Metal-Catalyzed Acyl Transfer Reactions of Enol Esters: Role of $Y_5(O^iPr)_{13}O$ and $(thd)_2Y(O^iPr)$ as Transesterification Catalysts

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Supporting Information

General. All catalyzed reactions were carried out under an inert atmosphere of nitrogen in a Vacuum Atmospheres drybox, or by Schlenk techniques. Methylene chloride was distilled from calcium hydride under nitrogen and stored over molecular sieves. All chemicals were purchased from Aldrich Chemical Company unless otherwise noted. Analytical TLC was done on E. Merck precoated (0.25 mm) silica gel 60 F_{254} plates. Column chromatography was conducted by using silica gel 40 (Scientific Adsorbents Incorporated, Microns Flash). ^{1}H NMR spectra were recorded on a Brucker AM-200, AM-250 and AM-300 spectrometers in $CDCl_3$. Gas chromatographic analyses were performed on a Hewlett-Packard 5890 equipped with an HP-ultra-1 crosslinked methyl silicone capillary column (25 m length x 0.2 mm i.d.) and an FID detector connected to an HP 3396 integrator. As carrier gas helium was used. The retention times recorded are reported with programmed runs as indicated under each experiments. In all cases base line separation of the relevant components were observed**.** GC separations of enantiomers of the amino acid esters were accomplished using Chirasil L-Val on WCOT fused silica (25 m x 0.25 mm, 0.12 mm film thickness) capillary GC column purchased from Chrompack (1130 Route 202 South, Raritan, New Jersey 08869). Isopropenyl benzoate,[1] t-butyl cholate,[2] epoxygeraniol,[3] diphenylallyl alcohol[4] and benzyl 2-amino-4,6-O-benzylidene-2-deoxy-_-D-glucopyranoside[5] were prepared according to the procedures described in the literature. The yttrium complexes $Y_5(O^iPr)_{13}O$ (**2**)[6] and $(thd)_2Y(O^iPr)$ (**3**)[7] have also been described in the literature, and the former is available from Strem Chemicals.

Reactions listed in the Table

Benzyl acetate (Table, entry 1). The mixture of benzyl alcohol (109.2 mg; 1 mmol), $Y_5(O^iPr)_{13}O$ (6.2 mg; 0.005 mmol) and isopropenyl acetate (1 mL, 9.1 mmol) was stirred for 1 h at room temperature, and evaporated in vacuo to get a quantitative yield of the product.

Control experiments: Reaction in the absence of a catalyst. A mixture of benzyl alcohol (108.7 mg, 1 mmol) and vinyl acetate (1 mL) was stirred at room temperature for 96 h, and the mixture was analyzed by gas chromatography. No trace of products was observed. In a separate experiment, the reaction was repeated under strictly anhydrous conditions using a flask and a stir bar, both rinsed with 10% HCl, 6N NaOH, water and finally acetone. No reaction was observed for several days.

Preparative run using vinyl acetate with 1/2000 equivalents of the catalyst (Table entry 13). A mixture of benzyl alcohol (1087.2 mg; 10 mmol), $Y_5(O^iPr)_{13}O$ (6.2 mg; 0.005 mmol), and vinyl acetate (4 mL; 43.4 mmol) was stirred for 42 h at room temperature, and the product was collected by evaporation of the excess solvent and reagents in vacuo to get a quantitative yield .

Attempted reaction with isopropenyl acetate and 1/2000 equivalents of the catalyst: A mixture of benzyl alcohol (1093.4 mg; 10.1 mmol), $Y_5(O^iPr)_{13}O$ (6.2 mg; 0.005 mmol) and isopropenyl acetate (4 mL; 36.3 mmol) was stirred for 11 h at room temperature. The reaction mixture was analyzed by gas chromatography. Less than 2% conversion was observed.

_-*Methylbenzyl acetate (Table, entry 2).* The mixture of α-methylbenzyl alcohol (123.4 mg; 1 mmol), $Y_5(O^iPr)_{13}O$ (10.5 mg; 0.0085 mmol) and isopropenyl acetate (1 mL, 9.1 mmol) was stirred for 1.5 h at room temperature, and evaporated in vacuo to get a quantitative yield of the product (GC, NMR).

Cyclohexyl acetate (Table, entry 3). The mixture of cyclohexanol (102.8 mg; 1 mmol), $Y_5(O^iPr)_{13}O$ (6.2 mg; 0.005 mmol) and isopropenyl acetate (1 mL) was stirred for 1.5 h at room temperature, and evaporated in vacuo to get a quantitative yield of the product (GC).

Cyclohexyl acetate. Preparative run: The mixture of cyclohexanol (553.4 mg; 5.5 mmol), $Y_5(O^iPr)_{13}O$ (31.2 mg; 0.0254 mmol) and isopropenyl acetate (5 mL) was stirred for 3 h at room temperature (95% GC yield). The mixture was passed through a short column, hexane as the eluant, and evaporated on rotavapor (at 50 ^oC water bath) and evaporated in vacuo for 2 min to get 735.7 mg (94% yield) of the product.

1,2-diacetoxy-1-phenyl-ethane (Table entry 4). The mixture of 1-phenyl-1,2-ethanediol (138.4 mg; 1 mmol), $Y_5(O^iPr)_{13}O$ (12.6 mg; 0.01 mmol) and isopropenyl acetate (1 mL) was stirred for 1.5 h at room temperature, and evaporated in vacuo to give diacetylated product (99 % GC yield) as an oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 2.02 (s, 3 H, -OAc), 2.08 (s, 3 H, -OAc), 4.24-4.36 (m, ABX, 2 H, PhCHC<u>H</u>$_2$), 6.00 (dd, *J* = 4.2, 7.6 Hz, 1 H, PhC<u>H</u>CH$_2$), 7.27-7.35 (m, 5 H, Ph); GC (60°C/5min-20°C/min-250°C) t_R = 12.62 min.

Reactions listed in equations 2-11

Comparison of vinyl acetate and isopropenyl acetate for the synthesis of cyclohexyl acetate (eq 2). (a) A mixture of cyclohexanol (101.2 mg, 1 mmol), $Y_5(O^iPr)_{13}O$ (6.2 mg, 0.005 mmol) and *isopropenyl acetate* (1 mL, 9.1 mmol) was stirred for 1.5 h at room temperature, and the mixture was concentrated in vacuo to get 96% yield of the expected product. (GC and ^{1}H NMR).
(b) A mixture of cyclohexanol (101.7 mg; 1 mmol), $Y_5(O^iPr)_{13}O$ (6.2 mg; 0.005 mmol) and *vinyl acetate* (1 mL, 10.9 mmol) was stirred for 1.5 h at room temperature, and the mixture was concentrated in vacuo to get 67% yield of the expected product (GC and ^{1}H NMR).

^{t}Butyl 3-O-acetyl cholate (eq 4). To the solution of ^{t}butyl cholate (117.6 mg; 0.25 mmol), and $Y_5(O^iPr)_{13}O$ (9.3 mg; 0.0075 mmol) in toluene (1 mL), isopropenyl acetate (1 mL, 9.1 mmol) was added. The reaction mixture was stirred for 24 h at room temperature. Flash chromatography of the crude product with ethyl acetate-hexane (1:1) as eluant, gave ^{t}butyl 3-*O*-acetyl-cholate (117.8 mg, 93 % yield) as a white solid. TLC (EtOAc/hexane (2:3)) R_f = 0.34; ^{1}H NMR (300 MHz, $CDCl_3$) δ *inter alia* 3.85 (q, 1 H, HO-C(7)-<u>H</u>), 3.99 (t, 1 H, HO-C(12)-<u>H</u>), 4.57 (m, 1 H, AcO-C(3)-<u>H</u>); (Lit. ref. 2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 68.3 (d), 72.9 (d), 74.3 (d), 79.9 (s), 170.7 (s), 173.6 (s).

(2S, 3S)-3-methyl-3-(4-methylpent-3-enyl)oxiranemethanol acetate (eq 5). A mixture of (2*S*, 3*S*)-epoxygeraniol (170.4 mg; 1 mmol), $Y_5(O^iPr)_{13}O$ (6.2 mg; 0.005 mmol) and vinyl acetate (1 mL, 9.1 equiv.) was stirred for 5 min at room temperature. Gas chromatographic analysis showed an exceptionally clean reaction, with nearly quantitative conversion of the starting material. The solvent was evaporated in vacuo, and the crude product was passed through a short column using hexane as eluant, to get 141.7 mg (67% yield) of the acetate. Under comparable conditions, reaction with isopropenyl acetate was found to proceed to ~ 40% conversion in 4 h.
^{1}H NMR (300 MHz, $CDCl_3$) *inter alia* δ 2.90 (dd, *J* = 6, 6 Hz, 1 H), 4.09 (ABX, υ_A = 4.22, υ_B = 3.96, J_{AB} = 12 Hz, J_{AX} = 6 Hz, J_{BX} = 6 Hz, 2 H), 5.00 (m, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) _ 16.6 (q), 17.4 (q), 20.5 (q), 23,4 (t), 25.4 (q), 38.1 (t), 59.4 (d), 60.3 (s), 63.2 (t), 123.1 (d), 131.9 (s), 170.5 (s).

Synthesis of cinnamyl acetate (Table entry 5). A mixture of cinnamyl alcohol (141.2 mg; 1 mmol), $Y_5(O^iPr)_{13}O$ (6.4 mg; 0.005 mmol) and isopropenyl acetate (1 mL; 9.1 mmol) was stirred for 10 min at room temperature. Gas chromatographic analysis showed an exceptionally clean reaction, with nearly quantitative conversion (>99%) of the starting material. The solvent was evaporated in vacuo to give acetate product as an oil.

Preparative run using vinyl acetate with 1/2000 equivalents of the catalyst (Table entry 12). A mixture of cinnamyl alcohol (1370.1 mg; 10.2 mmol), $Y_5(O^iPr)_{13}O$ (6.2 mg; 0.005 mmol) and vinyl acetate (4 mL; 4.3 equiv.) was stirred for 48 h at room temperature. Flash chromatography, with ethyl acetate-hexane (1:3) as eluant, gave 1287.0 mg (72% yield) of cinnamyl acetate. ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.09 (s, 3 H, -COC<u>H</u>$_3$), 4.73 (d, *J* = 6.4 Hz, 2 H, -C<u>H</u>$_2$OAc), 6.29 (dt, *J* = 15.9, 6.4 Hz, 1 H, PhCH=C<u>H</u>-), 6.65 (d, *J* = 15.9 Hz, 1 H, PhC<u>H</u>=CH-), 7.25-7.41 (m, -Ph,); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.7 (q), 64.8 (t), 123.1 (d), 126.4 (d), 127.9 (d), 128.4 (d), 134.0 (d), 136.1 (s), 170.5 (s); GC (60°C/5min-20°C/min-250°C) t_R = 13.052.

(E)-1,3-Diphenylallyl acetate (eq 6). The mixture of 1,3-diphenylallyl alcohol (2101.4 mg; 10 mmol), $Y_5(O^iPr)_{13}O$ (123.4 mg; 0.1 mmol) and isopropenyl acetate (10 mL) was stirred for 1.5 h at room temperature. Removal of the solvent, followed by flash chromatography on silica gel with ethyl acetate-hexane (1:9) as the eluant, gave 2279 mg (90 % yield) of the allyl acetate.
^{1}H NMR (300 MHz, $CDCl_3$) δ 2.15 (s, 3 H), 6.37 (dd, J = 15.7 Hz, 6.8 Hz, 1H), 6.47 (d, J = 6. 7 Hz, 1 H), 6.66 (d, *J* = 15.7 Hz, 1 H), 7.25-7.43 (m, aromatic); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.3 (q), 76.1 (d), 126.7 (d), 127.0 (d), 127.5 (d), 128.1 (d), 128.6 (d), 132.6 (d), 136.2 (s). 139.2 (s), 170.0 (s); GC(60°C/5min-20°C/min-250°C) t_R = 17.19 min.

3-Hydroxybenzyl acetate (eq 7). A mixture of 3-hydroxybenzyl alcohol (621.2 mg; 5 mmol), $Y_5(O^iPr)_{13}O$ (32.3 mg; 0.026 mmol) and vinyl acetate (5 mL) was stirred for 18 h at room temperature. Flash chromatography, with ethyl acetate-hexane (1:4) as eluant, gave 776.2 mg (93 % yield) of 3-hydroxybenzyl acetate isolated. White solid, TLC (EtOAc/hexane (1:4)) R_f = 0.23; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.12 (s, 3 H), 5.07 (s, 2 H), 6.18 (s, 1 H), 6.80-6.91 (m, 3 H), 7.22 (t, *J* = 7.8 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.9 (q), 66.3 (t), 115.1 (d), 115.3 (d), 120.1 (d), 129.8 (d), 137.3 (s), 156.1 (s), 171.8 (s); GC (temperature program: 60°C/5min-20°C/min-250°C) t_R = 13.30 min.

(S)-N-Ac-Phenylalanine ethyl ester (eq 8). (*L*)-Phenylalanine ethyl ester (192.3 mg; 1 mmol) and isopropenyl acetate (1 mL, 9.1 mmol) without any catalysts was stirred for 24 h at room temperature. The excess isoproenyl acetate was evaporated in vacuo to get a quantitative yield

of the product (GC and NMR). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.22 (t, *J* = 7 Hz, 3 H, -$OCH_2C\underline{H}_3$), 1.96 (s, 3 H, -NAc), 2.99-3.12 (m, ABX, 2 H, $PhC\underline{H}_2CHNHAc$), 4.15 (q, *J* = 7 Hz, 2 H, -$OC\underline{H}_2CH_3$), 4,85 (ddd, *J* = 7.4, 6, 5.8 Hz, 1 H, $PhCH_2C\underline{H}NHAc$), 6.04 (d, *J* = 7.4 Hz, 1 H, $PhCH_2C\underline{H}NAc$), 7.10 (dd, J = 7.2, 2 Hz, 2 H, -Ph), 7.19-7.30 (m, 3 H, -Ph); GC (60°C/5min-20°C/min-250°C) t_R = 14.35. The absence of any racemization was confirmed by GC analysis of the product on Chirasil S-val column where base line separation of enantiomers have been observed on an authentic sample of the racemic product.[8]

Reaction of (S)-Phenylalanine ethyl ester with isopropenyl acetate in the presence of $Y_5(O^iPr)_{13}O$. A mixture of (*L*)-Phenylalanine ethyl ester (192.1 mg; 1 mmol), $Y_5(O^iPr)_{13}O$ (6.1 mg; 0.005 mmol) and isopropenyl acetate(1 mL, 9.1 mmol) was stirred for 24 h at room temperature. The excess isopropenyl acetate was removed in vacuo and the product was analyzed by GC and NMR to reveal ~4% conversion into the amide. *(S)-Phenylalanine ethyl ester:* ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.21 (t, *J* = 7 Hz, 3 H, -$OCH_2C\underline{H}_3$), 1.48 (s, -NH_2), 2.95 (ABX, υ_A = 3.05, υ_B = 2.84, J_{AB} = 13.5 Hz, J_{AX} = 5.4 Hz, J_{BX} = 7.8 Hz, 2 H, $PhC\underline{H}_2$), 3.68 (dd, *J* = 5.4, 7.8 Hz, 1 H, $PhCH_2C\underline{H}NH_2$), 4,14 (q, *J* = 7 Hz, 2 H, -$OC\underline{H}_2CH_3$), 7.16-7.28 (m, 5 H, -Ph); GC (60°C/5min-20°C/min-250°C) t_R = 12.43.

(R)-N-Acetyl Phenylglycine methyl ester (eq 8). A mixture of (*R*)-Phenylglycine methyl ester (166.7 mg; 1 mmol) and isopropenyl acetate (1mL, 9.1 mmol) was stirred for 24 h at room temperature without any catalysts, the low boiling components were removed on the pump and the product was analyzed by GC and NMR. ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.89 (s, 3 H, -NAc), 3.59 (s, 3 H, -OMe), 5.46 (d, *J* = 6.6 Hz, 1 H, $PhC\underline{H}$), 6.56 (d, *J* = 6.6 Hz, 1 H, -$N\underline{H}Ac$), 7.19-7.24 (m, 5 H, -Ph); GC (60°C/5min-20°C/min-250°C) t_R = 13.29.

Reaction of (R)-Phenylglycine methyl ester with isopropenyl acetate in the presence of $Y_5(O^iPr)_{13}O$. The mixture of (*R*)-Phenylglycine methyl ester (165.4 mg; 1 mmol), $Y_5(O^iPr)_{13}O$ (6.2 mg; 0.005 mmol)and isopropenyl acetate (1mL, 9.1 mmol) was stirred for 24 h at room temperature, and evaporated in vacuo. Analysis by GC and NMR showed mostly starting material. *(R)-Phenylglycine methyl ester:* ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.80 (br, 2 H, -NH_2), 3.57 (s, 3 H, -OMe), 4.49 (s, 1 H, $PhC\underline{H}$), 7.18-7.25 (m, 5 H, -Ph); GC (60°C/5min-20°C/min-250°C) t_R = 11.16.

Reaction of aminoacid ester with isopropenyl aceateunder stoichiometric conditions.

A mixture of (L)-phenylalanine ethyl ester (1 mmol), and isopropenyl acetate (1.09 mmol) in CH_2Cl_2 (1 mL) was stirred at room temperature for 22 h. Conversion (21.5%) was

determined by GC. Under identical conditions (o.54 mmol each of the reagents in 0.6 mL benzene) in benzene 55% conversion was observed in in 22 h.

Benzyl 2-amino-3-O-acetyl-4,6-O-benzylidene-2-deoxy-α-D-glucopyranoside (eq 9). A mixture of benzyl 2-amino-4,6-*O*-benzylidene-2-deoxy-α-*D*-glucopyranoside (177.3 mg; 0.5 mmol), $Y_5(O^iPr)_{13}O$ (18.5 mg; 0.015 mmol), isopropenyl acetate (2 mL) and toluene (1 mL, 9.1 mmol) was stirred for 2 h at room temperature. Isolation of the product by evaporation of the solvent followed by flash chromatography on silica gel with ethyl acetate as eluant, gave 161 mg (82 % yield) of the acetoxy compound. Solid (mp > 220 ^oC); TLC (EtOAc) R_f = 0.3; ^1H NMR (300 MHz, $CDCl_3$) δ 1.48 (br, NH_2), 2.13 (s, 3 H, -OAc), 2.95 (dd, J = 10.0, 3.6 Hz, 1 H, H_2), 3.56 (dd, J = 9.5, 9.5 Hz, 1 H, H_4), 3.74 (dd, J = 10.2, 10.2 Hz, 1 H, H_{6ax}), 3.96 (ddd, J = 10.2, 9.5, 4.8 Hz, 1 H, H_5), 4.24 (dd, J = 10.2, 4.8 Hz, 1 H, H_{6eq}), 4.66 (ABq, J_{AB} = 11.7 Hz, $\Delta\upsilon_{AB}$ = 60.9 Hz, 2 H, PhC$\underline{H}_2$O), 4.97 (d, J = 3.6 Hz, 1 H, H_1), 5.28 (dd, J = 10.0, 9.5 Hz, 1 H, H_3), 5.49 (s, 1 H, PhC$\underline{H}$), 7.31-7.46 (m, aromatic, 2 x Ph); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.0 (q), 55.5 (d), 63.1 (d), 69.0 (t), 70.1 (t), 73.5 (d), 79.7 (d), 99.8 (d), 101.4 (d), 126.1 (d), 128.0 (d), 128.1 (d), 128.2 (d), 128.5 (d), 128.9 (d), 136.9 (s), 137.2 (s), 170.7 (s); Anal. calcd. for $C_{22}H_{25}NO_6$: C, 66.14; H, 6.31; N, 3.51. Found: C, 66.30; H, 6.33; N, 3.38.

Selective O vs N-Acylation: 2-Piperidinemethanol acetate (eq. 10.) A mixture of 2-piperidinemethanol (230.3 mg; 2 mmol), $Y_5(O^iPr)_{13}O$ (12.3 mg; 0.01 mmol) and isopropenyl acetate (1 mL; 4.5 equiv.) was stirred for 5 min at room temperature. Gas chromatographic analysis showed an exceptionally clean reaction, with nearly quantitative conversion of the starting material. The solvent was evaporated in vacuo to give *O*-acylation product as oil. IR (neat): 1729.9 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) *inter alia* δ 3.69-3.96 (m, 2 H, ABX, -C$\underline{H}_2$OAc), 2.96 (m, 1 H, H_2), 2.66 (m, 1 H, $H_{6'}$), 2.51 (m, 1 H, $H_{6''}$), 1.94 (s, 3 H, -COC$\underline{H}_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.6 (q), 24.0 (t), 26.0 (t), 28.5 (t), 46.3 (t), 54.9 (d), 68.6 (t), 170.6 (s); GC (60^oC/5min-20^oC/min-250^oC) t_R = 10.937. Amine oxalate salt preparation: The crude product was dissolved in ethyl acetate and added to a ethyl acetate solution containing oxalic acid dihydrate (251.9 mg; 2 mmol) to form amine oxalate salt. The salt was recrystallized from EtOAc/$CHCl_3$ to give white fine crystals. Anal. Calcd for $C_{10}H_{17}NO_6$: C, 48.56; H, 6.93; N, 5.67. Found: C, 48.70; H, 6.98; N, 5.72.

Selective O vs N-Acylation: Reaction of a 1:1 mixture of alcohol, amine and isopropenyl acetate in the presence of 1 mol% of $Y_5(O^iPr)_{13}O$ (eq. 11). A mixture of α-methylbenzyl alcohol (122.5 mg; 1 mmol), *L*-(-)-α-phenylethylamine (121.6 mg; 1 mmol), isopropenyl acetate (107.0 mg; 1 mmol), $Y_5(O^iPr)_{13}O$ (12.2 mg; 0.01 mmol) and benzene (1 mL) was stirred for 4 h at room

temperature. Analysis of the crude product by GC showed the product to be a mixture of amine (31%), the acetate ester (49%), acetone imine of α-methylbenzyl amine (18%) and <0.1 % of the acetamide. ^{1}H and ^{13}C NMR confirmed the structures of the major components. The benzylic proton absorption characteristic of the acetamide (δ 5.08) was absent in the ^{1}H NMR spectrum. Absence of the signals due to the CH_3C(O)-N in proton (δ 1.91) and carbon (δ 21.63, 169.09) NMR also confirmed the exclusive *O*-acylation.

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