



Supporting Information

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A Tandem Intermolecular Radical Addition–Oxidation Reaction Converts Alkenylsilanes into Ketones with Air as an Oxidant

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General Methods ^1H NMR (300 MHz) and ^{13}C NMR (75.3 MHz) spectra were taken on Varian GEMINI 300 or MERCURY 300 spectrometer in CDCl_3 as a solvent, and chemical shifts were given in δ value with tetramethylsilane as an internal standard. IR spectra were determined on a JASCO IR-810 spectrometer. Mass spectra were determined on a JEOL JMS-700 spectrometer. TLC analyses were performed on commercial glass plates bearing 0.25 mm layer of Merk Silica gel 60F₂₅₄. Column chromatography was done with silica gel (Wakogel 200 mesh). The analyses were carried out at the Elemental Analysis Center of Kyoto University. Triethylborane was purchased from Aldrich and used for reactions as hexane or methanol solutions (1.0 M). Benzene was dried over slices of sodium. Commercially available distilled water was used for the reaction in water. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification.

Experimental and Compound Data

General Procedure for the Preparation of Aldehydes from α -Iodoalkylsilanes

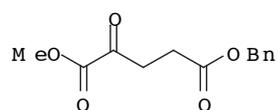
Under air atmosphere, a solution of iodide **3a** (250 mg, 0.5 mmol), H_3PO_2 (0.275 mL, 50% aqueous solution, 2.5 mmol), and pyridine (0.2 mL, 2.5 mmol) in benzene (3 mL) was stirred for 5 min. To the mixture, a solution of Et_3B in hexane (1.5 mL, 1.0 M, 1.5 mmol) was added dropwise in five portions at intervals of 1 h at room temperature. (**Caution:** A concentrated solution of Et_3B may ignite in air. We recommend the use of a diluted 1.0 M solution.) After the addition of all the solution of Et_3B , the mixture was stirred for additional 1 h. The reaction mixture then extracted with ether (10 mL \times 3). The organic layers were dried over anhydrous Na_2SO_4 and concentrated in vacuo. Purification by silica gel column chromatography provided aldehyde **4a** (65 mg, 0.34 mmol) in 68% yield.

General Procedure for the Tandem Radical Addition–Oxidation Reaction

A 30-mL two-necked round bottomed flask with a septum, a gas inlet 3-way tap and a stirring bar was charged with 2-silylpropene (**2b**, 119 mg, 0.5 mmol), benzyl iodoacetate (201 mg, 0.75 mmol), NH_4Cl (802 mg, 15 mmol), and distilled water (5 mL). The tap was connected to air and argon balloons at each inlet. The mixture was stirred for 5 min under air atmosphere, and then purged with argon. A solution of Et_3B in methanol (1.0 mL, 1.0 M, 1.0 mmol) was introduced dropwise in five portions at intervals of 1 h at room temperature. (**Caution:** An addition of Et_3B in methanol to an aqueous mixture under air may cause fire. Accordingly, a solution of Et_3B was added under argon atmosphere. Before the addition, air was purged off by the stream of argon. To the mixture, a solution of Et_3B in methanol (0.2 mL, 1.0 M) was added dropwise at room temperature. The reaction flask was then connected to the balloon of air, and the mixture was

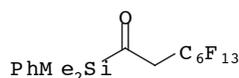
stirred for 1 h. This sequence was repeated at each addition of Et₃B.) The mixture was stirred for additional 1 h after the final addition of Et₃B. The reaction mixture then extracted with ether (10 mL × 3). The organic layers were dried over anhydrous Na₂SO₄ and concentrated in vacuo. Purification by silica gel column chromatography provided ketone **4c** (83 mg, 0.40 mmol) in 80% yield.

5-Benzyl 1-Methyl 2-Oxopentanedioate (**4l**)



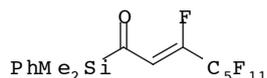
IR (neat) 2930, 2858, 1732, 1492, 1163, 1109, 974, 793, 739, 700 cm⁻¹; ¹H NMR (CDCl₃) δ 2.73 (t, *J* = 6.6 Hz, 2H) 3.17 (t, *J* = 6.6 Hz, 2H), 3.87 (s, 3H), 5.12 (s, 2H), 7.31–7.40 (m, 5H); ¹³C NMR (CDCl₃) δ 27.66, 34.14, 53.04, 66.75, 128.23, 128.32, 128.57, 135.60, 160.89, 171.76, 192.19. Found: C, 62.66; H, 5.57%. Calcd for C₁₃H₁₄O₅: C, 62.39; H, 5.64%.

1-(Dimethylphenylsilyl)-3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctan-1-one (**4m**)



Not isolated. ¹H NMR (CDCl₃) δ 0.23 (s, 3H), 0.34 (s, 3H), 3.21 (t, *J*_{H-F} = 19.2 Hz, 2H).

1-(Dimethylphenylsilyl)-3,4,4,5,5,6,6,7,7,8,8,8-dodecafluorooct-(2Z)-en-1-one (**4n**)



IR (neat) 1682, 1609, 1429, 1337, 1240, 1144, 1113, 970, 816, 789, 723, 698 cm⁻¹; ¹H NMR (CDCl₃) δ 0.53 (s, 3H), 0.54 (s, 3H), 6.08 (d, *J*_{H-F} = 37.2 Hz, 1H), 7.35–7.46 (m, 3H), 7.48–7.53 (m, 3H); ¹³C NMR (CDCl₃) δ -5.13, -5.09, 116.30, 128.24, 130.30, 132.66, 134.01, 148.47, 148.87,

149.26, 152.21, 152.60, 152.99. Found: C, 40.59; H, 2.56%. Calcd for C₁₆H₁₂F₁₂OSi: C, 40.34; H, 2.54%.