Supporting Information

Silver Technology for Stabilization of Simple (Z)-Enethiols: Stereoselective Synthesis and Reaction of Silver (Z)-Enethiolates

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Scheme S1. ^1H NMR chemical shifts (δ values in ppm) of α and β vinylic protons.

This chemical shift change will be due to the following equilibrium.

Scheme S2. (Z)-1-Decenyl *iso*-propyl sulfide was recovered quantitatively without isomerization, during the methylation of silver (Z)-1-decenylthiolate (**1a**) with methyl iodide.

Scheme S3. A possible mechanism of the isomerization of silver enethiolates **1** and of inhibition of the isomerization by TEMPO.

a)

b)

Figure S1. ESI-MS spectra (negative) in CH₂Cl₂-MeOH (1:1) showing the most prominent ion peak of hexamers [1₆-Ag]⁻. a) **1a**. b) **1b**.

Figure S2. ^1H NMR spectra of silver (Z)-1-decenylthiolate (**1a**) in CDCl_3 in the presence and absence of Bu_4NX ($\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$).

General Information. IR spectra were recorded on Perkin Elmer 1720 FT-IR spectrometers. ^1H NMR and ^{13}C NMR spectra were obtained on a JEOL JNM-AL300 or JNM-AL400 spectrometers. Chemical shifts (δ) are reported in parts per million (ppm) downfield from internal Me_4Si . Mass spectra (MS) were obtained on a JEOL JMS-DX300 spectrometer. Preparative thin-layer chromatography (TLC) was carried out on precoated plates of silica gel (MERCK, silica gel F-254). Melting points were determined with a Yanaco micro melting points apparatus and are uncorrected. Dichloromethane was dried over CaH_2 and distilled.

Substrates. (Z)-S-(1-Hexenyl)thioimidonium tetrafluoroborate **2b** (R = Bu, Ar = Ph) was prepared according to a literature method.¹

Reaction of (E)-1-Decenyl(phenyl)(tetrafluoroborato)- λ^3 -iodane (3a) with 4-Chloro-N,N-dimethylbenzenecarbothioamide.¹ To a stirred solution of λ^3 -iodane **3a**² (207 mg, 0.48 mmol) in dichloromethane (4 mL) was added *p*-chloro-N,N-dimethylthiobenzamide (96 mg, 0.48 mmol) at room temperature under nitrogen and the mixture was stirred for 3 days. After cooling, the mixture was concentrated *in vacuo*. Purification of the crude product by repeated decantation with hexane at $-78\text{ }^\circ\text{C}$ gave (Z)-S-vinylthioimidonium tetrafluoroborate **2a** (R = *n*-C₈H₁₇, Ar = *p*-ClC₆H₄, 199 mg, 97%) as a yellow oil. IR (neat) 2927, 2856, 1624, 1489, 1458, 1404, 1288, 1100-1000, 829, 729 cm⁻¹; ^1H NMR (400 MHz, CDCl₃) δ 7.58 (d, *J* = 7.3 Hz, 2H), 7.44 (d, *J* = 7.3 Hz, 2H), 6.02 (dt, *J* = 9.2, 7.3 Hz, 1H), 5.40 (d, *J* = 9.2 Hz, 1H), 3.84 (s, 3H), 3.51 (s, 3H), 2.27 (dt, *J* = 7.3, 7.0 Hz, 2H), 1.45-1.20 (m, 12H), 0.89 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (75 MHz, CDCl₃) δ 187.6, 144.1, 138.9, 130.1, 129.0, 128.5, 113.7, 47.6, 45.2, 31.8, 29.4, 29.3, 29.2, 29.1, 28.4, 22.6, 14.1; HRMS (ESI) calcd for C₁₉H₂₉CINS [(M-BF₄)⁺] 338.1709, found 338.1707.

Preparation of Silver (Z)-1-Decenylthiolate (1a). A suspension of (Z)-S-vinylthioimidonium tetrafluoroborate **2a** (199 mg, 0.47 mmol) and silver acetate (94 mg, 0.56 mmol) in THF (3 mL) and water (0.75 mL) was stirred at room temperature for 2 h under nitrogen in the dark. To the resulting yellow suspension was added water and the mixture was extracted with dichloromethane. The organic phase was filtered and concentrated under an aspirator vacuum to give an oily residue, which was purified by repeated decantation with methanol and then with ethyl acetate. The attempted recrystallization from dichloromethane-hexane at $4\text{ }^\circ\text{C}$ in the dark afforded silver (Z)-enethiolate **1a** (99.8 mg, 77%) as a yellow powder. Mp $75\text{--}77\text{ }^\circ\text{C}$ (decomp.); IR (Nujol) 2981, 2833, 1625, 1600, 1469, 1454, 1377, 1346, 1053, 721, 666 cm⁻¹; ^1H NMR (400 MHz, CDCl₃) δ 6.30 (d, *J* = 7.3 Hz, 1H), 5.68 (dt, *J* = 7.3, 6.6 Hz, 1H), 2.39 (q, *J* = 6.6 Hz, 2H), 1.46-1.20 (m, 12H), 0.89 (t, *J* = 6.6 Hz, 3H); ^{13}C NMR (75 MHz, CDCl₃) δ 136.4, 120.7, 32.0, 29.9, 29.5, 29.2, 22.7, 14.1; FAB MS (negative) *m/z* (relative intensity) 171 [(M-Ag)⁻, 68], 153 (52), 87 (100). Anal. Calcd for C₁₀H₁₉SAg·1/4 H₂O: C, 42.34; H, 6.92. Found: C, 42.21; H, 6.62.

Preparation of Silver (Z)-1-Hexenylthiolate (1b). A suspension of (Z)-S-vinylthioimidonium tetrafluoroborate **2b** (906 mg, 2.7 mmol) and silver acetate (541 mg, 3.2 mmol) in THF (6 mL) and water (1.5 mL) was stirred at room temperature for 2 h under nitrogen in the dark. To the resulting yellow suspension was added water and the mixture was extracted with dichloromethane. The organic phase was filtered and concentrated under an aspirator vacuum to give an oily residue,

which was purified by repeated decantation with methanol and then with ethyl acetate. The attempted recrystallization from dichloromethane-hexane at 4 °C in the dark afforded silver (Z)-enethiolate **1b** (486 mg, 80%) as a yellow powder. Mp 93-95 °C (decomp.); IR (Nujol) 2947, 2897, 2848, 1597, 1456, 1329, 690 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 6.33 (d, *J* = 7.7 Hz, 1H), 5.65 (dt, *J* = 7.7, 7.3 Hz, 1H), 2.40 (q, *J* = 7.3 Hz, 2H), 1.47-1.30 (m, 4H), 0.91 (t, *J* = 6.6 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 135.3, 122.1, 31.3, 28.6, 22.7, 14.2. Anal. Calcd for C₆H₁₁SAg·1/4 H₂O: C, 31.66; H, 5.09. Found: C, 31.45; H, 4.72.

General Procedure for Direct Methylation of Silver (Z)-Enethiolate 1a with Methyl Iodide (Table 1). A Typical Example (Entry 1). To a stirred solution of silver (Z)-enethiolate **1a** (9.1 mg, 0.032 mmol) in hexane (2 mL) was added methyl iodide (46.5 mg, 0.32 mmol) at room temperature under nitrogen in the dark and the mixture was stirred for 7 h. The resulting yellow suspension was filtered and the precipitate was washed with dichloromethane. The organic phase was concentrated under an aspirator vacuum to give an oil, which was purified by preparative TLC (ethyl acetate:hexane = 3:7) to yield a mixture of stereoisomers of 1-decenyl methyl sulfide (**4a**) (4.6 mg, 77%) as a colorless oil. The *Z:E* ratio (80:20) of **4a** was determined by ¹H NMR of a crude oil. (Z)-**4a**:^{3,4} IR (neat) 1608 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 5.86 (d, *J* = 9.1 Hz, 1H), 5.53 (dt, *J* = 9.1, 6.9 Hz, 1H), 2.27 (s, 3H), 2.10 (q, *J* = 6.9 Hz, 2H), 1.44-1.19 (m, 12H), 0.88 (t, *J* = 6.2 Hz, 3H).

General Procedure for Alkylation of Silver (Z)-Enethiolates 1 in the Presence of Bu₄NX (Table 2). A Typical Example (Entry 4). To a stirred solution of Bu₄NI (17.5 mg, 0.047 mmol) in dichloromethane (2 mL) was added silver (Z)-enethiolate **1a** (13.2 mg, 0.047 mmol) at room temperature under nitrogen in the dark and the resulting yellow solution was stirred for 0.5 h. Methyl iodide (20 mg, 0.14 mmol) was added and the mixture was stirred at room temperature for 3 h. After addition of water, the mixture was extracted with dichloromethane. The combined organic phase was washed with water, dried over anhydrous Na₂SO₄, filtered, and concentrated under an aspirator vacuum to give an oil, which was purified by preparative TLC (hexane) to yield a mixture of stereoisomers of methyl sulfide **4a** (6.8 mg, 77%). The *Z:E* ratio (97:3) of **4a** was determined by ¹H NMR of a crude oil.

(Z)-1-Hexenyl Methyl Sulfide (Entry 5):⁵ a colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 5.86 (d, *J* = 9.1 Hz, 1H), 5.53 (dt, *J* = 9.1, 7.3 Hz, 1H), 2.27 (s, 3H), 2.11 (q, *J* = 7.3 Hz, 2H), 1.44-1.28 (m, 4H), 0.91 (t, *J* = 7.3 Hz, 3H).

(Z)-1-Decenyl Ethyl Sulfide (Entry 6):⁶ a colorless oil; IR (neat) 1608 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 5.91 (d, *J* = 9.1 Hz, 1H), 5.57 (dt, *J* = 9.1, 6.9 Hz, 1H), 2.67 (q, *J* = 6.9 Hz, 2H), 2.11 (q, *J* = 6.9 Hz, 2H), 1.44-1.20 (m, 15H), 0.88 (t, *J* = 6.9 Hz, 3H).

(Z)-1-Hexenyl Ethyl Sulfide (Entry 7): a colorless oil; IR (neat) 2956, 2925, 2854, 1456, 1377, 1263 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 5.91 (d, *J* = 9.1 Hz, 1H), 5.57 (dt, *J* = 9.1, 7.3 Hz, 1H), 2.67 (q, *J* = 7.3 Hz, 2H), 2.12 (q, *J* = 7.3 Hz, 2H), 1.44-1.25 (m, 4H), 1.29 (t, *J* = 7.3 Hz, 3H), 0.91 (t, *J* = 7.3 Hz, 3H); MS *m/z* (relative intensity) 144 (M⁺, 60), 115 (41), 101 (100), 82 (34), 73 (68), 67 (74); HRMS calcd for C₈H₁₆S (M⁺) 144.0973, found 144.0990.

(Z)-1-Decenyl *iso*-Propyl Sulfide (Entry 8): a colorless oil; IR (neat) 2958, 2924, 2854, 1607, 1462, 1243, 770 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 5.98 (d, $J = 9.4$ Hz, 1H), 5.58 (dt, $J = 9.4$, 7.0 Hz, 1H), 3.05 (sept, $J = 6.6$ Hz, 1H), 2.11 (dt, $J = 7.0$, 6.8 Hz, 2H), 1.42-1.21 (m, 12H), 1.31 (d, $J = 6.6$ Hz, 6H), 0.87 (t, $J = 6.6$ Hz, 3H); MS m/z (relative intensity) 215 (30), 214 (M^+ , 10), 207 (89), 167 (90), 149 (100), 135 (40), 124 (45), 107 (67), 97 (97), 81 (95); HRMS calcd for $\text{C}_{13}\text{H}_{26}\text{S}$ (M^+) 214.1755, found 214.1734.

(Z)-1-Decenyl Benzyl Sulfide (Entry 10): a colorless oil; IR (neat) 3029, 2925, 2853, 1604, 1495, 1454, 1240, 1070, 746, 697 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.36-7.28 (m, 5H), 5.89 (d, $J = 9.2$ Hz, 1H), 5.55 (dt, $J = 9.2$, 7.0 Hz, 1H), 3.86 (s, 2H), 2.09 (q, $J = 7.0$ Hz, 2H), 1.39-1.16 (m, 12H), 0.88 (t, $J = 6.6$ Hz, 3H); MS m/z (relative intensity) 262 (M^+ , 23), 171 (25), 91 (100), 81 (27); HRMS calcd for $\text{C}_{17}\text{H}_{26}\text{S}$ (M^+) 262.1755, found 262.1731.

(Z)-1-Hexenyl Benzyl Sulfide (Entry 11):⁷ a colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 7.37-7.28 (m, 5H), 5.89 (d, $J = 9.1$ Hz, 1H), 5.55 (dt, $J = 9.1$, 7.3 Hz, 1H), 3.86 (s, 2H), 2.10 (q, $J = 7.3$ Hz, 2H), 1.40-1.22 (m, 4H), 0.87 (t, $J = 6.6$ Hz, 3H).

(Z)-1-Decenyl Allyl Sulfide (Entry 12): a colorless oil; IR (neat) 2925, 2853, 1636, 1607, 1457, 1228, 987, 916, 771 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 5.87 (d, $J = 9.1$ Hz, 1H), 5.84 (ddt, $J = 17.6$, 10.6, 7.3 Hz, 1H), 5.58 (dt, $J = 9.1$, 6.9 Hz, 1H), 5.16 (d, $J = 17.6$ Hz, 1H), 5.11 (d, $J = 10.6$ Hz, 1H), 3.28 (d, $J = 7.3$ Hz, 2H), 2.11 (q, $J = 6.9$ Hz, 2H), 1.43-1.18 (m, 12H), 0.88 (t, $J = 6.5$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 134.5, 130.2, 123.3, 117.1, 36.4, 31.9, 29.4, 29.3, 29.3, 29.3, 29.0, 22.7, 14.1; MS m/z (relative intensity) 212 (M^+ , 27), 171 (13), 113 (80), 99 (51), 95 (56), 85 (64), 81 (79), 79 (100), 67 (84); HRMS calcd for $\text{C}_{13}\text{H}_{24}\text{S}$ (M^+) 212.1599, found 212.1541.

(Z)-1-Decenyl (*E*)-Cinnamyl Sulfide (Entry 13): a colorless oil; IR (neat) 3028, 2924, 2854, 1606, 1464, 1223, 962, 750, 692 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.37 (d, $J = 7.7$ Hz, 2H), 7.31 (t, $J = 7.7$ Hz, 2H), 7.23 (t, $J = 7.7$ Hz, 1H), 6.49 (d, $J = 15.4$ Hz, 1H), 6.22 (dt, $J = 15.4$, 6.9 Hz, 1H), 5.92 (d, $J = 9.1$ Hz, 1H), 5.58 (dt, $J = 9.1$, 6.9 Hz, 1H), 3.45 (d, $J = 6.9$ Hz, 2H), 2.12 (q, $J = 6.9$ Hz, 2H), 1.42-1.19 (m, 12H), 0.87 (t, $J = 6.6$ Hz, 3H); MS m/z (relative intensity) 288 (M^+ , 6), 117 (100), 115 (20), 91 (15); HRMS calcd for $\text{C}_{19}\text{H}_{28}\text{S}$ (M^+) 288.1912, found 288.1891.

(Z)-1-Decenyl Phenacyl Sulfide (Entry 14): a colorless oil; IR (neat) 3060, 2925, 2854, 1680, 1599, 1579, 1448, 1277, 1014, 68 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.97 (d, $J = 7.3$ Hz, 2H), 7.58 (t, $J = 7.3$ Hz, 1H), 7.47 (t, $J = 7.3$ Hz, 2H), 5.97 (d, $J = 9.1$ Hz, 1H), 5.65 (dt, $J = 9.1$, 6.9 Hz, 1H), 3.95 (s, 2H), 2.07 (q, $J = 6.9$ Hz, 2H), 1.37-1.14 (m, 12H), 0.87 (t, $J = 6.9$ Hz, 3H); MS m/z (relative intensity) 290 (M^+ , 8), 120 (19), 105 (100), 77 (29); HRMS calcd for $\text{C}_{18}\text{H}_{26}\text{OS}$ (M^+) 290.1704, found 290.1693.

Reaction of Silver (Z)-Enethiolate 1a with Dichloromethane in the Presence of Bu_4NI . To a stirred solution of Bu_4NI (182 mg, 0.49 mmol) in dichloromethane (2 mL) was added silver (Z)-enethiolate **1a** (23.1 mg, 0.082 mmol) at room temperature under nitrogen in the dark and the resulting yellow solution was stirred for 24 h. After addition of water, the mixture was extracted with dichloromethane. The combined organic phase was washed with water, dried over anhydrous

Na₂SO₄, filtered, and concentrated under an aspirator vacuum to give an oil, which was purified by preparative TLC (dichloromethane:hexane = 7:3) to yield a 94:6 mixture of *Z,Z*- and *E,Z*-isomers of dithioacetal **6** (11.8 mg, 81%) as a colorless oil: IR (neat) 2954, 2924, 2853, 1604, 1494, 1454, 1240, 1070, 747, 697 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 6.06 (d, *J* = 9.1 Hz, 2H), 5.69 (dt, *J* = 9.1, 6.9 Hz, 2H), 3.87 (s, 2H), 2.12 (q, *J* = 6.9 Hz, 4H), 1.44-1.17 (m, 24H), 0.88 (t, *J* = 6.6 Hz, 6H); MS *m/z* (relative intensity) 356 (M⁺, 50), 185 (100), 137 (9), 95 (30), 87 (66), 81 (30): HRMS calcd for C₂₁H₄₀S₂ (M⁺) 356.2571, found 356.2577.

Reaction of Silver (Z)-Enethiolate 1a with 2,4-Dinitrochlorobenzene in the Presence of Bu₄NI. To a stirred solution of Bu₄NI (17.4 mg, 0.047 mmol) in dichloromethane (2 mL) was added silver (Z)-enethiolate **1a** (13.2 mg, 0.047 mmol) at room temperature under nitrogen in the dark and the resulting yellow solution was stirred for 0.5 h. A solution of 1-chloro-2,4-dinitrobenzene (7.9 mg, 0.039 mmol) in dichloromethane (1 mL) was added and the mixture was stirred at room temperature for 48 h. After addition of water, the mixture was extracted with dichloromethane. The combined organic phase was washed with water, dried over anhydrous Na₂SO₄, filtered, and concentrated under an aspirator vacuum to give an oil, which was purified by preparative TLC (ethyl acetate:hexane = 6:4) to yield (Z)-1-decenyl 2,4-dinitrophenyl sulfide (12.2 mg, 93%) as a yellow oil: IR (neat) 3105, 2926, 2855, 1594, 1522, 1339, 1051, 917, 833, 736 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 9.09 (d, *J* = 2.6 Hz, 1H), 8.34 (dd, *J* = 8.8, 2.6 Hz, 1H), 7.66 (d, *J* = 8.8 Hz, 1H), 6.45 (dt, *J* = 9.1, 6.9 Hz, 1H), 6.19 (d, *J* = 9.1 Hz, 1H), 2.39 (q, *J* = 6.9 Hz, 2H), 1.51-1.41 (m, 2H), 1.38-1.17 (m, 10H), 0.87 (t, *J* = 6.6 Hz, 3H); MS *m/z* (relative intensity) 338 (M⁺, 57), 239 (32), 183 (100), 137 (66), 95 (32), 83 (48): HRMS calcd for C₁₆H₂₂O₄N₂S (M⁺) 338.1300, found 338.1291.

Michael Addition of Silver (Z)-Enethiolate 1a to 2-Cyclohexenone in the Presence of LiI. To a stirred solution of LiI (39.8 mg, 0.30 mmol) in dichloromethane (2 mL) was added silver (Z)-enethiolate **1a** (13.6 mg, 0.05 mmol) and 2-cyclohexenone (3.7 mg, 0.038 mmol) at room temperature under nitrogen in the dark and the mixture was stirred at room temperature for 4 h. The resulting suspension was filtered and the precipitate was washed with dichloromethane. After addition of water, the mixture was extracted with dichloromethane. The combined organic phase was washed with water, dried over anhydrous Na₂SO₄, filtered, and concentrated under an aspirator vacuum to give an oil, which was purified by preparative TLC (dichloromethane:ethyl acetate = 9:1) to yield 3-[(Z)-1-decenylthio]cyclohexanone (8.1 mg, 81%) as a colorless oil: IR (neat) 2925, 2854, 1715, 1457, 1313, 1220 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 5.92 (d, *J* = 9.2 Hz, 1H), 5.68 (dt, *J* = 9.2, 7.0 Hz, 1H), 3.21-3.11 (m, 1H), 2.73 (dd, *J* = 14.6, 3.6 Hz, 1H), 2.46-2.25 (m, 3H), 2.22-2.03 (m, 4H), 1.83-1.65 (m, 2H), 1.43-1.18 (m, 12H), 0.88 (t, *J* = 6.6 Hz, 3H); MS *m/z* (relative intensity) 268 (M⁺, 9), 207 (100), 191 (11), 171 (13), 97 (72), 69 (96): HRMS calcd for C₁₆H₂₈OS (M⁺) 268.1861, found 268.1839.

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