Supporting Information
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Supporting Information

Metal-Free Relay Oxidation: Valuable Synthesis of Acylsilane and Ketones Under Aerobic Oxidation

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General information

All reagents and solvents were used after purification according to general methods. Flash column chromatography was performed over silica (200-300 mesh). $^1$H-NMR and $^{13}$C-NMR spectra were recorded at 400 and 100 MHz, respectively on Advance (Brucker) 400 MHz Nuclear Magnetic Resonance Spectrometer, and were referenced to the internal solvent signals. Thin layer chromatography was performed using silica gel; F$_{254}$ TLC plates and visualized with ultraviolet light. The products of Michael adducts$^1$, most of the products of retro-Brook arrangement$^2$, and ketones$^3$, were simple and known and confirmed by MS, and usual spectral methods ($^1$H-NMR, $^{13}$C-NMR). The ESI-MS analysis of the samples was operated on an LCQ advantage mass spectrometer (ThermoFisher Company, USA), equipped with an ESI ion source in the positive ionization mode, with data acquisition using the Xcalibur software (Version 1.4). The ESI-HR-MS analysis of the samples was operated on a micrOTOF-Q II (Brucker).

2. General Procedure for the synthesis of α-hydroxysilane through retro-Brook arrangement$^2$

Sec-Butyllithium (1.3 equiv) was added to a solution of aromatic silyl ether 7 (Scheme S1) in THF at -78°C under argon. The resulting orange solution was then stirred at this temperature for several hours. The reaction mixture was allowed to warm to room temperature and stirred for 10 hours, then poured into water, and extracted into EtOAc. The combined extracts were dried over magnesium sulfate, and concentrated under reduced pressure to give the crude product. The product was purified by column chromatography (silica gel, petroleum/ethyl acetate mixtures). Most of the products in the retro-Brook arrangement are known and confirmed by MS, and usual spectral methods ($^1$H-NMR, $^{13}$C-NMR).
Scheme S1. The synthesis of α-hydroxysilane through retro-Brook arrangement

(tert-butyldiphenylsilyl)(4-fluorophenyl)methanol: $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 1.09 (d, $J$ = 1.6 Hz, 9H, CH$_3$), 1.83 (br s, 1H, OH), 5.20 (s, 1H, CH), 6.75 (t, $J$ = 8.0 Hz, 2H, ArH), 6.86 (dt, $J_1$ = 2.4, $J_2$ = 5.6 Hz, 2H, ArH), 7.26-7.41 (m, 6H, ArH), 7.54 (d, $J$ = 7.6 Hz, 2H, ArH), 7.66 (d, $J$ = 7.6 Hz, 2H, ArH) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 18.97, 28.52, 68.43, 114.57, 114.78, 127.63, 127.67, 128.34, 128.41, 129.57, 129.60, 132.95, 132.97, 137.00, 137.03, 139.32, 139.35, 162.07, 162.70 ppm; FT-IR: $\nu$ (cm$^{-1}$) = 3532.7, 3070.9, 2958.6, 2927.3, 2891.8, 2855.3, 1600.6, 1505.6,
1462.1, 1428.1, 1389.6, 1361.5, 1224.1, 1158.8, 1106.9, 1016.0, 840.3, 821.6, 782.5, 740.6, 700.0, 606.7, 565.2, 528.0, 502.7, 482.2, 448.8 cm⁻¹; GC-MS (EI): m/z = 364.2, ([M]⁺, C₂₃H₂₅FOSi).

(tert-butyldiphenylsilyl)(m-tolyl)methanol: ¹H NMR (400 MHz, CDCl₃): δ = 1.09 (s, 9H, CH₃), 1.73 (br s, 1H, OH), 2.09 (s, 3H, CH₃), 5.20 (s, 1H, CH), 6.59 (s, 1H, ArH), 6.81 (d, J = 7.2 Hz, 1H, ArH), 6.87 (d, J = 7.6 Hz, 1H, ArH), 6.99 (t, J = 7.6 Hz, 1H, ArH), 7.23-7.39 (m, 6H, ArH), 7.57 (d, J = 7.6 Hz, 2H, ArH), 7.67 (d, J = 6.8 Hz, 2H, ArH); ppm. FT-IR: ν (cm⁻¹) = 3532.7, 3071.0, 3046.9, 2956.8, 2930.3, 2892.3, 2857.1, 1603.8, 1486.0, 1471.7, 1462.1, 1427.1, 1391.7, 1361.9, 1106.1, 999.2, 820.4, 788.6, 739.1, 700.1, 605.3, 506.4, 483.6, 443.1 cm⁻¹; GC-MS (EI): m/z = 360.2 ([M]⁺, C₂₄H₂₈OSi).

(tert-butyldiphenylsilyl)(3-fluorophenyl)methanol: ¹H NMR (400 MHz, CDCl₃): δ = 1.12 (s, 9H, CH₃), 1.75 (br s, 1H, OH), 5.24 (s, 1H, CH), 6.60 (d, J = 10.4Hz, 1H, ArH), 6.67 (d, J = 8.0 Hz, 1H, ArH), 6.73 (dt, J = 8.4, 2.4 Hz, 1H, ArH), 6.98-7.03 (m, 1H, ArH), 7.30 (t, J = 7.2 Hz, 2H, ArH), 7.34 (t, J = 7.2 Hz, 2H, ArH), 7.39-7.42 (m, 2H, ArH), 7.55 (d, J = 6.8 Hz, 2H, ArH), 7.66 (d, J = 6.8 Hz, 2H, ArH) ppm. FT-IR: ν (cm⁻¹) = 3535.3, 3441.5, 3072.2, 3049.4, 2958.2, 2931.2, 2893.8, 2857.8, 1611.0, 1586.7, 1486.0, 1472.5, 1392.5, 1362.8, 1259.7, 1128.9, 1106.3, 999.7, 950.4, 872.8, 820.3, 786.7, 766.5, 739.5, 699.2, 674.6, 623.2, 506.3, 486.0, 459.8 cm⁻¹; GC-MS (EI): m/z = 364.2 ([M]⁺, C₂₃H₂₅FOSi).
3. General Procedure for Metal-Free Relay Oxidation of $\alpha$-hydroxysilane to acylsilanes and aromatic alcohols to ketones$^3$

To a solution of the Michael adduct $3^{[1]}$ derived from 5,5-dimethylcyclohexane-1,3-dione and chalcone (0.45 mmol) in DCE (1 mL), 0.3 mmol of $\alpha$-hydroxysilane or aromatic alcohol was added, and the resulting solution was stirred at room temperature for 24-36h. TLC indicated the completion of the reaction. The product, acylsilane or aromatic ketone was purified by column chromatography (silica gel, petroleum ethyl acetate mixtures). Most of these ketones products are known and confirmed by MS, and usual spectral methods ($^1$H-NMR, $^{13}$C-NMR).

(tert-butyldiphenylsilyl)(phenyl)methanone: $^1$H NMR (400 MHz, CDCl$_3$): 1.14 (s, 9H), 7.22 (q, J = 15.2 Hz, 2H), 7.31-7.43 (m, 7H), 7.62 (d, J = 7.2 Hz, 2H), 7.68 (dd, J =1.2, 8.0 Hz, 4H); $^{13}$C NMR (100 MHz, CDCl$_3$): 19.2, 27.6, 128.2, 128.3, 128.5, 129.9, 132.7, 133.0, 136.4, 142.3, 233.0 (SiCOPh); FT-IR: $\nu$ (cm$^{-1}$) = 3447.9, 3069.0, 2932.7, 2857.2, 1685.7, 1614.8, 1575.1, 1426.7, 1204.8, 1172.4, 1108.8, 770.7, 700.0; HRMS (ESI, m/z): Calcd. for [C$_{23}$H$_{24}$OSi+H]+, 345.1675, found, 345.1669.

(tert-butyldiphenylsilyl)(m-tolyl)methanone: $^1$H NMR (400 MHz, CDCl$_3$): 1.33 (s, 9H), 2.28 (s, 3H), 7.14 (t, J = 7.6Hz, 1H), 7.25 (t, J = 7.6 Hz, 1H), 7.43-7.51 (m,6H), 7.59 (d, J = 8Hz, 1H), 7.65 (s, 1H), 7.86 (t, J = 6.8 Hz, 4H); $^{13}$C NMR (100 MHz, CDCl$_3$): 19.18, 21.31, 27.69, 126.39, 128.17, 128.48, 129.92, 133.19, 133.46, 136.37, 137.96, 142.47, 233.13(SiCOAr); FT-IR: $\nu$ (cm$^{-1}$) = 3071.4, 3050.0, 2931.0, 2857.9, 1611.2, 1585.5, 1473.5, 1244.6, 1148.2, 1107.7, 819.7, 740.0, 700.0, 607.2; HRMS
(ESI, m/z): Calcd. for [C23H24OSi+H]+, 359.1831, found, 359.1831.

(tert-butyldiphenylsilyl)(3-methoxypenyl)methanone: \(^1\)H NMR (400 MHz, CDCl\(_3\)): 1.27 (s, 9H), 3.57 (s, 3H), 6.99 (dd, J = 2.0, 8.0 Hz, 1H), 7.14 (t, J = 7.6 Hz, 1H), 7.33-7.48 (m, 8H), 7.81 (t, J = 6.4 Hz, 4H); \(^1\)C NMR (100 MHz, CDCl\(_3\)): 19.22, 27.66, 55.25, 111.52, 120.32, 121.68, 128.19, 129.36, 129.96, 133.12, 136.41, 143.61, 159.61, 232.56 (SiCOAr); FT-IR: \(\nu\) (cm\(^{-1}\)) = 3071.5, 2933.6, 2858.1, 1613.9, 1578.1, 1483.2, 1463.3, 1427.3, 1257.5, 1153.3, 1107.7, 1040.2, 819.6, 791.6, 740.7, 700.7, 688.2; HRMS(ESI, m/z): Calcd. for [C24H26O2Si+H]+, 375.1780, found, 375.1792.

(tert-butyldiphenylsilyl)(3-methoxypenyl)methanone: \(^1\)H NMR (400 MHz, CDCl\(_3\)): 1.26 (s, 9H), 7.06-7.11 (m, 1H), 7.14-7.19 (m, 1H), 7.41-7.48 (m, 8H), 7.79 (t, J = 6.4 Hz, 4H); \(^1\)C NMR (100 MHz, CDCl\(_3\)): 19.19, 27.52, 113.90, 114.11, 119.55, 119.77, 125.02, 125.05, 128.29, 129.89, 129.97, 130.14, 132.53, 136.34, 144.15, 144.20, 161.56, 164.02, 231.73 (SiCOAr); FT-IR: \(\nu\) (cm\(^{-1}\)) = 3072.1, 2932.9, 2858.9, 1617.8, 1583.5, 1479.2, 1428.3, 1243.4, 1153.7, 1108.2, 815.8, 789.7, 740.4, 700.3, 685.4; HRMS(ESI, m/z): Calcd. for [C24H26FOSi+H]+, 363.1580, found, 363.1594.
(tert-butyldiphenylsilyl)(4-fluoropentyl)methanone: $^1$H NMR (400 MHz, CDCl$_3$): 1.25, 6.91 (t, J = 8.0 Hz, 2H), 7.40-7.49 (m, 6H), 7.75-7.80 (m, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$): 19.20, 27.52, 115.34, 115.56, 128.27, 130.08, 131.06, 131.16, 132.80, 136.36, 138.81, 138.84, 164.14, 166.67, 230.82 (SiCOAr); FT-IR: $\nu$ (cm$^{-1}$) = 3447.8, 3075.1, 2959.9, 2934.3, 2856.2, 1613.8, 1580.4, 1500.9, 1427.7, 1225.6, 1204.4, 1155.3, 1098.1, 846.9, 819.6, 742.4, 698.1; HRMS (ESI, m/z): Calcd. for [C$_{23}$H$_{23}$FOSi+H]$^+$, 363.1580, found, 363.1590.

The synthesis of 2-benzyl-3-hydroxy-5,5-dimethylcyclohex-2-enone and its similarities were carried out according to previous reports$^{[4]}$.

$^1$H NMR (400 MHz, [D$_6$]DMSO$_2$): $\delta = 0.98$ (s, 6H, CH$_3$), 2.26 (br s, 4H, CH$_2$), 3.49 (s, 2H, CH$_2$), 7.08 (t, J = 7.2Hz, 1H, ArH), 7.14 (d, J = 7.6Hz, 2H, ArH), 7.19 (t, J = 7.6Hz, 2H, ArH). $^{13}$C NMR (100 MHz, [D$_6$]DMSO): $\delta = 142.3$, 128.6, 128.3, 125.6, 113.2, 32.1, 28.5, 27.6.

$^1$H NMR (400 MHz, [D$_6$]DMSO$_2$): $\delta = 0.99$ (s, 6H, CH$_3$), 1.23 (s, 9H, CH$_3$), 2.25 (s, 4H, CH$_2$), 3.43 (s, 2H, CH$_2$), 7.04 (d, J = 8.4Hz, 2H, ArH), 7.20 (d, J = 8.4Hz, 2H, ArH). $^{13}$C NMR (100 MHz, [D$_6$]-DMSO): $\delta = 147.8$, 139.2, 128.2, 125.0, 113.3, 34.4, 32.1, 31.7, 28.5, 27.0.
References


Selected NMR Spectra of \(\alpha\)-hydroxysilane and acylsilanes