δ 0.8-0.9 (m, 12 H), 1.0-1.65 (m, 18 H), 3.6-3.7 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.66, 19.71, 22.60, 22.70, 24.35, 24.77, 27.95, 29.51, 32.77, 37.25, 37.35, 37.48, 39.34, 39.94, 61.22; MS (CI) *m/z* (%) 227 (73) [M^+ - 1]; IR (neat) 3318, 2922, 1463, 1054 cm^{-1}.

Optical Purification of Alcohols 5 and 6. Repesentative Procedure.[q] A mixture of alcohol **5** (560 mg, 3.54 mmol), *p*-phenylene diisocyanate (283 mg, 1.77 mmol), and 1,4-diazabicyclo[2,2,2]octane (5 mg) in benzene (5 mL) was stirred at 50 °C for 1 h. The crude product was purified by flash chromatography to give 800 mg of the corresponding bisurethane. Yield, 95%; Mp. 118-120 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 0.85-0.95 (m, 18 H), 1.1-1.75 (m, 20 H), 4.15-4.25 (m, 4 H), 6.64 (bs, 2 H), 7.3 (bs, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.48 (2C), 22.56 (2 C), 22.65 (2 C), 24.59 (2 C), 27.92 (2 C), 29.75 (2 C), 35.87 (2 C), 37.15 (2 C), 39.18 (2 C), 63.83 (2 C), 119.59 (4 C), 133.59 (2 C), 153.87 (2 C); MS (EI, 70 eV) *m/z* (%) 476 (75) [M^+]; Anal. Cacld. For $C_{28}H_{48}N_2O_4$: C, 70.55; H, 10.15; N, 5.88. Found: C, 70.53; H, 10.18; N, 5.8; IR (KBr) 3321, 2925, 1696, 1526, 1079 cm^{-1}. After recrystallization from MeOH, the melting point of the bisurethane was raised to 122.5-123.5 °C. Yield 78%; $[\alpha]_D^{23}$ +3.8° (c 1.8, $CHCl_3$). A sample of the purified bisurethane (1.0 g) was refluxed with 2 N NaOEt ethanol solution (20 mL) for 2 h to produce the alcohol **5** in 96% ee (95% yield).

Similarly, alcohol **6** of 96% *R* at the C-3 was purified up to 99% *R* at the C-3 in 65% recovery yield.

References and Notes

a. Erker, G.; Aulbach, M.; Knickmeier, M.; Wingbermuhle, D.; Kruger, C., Nolte, M.; Werner, S. *J. Am. Chem. Soc*. **1993**, 115, 4590.

b. Dolbier, W. R. Jr.; Rong, X.X.; Bartberger, M. D.; Koroniak, H.; Smart, B. E.; Yang, Z.-Y. *J. Chem. Soc., Perkin Trans. 2*, **1998**, 219.

c. Al-Husaini, A. H.; Muqtar, M.; Ali, S. A. *Tetrahedron* **1991**, *47*, 7719.

d. Ziegler, K.; Martin, H.; Krupp, F. *Liebigs Ann. Chem.* **1960**, *629*, 14.

e. Odinokov, V. N.; Akhmetova, V. R.; Khasanov, Kh. D.; Abduvakhabov, A. A.; Khalilov, L. M.; Cheskis, B. A.; Moiseenkov, A. M.; Tolstikov, G. A. *J. Org. chem.. USSR (Engl. Transl.)* **1992**, *28*, 908.

f. Pempo, D.; Cintrat, J.-C.; Parrain, J.-L.; Santalli, M. *Tetrahedron* **2000**, *56*, 5493.

g. Cohen, N.; Eichel, w. F.; Lopresti, R. J.; Neukom, C.; and Saucy, G. *J. Org. Chem*. **1976**, 41, 3505.

h. Levene, P. A.; Marker, R. E. *J. Biol. Chem*. **1935**, *110*, 311.

i. Mori, K; Tamada, S. *Tetrahedron* **1979**, *35*, 1279.

j. Helmchen, G.; Schmierer, R. *Tetrahedron Lett*. **1983**, *24*, 1235.

k. Shionozaki, Y.; Shibata, T. *Ger. Offen*. **1987**, 7pp.

l. Tsunoda, T.; Nagaku, M.; Nagino, C.; Kawamura, Y.; Ozaki, F.; Hioki, H.; Itô, S. *Tetrahedron Lett.* **1995**, *36*, 2531.

m. Raederstorff, D.; Shu, A. Y. L.; Thompson, J. E.; Djerassi, C. *J Org. Chem*. **1987**, *52*, 2529.

n. Dess, D. B.; Martin, J. C. *J. Org. Chem*. **1983**, *48*, 4156.

o. Gäbler, A.; Boland, W.; Preiss, U.; Simon, H. *Helv. Chim. Acta* **1991**, *74*, 1773.

p. Gramatica, P.; Manitto, P.; Monti, D.; Speranza, G. *Tetrahedron* **1986**, *24*, 6687.

q. Huo, S.; Negishi, N. *Org. Lett*. **2001**, *3*, 3253.