Supporting Information

RuCl₃/CeCl₃/NaIO₄ – A new bimetallic oxidation system for the mild and efficient dihydroxylation of unreactive olefins.

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General Remarks. General Remarks. Petroleum ether refers to that fraction boiling in the range 35 – 60 °C. HPLC-grade acetonitrile was purchased from Aldrich, ethyl acetate was purified by distillation over CaCl_2 prior to use. RuCl_3 was obtained from Aldrich. A stock solution was prepared calculating with $\text{RuCl}_3(\text{H}_2\text{O})_2$ and dissolving the catalyst (2.44 g, 10 mmol) in 100 mL water (0.1 M)). The deep brown solution can be stored on the bench for weeks without loss of activity. Literature-known compounds **2**¹, **5**¹, **7**², **9**¹, **11**¹, **13**¹ and **15**¹ were characterized by ^1H NMR, ^{13}C NMR and IR-spectroscopic data and comparison of these data with the literature reports.

General Procedure. In a 50-mL round-bottomed flask equipped with magnetic stirring bar and overpressure valve NaIO_4 (642 mg, 3 mmol) and $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ (74.6 mg, 0.2 mmol, 10 mol%) were stirred in 0.9 mL H_2O and gently heated until a bright yellow suspension was formed. After cooling to 0 °C ethyl acetate (2.5 mL) and acetonitrile (3 mL) were added and the suspension was stirred for 2 min. A 0.1 M aqueous solution of RuCl_3 (100 μL , 0.01 mmol) was added and the mixture was stirred for 2 min. A solution of the olefin (2 mmol) in ethyl acetate (0.5 mL) was added in one portion and the resulting slurry was stirred until all starting material was consumed. Solid Na_2SO_4 (1 g) was added followed by ethyl acetate (6 mL). The solid was filtered off and the filtercake was washed several times with ethyl acetate. The filtrate was washed with sat. Na_2SO_3 -solution (3 mL), the organic layer was dried over Na_2SO_4 and concentrated in vacuum. The crude product was purified by flash-chromatography.

(2S*,3R*)-2,3-Dihydroxy-3-phenyl-propionic acid methyl ester (2). (322 mg, 1.64 mmol, 82 %). White solid. m.p. 79 °C. R_f 0.30 (4:1 pentane / ethyl acetate). ¹H NMR (400 MHz, CDCl₃). δ 7.38-7.22 (m, 5H), 4.94 (d, 1H), 4.28 (d, 1H), 3.70 (s, 3H), 3.49 (s, 2H) ppm. ¹³C NMR (100 MHz, CDCl₃). δ 173.2, 140.0, 128.4, 128.2, 126.3, 75.0, 74.5, 52.7 ppm. IR (KBr): ν 3495 (s), 3378 (s), 3086 (m), 3062 (m), 3038 (m), 3007 (m), 2954 (s), 2931 (m), 1732 (s), 1493 (s), 1458 (s), 1324 (s), 1308 (s), 1104 (s), 1083 (s) cm⁻¹.

(2S*,3R*)-2,3-Dihydroxy-1,3-diphenyl-propan-1-one (5). (397 mg, 1.36 mmol, 68 %). White solid. m.p. 117 °C. R_f 0.15 (3:1 pentane / ethyl acetate). ¹H NMR (400 MHz, CDCl₃). δ 7.41-7.78 (m, 10H), 6.36 (d, 1H), 5.01 (d, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃). δ 189.7, 130.7, 130.6, 130.1, 129.1, 128.9, 128.7, 128.6, 128.5, 88.7, 87.8 ppm. IR (KBr): ν 3434 (s), 3065 (w), 2929 (m), 2857 (w), 1694 (s), 1598 (m), 1579 (m), 1450 (m), 1284 (s), 1227 (s), 1113 (s) cm⁻¹.

(1R*,2S*)-3-(tert-Butyl-dimethyl-silanyloxy)-1-phenyl-propane-1,2-diol (7). (458 mg, 1.62 mmol, 81 %). White solid. m.p. 59 °C. R_f 0.56 (7:1 pentane / ethyl acetate). ¹H NMR (400 MHz, CDCl₃). δ 7.40-7.34 (m, 4H), 7.32-7.28 (m, 1H), 4.72 (d, 1H), 3.73-3.69 (m, 1H), 3.64 (dd, 1H), 3.56 (dd, 1H), 3.15 (s, 1H), 2.69 (s, 1H), 0.92 (s, 9H), 0.07 (s, 3H), 0.065 (s, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃). δ 140.7, 128.6, 128.1, 126.8, 75.6, 74.9, 64.2, 26.0, 12.9, -5.3, -5.4 ppm. IR (KBr): ν 3374 (s), 3286 (s), 3086 (w), 3062 (w), 3029 (w), 2954 (s), 2929 (s), 2883 (m), 2856 (s), 1471 (m), 1402 (m), 1251 (s), 1114 (s) cm⁻¹.

(1S*,2R*)-1-(5,5-Dimethyl-1,3-dioxan-2-yl)-2-phenyl ethane-1,2-diol (9). (439 mg, 1.74 mmol, 87 %). White solid. m.p. 126 °C. R_f 0.84 (3:1 pentane / ethyl acetate). ¹H NMR (400 MHz, CDCl₃). δ 7.41-7.24 (m, 5H), 4.99 (d, 1H), 4.46 (d, 1H), 3.68 (d, 2H), 3.64 (dd, 1H), 3.43 (d, 2H), 3.18 (s, 1H), 2.60 (s, 1H), 1.20 (s, 3H), 0.72 (s, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃). δ 140.7, 128.5, 127.8, 126.6, 101.2, 77.3, 75.5, 72.5, 31.3, 30.6, 23.1, 21.8 ppm. IR (KBr): ν 3447 (s, br), 3362 (s, br), 2955 (m), 2871 (m), 1495 (m), 1473 (m), 1396 (m), 1091 (s), 1030 (s) cm⁻¹.

(1S*,2R*)-1-Methyl-cyclohexane-1,2-diol (11). (213 mg, 1.64 mmol, 82 %). White solid. m.p. 67 °C. R_f 0.78 (3:1 pentane / ethyl acetate). ¹H NMR (400 MHz, CDCl₃). δ 3.27 (t, 1H), 2.34 (s, 2H), 1.79-1.72 (m, 1H), 1.68-1.54 (m, 5H), 1.41-1.30 (m, 2H), 1.22 (s, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃). δ 82.5, 72.2, 37.2, 37.0, 29.0, 22.0 ppm. IR (KBr): ν 3326 (s), 2991

(m), 2938 (s), 2881 (s), 2860 (s), 1716 (m), 1458 (m), 1444 (m), 1405 (m), 1370 (m), 1151 (s), 1087 (s), 1063 (s) cm^{-1} .

(3*S*^{*},4*S*^{*})-3,4-Dihydroxychroman-2-one (13). (335 mg, 1.86 mmol, 93 %). White solid. m.p. 142 °C. R_f 0.58 (1:1 pentane / ethyl acetate). ^1H NMR (400 MHz, MeOH(d_4)). δ 7.45-7.39 (m, 2*H*), 7.20 (t, 1*H*), 7.07 (d, 1*H*), 4.92-4.87 (m, 2*H*), 4.79 (d, 1*H*), 4.69 (dd, 1*H*) ppm. ^{13}C NMR (100 MHz, CDCl_3). δ 170.1, 152.0, 131.2, 130.3, 125.3, 117.3, 71.6, 70.1 ppm. IR (KBr): ν 3431 (s), 3308 (s), 2887 (w), 1774 (s), 1487 (m), 1461 (s), 1158 (s), 1129 (s), 1113 (s), 1066 (s) cm^{-1} .

(2*S*^{*},3*S*^{*})-2,3-Dihydroxycyclohexanone (15). (215 mg, 1.65 mmol, 83 %). White solid. m.p. 52 °C. R_f 0.25 (3:2 pentane / ethyl acetate). ^1H NMR (400 MHz, CDCl_3). δ 4.35-4.39 (m, 1*H*), 4.13 (dd, 1*H*), 3.49 (s, 2*H*), 2.49 (dq, 1*H*), 2.32 (dt, 1*H*), 2.03-2.14 (m, 2*H*), 1.75-1.82 (m, 2*H*) ppm. ^{13}C NMR (100 MHz, CDCl_3). δ 210.2, 77.5, 72.8, 39.1, 29.0, 21.2 ppm. IR (KBr): ν 3405 (s), 2949 (m), 1718 (s), 1140 (m), 1107 (m) 1075 (m) cm^{-1} .

(2*S*^{*},3*R*^{*})-2-(2,3-Dihydroxy-3-phenyl-propyl)-isoindole-1,3-dione (17). (541 mg, 1.82 mmol, 91 %). White solid. m.p. 105 °C. R_f 0.44 (1:1 pentane / ethyl acetate). ^1H NMR (400 MHz, CDCl_3). δ 7.79 (dd, 2*H*), 7.68 (dd, 2*H*), 7.40-7.35 (m, 2*H*), 7.34-7.28 (m, 2*H*), 7.26-7.21 (m, 1*H*), 4.60 (d, 1*H*), 4.09 (ddd, 1*H*), 3.86 (dd, 1*H*), 3.72 (dd, 1*H*), 2.61 (s, 2*H*) ppm. ^{13}C NMR (100 MHz, CDCl_3). δ 168.9, 140.2, 134.3, 132.0, 128.7, 128.3, 126.8, 123.6, 75.0, 73.4, 41.0 ppm. IR (KBr): ν 3502 (s), 3465 (s), 3398 (s), 3315 (s), 3088 (w), 3060 (w), 3030 (w), 3005 (w), 2928 (m), 1775 (s), 1694 (s), 1612 (m), 1467 (m), 1450 (m), 1427 (s), 1398 (s), 1257 (s) cm^{-1} ; elemental analysis calcd. (%) for $\text{C}_{17}\text{H}_{15}\text{NO}_4$ (297.31): C 68.68, H 5.09; found: C 68.63, H 5.12.

(2*S*^{*},3*R*^{*})-3-(2,3-Dihydroxy-3-phenyl-propionyl)-oxazolidin-2-one (19). (432 mg, 1.72 mmol, 86 %). White solid. m.p. 124 °C. R_f 0.16 (1:2 pentane / ethyl acetate). ^1H NMR (400 MHz, CDCl_3). δ 7.53-7.47 (m, 2*H*), 7.41-7.35 (m, 2*H*), 7.34-7.28 (m, 1*H*), 5.37 (s, 1*H*), 5.16 (d, 1*H*), 4.57-4.44 (m, 2*H*), 4.18-4.01 (m, 2*H*), 3.58 (s, 1*H*), 2.73 (s, 1*H*) ppm. ^{13}C NMR (100 MHz, CDCl_3). δ 194.5, 192.4, 140.2, 128.5, 128.1, 126.3, 74.4, 73.7, 63.3, 42.8 ppm. IR (KBr): ν 3463 (s), 3060 (w), 3026 (w), 2992 (w), 2928 (w), 2894 (w), 1760 (s), 1710 (s), 1490 (m), 1477 (m), 1391 (s), 1325 (s), 1229 (s), 1095 (s) cm^{-1} ; elemental analysis calcd. (%) for $\text{C}_{12}\text{H}_{13}\text{NO}_5$ (251.08): C 57.37, H 5.22; found: C 57.41, H 5.18.

(3R*,4S*)-1-Benzyl-3,4-dihydroxy-3,4-dimethyl-pyrrolidine-2,5-dione (21). (443 mg, 1.78 mmol, 89 %). White solid. m.p. 89 °C. R_f 0.12 (1:1 pentane / ethyl acetate). ¹H NMR (400 MHz, CDCl₃). δ 7.27 (s, 5H), 4.61 (s, 2H), 4.23 (s, 2H), 1.33 (s, 6H) ppm. ¹³C NMR (100 MHz, CDCl₃). δ 178.9, 136.5, 130.2, 129.6, 129.4, 76.9, 43.7, 20.1 ppm. IR (KBr): ν 3450 (s), 2991 (w), 1703 (s), 1404 (m), 1343 (m), 1134 (s), 1070 (m), 699 (s) cm⁻¹; elemental analysis calcd. (%) for C₁₃H₁₅NO₄ (249.26): C 62.64, H 6.07; found: C 62.65, H 6.08.

References

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- (2) Ko, S. Y.; Malik, M.; Dickinson, F. J. *Org. Chem.* **1994**, 59, 2570.

^1H NMR spectra