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

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Supporting Information

Experimental section

All the ^{1}H 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 (d) 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 Köfler melting point apparatus and are uncorrected. Yields refer to isolated material judged to be ≥ 95% pure by ^{1}H 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 ^{o}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 NH_4Cl solution (9 mL). The organic phase was washed with brine (9 mL), dried over $MgSO_4$, 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 Et_2O, 1.85 mL, 1.99 mmol) was added to a solution of **1** (207 mL, 1.63 mmol) in Et_2O (8 mL). After 18.5 h of refluxing, standard workup and purification provided **2** as a clear liquid (273 mg, 88%).

^{1}H NMR (300 MHz): d 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). ^{13}C NMR (75 MHz): d 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 $C_{12}H_{18}Si$: 190.1180. Found 190.1178.

1-Methyl -1-(a-styrenyl)siletane (5)

a-Styrenylmagnesium bromide[1] (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 Et_2O (6 mL). After 17 h of refluxing, standard work up and purification afforded **5** as a clear liquid (1.49 g, 97%).

^{1}H NMR (300 MHz): d 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). ^{13}C NMR (75 MHz): d 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 $C_{12}H_{16}Si$: 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 ^{o}C, workup and purification by column chromatography (*n*-heptane) afforded siletane **7** as a clear colorless oil (420 mg, 77%).

^{1}H NMR (300 MHz): d 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). ^{13}C 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 Et_2O, 1.95 mL, 2.11 mmol) was added to a solution of **1** (127 mL, 1.0 mmol) in Et_2O (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%).

^{1}H NMR (300 MHz): d 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). ^{13}C 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 Et_2O, 1.0 mL, 2.0 mmol) was added to a solution of **1** (207 mL, 1.63 mmol) in Et_2O (9 mL). After refluxing overnight, standard workup and purification provided **9** as a clear liquid (266 mg, 96%).

^{1}H NMR (300 MHz): d 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). ^{13}C NMR (75 MHz): d 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 $C_{11}H_{16}Si$: 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 mL, 1.55 mmol) in Et_2O (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%).

^{1}H NMR (300 MHz): d 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). ^{13}C NMR (75 MHz): d 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 $C_{11}H_{16}OSi$: 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 mL, 2.86 mmol) in Et_2O (9 mL). After 17.5 h of stirring at 40 ^{o}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.

^{1}H NMR (300 MHz): d 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). ^{13}C NMR (75 MHz): d 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, CH_2Cl_2, cm^{-1}): 3022, 2960, 1916, 1541, 1409.

HRMS (EI$^+$): Calcd for $C_{11}H_{16}OSi$: 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 mL, 3.93 mmol) in THF. After overnight stirring at 40 ^{o}C, usual work up and purification by column chromatography (*n*-heptane) gave the title compound as a colorless oil (828 mg, 92%).

^{1}H NMR (300 MHz): d 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). ^{13}C NMR (75 MHz): d 138.0, 134.9, 134.2 (d, J_{C-F} = 31.2 Hz), 134.0, 130.7, 129.3, 125.1 (q, J_{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 hydrazide[2] (358 mg, 1.20 mmol) is added to a solution of **5** (216 mg, 1.15 mmol) in CH_3OH (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 $NaHCO_3$ solution (2 x 10 mL) and brine (10 mL). The organic phase was then dried over $MgSO_4$, filtered, and concentrated under reduced pressure. Purification by flash column chromatography (hexanes) yielded **6** as a clear liquid (195 mg, 89%).

^{1}H NMR (300 MHz): d 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). ^{13}C NMR (75 MHz): d 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 $C_{12}H_{18}Si$: 190.1178. Found 190.1169.

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

KF $2H_2O$ (342 mg, 3.63 mmol) and $KHCO_3$ (365 mg, 3.64 mmol) were added to a solution of **2** (342 mg, 1.80 mmol) in 8 mL of THF/CH_3OH (1:1). The resulting mixture was cooled in an ice bath, and H_2O_2 (30% in H_2O, 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 $Na_2S_2O_3$ (6 mL) and brine (6 mL). The combined aqueous phases were extracted with CH_2Cl_2 (3x 20 mL).[3] The combined organic phases were dried over $MgSO_4$, 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).

^{1}H NMR (300 MHz): d 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)

KF $2H_2O$ (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]

^{1}H 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 $C_{12}H_{29}O_2Si$: 233.1937. Found 233.1935.

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

KF $2H_2O$ (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%).

^{1}H NMR (300 MHz): d 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 $2H_2O$ (294 mg, 3.12 mmol) and $KHCO_3$ (318 mg, 3.17 mmol) were added to a solution of **10** (293 mg, 1.52 mmol) in 7 mL of THF/CH_3OH. The mixture was cooled, and H_2O_2 (30% in H_2O, 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%).

^{1}H NMR (300 MHz): d 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 $2H_2O$ (359 mg, 3.82 mmol) and $KHCO_3$ (344 mg, 3.43 mmol) were added to a solution of **2** (395 mg, 1.66 mmol) in 8 mL of THF/CH_3OH. The mixture was cooled, and the H_2O_2 (30% in H_2O, 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%).

^{1}H NMR (300 MHz): d 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 $2H_2O$ (211 mg, 2.02 mmol) and $KHCO_3$ (225 mg, 2.24 mmol) were added to a solution of **2** (285 mg, 1.02 mmol) in 8 mL of THF/CH_3OH. The suspension was then cooled at 0 ^oC to which, H_2O_2 (30% in H_2O, 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/Et_2O 80:20) provided **20** as a colorless oil that crystallized upon

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

^{1}H NMR (300 MHz): d 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, KF $2H_2O$ (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 $Na_2S_2O_3$ (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%).

^{1}H NMR (300 MHz): d 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 C_8H_8O: 120.0575. Found 120.0575.

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

KF $2H_2O$ (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

H_2O, 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%).

^{1}H NMR (300 MHz): d 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 $C_8H_{10}O$: 122.0732. Found 120.0727.

Mechanistic Study in Deuterated Solvents

KF $2H_2O$ (177 mg, 1.88 mmol) and $KHCO_3$ (169 mg, 1.69 mmol) were added to a solution of 1,1-dimethylsiletane (83 mg, 0.82 mmol) in 0.75 mL of THF-d_8 and 1 g of CH_3OH-d_4. The resulting mixture was cooled in an ice bath, and H_2O_2 (30% in H_2O, 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 ^{1}H NMR for 3 days (due to smaller excess of H_2O_2), 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 ^{1}H NMR analysis, which confirmed a 1:1 ratio of silanes. The reaction mixture was then exposed to air and 2 mL of THF/CH_3OH (1:1) was added, followed by KF $2H_2O$ (85 mg, 0.91 mmol) and $KHCO_3$ (88 mg, 0.88 mmol). The mixture was cooled in an ice bath and H_2O_2 (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 ^{1}H 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/H_2O/AcOH (1:1:3, 50 mL) was added slowly to siletane **7** (300 mg, 1.00 mmol) over 5 min at 0 ^oC. After 10 min, the clear solution was warmed up to room temperature and stirred for 1 h. The reaction mixture was then partitioned between Et_2O (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 $NaHCO_3$ (2 x 20 mL), brine (20 mL), dried over Na_2SO_4 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%).

^{1}H NMR (300 MHz): d 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). ^{13}C NMR (75 MHz): d: 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 Et_2O, 30 mL, 85 mmol) was added to a solution of 1,1-dichlorosilacyclobutane (5.99 g, 42 mmol) in Et_2O (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).

^{1}H NMR (300 MHz): d 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 $2H_2O$ (379 mg, 4 mmol) and $KHCO_3$ (410 mg, 4 mmol) were added to a solution of **13** (444 mg, 1.98 mmol) in 8 mL of THF/CH_3OH. The mixture was cooled, and the H_2O_2 (30% in H_2O, 6.80 g, 60 mmol) was added. Work up and flash column chromatography (Et_2O/Hexanes: 20/80) provided **15** as a white powder (284 mg, 76% over two steps).

^{1}H NMR (300 MHz): d 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).