Supporting Information
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Supporting Information for
A Simple, General, and Highly Chemoselective Acetylation of Alcohols Using Ethyl Acetate as the Acetyl Donor Catalyzed by a Tetranuclear Zinc Cluster

Takanori Iwasaki, Yusuke Maegawa, Yukiko Hayashi, Takashi Ohshima* and Kazushi Mashima*

Department of Chemistry, Graduate School of Engineering Science, Osaka University, Toyonaka, Osaka 560-8531, Japan
*To whom the correspondence should be addressed.
E-mail: ohshima@chem.es.osaka-u.ac.jp; mashima@chem.es.osaka-u.ac.jp

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a Reaction conditions: alcohol 2 (1.0 mmol), amine 6 (1.0 mmol), Zn₄(OCOCF₃)₆O (1) (5 mol% on zinc), and EtOAc (1.7 mL) were refluxed for 18 hours in an argon atmosphere. b GC yield.

Scheme S1

1) Zn₄(OCOCF₃)₆O (1) (1.25 mol%) EtOAc (17 eq) reflux, 12 h
2) (Boc)₂O, Et₃N
   Ac₂O (1.0 eq)
   Et₃N, CH₂Cl₂
   0 °C to rt, 18 h
3) Ac₂O (5.0 eq)
   Et₃N, CH₂Cl₂
   0 °C to rt, 18 h

BocN
97%
Boc-9
AcN
95%
10
AcN
>99%
11
**General:** Nuclear magnetic resonance (1H NMR, 13C NMR, and 19F NMR) spectra were measured on a Varian MERCURY300-C/H spectrometer operating at 300 MHz (1H NMR), 75 MHz (13C NMR), and 282 MHz (19F NMR), in 5 mm NMR tubes. All 1H NMR chemical shifts were reported in ppm relative to internal references of TMS at δ 0.00. All 13C NMR chemical shifts were reported in ppm relative to carbon resonance in chloroform-d$_6$ at δ 77.00, THF-d$_8$ at δ 25.20, and DMSO- d$_6$ at δ 39.70. The 19F NMR chemical shifts were reported in ppm relative to external reference of α,α,α-trifluorotoluene at δ –63.90. Low and high resolution mass spectra were recorded by JEOL JMS-700. IR spectra were recorded on Jasco FT/IR-410 spectrometer. Elemental analyses were conducted by Perkin-Elmer 2400II. Melting points were measured using Yanaco micro melting point apparatus. GC analyses were recorded on a Shimadzu GC-14A gas chromatograph with J&W Scientific DB-5 column. All catalytic reactions were carried out by the standard Schlenk techniques under an argon atmosphere. Ethyl acetate was distilled from phosphorus(V) oxide. Alcohol 2e was synthesized according to the literature.1 Alcohols 2f-i were prepared by the standard protection reactions2 of p-xylene glycol with 1 equivalent of protecting reagent using 1,4-dioxane as a solvent due to the less solubility of p-xylene glycol. D-Glucose derivative 2m was prepared according to the literature.3 All other commercially available alcohols were used as received. Authentic esters 3s-u and amides 7s-u were prepared by standard acylation reaction using acetic anhydride in pyridine.2,4–9

**Preparation of tetranuclear zinc cluster 1.** Under an inert atmosphere of argon, zinc trifluoroacetate hydrate (845 mg, 2.73 mmol as a monohydrate) was heated at 120 °C for 4 h under reduced pressure (≤0.02 mmHg) to remove water. The resulting dry powder was then heated at 360 °C on a sand bath, and μ-oxo-tetranuclear zinc cluster 1 was sublimed from the reaction mixture. The zinc cluster was collected and stored under an inert atmosphere of argon (545 mg, 84%); white solid; IR (nujol NaCl, v/cm–1) 2923, 1701, 1202, 856, 796, 730; 13C NMR (75 MHz, THF-d$_6$, 35 °C) δ 117.0 (q, $J_{C,F} = 288$ Hz, CF$_3$COO), 163.8 (q, $J_{C,F} = 38$ Hz, CF$_3$COO); 19F NMR (282 MHz, THF-d$_8$, 35 °C) δ –78.88 (s); MS (ESI) m/z (relative intensity) 933 ([M+2H$_2$O+H$^+$], 3); Anal. calcd for C$_{12}$F$_{18}$O$_{13}$Zn$_4$: C15.08%; found C 15.52%.
General procedure for the acetylation of various alcohols catalyzed by tetranuclear zinc cluster. 

Zn₄(OCOCF₃)₆O (1) (0.038 mmol), alcohol 2 (3.0 mmol), and ethyl acetate (5.0 mL, 0.6 M) were refluxed for periodic time in an argon atmosphere (see right figure). The resulting mixture was concentrated and purified by silica gel column chromatography to give acetylated product 3.

4-Nitrobenzyl acetate (3a)

Purified by flush column chromatography (silica gel, Hexane/EtOAc = 8/1); white solid; mp 78-79 °C; IR (film NaCl, ν/cm⁻¹) 3074, 1738, 1602, 1520, 1449, 1346, 1254, 1240, 837, 742; ¹H NMR (300 MHz, CDCl₃, 35 °C) δ 2.15 (s, 3H, acetyl), 5.20 (s, 2H, benzyl), 7.51 (d, J = 8.7 Hz, 2H, Ar), 8.22 (d, J = 8.7 Hz, 2H, Ar); ¹³C NMR (75 MHz, CDCl₃, 35°C) δ 20.86, 64.76, 123.68, 128.28, 143.10, 147.65, 170.24; MS (EI) m/z (relative intensity) 195 ([M]+, 32), 153 (100), 136 (20); HRMS (EI) m/z calcd. for C₉H₈NO₄ 195.0532 found 195.0560.

Benzyl acetate (3b)

Purified by flush column chromatography (silica gel, Hexane/EtOAc = 20/1); colorless oil; IR (neat NaCl, ν/cm⁻¹) 3034, 1742, 1281, 1362, 1230, 1027, 912, 734, 698; ¹H NMR (300 MHz, CDCl₃, 35 °C) δ 2.05 (s, 3H, acetyl), 5.08 (s, 2H, benzyl), 7.3 (m, 5H, Ph); ¹³C NMR (75 MHz, CDCl₃, 35°C) δ 20.78, 66.05, 127.90, 127.93, 128.25, 135.79, 170.31; MS (EI) m/z (relative intensity) 150 ([M]+, 39), 108 (100), 91 (57); HRMS (EI) m/z calcd. for C₉H₁₀O₂ 150.0681 found 150.0659.

4-Chlorobenzyl acetate (3c)

Purified by flush column chromatography (silica gel, Hexane/EtOAc = 20/1); colorless oil; IR (neat NaCl, ν/cm⁻¹) 2956, 1739, 1494, 1379, 1362, 1227, 1094, 1030, 1015, 806; ¹H NMR (300 MHz, CDCl₃, 35 °C) δ 2.08 (s, 3H, acetyl), 5.05 (s, 2H, benzyl), 7.2–7.3 (m, 4H, Ar); ¹³C NMR (75 MHz, CDCl₃, 35°C) δ 20.84, 65.29, 128.52, 129.38, 133.89, 134.36, 170.31; MS (EI) m/z (relative intensity) 184 ([M]+, 13), 142 (20), 125 (21); HRMS (EI) m/z calcd. for C₉H₈O₂Cl 184.0291 found 184.0272.

4-Bromobenzyl acetate (3d)
Purified by flush column chromatography (silica gel, Hexane/EtOAc = 20/1); colorless oil; IR (neat NaCl, v/cm⁻¹) 2955, 1746, 1490, 1377, 1362, 1227, 1071, 1031, 1012, 801; ¹H NMR (300 MHz, CDCl₃, 35 °C) δ 2.08 (s, 3H, acetyl), 5.04 (s, 2H, benzyl), 7.21 (d, J = 8.7 Hz, 2H, Ar), 7.47 (d, J = 8.7 Hz, 2H, Ar); ¹³C NMR (75 MHz, CDCl₃, 35°C) δ 20.89, 65.35, 122.07, 129.69, 131.51, 134.86, 170.33; MS (EI) m/z (relative intensity) 230 ([M⁺]⁺, 52), 228 ([M⁺⁻²Br]⁺, 53), 188 (94), 186 (98), 171 (58), 169 (60); HRMS (EI) m/z calcd. for C₉H₉O₂⁻²⁹Br 227.9786 found 227.9835, calcd. for C₉H₉O₂⁻⁸¹Br 229.9765 found 229.9774.

4-(tert-Butyldimethylsiloxy)benzyl acetate (3e)

Purified by flush column chromatography (silica gel, Hexane/EtOAc = 40/1); colorless oil; IR (neat NaCl, v/cm⁻¹) 2956, 2859, 1741, 1611, 1513, 1254, 1169, 1026, 915, 840, 782, 734, 695; ¹H NMR (300 MHz, CDCl₃, 35 °C) δ 0.20 (s, 6H, SiCH₃), 0.98 (s, 9H, Si tert-Bu), 2.07 (s, 3H, acetyl), 5.02 (s, 2H, benzyl), 6.81 (d, J = 8.1 Hz, 2H, Ar), 7.21 (d, J = 8.1 Hz, 2H, Ar); ¹³C NMR (75 MHz, CDCl₃, 35°C) δ –4.30, 18.28, 21.09, 25.74, 66.10, 119.98, 128.63, 129.79, 155.64, 170.64; MS (EI) m/z (relative intensity) 280 ([M⁺]⁺, 27), 223 (15), 117 (100); HRMS (EI) m/z calcd. for C₁₅H₂₄O₃Si 280.1495 found 280.1493.

4-(Triethylsiloxymethyl)benzyl acetate (3f)

Purified by flush column chromatography (silica gel, Hexane/EtOAc = 20/1 to 4/1); colorless oil; IR (neat NaCl, v/cm⁻¹) 2955, 2876, 1744, 1517, 1458, 1415, 1379, 1362, 1228, 1092, 1019, 971, 820, 742; ¹H NMR (300 MHz, CDCl₃, 35 °C) δ 0.65 (q, J = 7.5 Hz, 6H, CH₂CH₃), 0.98 (t, J = 7.5 Hz, 9H, CH₂CH₃), 2.08 (s, 3H, acetyl), 4.73 (s, 2H, benzyl), 5.09 (s, 2H, benzyl), 7.32 (m, 4H, Ar); ¹³C NMR (75 MHz, CDCl₃, 35°C) δ 4.51, 6.70, 20.92, 64.39, 66.13, 126.32, 128.21, 134.62, 141.54, 170.76; MS (EI) m/z (relative intensity) 294 ([M⁺]⁺, 1), 265 (62), 145 (100), 103 (39), 75 (20); HRMS (EI) m/z calcd. for C₁₆H₂₆O₃Si 294.1651 found 294.1646.

4-(Methoxyethoxymethoxymethyl)benzyl acetate (3g)
Purified by flush column chromatography (silica gel, Hexane/EtOAc = 4/1); colorless oil; IR (neat NaCl, v/cm\(^{-1}\)) 2884, 1739, 1456, 1380, 1363, 1229, 1172, 1049, 850, 814, 733; \(^1\)H NMR (300 MHz, CDCl\(_3\), 35 °C) \(\delta\) 2.08 (s, 3H, acetyl), 3.39 (s, 3H, \(\text{CH}_3\text{O}\)), 3.5–3.6 (m, 2H, \(\text{CH}_2\text{CH}_2\)), 3.7 (m, 2H, \(\text{CH}_2\text{CH}_2\)), 4.62 (s, 2H, \(\text{CH}_2\text{O}\)), 4.79 (s, 2H, \(\text{CH}_2\text{O}\)), 5.09 (s, 2H, \(\text{CH}_2\text{O}\)), 7.3 (m, 4H, Ar); \(^{13}\)C NMR (75 MHz, CDCl\(_3\), 35°C) \(\delta\) 20.80, 58.85, 65.87, 66.87, 68.84, 71.69, 94.74, 127.88, 128.22, 135.33, 137.99, 170.59; MS (EI) m/z (relative intensity) 179 ([M–MEM]\(^+\), 30), 163 (40), 132 (25), 104 (32), 84 (100).

4-(Acetoxymethyl)benzyl benzoate (3h)

Purified by flush column chromatography (silica gel, Hexane/EtOAc = 10/1 to 4/1); white solid; mp 32–33 \(^\circ\)C; IR (neat NaCl, v/cm\(^{-1}\)) 2955, 1722, 1602, 1451, 1372, 1315, 1271, 1176, 1110, 1070, 1026, 967, 817, 712; \(^1\)H NMR (300 MHz, CDCl\(_3\), 35 °C) \(\delta\) 2.09 (s, 3H, acetyl), 5.11 (s, 2H, benzyl), 5.36 (s, 2H, benzyl), 7.3–7.6 (m, 7H, Ar), 8.0–8.1 (m, 2H, Ar); \(^{13}\)C NMR (75 MHz, CDCl\(_3\), 35°C) \(\delta\) 20.88, 65.85, 66.24, 128.34, 128.44, 129.66, 130.09, 133.01, 136.05, 136.16, 166.30, 170.69; MS (FAB) m/z (relative intensity) 285 ([M+1]\(^+\), 4), 225 (52), 163 (83), 105 (100).

4-(Acetoxymethyl)benzyl pivalate (3i)

Purified by flush column chromatography (silica gel, Hexane/EtOAc = 10/1 to 4/1); colorless oil; IR (neat NaCl, v/cm\(^{-1}\)) 2974, 1735, 1481, 1460, 1397, 1363, 1282, 1229, 1150, 1033, 968, 815; \(^1\)H NMR (300 MHz, CDCl\(_3\), 35 °C) \(\delta\) 1.23 (s, 9H, tert-Bu), 2.09 (s, 3H, acetyl), 5.10 (s, 4H, benzyl), 7.3–7.4 (m, 4H, Ar); \(^{13}\)C NMR (75 MHz, CDCl\(_3\), 35°C) \(\delta\) 20.86, 27.13, 38.74, 65.59, 65.87, 127.83, 128.33, 135.74, 136.56, 170.68, 178.15; MS (EI) m/z (relative intensity) 264 ([M]+, 1), 204 (42), 163 (80), 120 (49), 85 (37), 57 (100); HRMS (EI) m/z calcd. for C\(_{13}\)H\(_{20}\)O\(_4\) 264.1362 found 264.1363.

Octadecanyl acetate (3j)

Purified by flush column chromatography (silica gel, Hexane/EtOAc = 20/1); colorless wax; IR (neat NaCl, v/cm\(^{-1}\)) 2918, 1747, 1467, 1365, 1242, 1039, 910, 735, 648, 607; \(^1\)H NMR (300 MHz,
CDCl₃, 35 °C) δ 0.88 (t, J = 6.9 Hz, 3H, CH₃(CH₂)₁₇), 1.3 (brs, 30H, CH₂), 1.6 (m, 2H, CH₂), 2.03 (s, 3H, acetyl), 4.05 (t, J = 6.6 Hz, 2H, CH₂OAc); ¹³C NMR (75 MHz, CDCl₃, 35°C) δ 14.16, 21.02, 22.76, 26.01, 28.72, 29.34, 29.43, 29.59, 29.64, 29.76, 32.00, 64.64, 170.90; MS (EI) m/z (relative intensity) 312 ([M]+, 1), 252 (25), 224 (13); HRMS (EI) m/z calcd. for C₂₀H₄₀O₂ 312.3028 found 312.3024.

**Cinnamyl acetate (3k)**

Purified by flush column chromatography (silica gel, Hexane/EtOAc = 20/1); colorless oil; IR (neat NaCl, v/cm⁻¹) 2944, 1738, 1495, 1449, 1362, 1231, 1026, 966, 910, 744, 693; ¹H NMR (300 MHz, CDCl₃, 35 °C) δ 2.07 (s, 3H, acetyl), 4.71 (m, 2H, CH₂OAc), 6.26 (dt, J = 15.6, 6.1 Hz, 1H, PhCH=CH), 6.63 (d, J = 15.6 Hz, 1H, PhCH=CH), 7.2–7.4 (m, 5H, Ph); ¹³C NMR (75 MHz, CDCl₃, 35°C) δ 20.93, 64.93, 123.09, 126.43, 127.86, 128.40, 133.95, 136.07, 170.43; MS (EI) m/z (relative intensity) 176 ([M]+, 15), 134 (19), 115 (32), 105 (15); HRMS (EI) m/z calcd. for C₁₁H₁₂O₂ 176.0837 found 176.0817.

(E)-3,7-Dimethylocta-2,6-dienyl acetate (Geranyl acetate) (3l)

Purified by flush column chromatography (silica gel, Hexane/EtOAc = 20/1); colorless oil; IR (neat NaCl, v/cm⁻¹) 2968, 2925, 2914, 1741, 1671, 1444, 1366, 1232, 1108, 1024, 955, 830; ¹H NMR (300 MHz, CDCl₃, 35 °C) δ 1.60 (s, 3H, acetyl), 1.68 (s, 3H, CH₃), 1.70 (s, 3H, CH₃), 2.04 (s, 3H, CH₃), 2.0–2.1 (m, 4H, CH₂CH₂), 4.59 (d, J = 7.2 Hz, 2H, OCH₂), 5.1 (m, 1H, CH=), 5.3 (m, 1H, CH=); ¹³C NMR (75 MHz, CDCl₃, 35 °C) δ 16.32, 17.54, 20.86, 25.52, 26.25, 25.45, 61.26, 118.35, 123.71, 131.65, 142.02, 170.86; MS (EI) m/z (relative intensity) 196 ([M]+, 1), 121 (23), 93 (39), 69 (100); HRMS (EI) m/z calcd. for C₁₂H₂₀O₂ 196.1463 found 196.1441.

6-O-Acetyl-3,5-O-benzylidene-1,2-O-isopropylidene-α-D-glucofranose (3m)

Purified by flush column chromatography (silica gel, Hexane/EtOAc = 8/1 to 4/1); white solid; mp 128-129 °C; IR (film NaCl, v/cm⁻¹) 2988, 2937, 1744, 1456, 1375, 1233, 1142, 1081, 1015, 760, 700; ¹H NMR (300 MHz, CDCl₃, 35 °C) δ 1.34 (s, 3H, C(CH₃)₂), 1.52 (s, 3H, C(CH₃)₂), 2.11
(s, 3H, *acetyl*), 4.07 (m, 1H), 4.28 (dd, *J* = 11.7, 4.8 Hz, 1H), 4.46 (d, *J* = 6.0 Hz, 1H),
4.49 (dd, *J* = 7.2, 4.8 Hz, 1H), 4.6–4.7 (m, 1H), 5.78 (s, 1H, *benzyl*), 6.04 (d, *J* = 3.6 Hz, 1H),
7.3–7.5 (m, 5H, *Ph*); 13C NMR (75 MHz, CDCl$_3$, 35°C) δ 20.92, 26.21, 26.81,
62.81, 71.77, 72.59, 77.72, 83.85, 94.38, 105.01, 111.91, 126.05, 128.15, 129.02,
137.39, 170.25; MS (EI) *m/z* (relative intensity) 350 ([M$^+$], 15), 335 (9); HRMS (EI)
*m/z* calcd. for C$_{18}$H$_{22}$O$_7$ 350.1366 found 350.1385; $\lbrack \alpha \rbrack_{25}^{289} +14.4$ (c 1.0, CHCl$_3$).

(1S,2R,5S)-2-Isopropyl-5-methylcyclohexyl *acetate* (menthyl acetate) (3n)$^{11}$
Purified by flush column chromatography (silica gel, Hexane/EtOAc = 20/1); colorless oil; IR (neat NaCl, $\nu$/cm$^{-1}$) 2958, 2871, 2256, 1721,
1456, 1371, 1247, 1025, 909, 734; 1H NMR (300 MHz, CDCl$_3$, 35°C) δ 0.77 (d, *J* = 7.2 Hz, 3H, CHCH$_3$), 0.8–1.1 (m, 3H, Cy), 0.90 (d, *J* = 6.9 Hz, 3H, CH(CH$_3$)$_2$), 0.90 (d, *J* = 6.6 Hz, 3H, CH(CH$_3$)$_2$), 1.3–2.0 (m, 6H, Cy and CH(CH$_3$)$_2$), 2.02 (s, 3H, *acetyl*), 4.68
(ddd, *J* = 11.1, 11.1, 4.5 Hz, 1H, OCH$_3$); 13C NMR (75 MHz, CDCl$_3$, 35°C) δ 16.51,
20.75, 21.30, 22.03, 23.67, 26.45, 31.43, 34.35, 41.00, 47.09, 74.12, 170.32; MS (FAB)
*m/z* (relative intensity) 197 ([M–H$^+$], 35), 154 (92), 136 (86); $\lbrack \alpha \rbrack_{25}^{289} +82.3$ (c 1.1, CHCl$_3$).

**β-Sitosterol acetate (3o)$^{18}$**
Purified by flush column chromatography (silica gel, Hexane/EtOAc = 40/1); white solid;
mp 136-138 °C; IR (film NaCl, $\nu$/cm$^{-1}$) 2941, 1731, 1466, 1374, 1249, 1038; 1H NMR (300
MHz, CDCl$_3$, 35°C) δ 0.68 (s, 3H, CH$_3$), 0.8–2.0 (m, 39H), 1.02 (s, 3H, CH$_2$), 2.02 (s, 3H, *acetyl*), 2.32 (bd, *J* = 7.8 Hz, 2H), 4.5–4.6 (m, 1H, CHOAc), 5.4 (m, 1H, CH=C);
13C NMR (75 MHz, CDCl$_3$, 35°C) δ 11.97, 12.10, 18.90, 19.18, 19.39, 19.90, 21.15,
21.45, 23.22, 24.39, 26.31, 27.89, 28.31, 29.34, 31.98, 34.07, 35.96, 36.23, 36.68, 37.10,
38.22, 39.84, 42.40, 45.96, 50.15, 56.14, 56.76, 73.97, 122.51, 139.56, 170.21; MS (EI)
*m/z* (relative intensity) 455 ([M–H$^+$], 2), 397 (65), 383 (58); $\lbrack \alpha \rbrack_{25}^{289} –44.6$ (c 1.0, CHCl$_3$).
Stigmasterol acetate (3p)<sup>19</sup>
Purified by flush column chromatography (silica gel, Hexane/EtOAc = 20/1); white solid; mp 144-146 °C; IR (film NaCl, $\nu$cm<sup>-1</sup>) 2937, 2359, 1731, 1507, 1456, 1370, 1262, 1136, 1038, 971, 798; $^1$H NMR (300 MHz, CDCl<sub>3</sub>, 35 °C) $\delta$ 0.70 (s, 3H, CH$_3$), 0.8–2.3 (m, 21H), 2.02 (s, 3H, acetyl), 4.6 (m, 1H, CHOAc), 5.02 (dd, $J = 15.4, 9.0$ Hz, 1H, CH=CH), 5.16 (dd, $J = 15.4, 8.5$ Hz, 1H, CH=CH), 5.7 (m, 1H, CH=C); $^{13}$C NMR (75 MHz, CDCl<sub>3</sub>, 35°C) δ 12.17, 12.33, 19.11, 19.41, 21.15, 21.32, 21.48, 24.46, 25.47, 27.90, 28.96, 31.96, 31.99, 36.71, 37.11, 38.23, 39.74, 40.50, 42.31, 50.18, 51.30, 56.05, 56.86, 73.98, 122.52, 129.26, 138.16, 139.58, 170.24; MS (EI) $m/z$ (relative intensity) 453 ([M–H]+, 2), 395 (68), 255 (20); $[\alpha]_{25}^{25}$ = 55.5 (c 1.0, CHCl<sub>3</sub>).

Cholecalciferol acetate (3q)<sup>20</sup>
Purified by flush column chromatography (silica gel, Hexane/EtOAc = 40/1); white wax; IR (neat NaCl, $\nu$cm<sup>-1</sup>) 2950, 2869, 1741, 1467, 1440, 1375, 1241, 1031, 892, 834, 715, 607; $^1$H NMR (300 MHz, CDCl<sub>3</sub>, 35 °C) $\delta$ 0.54 (s, 3H, CH$_3$), 0.9–2.8 (m, 36H), 2.02 (s, 3H, acetyl), 4.83 (d, $J = 1.8$ Hz, 1H, C=CH$_2$), 4.9–5.0 (m, 1H, CHOAc), 5.05 (d, $J = 1.8$ Hz, 1H, C=CH$_2$), 6.03 (d, $J = 11.1$ Hz, 1H, CH=CH), 6.21 (d, $J = 11.1$ Hz, 1H, CH=CH); $^{13}$C NMR (75 MHz, CDCl<sub>3</sub>, 35°C) δ 12.04, 18.91, 22.29, 22.58, 22.83, 23.61, 23.94, 27.69, 28.03, 29.10, 32.24, 36.15, 36.20, 36.23, 39.54, 40.61, 42.18, 45.92, 56.38, 56.67, 71.73, 112.52, 117.42, 122.32, 134.17, 142.12, 144.49, 170.17; MS (EI) $m/z$ (relative intensity) 426 ([M]+, 2); HRMS (EI) $m/z$ calcd. for C$_{29}$H$_{46}$O$_2$ 426.3498 found 426.3509; $[\alpha]_{25}^{25}$ = 25.4 (c 1.0, CHCl<sub>3</sub>).

Testosterone acetate (3r)<sup>21</sup>
Purified by flush column chromatography (silica gel, Hexane/EtOAc = 6/1 to 4/1); white solid; mp 143-145 °C; IR (film NaCl, $\nu$cm<sup>-1</sup>) 2949, 2908, 2849, 1733, 1669, 1615, 1434, 1374, 1354, 1250, 1186, 1044, 861; $^1$H NMR (300 MHz, CDCl<sub>3</sub>, 35 °C) $\delta$ 0.84 (s, 3H, CH$_3$), 0.9–1.2 (m, 3H), 1.19 (s, 3H, CH$_3$), 1.3–1.9
(m, 1H), 2.0–2.5 (m, 6H), 2.04 (s, 3H, acetyl), 4.60 (dd, $J = 9.0, 7.8$ Hz, 1H, CHOAc), 5.72 (s, 1H, C=CH); $^{13}$C NMR (75 MHz, CDCl$_3$, 35°C) δ 12.08, 17.48, 20.62, 21.15, 23.52, 27.54, 31.57, 32.77, 33.96, 35.49, 35.78, 36.69, 38.65, 42.51, 50.31, 53.76, 82.39, 123.83, 170.51, 170.79, 198.94; MS (EI) m/z (relative intensity) 330 ([M]$^+$, 24), 288 (25), 228 (22); HRMS (EI) m/z calcd. for C$_{21}$H$_{30}$O$_3$ 330.2195 found 330.2199; $[\alpha]_{25}^{2589}$ +82.2 (c 1.0, CHCl$_3$).

**β-Estradiol 17-acetate (5)**

Purified by flush column chromatography (silica gel, Hexane/EtOAc = 4/1); white solid; mp >200 °C; IR (film NaCl, v/cm$^{-1}$) 3419, 2930, 1706, 1497, 1457, 1373, 1274, 1037; $^1$H NMR (300 MHz, DMSO, 35°C) δ 0.77 (s, 3H, CH$_3$), 1.2–1.8 (m, 10 H, CH, CH$_2$), 1.99 (s, 3H, acetyl), 2.0–2.2 (m, 3H, CH, CH$_2$), 2.7 (bs, 2H, benzyl), 4.60 (t, $J = 8.1$ Hz, 1H, OCH), 6.43 (d, $J = 2.1$ Hz, 1H, Ar), 6.50 (dd, $J = 8.4, 2.1$ Hz, 1H, Ar), 7.02 (d, $J = 8.4$ Hz, 1H, Ar), 8.91 (s, 1H, OH); $^{13}$C NMR (75 MHz, DMSO, 35°C) δ 12.08, 20.96, 22.91, 26.01, 26.96, 27.31, 29.20, 36.62, 38.43, 42.62, 43.33, 49.20, 81.93, 112.72, 114.92, 125.93, 130.09, 136.98, 154.85, 170.11; MS (EI) m/z (relative intensity) 314 ([M]$^+$, 100), 254 (30); HRMS (EI) m/z calcd. for C$_{20}$H$_{26}$O$_3$ 314.1882 found 314.1891; $[\alpha]_{25}^{2589}$ +41.5 (c 1.0, CHCl$_3$).

**General procedure for the O-selective acetylation of 4-piperidinemethaol (8) catalyzed by tetranuclear zinc cluster 1.** Zn$_4$(OCOCF$_3$)$_6$O (I) (0.038 mmol), 4-piperidinemethaol (8) (346 mg, 3.0 mmol), and ethyl acetate (5.0 mL, 0.6 M) were refluxed for 12 hours in an argon atmosphere. The resulting mixture was cooled, treated with Boc$_2$O and triethylamine, and purified by silica gel column chromatography to give N-protected aminoester Boc-9.

**tert-Butyl 4-(acetoxymethyl)piperidine-1-carboxylate (Boc-9)**

Purified by flush column chromatography (silica gel, Hexane/EtOAc = 10/1 to 4/1); colorless oil; IR (neat NaCl, v/cm$^{-1}$) 2939, 2856, 1744, 1693, 1423, 1365, 1245, 1174, 1038, 982, 920, 866, 733; $^1$H NMR (300 MHz, CDCl$_3$, 35°C) δ 1.1–1.3 (m, 2H, piperidine), 2.0–2.7 (m, 6H, piperidine), 4.60 (t, $J = 8.1$ Hz, 1H, OCH), 6.43 (d, $J = 2.1$ Hz, 1H, Ar), 6.50 (dd, $J = 8.4, 2.1$ Hz, 1H, Ar), 7.02 (d, $J = 8.4$ Hz, 1H, Ar), 8.91 (s, 1H, OH); $^{13}$C NMR (75 MHz, DMSO, 35°C) δ 12.08, 20.96, 22.91, 26.01, 26.96, 27.31, 29.20, 36.62, 38.43, 42.62, 43.33, 49.20, 81.93, 112.72, 114.92, 125.93, 130.09, 136.98, 154.85, 170.11; MS (EI) m/z (relative intensity) 314 ([M]$^+$, 100), 254 (30); HRMS (EI) m/z calcd. for C$_{20}$H$_{26}$O$_3$ 314.1882 found 314.1891; $[\alpha]_{25}^{2589}$ +41.5 (c 1.0, CHCl$_3$).
1.46 (6, 9H, C(CH₃)₃), 1.7–1.8 (m, 3H, piperidine), 2.05 (s, 3H, acetyl), 2.7 (m, 2H, piperidine), 3.93 (d, \( J = 6.6 \) Hz, 2H, OCH₃), 4.1 (d-like, 2H, piperidine); \(^{13}\)C NMR (75 MHz, CDCl₃, 35 °C) δ 20.69, 28.33, 28.37, 28.61, 35.49, 43.35, 68.33, 79.30, 154.69, 170.87; MS (EI) \( m/z \) (relative intensity) 257 (\([M^+], 1\)), 200 (8), 184 (8), 142 (11), 114 (33), 84 (30), 57 (56); HRMS (EI) \( m/z \) calcd. for C₁₃H₂₃NO₄ 257.1627 found 257.1642.

**General procedure for acetylation of 4-piperidinemethanol (8) by acetic anhydride.**

To a solution of 4-piperidinemethanol (8) (345 mg, 3.0 mmol) and triethylamine (2.1 mL) in CH₂Cl₂ (5.0 mL), 1.0 eq or 5.0 eq of acetic anhydride was added with ice-bath cooling followed by stirring at room temperature for 18 hours. Resulting mixture was concentrated and purified by silica gel column chromatography to give corresponding acetylated products 10 (in the case of using 1.0 eq of acetic anhydride, 471 mg, >99% yield) and 11 (in the case of using 5.0 eq of acetic anhydride, 568 mg, 95% yield), respectively.

**(1-Acetylpiperidin-4-yl)methanol (10)**

Purified by flush column chromatography (silica gel, EtOAc to EtOAc/MeOH = 100/5); colorless oil; IR (neat NaCl, \( \nu/cm^{-1} \)) 3389, 2922, 2863, 1622, 1455, 1371, 1315, 1271, 1091, 1040, 920, 731; \(^1\)H NMR (300 MHz, CDCl₃, 35 °C) δ 1.1–1.2 (m, 2H, piperidine), 1.7–1.9 (m, 3H, piperidine), 2.08 (s, 3H, acetyl), 2.5–2.6 (m, 1H, piperidine), 3.0–3.1 (m, 1H, piperidine), 3.23 (br, 1H, OH), 3.5 (m, 2H, OCH₃), 3.8–3.9 (m, 1H, piperidine), 4.6 (m, 1H, piperidine); \(^{13}\)C NMR (75 MHz, CDCl₃, 35 °C) δ 21.22, 28.20, 29.14, 38.56, 41.42, 46.01, 66.71, 168.87; MS (EI) \( m/z \) (relative intensity) 157 (\([M^+], 5\)), 86 (65), 84 (100); HRMS (EI) \( m/z \) calcd. for C₈H₁₅NO₂ 175.1103 found 175.1087.

**(1-Acetylpiperidin-4-yl)methyl acetate (11)**

Purified by flush column chromatography (silica gel, Hexane/EtOAc = 1/4); colorless oil; IR (neat NaCl, \( \nu/cm^{-1} \)) 2942, 1735, 1624, 1453, 1365, 1242, 1038, 981; \(^1\)H NMR (300 MHz, DMSO, 35 °C) δ 0.9–1.2 (m, 2H, piperidine), 1.6–1.9 (m, 3H, piperidine), 1.96 (s, 3H, acetyl), 1.99 (s, 3H, acetyl), 2.4–2.5 (m, 1H, piperidine), 2.9–3.0 (m, 1H, piperidine), 3.8 (m, 1H, piperidine), 3.86 (d, \( J = 6.3 \) Hz, 2H, OCH₃), 4.3–4.4 (m, 1H, piperidine); \(^{13}\)C NMR (75
MHz, DMSO, 35°C) δ 20.74, 21.39, 28.22, 28.99, 35.11, 40.65, 45.60, 67.84, 168.19, 170.58; MS (EI) m/z (relative intensity) 199 ([M]+, 56), 156 (72), 114 (46), 96 (52); HRMS (EI) m/z calcd. for C_{10}H_{17}NO_{3} 199.1208 found 199.1236.

References
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