Supporting Information

Synthesis of Primary Amines by the Electrophilic Amination of Grignard Reagents with 1,3-Dioxolan-2-one *O*-Sulfonyloxime

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Experimental

General

¹H NMR (400 MHz) and ¹³C NMR (100 MHz) spectra were recorded on JEOL AL 400 spectrometer in CDCl₃ [using CHCl₃ (for ¹H, δ = 7.24) and CDCl₃ (for ¹³C, δ = 77.0) as an internal standard] or DMSO-*d*₆ [using DMSO (for ¹H, δ = 2.49) and DMSO-*d*₆ (for ¹³C, δ = 39.70) as an internal standard]. IR spectra were recorded on a Horiba FT 300-S spectrometer by ATR method. The melting points were uncorrected. Elemental analyses were carried out at The Elemental Analysis Laboratory, Department of Chemistry, Faculty of Science, The University of Tokyo. Column chromatography was performed on silica gel (Fuji Silysia Silica gel PSQ-100B). Preparative TLC (PTLC) was performed on a silica gel (Wakogel B-5F). Tetrahydrofuran (THF) and diethyl ether (Et₂O) were freshly distilled from sodium benzophenone ketyl under an argon atmosphere. Toluene was distilled, and water was azeotropically removed. Dichloromethane and acetonitrile were distilled twice from P₂O₅ then from CaH₂, and stored over molecular sieves 4A. Chlorobenzene was distilled from CaH₂ and stored over molecular sieves 4A. Methanol was distilled from Mg and stored over molecular sieves 4A. Ethanol was distilled from Na and stored over molecular sieves 4A. Triethylamine was distilled from CaH₂ and stored over KOH. Pyridine was distilled from CaH₂. Phenylcarbonimidic dichloride was purchased from Tokyo Chemical Industry. Phenylmagnesium bromide, 4-methylphenylmagnesium bromide, 2,6-dimethylphenylmagnesium bromide, 2-methoxyphenylmagnesium bromide, 3-methoxyphenylmagnesium bromide, 4-methoxyphenylmagnesium bromide, 2,4-dimethoxyphenylmagnesium bromide, 4-fluorophenylmagnesium bromide, 4-trifluoromethylphenylmagnesium bromide, 1-naphthylmagnesium bromide, phenethylmagnesium bromide, 2-phenylpropylmagnesium bromide, 1-methyl-2-phenylethylmagnesium bromide, cyclohexylmagnesium bromide were prepared according to the general procedure.¹ 1-Adamantylmagnesium bromide,² and 1-norbornylmagnesium chloride³ were prepared according to the references. All the Grignard reagents were used after the titration by the literature procedure.⁴

2-Phenylimino-4,4,5,5-tetramethyl-1,3-dioxolane (5a):⁵ To a suspension of NaH (6.36 g, 264 mmol) in THF (250 mL) was slowly added pinacol (15.2 g, 128 mmol) in THF (60 mL) at 0 °C under an argon atmosphere, then phenylcarbonimidic dichloride⁶ (**4**) (20.5 g, 128 mmol) in THF (40 mL) was added for 15 min. This mixture was stirred at room temperature for 30 min. After the reaction was quenched with pH 9 buffer, the mixture was extracted three times with ethyl acetate. The combined extracts were washed with brine and dried over anhydrous sodium sulfate. The ethyl acetate was removed in vacuo to give 4,4,5,5-tetramethyl-2-phenylimino-1,3-dioxolane (**5a**) (22.5 g, 87%), which was used without further purification. Colorless needles; mp 82-84 °C (hexane/ethyl acetate); IR (ZnSe) 2983, 1697, 1593, 1487, 1292, 1140, 1011, 993, 777, 704 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 1.37 (6H, s), 1.39 (6H, s), 7.00 (1H, t, *J* = 7.4 Hz), 7.08 (2H, d, *J* = 7.4 Hz), 7.24 (2H, t, *J* = 7.4 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 22.1, 22.2, 84.6, 87.1, 122.9, 123.3, 128.4, 145.5, 151.8; Anal. Found: C, 71.16; H, 7.82; N, 6.33%. Calcd for C₁₃H₁₇NO₂: C, 71.21, H, 7.81; N, 6.39%.

4,4,5,5-Tetramethyl-1,3-dioxolan-2-one Oxime (6): To a solution of 4,4,5,5-tetramethyl-2-phenylimino-1,3-dioxolane (**5a**) (26.7 g, 122 mmol) in ethanol (300 mL) was added triethylamine (61.7 g, 611 mmol) and NH₂OH·HCl (34.1 g, 491 mmol), and this mixture was stirred at room temperature for 24 h. After the reaction was quenched with pH 9 buffer, the mixture was extracted three times with ethyl acetate. The combined extracts were washed successively with water and brine,

and dried over anhydrous sodium sulfate. The ethyl acetate was removed in vacuo and the crude materials were purified by flash column chromatography (hexane/ethyl acetate = 1/1 - 1/4) to give 4,4,5,5-tetramethyl-1,3-dioxolan-2-one oxime (**6**) (16.7 g, 86%). Colorless needles; mp 132-134 °C (hexane/ethyl acetate); IR (ZnSe) 3330, 2987, 2943, 1707, 1379, 1321, 1140, 1022, 661 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 1.33 (6H, s), 1.38 (6H, s), 6.82 (1H, br); ¹³C NMR (100 MHz, CDCl₃) δ 22.0, 22.2, 86.2, 87.7, 157.3; Anal. Found: C, 52.55; H, 8.18; N, 8.53%. Calcd for C₇H₁₃NO₃: C, 52.82; H, 8.23; N, 8.80%.

Typical Procedure for the Preparation of *O*-Sulfonyloxime (3**) (Preparation of 4,4,5,5-tetramethyl-1,3-dioxolan-2-one *O*-phenylsulfonyloxime (**3a**) is described below):** To a solution of 4,4,5,5-tetramethyl-1,3-dioxolan-2-one oxime (**6**) (4.49 g, 22.8 mmol) and triethylamine (5.90 mL, 42.3 mmol) in dichloromethane (100 mL) was slowly added benzenesulfonyl chloride (5.59 g, 31.6 mmol) in dichloromethane (15 mL) at 0 °C under an argon atmosphere, and the mixture was stirred at room temperature for 1 h. After the reaction was quenched with ice water, the mixture was extracted three times with ethyl acetate. The combined extracts were washed with brine and dried over anhydrous sodium sulfate. The ethyl acetate was removed in vacuo and the crude materials were purified by recrystallization (hexane/ethyl acetate) to give 4,4,5,5-tetramethyl-1,3-dioxolan-2-one *O*-phenylsulfonyloxime (**3a**) (7.40 g, 88%). Colorless crystal; mp 94-96 °C (hexane/ethyl acetate); IR (ZnSe) 2987, 1792, 1651, 1356, 1190, 1032, 870, 725, 652, 557 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 1.32 (6H, s), 1.36 (6H, s), 7.50 (2H, t, *J* = 7.4 Hz), 7.61 (1H, t, *J* = 7.4 Hz), 7.97 (2H, d, *J* = 7.4 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 22.0, 22.1, 88.8, 90.0, 128.7, 128.9, 133.6, 135.2, 163.6; Anal. Found: C, 52.10; H, 5.80; N, 4.50%. Calcd for C₁₃H₇NO₅S: C, 52.16; H, 5.72; N, 4.68%.

4,4,5,5-Tetramethyl-1,3-dioxolan-2-one *O*-Tosyloxime (3b**):** Colorless crystal; mp 159 °C dec. (hexane-ethyl acetate); IR (ZnSe) 2987, 1678, 1352, 1192, 1174, 1041, 872, 816, 719, 663, 652 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 1.31 (6H, s), 1.35 (6H, s), 2.40 (3H, s), 7.29 (2H, d, *J* = 8.4 Hz), 7.83 (2H, d, *J* = 8.4 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 21.7, 21.9, 22.0, 88.7, 90.0, 128.9, 129.3, 132.2, 144.5, 163.4; Anal. Found: C, 53.40; H, 6.07; N, 4.36%. Calcd for C₁₄H₁₉NO₅S: C, 53.66; H, 6.11; N, 4.47%.

4,4,5,5-Tetramethyl-1,3-dioxolan-2-one *O*-Mesitylphenylsulfonyloxime (3c**):** Colorless crystal; mp 152-154 °C (hexane-ethyl acetate); IR (ZnSe) 2981, 1680, 1360, 1340, 1192, 1176, 1028, 804, 719, 660 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 1.29 (6H, s), 1.35 (6H, s), 2.27 (3H, s), 2.64 (6H, s), 6.92 (2H, s); ¹³C NMR (100 MHz, CDCl₃) δ 21.1, 21.8, 21.9, 22.8, 88.6, 89.7, 130.2, 131.3, 140.7, 143.0, 163.4; Anal. Found: C, 56.03; H, 6.75; N, 3.99%. Calcd for C₁₆H₂₃NO₅S: C, 56.29; H, 6.79; N, 4.10%.

4,4,5,5-Tetramethyl-1,3-dioxolan-2-one *O*-Mesyloxime (3d**):** Colorless crystal; mp 105-106 °C (hexane-ethyl acetate); IR (ZnSe) 1672, 1352, 1178, 1138, 1034, 964, 872, 814, 715, 650 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 1.42 (6H, s), 1.44 (6H, s), 3.09 (3H, s); ¹³C NMR (100 MHz, CDCl₃) δ 22.0, 22.1, 35.6, 89.1, 90.3, 163.5; Anal. Found: C, 40.46; H, 6.31; N, 5.62%. Calcd for C₈H₁₅NO₅S: C, 40.50; H, 6.37; N, 5.90%.

Typical Procedure for the Preparation of Aniline Hydrochlorides by the Reaction of 1,3-Dioxolan-2-one Oxime **3 with Aryl Grignard Reagents:** To a solution of 4,4,5,5-tetramethyl-1,3-dioxolan-2-one *O*-phenylsulfonyloxime (**3a**) (593 mg, 1.98 mmol) in chlorobenzene (15 mL) was added dropwise an ether solution of phenylmagnesium bromide (0.96 M, 2.3 mL, 2.2 mmol) at 0 °C under an argon atmosphere, and this mixture was stirred at the same temperature for 30 min. After the reaction was quenched with pH 9 buffer at 0 °C, the mixture was extracted three times with ethyl acetate. The combined extracts were washed with brine and dried over anhydrous sodium sulfate. The ethyl acetate was removed in vacuo. To the crude imine in methanol (10 mL) was added hydrochloride in ether (1.0 M, 4.0 mL) at 0 °C, and this mixture was stirred at room temperature for 1.5 h. Volatile materials were removed in vacuo, and to the resulting mixture was added anhydrous ether (40 mL). Insoluble materials were collected by filtration to give aniline hydrochloride (**7a**) (239 mg, 93%).

Spectral Data. Aniline Hydrochloride (7a**):** White powder; ¹H NMR (400 MHz, DMSO-*d*₆) δ 7.36-7.39 (3H, m), 7.47 (2H, dd, *J* = 7.8 Hz, 7.8 Hz), 10.37 (3H, br); ¹³C NMR (100 MHz, DMSO-*d*₆) δ 123.2, 127.9, 129.8, 132.2.

4-Methylaniline Hydrochloride (7b):⁸ Pale yellow powder; ¹H NMR (400 MHz, DMSO-*d*₆) δ 2.30 (3H, s), 7.27 (4H, m), 10.45 (3H, br); ¹³C NMR (100 MHz, DMSO-*d*₆) δ 20.8, 123.2, 129.2, 130.1, 137.5.

2-Methoxyaniline Hydrochloride (7c):⁷ Pale purple powder; ¹H NMR (400 MHz, DMSO-*d*₆) δ 3.85 (3H, s), 7.00 (1H, dd, *J* = 7.2 Hz), 7.17 (1H, d, *J* = 7.2 Hz), 7.36 (1H, dd, *J* = 7.2 Hz), 7.50 (1H, d, *J* = 7.2 Hz), 10.19 (3H, br); ¹³C NMR (100 MHz, DMSO-*d*₆) δ 56.3, 112.5, 120.7, 120.8, 124.1, 129.3, 152.4.

3-Methoxyaniline Hydrochloride (7d):⁹ Pale yellow powder; ¹H NMR (400 MHz, DMSO-*d*₆) δ 3.75 (3H, s), 6.95 (3H, br), 7.37 (1H, t, *J* = 7.8 Hz), 10.41 (3H, br); ¹³C NMR (100 MHz, DMSO-*d*₆) δ 55.6, 109.3, 113.2, 115.3, 130.7, 133.3, 159.9.

4-Methoxyaniline Hydrochloride (7e):⁹ Pale yellow powder; ¹H NMR (400 MHz, DMSO-*d*₆) δ 3.74 (3H, s), 7.01 (2H, d, *J* = 8.4 Hz), 7.32 (2H, d, *J* = 8.4 Hz), 10.36 (3H, br); ¹³C NMR (100 MHz, DMSO-*d*₆) δ 55.6, 114.9, 124.2, 124.6, 158.7.

2,4-Dimethoxyaniline Hydrochloride (7f):⁷ Pale purple powder; ¹H NMR (400 MHz, DMSO-*d*₆) δ 3.75 (3H, s), 3.84 (3H, s), 6.56 (1H, d, *J* = 8.4 Hz), 6.72 (1H, s), 7.44 (1H, d, *J* = 8.4 Hz), 10.13 (3H, br); ¹³C NMR (100 MHz, DMSO-*d*₆) δ 55.8, 56.4, 99.7, 105.1, 113.0, 124.8, 153.4, 160.1.

4-Fluoroaniline Hydrochloride (7g): White powder; mp >200 °C (isopropylalcohol); IR (ZnSe) 2819, 2544, 1558, 1506, 1238, 1161, 1101, 825, 739, 633 cm⁻¹; ¹H NMR (400 MHz, DMSO-*d*₆) δ 7.30-7.34 (2H, m), 7.43-7.46 (2H, m), 10.45 (3H, br); ¹³C NMR (100 MHz, DMSO-*d*₆) δ 116.6 (d, *J* = 23.1 Hz), 125.4 (d, *J* = 8.3 Hz), 128.4, 161.1 (d, *J* = 243 Hz); Anal. Found: C, 48.58; H, 4.89; N, 9.25%. Calcd for C₆H₇ClFN: C, 48.83; H, 4.78; N, 9.49%.

4-Trifluoromethylaniline Hydrochloride (7h):¹⁰ White powder; ¹H NMR (400 MHz, DMSO-*d*₆) δ 7.30 (2H, d, *J* = 8.4 Hz), 7.66 (2H, d, *J* = 8.4 Hz), 9.71 (3H, br); ¹³C NMR (100 MHz, DMSO-*d*₆) δ 117.2, 120.6, 124.5 (q, *J* = 269 Hz), 126.7-126.8 (m), 141.8.

2,6-Dimethylaniline Hydrochloride (7i):⁹ White powder; ¹H NMR (400 MHz, DMSO-*d*₆) δ 2.37 (6H, s), 7.11 (3H, m), 9.80 (3H, br); ¹³C NMR (100 MHz, DMSO-*d*₆) δ 18.2, 127.4, 129.0, 129.8, 131.5.

1-Naphtylammonium Chloride (7j):⁹ White powder; ¹H NMR (400 MHz, DMSO-*d*₆) δ 7.54-7.72 (4H, m), 7.93-8.02 (2H, m), 8.12 (1H, d, *J* = 7.2), 10.53 (3H, br); ¹³C NMR (100 MHz, DMSO-*d*₆) δ 120.2, 122.2, 125.6, 126.5, 126.9, 127.0, 127.8, 128.3, 128.8, 133.7.

Typical Procedure for the Preparation of Alkylamine Hydrochlorides by the Reaction of 1,3-Dioxolan-2-one Oxime 3 with Alkyl Grignard Reagents: To a solution of 4,4,5,5-tetramethyl-1,3-dioxolan-2-one *O*-phenylsulfonyloxime (**3a**) (602 mg, 2.01 mmol) in chlorobenzene (14 mL) was added dropwise an ether solution of 1-adamantylmagnesium bromide (0.63 M, 3.5 mL, 2.2 mmol) at 0 °C under an argon atmosphere, and this mixture was stirred at the same temperature for 30 min. After the reaction was quenched with pH 9 buffer at 0 °C, the mixture was extracted three times with ethyl acetate. The combined extracts were washed with brine and dried over anhydrous sodium sulfate. The ethyl acetate was removed in vacuo. To the crude imine in ethanol (10 mL) was added 6.0 M HCl (1.3 mL, 8.0 mmol) and this mixture was stirred at reflux for 10 h. After removing ethanol in vacuo, 5.0 M NaOH (5.0 mL, 25 mmol) was added to the resulting mixture. The mixture was extracted three times with dichloromethane and the combined extracts were washed with brine and dried over anhydrous sodium sulfate. The dichloromethane was removed in vacuo, and hydrochloride in ether (1.0 M, 4.0 mL) was added to the crude mixture in methanol (10 mL) at 0 °C. After stirring this mixture for 5 min, volatile materials were removed in vacuo. To the resulting mixture was added anhydrous ether (40 mL). Insoluble materials were collected by filtration to give 1-adamantylammonium chloride (**7o**) (334 mg, 89%).

Spectral Data. 2-Phenethylammonium Chloride (7k):⁷ White powder; ¹H NMR (400 MHz, DMSO-*d*₆) δ 2.89-2.92 (2H, m), 2.97 (2H, br), 7.20-7.24 (3H, m), 7.30 (2H, t, *J* = 7.4 Hz), 8.31 (3H, br); ¹³C NMR (100 MHz, DMSO-*d*₆) δ 33.1, 40.1, 126.7, 128.66, 128.69, 137.6.

2-Phenylpropylammonium Chloride (7l): White powder; mp 143-144 °C (hexane-benzene-isopropylalcohol); IR (ZnSe) 3116, 2877, 1570, 1489, 1149, 1011, 989, 841, 746, 698 cm⁻¹; ¹H NMR

(400 MHz, DMSO- d_6) δ 1.25 (3H, d, J = 7.2 Hz), 2.94 (2H, br), 3.05-3.14 (1H, m), 7.21-7.34 (5H, m), 8.21 (3H, br); ^{13}C NMR (100 MHz, DMSO- d_6) δ 19.5, 37.5, 45.1, 126.9, 127.2, 128.7, 143.1; Anal. Found: C, 62.75; H, 8.39; N, 8.01%. Calcd for $\text{C}_9\text{H}_{14}\text{ClN}$: C, 62.97; H, 8.22; N, 8.16%.

1-Methyl-2-phenylethylammonium Chloride (7m):¹¹ White powder; ^1H NMR (400 MHz, DMSO- d_6) δ 1.10 (3H, d, J = 6.4 Hz), 2.61-2.67 (1H, m), 3.06-3.10 (1H, m), 3.33-3.37 (1H, m), 7.23 (2H, t, J = 7.2 Hz), 7.29-7.33 (3H, m), 8.30 (3H, br); ^{13}C NMR (100 MHz, DMSO- d_6) δ 17.6, 22.2, 48.2, 126.8, 128.7, 129.3, 137.0.

Cyclohexylammonium Chloride (7n):⁹ White powder; ^1H NMR (400 MHz, DMSO- d_6) δ 1.01-1.11 (1H, m), 1.16-1.32 (4H, m), 1.53-1.57 (1H, m), 1.67-1.70 (2H, m), 1.89-1.92 (2H, m), 2.85-2.92 (1H, m), 8.19 (3H, br); ^{13}C NMR (100 MHz, DMSO- d_6) δ 23.9, 24.8, 30.4, 49.4.

1-Adamantylammonium Chloride (7o):⁷ White powder; ^1H NMR (400 MHz, DMSO- d_6) δ 1.54 (3H, d, J = 12.2 Hz), 1.62 (3H, d, J = 12.2 Hz), 1.79 (6H, s), 2.05 (3H, s), 8.18 (3H, br); ^{13}C NMR (100 MHz, DMSO- d_6) δ 28.5, 35.4, 40.1, 51.1.

1-Norbornylammonium Chloride (7p):¹⁰ To a suspension of magnesium bromide diethyl etherate (800 mg, 3.10 mmol) in THF (2 mL) was added dropwise a hexane and cyclohexane solution of norbornane lithium (0.60 M, 4.3 mL, 2.6 mmol) at 0 °C under an argon atmosphere, and this mixture was stirred at room temperature for 1 h. A solution of 4,4,5,5-tetramethyl-1,3-dioxolan-2-one *O*-phenylsulfonyloxime (**3a**) (292 mg, 0.975 mmol) in dichloromethane (10 mL) was added to the mixture. After the reaction mixture was stirred at room temperature for 10 min, the reaction was quenched with pH 9 buffer at 0 °C. The mixture was extracted three times with ethyl acetate. The combined extracts were washed with brine and dried over anhydrous sodium sulfate. The ethyl acetate was removed in vacuo. To the crude imine in ethanol (5 mL) was added 6.0 M HCl (0.67 mL, 4.0 mmol) and this mixture was stirred at reflux for 10 h. After the ethanol was removed in vacuo, water was added and the mixture was washed with ethyl acetate twice. The aqueous solution was removed in vacuo, and recrystallization of the residual solid from 2-propanol-ether gave 1-norbornylammonium chloride (**7p**) (92.5 mg, 64%). White powder; ^1H NMR (400 MHz, DMSO- d_6) δ 1.32-1.40 (2H, m), 1.50-1.57 (4H, m), 1.65-1.73 (4H, m), 2.17 (1H, s), 8.55 (3H, br); ^{13}C NMR (100 MHz, DMSO- d_6) δ 29.4, 32.1, 35.0, 40.9, 60.9.

***N*-Cyclohexylbenzamide:**¹⁰ To a solution of 4,4,5,5-tetramethyl-1,3-dioxolan-2-one *O*-phenylsulfonyloxime (**3a**) (596 mg, 1.99 mmol) in chlorobenzene (10 mL) was added dropwise an ether solution of cyclohexylmagnesium bromide (0.88 M, 2.5 mL, 2.2 mmol) at 0 °C under an argon atmosphere, and this mixture was stirred at the same temperature for 30 min. After the reaction was quenched with pH 9 buffer at 0 °C, the mixture was extracted three times with ethyl acetate. The combined extracts were washed with brine and dried over anhydrous sodium sulfate. The ethyl acetate was removed in vacuo. To the crude imine in ethanol (9 mL) was added 6.0 M HCl (1.3 mL, 8.0 mmol) and this mixture was stirred at reflux for 6 h, then ethanol was removed in vacuo. To the residue in dichloromethane (6 mL) was added triethylamine (1.7 mL, 12 mmol) and successively a solution of benzoyl chloride (560 mg, 4.0 mmol) in dichloromethane (2 mL) was added slowly at 0 °C. After the resulting solution was stirred at room temperature for 30 min, the reaction was quenched with water. The mixture was extracted three times with ethyl acetate, and the combined extracts were washed successively with sat. NaHCO_3 and brine. The ethyl acetate solution was dried over anhydrous sodium sulfate, and the ethyl acetate was removed in vacuo. The crude materials were purified by flash column chromatography (hexane/ethyl acetate = 4/1 – 1/1) to give *N*-cyclohexylbenzamide (372 mg, 92%). Colorless prism; IR (ZnSe) 3311, 2929, 2850, 1626, 1577, 1533, 1329, 1151, 1082, 692 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 1.12-1.26 (3H, m), 1.34-1.45 (2H, m), 1.60-1.65 (1H, m), 1.70-1.75 (2H, m), 1.98-2.02 (2H, m), 3.91-3.99 (1H, m), 6.06-6.08 (1H, br), 7.36-7.40 (2H, m), 7.42-7.47 (1H, m), 7.71-7.74 (2H, m); ^{13}C NMR (100 MHz, CDCl_3) δ 24.9, 25.6, 33.2, 48.7, 126.7, 128.4, 131.1, 134.9, 166.5.

Typical Procedure for the Preparation of Azadienes by the Reaction of 1,3-Dioxolan-2-one Oxime 3a with Alkenyl Grignard Reagents: To a solution of 4,4,5,5-tetramethyl-1,3-dioxolan-2-one *O*-phenylsulfonyloxime (**3a**) (562 mg, 1.88 mmol) in chlorobenzene (12 mL) was added dropwise a

ether solution of 2-styrylmagnesium bromide (0.46 M, 4.5 mL, 2.1 mmol: prepared from 2-styrylbromide (*E/Z* = 1:1) and Mg in ether) at 0 °C under an argon atmosphere, and this mixture was stirred at room temperature for 2 h. After the reaction was quenched with pH 9 buffer at 0 °C, the mixture was extracted three times with ethyl acetate. The combined extracts were washed with brine and dried over anhydrous sodium sulfate. The ethyl acetate was removed in vacuo and the crude materials were purified by flash column chromatography (silica gel; hexane/ethyl acetate = 8/2) to give less polar (*Z*)-2-styrylimino-4,4,5,5-tetramethyl-1,3-dioxolan and more polar (*E*)-2-styrylimino-4,4,5,5-tetramethyl-1,3-dioxolan (**9b**) (48:52, total 461 mg, quant).

Spectral Data. **2-(2-Propenyl)imino-4,4,5,5-tetramethyl-1,3-dioxolan (9a):** Colorless crystal; mp 39-40 °C; IR (ZnSe) 2983, 1705, 1635, 1375, 1275, 1144, 1047, 996, 931, 823 cm⁻¹; ¹H NMR (400 MHz, DMSO-*d*₆) δ 1.34 (6H, s), 1.35 (6H, s), 1.84 (3H, s), 4.38 (2H, s); ¹³C NMR (100 MHz, DMSO-*d*₆) δ 22.1 (overlapped), 22.3, 84.3, 86.5, 99.6, 147.1, 150.5; Anal. Found: C, 65.43; H, 9.43; N, 7.48%. Calcd for C₁₀H₁₇NO₂: C, 65.54; H, 9.35; N, 7.64%.

(E)-2-Styrylimino-4,4,5,5-tetramethyl-1,3-dioxolan (E-9b): Pale yellow crystal; mp 116-118 °C (hexane-ethyl acetate); IR (ZnSe) 3036, 1675, 1631, 1597, 1271, 1138, 982, 850, 755, 661 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 1.37 (6H, s), 1.40 (6H, s), 6.36 (1H, d, *J* = 13.4 Hz), 7.12 (1H, t, *J* = 7.6 Hz), 7.24 (2H, dd, *J* = 7.6 Hz, 7.6 Hz), 7.34 (2H, d, *J* = 7.6 Hz), 7.37 (1H, d, *J* = 13.4 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 22.2, 22.3, 85.4, 87.2, 122.2, 125.7, 126.0, 128.3, 132.1, 137.6, 154.6; Anal. Found: C, 73.56; H, 7.95; N, 5.47%. Calcd for C₁₅H₁₉NO₂: C, 73.44; H, 7.81; N, 5.71%.

(Z)-2-Styrylimino-4,4,5,5-tetramethyl-1,3-dioxolan (Z-9b): Colorless crystal; mp 83-85 °C (hexane-ethyl acetate); IR (ZnSe) 3023, 1669, 1624, 1596, 1299, 1141, 1109, 984, 795, 695 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 1.39 (12H, br), 5.68 (1H, d, *J* = 8.8 Hz), 6.76 (1H, d, *J* = 8.8 Hz), 7.11 (1H, t, *J* = 7.2 Hz), 7.26 (2H, dd, *J* = 7.2 Hz, 7.2 Hz), 7.82 (2H, d, *J* = 7.2 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 22.2, 22.3, 85.4, 87.0, 118.2, 125.8, 127.9, 129.2, 131.2, 137.0, 154.7; Anal. Found: C, 73.28; H, 7.92; N, 5.53%. Calcd for C₁₅H₁₉NO₂: C, 73.44; H, 7.81; N, 5.71%.

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