Oxidation of Carbon–Silicon Bonds: The Dramatic Advantage of Strained Siletanes

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Supporting Information

Experimental section

All the ^1H and ^{13}C NMR spectra were recorded on a Mercury Varian 300 MHz or Inova Varian 500 MHz spectrometer using CDCl_3 as the deuterated solvent unless otherwise stated. The chemical shifts (δ) are reported in parts per million (ppm) using tetramethylsilane as the internal standard. The IR spectra were recorded on a Perkin Elmer Paragon 1000 FTIR spectrometer on NaCl discs. Low and high-resolution mass spectra were performed on a JEOL JMS600 apparatus. The melting points were determined on a Kfler melting point apparatus and are uncorrected. Yields refer to isolated material judged to be $\geq 95\%$ pure by ^1H NMR spectroscopy following silica gel chromatography.

Materials. All the chemicals were purchased from Aldrich or Acros and were used as received unless otherwise stated. Diethyl ether and THF were distilled over sodium and benzophenone under argon atmosphere. The Grignard reagents were purchased or prepared from the corresponding alkyl or aryl bromides and magnesium turnings, and titrated using a solution of I_2 in THF or Et_2O . The purifications of the compounds were performed on flash chromatography using silica gel F-254 (230-400 mesh particle size).

General procedure for the preparation of the siletanes 2, 5-12

The Grignard reagent was added dropwise to a solution of 1-chloro-1-methylsilacyclobutane (**1**) in Et_2O . The reaction mixture was then heated in a $40\text{ }^\circ\text{C}$ oil bath for the indicated length of time. After cooling to room temperature, the cloudy suspension was partitioned between a mixture of

hexanes (9 mL) and half-saturated NH₄Cl solution (9 mL). The organic phase was washed with brine (9 mL), dried over MgSO₄, filtered and concentrated under reduced pressure. Purification by flash column chromatography on silica gel using hexanes (unless otherwise stated) as the eluent provided the desired siletane.

1-Methyl-1-phenethylsiletane (**2**)

Phenethylmagnesium chloride (1.08 M in Et₂O, 1.85 mL, 1.99 mmol) was added to a solution of **1** (207 μ L, 1.63 mmol) in Et₂O (8 mL). After 18.5 h of refluxing, standard workup and purification provided **2** as a clear liquid (273 mg, 88%).

¹H NMR (300 MHz): δ 7.17-7.31 (m, 5H), 2.72-2.78 (m, 2H), 2.02-2.13 (m, 2H), 1.09-1.14 (m, 2H), 0.89-1.07 (m, 4H), 0.26 (s, 3H). ¹³C NMR (75 MHz): δ 145.0, 128.3, 127.9, 125.6, 29.8, 18.5, 18.3, 13.5, -1.6. IR (NaCl plate, thin film, cm⁻¹): 3062, 2961, 2925, 1603, 1495, 1409. HRMS (EI⁺) Calcd for C₁₂H₁₈Si: 190.1180. Found 190.1178.

1-Methyl -1-(α -styrenyl)siletane (**5**)

α -Styrenylmagnesium bromide¹ (0.83 M in THF, 10.0 mL, 8.3 mmol) was added to a solution of **1** (1.0 mL, 8.2 mmol) in Et₂O (6 mL). After 17 h of refluxing, standard work up and purification afforded **5** as a clear liquid (1.49 g, 97%).

¹H NMR (300 MHz): δ 7.22-7.35 (m, 5H), 6.06 (d, *J* = 2.7 Hz, 1H), 5.72 (d, *J* = 2.7 Hz, 1H), 2.07-2.18 (m, 2H), 1.08-1.31 (m, 4H), 0.36 (s, 3H). ¹³C NMR (75 MHz): δ 151.0, 142.9, 128.4, 127.0, 126.8, 126.4, 18.1, 14.7, -1.4. IR (NaCl plate, thin film, cm⁻¹): 3055, 2965, 1939, 1490, 1402. HRMS (EI⁺) Calcd for C₁₂H₁₆Si: 188.1021. Found 188.1014.

¹ The Grignard was prepared by following the procedure of Overman et al. *J. Am. Chem. Soc.* **1991**, *113*, 5354-5365.

1-[6-(*tert*-Butyldimethylsilanyloxy)hexyl]-1-methylsiletane (7)

6-(*tert*-Butyldimethylsilanyloxy)-1-hexylmagnesium bromide (0.75 M in THF, 22 mL, 17 mmol) was added to a solution of siletane **1** (1.35 mL, 11 mmol) in THF (25 mL). After 13 h at 40 °C, workup and purification by column chromatography (*n*-heptane) afforded siletane **7** as a clear colorless oil (420 mg, 77%).

¹H NMR (300 MHz): δ 3.60 (t, *J* = 6.3 Hz, 2H), 2.03-2.10 (m, 2H), 1.27-1.51 (m, 9H), 0.89-0.94 (m, 12H), 0.70-0.75 (m, 2H), 0.24 (s, 3H), 0.05 (s, 6H). ¹³C NMR (75 MHz): 63.3, 32.8, 31.6, 25.8, 23.6, 22.6, 18.2, 16.5, 14.0, -1.7, -5.3. IR (NaCl plate, thin film, cm⁻¹): 2928, 2856, 1472, 1462.

1,1-Diphenethylsiletane (8)

Phenethylmagnesium chloride (1.08 M in Et₂O, 1.95 mL, 2.11 mmol) was added to a solution of **1** (127 μ L, 1.0 mmol) in Et₂O (10 mL). After refluxing for 16 h, standard workup and purification by column chromatography (hexanes) provided siletane **8** as colorless viscous oil (240 mg, 86%).

¹H NMR (300 MHz): δ 7.20-7.45 (m, 10H), 2.78-2.90 (m, 2H), 1.90-2.20 (m, 2H), 1.58-1.79 (m, 2H), 1.01-1.30 (m, 8H). ¹³C NMR (75 MHz): 144.7, 128.4, 127.9, 125.7, 29.9, 19.4, 17.1, 12.1. IR (NaCl plate, thin film, cm⁻¹): 3061, 2923, 1603, 1495, 1454.

1-Methyl-1-(*o*-tolyl)siletane (**9**)

o-Tolylmagnesium bromide (2.01 M in Et₂O, 1.0 mL, 2.0 mmol) was added to a solution of **1** (207 μ L, 1.63 mmol) in Et₂O (9 mL). After refluxing overnight, standard workup and purification provided **9** as a clear liquid (266 mg, 96%).

¹H NMR (300 MHz): δ 7.51 (d, J = 7.1 Hz, 1H), 7.16-7.33 (m, 3H), 2.41 (s, 3H), 2.11-2.22 (m, 2H), 1.15-1.38 (m, 4H), 0.50 (s, 3H). ¹³C NMR (75 MHz): δ 146.1, 138.0, 133.8, 129.5, 129.3, 125.0, 22.2, 18.2, 14.5, -0.4. IR (NaCl plate, thin film, cm⁻¹): 3056, 2963, 2868, 1448. HRMS (EI⁺) Calcd for C₁₁H₁₆Si: 176.1026. Found 176.1021.

1-(3-Methoxyphenyl)-1-methylsiletane (**10**)

3-Methoxyphenylmagnesium bromide (1.03 M in THF, 1.30 mL, 1.33 mmol) is added to a solution of **1** (197 μ L, 1.55 mmol) in Et₂O (9 mL). After refluxing for 2 h, workup and purification by column chromatography (EtOAc/Hexanes: 5/95) provided **10** as a clear liquid (215 mg, 84%).

¹H NMR (300 MHz): δ 7.35 (apparent t, J = 7.7 Hz, 1H), 7.16-7.23 (m, 2H), 6.92-6.96 (m, 1H), 3.85 (s, 3H), 2.13-2.24 (m, 2H), 1.11-1.35 (m, 4H), 0.55 (s, 3H). ¹³C NMR (75 MHz): δ 159.1, 140.3, 129.1, 125.7, 118.9, 114.6, 55.1, 18.2, 14.3, -1.7. IR (NaCl plate, thin film, cm⁻¹): 2932, 1587, 1570, 1479. HRMS (EI⁺): Calcd for C₁₁H₁₆OSi: 192.0970. Found 192.0971.

1-Biphenyl-1-methylsiletane (**11**)

Biphenylmagnesium bromide (0.50 M in THF, 5.7 mL, 2.9 mmol) is added to a solution of **1** (363 μ L, 2.86 mmol) in Et₂O (9 mL). After 17.5 h of stirring at 40 °C, workup and purification

by column chromatography on silica gel (cyclohexane) provided **11** as a white solid (595 mg, 88%). M.pt. 38-40 °C.

¹H NMR (300 MHz): δ 7.70-7.73 (m, 2H), 7.59-7.65 (m, 4H), 7.43-7.48 (m, 2H), 7.34-7.39 (m, 1H), 2.16-2.27 (m, 2H), 1.15-1.39 (m, 4H), 0.59 (s, 3H). ¹³C NMR (75 MHz): δ 142.1, 140.9, 137.2, 133.9, 128.8, 127.4, 127.1, 126.6, 18.3, 14.4, -1.8. IR (NaCl plate, CH₂Cl₂, cm⁻¹): 3022, 2960, 1916, 1541, 1409.

HRMS (EI⁺): Calcd for C₁₁H₁₆OSi: 238.1178. Found 238.1171.

1-Methyl-1-(2-trifluoromethylphenyl)siletane (12)

2-Trifluoromethylphenylmagnesium bromide (1.05 M in THF, 17 mL, 17 mmol) was added to a solution of siletane **1** (500 μ L, 3.93 mmol) in THF. After overnight stirring at 40 °C, usual work up and purification by column chromatography (*n*-heptane) gave the title compound as a colorless oil (828 mg, 92%).

¹H NMR (300 MHz): δ 7.37-7.43 (m, 2H), 7.20-7.28 (m, 2H), 1.76-1.89 (m, 2H), 0.87-1.15 (m, 4H), 0.20 (s, 3H, Me). ¹³C NMR (75 MHz): δ 138.0, 134.9, 134.2 (d, $J_{\text{C-F}}$ = 31.2 Hz), 134.0, 130.7, 129.3, 125.1 (q, $J_{\text{C-F}}$ = 272.1 Hz), 17.4, 15.5, -0.4. IR (NaCl plate, thin film, cm⁻¹): 3015, 2963, 2919, 1597.

1-Methyl-1-(*sec*-phenethyl)siletane (6)

Under argon atmosphere, 2,4,6-triisopropylbenzenesulfonyl hydrazide² (358 mg, 1.20 mmol) is added to a solution of **5** (216 mg, 1.15 mmol) in CH₃OH (10 mL). The reaction mixture was stirred at ambient temperature for 4 h, at which time another portion of

² This hydrazide generates diimide at room temp in protic solvents. For a review on diimide reductions, see Pasto, D. J.; Taylor, R. T. Reduction with Diimide. *Org. React.* **1991**, 40, 91–155.

triisopropylbenzenesulfonyl hydrazide (175 mg, 0.59 mmol) was added. After 5 h of stirring at room temperature, the reaction mixture was diluted with hexanes (10 mL), and washed with half saturated NaHCO₃ solution (2 x 10 mL) and brine (10 mL). The organic phase was then dried over MgSO₄, filtered, and concentrated under reduced pressure. Purification by flash column chromatography (hexanes) yielded **6** as a clear liquid (195 mg, 89%).

¹H NMR (300 MHz): δ 7.26 (apparent t, J = 7.7 Hz, 2H), 7.09-7.13 (m, 3H), 2.41 (q, J = 7.4 Hz, 1H), 1.80-2.07 (m, 2H), 1.50 (d, J = 7.4 Hz, 3H), 0.86-1.13 (m, 4H), 0.15 (s, 3H). ¹³C NMR (75 MHz): δ 144.7, 128.2, 126.8, 124.5, 29.6, 17.7, 14.2, 12.9, -3.6. IR (NaCl plate, thin film, cm⁻¹): 3060, 3023, 1490, 1450. HRMS (EI⁺) Calcd. for C₁₂H₁₈Si: 190.1178. Found 190.1169.

Standard procedure for the siletane oxidations. Phenethyl alcohol [60-12-8] (3)

KF·2H₂O (342 mg, 3.63 mmol) and KHCO₃ (365 mg, 3.64 mmol) were added to a solution of **2** (342 mg, 1.80 mmol) in 8 mL of THF/CH₃OH (1:1). The resulting mixture was cooled in an ice bath, and H₂O₂ (30% in H₂O, 6.25 g, 55 mmol) was added dropwise. The reaction mixture was stirred at 0 °C for 10 min and then at ambient temperature for 6 h. The reaction mixture was then diluted with EtOAc (24 mL) and the aqueous layer removed. The organic phase was sequentially washed with a 1.0M aqueous Na₂S₂O₃ (6 mL) and brine (6 mL). The combined aqueous phases were extracted with CH₂Cl₂ (3x 20 mL).³ The combined organic phases were dried over MgSO₄, filtered and concentrated. Purification by flash column chromatography on silica gel (Hexanes/EtOAc: 9/1) provided phenethyl alcohol (170 mg, 78%), whose spectroscopic data was consistent with a commercially available sample.

³ For an alternative workup procedure, see compounds **14** and **15** (acetophenone and *sec*-phenethyl alcohol, below).

^1H NMR (300 MHz): δ 7.30-7.35 (m, 2H), 7.22-7.26 (m, 3H), 3.87 (t, J = 6.7 Hz, 2H), 2.88 (t, J = 6.5 Hz, 2H), 1.43 (s, 1H). LRMS (EI^+): 122.1 (M^+ , 38), 104.1 (32), 91.1 (100), 71.1 (36).

6-(*tert*-Butyldimethylsilanyloxy)hexan-1-ol (16)

$\text{KF}\cdot 2\text{H}_2\text{O}$ (242 mg, 1.69 mmol) and KHCO_3 (275 mg, 1.66 mmol) were added to a solution of **9** (230 mg, 0.77 mmol) in 6 mL of THF/ CH_3OH . The mixture was cooled, and H_2O_2 (30% in H_2O , 2.31 g, 23 mmol) was added. Work up and purification by column chromatography (Hexanes/Ether: 4:1) provided **16** as a colorless oil (122 mg, 82%), whose spectroscopic data was consistent with that reported previously.⁴

^1H NMR (300 MHz): 3.57-3.63 (m, 4H), 1.43-1.56 (m, 4H), 1.30-1.41 (m, 4H), 1.25 (bs, 1H, OH), 0.88 (s, 9H), 0.03 (s, 6H). ^{13}C NMR (75 MHz): 63.3, 63.1, 32.8, 31.6, 25.9, 22.6, 18.3, 14.0, -5.3. IR (NaCl plate, thin film, cm^{-1}): 3352, 2929, 2857, 1472, 1462. HRMS (ESI): Calcd for $\text{C}_{12}\text{H}_{29}\text{O}_2\text{Si}$: 233.1937. Found 233.1935.

***o*-Cresol [95-48-7] (17)**

$\text{KF}\cdot 2\text{H}_2\text{O}$ (283 mg, 3.01 mmol) and KHCO_3 (317 mg, 3.17 mmol) were added to a solution of **9** (276 mg, 1.52 mmol) in 8 mL of THF/ CH_3OH . The mixture was cooled, and H_2O_2 (30% in H_2O , 5.13 g, 45 mmol) was added. Work up and purification by column chromatography (Hexanes/ EtOAc : 10:1) provided **17** as a pale yellow liquid (122 mg, 74%).

^1H NMR (300 MHz): δ 7.06-7.14 (m, 2H), 6.85 (apparent t, J = 7.3 Hz, 1H), 6.77 (d, J = 8.1 Hz, 1H), 4.61 (s, 1H), 2.23 (s, 3H). LRMS (EI^+): 108.1 (M^+ , 100), 107.1 (80).

⁴ Mc Dougall, P.; Rico, J. G.; Oh, Y. I.; Condon, B. D. *J. Org. Chem.* **1986**, *51*, 3388-3390.

3-Methoxyphenol [150-19-6] (**18**)

KF·2H₂O (294 mg, 3.12 mmol) and KHCO₃ (318 mg, 3.17 mmol) were added to a solution of **10** (293 mg, 1.52 mmol) in 7 mL of THF/CH₃OH. The mixture was cooled, and H₂O₂ (30% in H₂O, 5.31 g, 47 mmol) was added. Work up and purification by column chromatography (Hexanes/EtOAc: 85/15) provided **18** as a pale yellow liquid (147 mg, 78%).

¹H NMR (300 MHz): δ 7.11-7.17 (m, 1H), 6.48-6.52 (m, 1H), 6.41-6.44 (m, 2H), 4.72 (s, 1H), 3.78 (s, 3H). LRMS (EI⁺): 124.1 (M⁺, 100), 94.1 (60), 81.0 (50), 66.6 (42).

4-Phenylphenol [92-69-3] (**19**).

KF·2H₂O (359 mg, 3.82 mmol) and KHCO₃ (344 mg, 3.43 mmol) were added to a solution of **2** (395 mg, 1.66 mmol) in 8 mL of THF/CH₃OH. The mixture was cooled, and the H₂O₂ (30% in H₂O, 5.72 g, 51 mmol) was added. Work up and purification by column chromatography (Hexanes/EtOAc: 75:25) provided **19** as a white solid (249 mg, 88%).

¹H NMR (300 MHz): δ 7.39-7.56 (m, 6H), 7.28-7.33 (m, 1H), 6.89-6.93 (m, 2H), 4.70 (s, 1H). LRMS (EI⁺): 170.1 (M⁺, 100).

2-Trifluoromethylphenol [444-30-4] (**20**)

KF·2H₂O (211 mg, 2.02 mmol) and KHCO₃ (225 mg, 2.24 mmol) were added to a solution of **2** (285 mg, 1.02 mmol) in 8 mL of THF/CH₃OH. The suspension was then cooled at 0 °C to which, H₂O₂ (30% in H₂O, 3.41 g, 31 mmol) was added over 10 min and the reaction mixture was stirred for 6 h at room temperature. Standard work up and purification by column chromatography (*n*-Pentane/Et₂O 80:20) provided **20** as a colorless oil that crystallized upon

standing. The ^1H NMR spectrum revealed solvent contamination in the sample, and attempts to remove the solvents without loss of phenol **20** under reduced pressure were unsuccessful.

^1H NMR (300 MHz): δ 7.51 (d, $J = 7.5$ Hz, 1H), 7.31 (apparent t, $J = 7.5$ Hz, 1H), 6.93-7.02 (m, 2H), 5.85 (s, 1H). LRMS (EI^+): 162.1 (M^+ , 20), 149 (m/z , 100), 122.1 (36), 71.1 (22).

Preparation of 14-15: Alternative work up procedure

Acetophenone [98-86-2] (14)

In air, $\text{KF}\cdot 2\text{H}_2\text{O}$ (385 mg, 4.10 mmol) and KHCO_3 (408 mg, 4.08 mmol) were added to a solution of **5** (366 mg, 1.95 mmol) in 8 mL of THF/ CH_3OH . The resulting mixture was cooled in an ice bath, and H_2O_2 (30% in H_2O , 6.67 g, 59 mmol) was added dropwise. The reaction mixture was stirred at 0 °C for 10 min and at ambient temperature for 6 h, and then was partitioned between EtOAc (24 mL) and H_2O (8 mL). The aqueous layer was extracted with CH_2Cl_2 (2 x 8 mL). The combined organic layers were sequentially washed with brine (8 mL), 1.0M aqueous $\text{Na}_2\text{S}_2\text{O}_3$ (8 mL), and brine (8 mL), and then dried over MgSO_4 , filtered and concentrated under reduced pressure. Purification by flash column chromatography (Hexanes/EtOAc: 9/1) provided **14** as a pale yellow liquid (182 mg, 78%).

^1H NMR (300 MHz): δ 7.95-7.98 (m, 2H), 7.55-7.60 (m, 1H), 7.45-7.50 (m, 2H), 2.61 (s, 3H).

HRMS (EI^+) Calcd for $\text{C}_8\text{H}_8\text{O}$: 120.0575. Found 120.0575.

***sec*-Phenethyl alcohol [98-85-1] (15).**

$\text{KF}\cdot 2\text{H}_2\text{O}$ (363 mg, 3.85 mmol) and KHCO_3 (378 mg, 3.77 mmol) were added to a solution of **6** (348 mg, 1.83 mmol) in 8 mL of THF/ CH_3OH . The mixture was cooled, and the H_2O_2 (30% in

H₂O, 6.31 g, 56 mmol) was added. Work up and purification by flash column chromatography (benzene) provided **15** as a pale yellow liquid (165 mg, 74%).

¹H NMR (300 MHz): δ 7.26-7.40 (m, 5H), 4.92 (quartet, J = 6.5 Hz, 1H), 1.76 (s, 1H), 1.51 (d, J = 6.4 Hz, 3H). HRMS (EI⁺) Calcd for C₈H₁₀O: 122.0732. Found 120.0727.

Mechanistic Study in Deuterated Solvents

KF·2H₂O (177 mg, 1.88 mmol) and KHCO₃ (169 mg, 1.69 mmol) were added to a solution of 1,1-dimethylsilane (83 mg, 0.82 mmol) in 0.75 mL of THF-*d*₈ and 1 g of CH₃OH-*d*₄. The resulting mixture was cooled in an ice bath, and H₂O₂ (30% in H₂O, 463 mg, 4.1 mmol) was added dropwise. The reaction mixture was stirred at 0 °C for 10 min, and then at ambient temperature. The reaction was monitored by ¹H NMR for 3 days (due to smaller excess of H₂O₂), at which point the ratio of propanediol to propanol was 1.5:1. The identity of propanediol and propanol in the NMR spectrum was confirmed by subsequent addition of authentic samples.

Competition between **3** and **24**

Under argon atmosphere, a flask was charged with **3** (42 mg, 0.22 mmol) and **24** (50 mg, 0.22 mmol). An aliquot of the mixture was taken for ¹H NMR analysis, which confirmed a 1:1 ratio of silanes. The reaction mixture was then exposed to air and 2 mL of THF/CH₃OH (1:1) was added, followed by KF·2H₂O (85 mg, 0.91 mmol) and KHCO₃ (88 mg, 0.88 mmol). The mixture was cooled in an ice bath and H₂O₂ (30% solution in water, 1.59 g, 14 mmol) was added dropwise. The reaction was stirred at 0°C for 10 min and at ambient temperature for 2 h. Following the usual workup, the crude mixture was analyzed by ¹H NMR (500 MHz) to show a 1.2:1 ratio of **24**:**3**.

6-(1-Methylsiletan-1-yl)hexan-1-ol (22)

A solution of THF/H₂O/AcOH (1:1:3, 50 mL) was added slowly to siletane **7** (300 mg, 1.00 mmol) over 5 min at 0 °C. After 10 min, the clear solution was warmed up to room temperature and stirred for 1 h. The reaction mixture was then partitioned between Et₂O (50 mL) and 1.0 M aqueous NaOH (50 mL). The organic layer was washed successively with 1.0 M aqueous NaOH (4 x 10 mL), saturated NaHCO₃ (2 x 20 mL), brine (20 mL), dried over Na₂SO₄ and concentrated under reduced pressure. Purification by column chromatography on silica gel (Hexanes/EtOAc: 8/2) afforded the title compound as a colorless viscous oil (161 mg, 87%).

¹H NMR (300 MHz): δ 3.64 (t, *J* = 6.7 Hz, 2H), 1.95-2.11 (m, 2H), 1.50-1.65 (m, 2H), 1.23-1.48 (m, 8H), 0.85-1.07 (m, 3H), 0.71-0.88 (m, 2H), 0.45 (s, 3H). ¹³C NMR (75 MHz): δ 62.8, 32.9, 32.7, 25.4, 23.5, 18.1, 16.4, 13.4, -1.7. IR (NaCl plate, thin film, cm⁻¹): 3335, 2920, 1462, 1409.

1,1-Diphenylsiletane (13)⁵

Phenylmagnesium bromide (2.83 M in Et₂O, 30 mL, 85 mmol) was added to a solution of 1,1-dichlorosilacyclobutane (5.99 g, 42 mmol) in Et₂O (20 mL) over 30 min. The cloudy suspension was stirred for another 30 min. and refluxed overnight. After usual workup and filtration on a short plug of silica gel (Hexanes/EtOAc:9/1), the title compound was obtained as a colorless liquid (9.34g, 98% crude yield).

¹H NMR (300 MHz): δ 7.50-7.85 (m, 4H), 7.30-7.53 (m, 6H), 2.14-2.36 (m, 2H), 1.40-1.60 (m, 4H).

⁵ The preparation of this compound is carried out by following a literature procedure: Grobe *et al.* *J. Organomet. Chem.* **1980**, 188, 25-52.

Phenol [108-95-2] (21)

KF·2H₂O (379 mg, 4 mmol) and KHCO₃ (410 mg, 4 mmol) were added to a solution of **13** (444 mg, 1.98 mmol) in 8 mL of THF/CH₃OH. The mixture was cooled, and the H₂O₂ (30% in H₂O, 6.80 g, 60 mmol) was added. Work up and flash column chromatography (Et₂O/Hexanes: 20/80) provided **15** as a white powder (284 mg, 76% over two steps).

¹H NMR (300 MHz): δ 7.22-7.28 (m, 2H), 6.93 (t, *J* = 8.5 Hz, 1H), 6.82-6.85 (m, 2 H), 4.74 (s, 1H).