Supporting Information for

N-Heterocyclic Carbene-Catalyzed Formal Cross-Coupling Reaction of α-Haloenals with Thiols: Organocatalytic Construction of sp² Carbon–Sulfur Bonds

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General Methods: Unless otherwise indicated, all reactions were conducted under nitrogen atmosphere in an oven-dried glassware with magnetic stirring bar. Column chromatograph was performed with silica gel (200~300 mesh) and analytical TLC on silica gel 60-F254. ¹H NMR (400 MHz, CDCl₃), ¹³C NMR (100 MHz, CDCl₃) spectra were recorded on 400 MHz spectrometer using deuterated chloroform as solvent, with tetramethylsilane as an internal standard and reported in ppm (δ). Infrared spectra were recorded on a FT/IR spectrophotometer and reported as wave number(cm⁻¹). EI mass spectra were measured on Agilent 7890A/5975C GC-MS and methanol or acetonitrile was used to dissolve the sample. High-resolution mass spectra (HRMS) were recorded on
FTICRMS. Thiols were obtained from commercial supplies and used without purification. α-Haloenals were synthesized according to literature. Anhydrous THF and toluene were distilled from sodium and benzophenone. CH$_2$Cl$_2$ and CH$_3$CN were distilled from calcium hydride. Petroleum ether (PE), where used, has a boiling range of 60–90 °C.

**Genera procedure for the synthesis α-thioenals:** A suspension of potassium carbonate (110mg, 0.8mmol) and IMes·HCl (9mg, 0.025mmol) in freshly distilled CH$_2$Cl$_2$ (2.0 mL) was stirred at ambient temperature for 0.5 h. Thiol (0.75mmol) and aldehyde (0.5mmol) were added subsequently and the solution was stirred at room temperature until full consume of the starting α-haloenal as indicated by TLC. The reaction mixture was then filtered through a short pad of silica gel and the silica gel was washed with 20 mL of 20% EtOAc in petroleum ether. After removal of the solvent under reduced pressure, the crude material was subjected to column chromatography (silica gel, PE-EtOAc, 10:1~100:1) to give the desired product.

**procedure for the synthesis IV:** A suspension of potassium carbonate (110mg, 0.8mmol) and IMes·HCl (9mg, 0.025mmol) in freshly distilled CH$_2$Cl$_2$ (2.0 mL) was stirred at ambient temperature for 0.5 h. Lithium chloride (26mg, 0.6mmol), Thiol (1.5mmol) and aldehyde (0.5mmol) were added subsequently and the solution was stirred at room temperature until full consume of the starting α-haloenal as indicated by TLC. The crude material was purified by column chromatography (silica gel, PE-Et$_2$O, 30:1) to afford the desired product.

**procedure for the Elimination of IV:** A suspension of potassium carbonate (42mg, 0.3mmol) and IMes·HCl (9mg, 0.025mmol) in freshly distilled CH$_2$Cl$_2$ (2.0 mL) was stirred at ambient temperature for 0.5 h. Bisulfenylated aldehyde (IV) was then added and the solution was stirred at room temperature until full consume of the starting Bisulfenylated aldehyde as indicated by TLC. The crude material was subjected to column chromatography (silica gel, PE-EtOAc, 10:1~100:1) to give the desired product.
Experimental Data:

**(Z)-2-(ethylthio)-3-phenylacrylaldehyde (3a)**

Purified with ethyl acetate/petroleum ether (1/50), yielding 107 mg (90%) of 3a as a yellow oil. R_f = 0.53 (1/15 ethyl acetate/petroleum ether); \(^1\)H NMR (400 MHz CDCl\(_3\)) \(\delta = 1.20\) (t, \(J = 7.42\) Hz, 3H), 2.98 (q, \(J = 7.41\) Hz, 2H), 7.43-7.49 (m, 3H), 7.60 (s, 1H), 7.93-7.96 (m, 2H), 9.59 (s, 1H); \(^13\)C NMR (100 MHz CDCl\(_3\)) \(\delta = 15.1, 26.7, 128.6, 130.6, 131.3, 134.2, 135.9, 152.0, 191.7\); IR (KBr) 2967.0, 2926.6, 1695.8, 1633.4, 1593.0, 1443.7, 1364.2, 1123.2, 756.1, 693.7, 527.3 cm\(^{-1}\); GC-MS (EI): m/z 192.0 (M\(^+\)); HRMS calcd for C\(_{11}\)H\(_{12}\)OS (EI): 192.0609; Found: 192.0611.

**(Z)-3-phenyl-2-(propylthio)acrylaldehyde (3b)**

Purified with ethyl acetate/petroleum ether (1/20), yielding 91 mg of 3b (88%) as a yellow oil. R_f = 0.53 (1/10 ethyl acetate/petroleum ether); \(^1\)H NMR (400 MHz CDCl\(_3\)) \(\delta = 0.93\) (t, \(J = 7.34\) Hz, 3H), 1.49-1.59 (m, 2H), 2.92 (t, \(J = 7.32\) Hz, 2H), 7.43-7.48 (m, 3H), 7.59 (s, 1H), 7.95-7.98 (m, 2H), 9.56 (s, 1H); \(^13\)C NMR (100 MHz CDCl\(_3\)) \(\delta = 13.2, 23.4, 34.4, 128.5, 130.6, 131.3, 134.3, 136.2, 151.9, 191.7\); IR (KBr) 2976.7, 1699.2, 1583.3, 1449.4, 1355.4, 1117.5, 763.7, 689.7, 523.8 cm\(^{-1}\); GC-MS (EI): m/z 206.0 (M\(^+\)); HRMS calcd for C\(_{12}\)H\(_{14}\)OS (EI): 206.0765; Found: 206.0767.

**(Z)-2-(butylthio)-3-phenylacrylaldehyde (3c)**

Purified with ethyl acetate/petroleum ether (1/50), yielding 101 mg (90%) of 3c as a yellow oil. R_f = 0.57 (1/10 ethyl acetate/petroleum ether); \(^1\)H NMR (400 MHz CDCl\(_3\)) \(\delta = 0.85\) (t, \(J = 7.32\) Hz, 3H), 1.30-1.39 (m, 2H), 1.46-1.54 (m, 2H), 2.94 (t, \(J = 7.42\) Hz, 2H), 7.43-7.48 (m, 3H), 7.58 (s, 1H), 9.58 (s, 1H); \(^13\)C NMR (100 MHz CDCl\(_3\)) \(\delta = 13.57, 21.75, 32.06, 32.15, 128.51, 130.56, 131.24, 134.26, 136.26, 151.77, 191.73\); IR (KBr) 2963.5, 2867.7, 1692.8, 1596.9, 1447.7, 1361.9, 1298.1, 1116.7, 758.6, 688.9, 529.3 cm\(^{-1}\); GC-MS (EI): m/z 220.0 (M\(^+\)); HRMS calcd for C\(_{13}\)H\(_{16}\)OS (EI): 220.0922; Found: 220.0925.
(Z)-2-(octadecylthio)-3-phenylacrylaldehyde (3d)
Purified with ethyl acetate/petroleum ether (1/100), yielding 142 mg (70%) of 3d as a yellow solid. Rf = 0.63 (1/10 ethyl acetate/petroleum ether); m.p. 53.3-54.5°C; 1H NMR (400 MHz CDCl3) δ = 0.88 (t, J = 6.84 Hz, 3H), 1.20-1.29 (m, 30H), 1.46-1.56 (m, 2H), 2.93 (t, J = 7.42 Hz, 2H), 7.42-7.48 (m, 3H), 7.59 (s, 1H), 7.93-7.97 (m, 2H), 9.58 (s, 1H), 13C NMR (100 MHz CDCl3) δ = 14.12, 22.69, 28.59, 28.80, 29.09, 29.36, 29.44, 29.52, 29.62, 29.65, 29.97, 31.92, 32.50, 128.49, 130.55, 131.24, 134.26, 136.27, 151.79, 191.72; IR (KBr) 2925.5, 2844.4, 1680.9, 1636.9, 1593.1, 1536.4, 1114.4, 727.4 cm⁻¹; HRMS calcd for C27H44OS (EI): 416.3113; Found: 416.3113.

(Z)-2-(benzylthio)-3-phenylacrylaldehyde (3e)
Purified with ethyl acetate/petroleum ether (1/30), yielding 110 mg (86%) of 3e as a yellow solid. Rf = 0.57 (1/5 ethyl acetate/petroleum ether); m.p. 36.8-38.7°C; 1H NMR (400 MHz CDCl3) δ = 4.17 (s, 2H), 7.15-7.22 (m, 5H), 7.40-7.41 (m, 3H), 7.53 (s, 1H), 7.81-7.83 (m, 2H), 9.51 (s, 1H), 13C NMR (100 MHz CDCl3) δ = 36.69, 127.17, 128.40, 128.45, 129.03, 130.65, 131.16, 134.04, 135.43, 137.42, 152.86, 191.66; IR (KBr) 3059.1, 2839.7, 1682.1, 1630.7, 1587.1, 1369.3, 1121.8, 757.8, 684.6, 516.6 cm⁻¹; GC-MS (EI): m/z 254.0 (M⁺); HRMS calcd for C16H14OS (EI): 254.0765; Found: 254.0763.

(Z)-2-(allylthio)-3-phenylacrylaldehyde (3f)
Purified with ethyl acetate/petroleum ether (1/50), yielding 61 mg (60%) of 3f as a yellow oil. Rf = (ethyl acetate/petroleum ether); 1H NMR (400 MHz CDCl3) δ = 3.58-3.60 (m, 2H), 4.96-5.01 (m, 2H), 5.65-5.76 (m, 1H), 7.42-7.48 (m, 3H), 7.62 (s, 1H), 7.91-7.95 (m, 2H), 9.54 (s, 1H); 13C NMR (100 MHz CDCl3) δ = 35.29, 117.91, 128.57, 130.75, 131.32, 133.67, 134.15,
135.20, 152.87, 191.49; IR (KBr) 2837.4, 1698.4, 1626.7, 1583.1, 1488.1, 1371.2, 1123.4, 911.5, 691.8, 525.1; GC-MS (EI): m/z 203.9 (M⁺); HRMS calcd for C₁₂H₁₂OS (EI): 204.0609; Found: 204.0611.

(Z)-methyl 2-(((3-oxo-1-phenylprop-1-en-2-yl)thio)acetate (3g)
Purified with ethyl acetate/petroleum ether (1/10), yielding 93 mg (79%) of 3g as a yellow oil. Rf = (ethyl acetate/petroleum ether); ¹H NMR (400 MHz CDCl₃) δ = 3.61 (s, 3H), 3.75 (s, 2H), 7.44-7.48 (m, 3H), 7.64 (s, 1H), 7.92-7.94 (m, 2H), 9.57 (s, 1H); ¹³C NMR (100 MHz CDCl₃) δ = 33.32, 52.40, 128.66, 130.99, 131.29, 133.77, 134.09, 153.24, 169.74, 191.16; IR (KBr) 2834.9, 1744.4, 1688.9, 1627.9, 1548.7, 1432.2, 1359.2, 1272.2, 756.4, 689.7; GC-MS (EI): m/z 236.0 (M⁺); HRMS calcd for C₁₂H₁₂O₃S (EI): 236.0507; Found: 236.0511.

(Z)-2-((furan-2-ylmethyl)thio)-3-phenylacrylaldehyde (3h)
Purified with ethyl acetate/petroleum ether (1/10), yielding 116 mg (92%) of 3h as a yellow solid. Rf = (ethyl acetate/petroleum ether); m.p. 37.0-38.8°C; ¹H NMR (400 MHz DMSO) δ = 4.24 (s, 2H), 6.12-6.13 (m, 1H), 6.29-6.30 (m, 1H), 7.45-7.50 (m, 4H), 7.82-7.84 (m, 2H), 7.95 (s, 1H), 9.59 (s, 1H); ¹³C NMR (100 MHz DMSO) δ = 27.61, 107.99, 110.48, 128.47, 130.60, 130.72, 133.77, 134.04, 142.62, 150.58, 153.09, 191.95; IR (KBr) 2834.4, 1684.7, 1630.3, 1595.1, 1361.3, 1127.6, 1011.4, 927.6, 742.4, 693.9; GC-MS (EI): m/z 243.9 (M⁺); HRMS calcd for C₁₄H₁₂O₂S (EI): 244.0558; Found: 244.0563.

(Z)-2-((isopropylthio)-3-phenylacrylaldehyde (3i)
Purified with ethyl acetate/petroleum ether (1/50), yielding 67 mg (65%) of 3i as a yellow oil. Rf = 0.48 (1/10 ethyl acetate/petroleum ether); ¹H NMR (400 MHz CDCl₃) δ = 1.22 (d, 6H, J = 6.72 Hz), 3.78-3.85 (m, 1H), 7.43-7.48 (m, 3H), 7.64 (s, 1H), 7.98-8.01 (m, 2H), 9.61 (s, 1H); ¹³C NMR (100 MHz CDCl₃) δ = 23.35, 36.22, 128.49, 130.67, 131.42, 134.28, 136.04, 152.63, 192.03; IR
(KBr) 2974.7, 2834.7, 1703.2, 1591.3, 1449.4, 1365.4, 1121.5, 767.7, 681.7, 523.8 cm\(^{-1}\);
GC-MS (EI): m/z 206.0 (M\(^+\)); HRMS calcd for C\(_{12}\)H\(_{14}\)OS (EI): 206.0765; Found: 206.0766.

**(Z)-2-(cyclohexylthio)-3-phenylacrylaldehyde (3j)**

Purified with ethyl acetate/petroleum ether (1/20), yielding 110 mg (90\%) of 3j as a yellow solid. R\(_f\) = 0.56 (1/10 ethyl acetate/petroleum ether); m.p. 77.5-78.1°C; \(^1\)H NMR (400 MHz CDCl\(_3\)) \(\delta = 1.18-1.35\) (m, 5H), 1.55-1.59 (m, 1H), 1.69-1.71 (m, 2H), 1.87-1.91 (m, 5H), 3.48-3.56 (m, 1H), 7.42-7.48 (m, 3H), 7.64 (s, 1H), 8.00-8.02 (m, 2H), 9.60 (s, 1H), \(^1^3\)C NMR (100 MHz CDCl\(_3\)) \(\delta = 25.62, 25.84, 33.57, 44.36, 128.47, 130.64, 131.43, 134.33, 135.42, 152.72, 192.12\); IR (KBr) 1938.7, 2834.7, 1693.2, 1637.3, 1571.3, 1365.4, 1121.5, 757.6, 691.7, 533.8 cm\(^{-1}\); GC-MS (EI): m/z 246.0 (M\(^+\)); HRMS calcd for C\(_{15}\)H\(_{18}\)OS (EI): 246.1078; Found: 246.1080.

**(Z)-2-(tert-butylthio)-3-phenylacrylaldehyde (3k)**

Purified with ethyl acetate/petroleum ether (1/50), yielding 58 mg (53\%) of 3k as a colorless oil. R\(_f\) = 0.48 (1/10 ethyl acetate/petroleum ether); \(^1\)H NMR (400 MHz CDCl\(_3\)) \(\delta = 1.28\) (s, 9H), 7.43-7.46 (m, 3H), 7.93 (s, 1H), 8.20-8.23 (m, 2H), 9.69 (s, 1H), \(^1^3\)C NMR (100 MHz CDCl\(_3\)) \(\delta = 31.58, 49.92, 128.40, 131.24, 132.15, 133.28, 134.30, 155.80, 193.85\); IR (KBr) 2966.7, 2824.7, 1703.2, 1627.3, 1591.3, 1365.4, 1093.5, 775.6, 663.7 cm\(^{-1}\); GC-MS (EI): m/z 220.0 (M\(^+\)); HRMS calcd for C\(_{13}\)H\(_{16}\)OS (EI): 220.0922; Found: 220.0923.

**(Z)-3-phenyl-2-(phenylthio)acrylaldehyde (3l)**

Purified with ethyl acetate/petroleum ether (1/50), yielding 86 mg (90\%) of 3l as a green-yellow oil. R\(_f\) = 0.51 (1/5 ethyl acetate/petroleum ether); \(^1\)H NMR (400 MHz CDCl\(_3\)) \(\delta = 7.14-7.18\) (m, 1H), 7.20-7.26 (m, 3H), 7.26-7.28 (m, 1H), 7.87 (s, 1H), 7.93-7.98 (m, 2H), 9.54 (s, 1H), \(^1^3\)C NMR (100 MHz CDCl\(_3\)) \(\delta = 126.7, 128.7, 129.0, 129.2, 131.2, 131.4, 133.1,
133.7, 133.8, 151.2, 190.8; IR (KBr) 3053.7, 2827.2, 1696.5, 1589.1, 1480.4, 1450.1, 1353.4, 1116.5, 743.0, 688.1, 536.4 cm\(^{-1}\); GC-MS (EI): m/z 240.0 (M\(^{+}\)); HRMS calcd for C\(_{13}\)H\(_{12}\)OS (EI): 240.0609; Found: 240.0611.

**(Z)-2-(ethylthio)-3-(4-methoxyphenyl)acrylaldehyde (3m)**

Purified with ethyl acetate/petroleum ether (1/20), yielding 92 mg (83%) of 3m as a yellow oil. \(R_f = 0.47\) (1/5 ethyl acetate/petroleum ether); \(^1\)H NMR (400 MHz CDCl\(_3\)) \(\delta = 1.19\) (t, \(J = 7.40\) Hz, 3H), 2.95 (q, \(J = 7.40\) Hz, 2H), 3.87 (s, 3H), 6.95-6.99 (m, 2H), 7.56 (s, 1H), 8.00-8.03 (m, 2H), 9.54 (s, 1H), \(^{13}\)C NMR (100 MHz CDCl\(_3\)) \(\delta = 15.05, 26.78, 55.44, 114.02, 127.09, 132.94, 133.59, 152.70, 161.64, 191.83\); IR (KBr) 2963.8, 2926.1, 2834.6, 1684.8, 1604.7, 1513.3, 1455.0, 1417.3, 1363.6, 1305.3, 1251.6, 1181.9, 1128.1, 1026.4, 828.7, 770.4, 668.6, 534.9 cm\(^{-1}\); GC-MS (EI): m/z 221.9 (M\(^{+}\)); HRMS calcd for C\(_{12}\)H\(_{14}\)O\(_2\)S (EI): 222.0715; Found: 222.0713.

**(Z)-3-(4-chlorophenyl)-2-(ethylthio)acrylaldehyde (3n)**

Purified with ethyl acetate/petroleum ether (1/50), yielding 94 mg (83%) of 3n as a yellow oil. \(R_f = 0.58\) (1/10 ethyl acetate/petroleum ether); \(^1\)H NMR (400 MHz CDCl\(_3\)) \(\delta = 1.19\) (t, \(J = 7.40\) Hz, 3H), 2.99 (q, \(J = 7.40\) Hz, 2H), 7.41-7.44 (m, 2H), 7.54 (s, 1H), 8.00-8.03 (m, 2H), 9.58 (s, 1H), \(^{13}\)C NMR (100 MHz CDCl\(_3\)) \(\delta = 15.10, 26.72, 128.81, 132.42, 132.66, 136.43, 136.52, 150.15, 191.38\); IR (KBr) 2984.7, 2918.7, 2834.7, 1703.2, 1581.3, 1477.3, 1375.4, 1131.5, 1085.5, 991.6, 813.6, 747.7, 681.7, 523.8 cm\(^{-1}\); GC-MS (EI): m/z 225.9 (M\(^{+}\)); HRMS calcd for C\(_{11}\)H\(_{11}\)ClOS (EI): 226.0219; Found: 226.0217.

**(Z)-2-(ethylthio)-3-(2-nitrophenyl)acrylaldehyde (3o)**

Purified with ethyl acetate/petroleum ether (1/20), yielding 94 mg (76%) of 3o as a brown-red oil. \(R_f = 0.46\) (1/5 ethyl acetate/petroleum ether); \(^1\)H NMR (400 MHz CDCl\(_3\)) \(\delta = 1.12\) (t, \(J = 7.42\) Hz, 3H), 2.84 (q, \(J = 7.40\) Hz, 2H),
7.57-7.66 (m, 2H), 7.70-7.74 (m, 1H), 8.02 (s,1H), 8.19-8.22(m, 1H), 9.70 (s, 1H), $^{13}$C NMR (100 MHz CDCl$_3$) δ = 14.86, 26.40, 124.91, 130.21 (d, 8.53 Hz), 131.59, 133.34, 138.88, 148.02, 190.73; IR (KBr) 2984.7, 2918.7, 2816.7, 1693.2, 1581.3, 1525.3, 1347.4, 1121.5, 859.6, 785.6, 747.7, 701.7, 673.7, 607.7, 513.8 cm$^{-1}$; GC-MS (EI): m/z 236.8 (M$^+$); HRMS calcd for C$_{11}$H$_{11}$NO$_3$S (EI): 237.0460; Found: 237.0466.

(Z)-2-(ethylthio)-3-(furan-2-yl)acrylaldehyde (3p)

Purified with ethyl acetate/petroleum ether (1/50), yielding 71 mg (78%) of 3p as a brown solid. R$_f$ = 0.49 (1/10 ethyl acetate/petroleum ether); m.p. 35.5-36.9°C; $^1$H NMR (400 MHz CDCl$_3$) δ = 1.23 (t, J = 7.40 Hz, 3H), 3.06 (q, J = 7.40 Hz, 2H), 6.60-6.62 (m, 1H), 7.47 (s, 1H), 7.51 (d, J = 3.60 Hz, 1H), 7.63 (dd, J = 1.76 Hz, 0.6 Hz,1H), 9.51 (s,1H), $^{13}$C NMR (100 MHz CDCl$_3$) δ = 15.36, 26.34, 113.16, 118.38, 131.98, 137.96, 145.49, 150.82, 190.29; IR (KBr) 3108.2, 2967.8, 2833.4, 1689.2, 1631.8, 1589.5, 1462.8, 1357.1, 1194.1, 1115.6, 1017.4, 946.5, 756.3, 656.6, 621.9, 508.7 cm$^{-1}$; GC-MS (EI): m/z 181.9 (M$^+$); HRMS calcd for C$_9$H$_{10}$O$_2$S (EI): 182.0402; Found: 184.0404.

(Z)-2-(benzylthio)hex-2-enal (3q)

Purified with ethyl acetate/petroleum ether (1/50), yielding 70 mg (64%) of 3q as a yellow solid. R$_f$ = 0.49 (1/20 ethyl acetate/petroleum ether); m.p. 36.8-38.7°C; $^1$H NMR (400 MHz CDCl$_3$) δ = 1.23 (t, J = 7.40 Hz, 3H), 1.26-1.35 (m, 2H), 2.32-2.38 (m, 2H), 3.99 (s,2H), 6.93 (t, J = 7.34 Hz,1H), 7.16-7.26 (m, 5H), 9.39 (s, 1H); $^{13}$C NMR (100 MHz CDCl$_3$) δ = 13.72, 21.45, 32.61, 36.37, 126.97, 128.31, 128.90, 137.09, 138.15, 162.48, 191.21; IR (KBr) 3034.5, 2965.5, 2919.6, 1696.9, 1596.8, 1498.3, 1450.8, 1166.8, 1083.1, 753.3, 699.1 cm$^{-1}$; GC-MS (EI): m/z 220.0 (M$^+$); HRMS calcd for C$_{13}$H$_{16}$OS (EI): 220.0922; Found: 220.0925.
2-(ethylthio)-3-phenylpropanal (3r)
Purified with ethyl acetate/petroleum ether (1/50), yielding 85 mg (80%) of 3r as a colorless oil. \( R_f = 0.59 \) (1/20 ethyl acetate/petroleum ether) ; \(^1\)H NMR (400 MHz CDCl\(_3\)) \( \delta = 1.21 \) (t, \( J=7.44 \) Hz, 3H), 2.36-2.49 (m, 2H), 2.88-2.93 (m,1H), 3.11-3.17 (m,1H), 3.39-3.44 (m,1H), 7.19-7.25 (m,3H), 7.28-7.32 (m,2H), 9.27 (s,1H), \(^{13}\)C NMR (100 MHz CDCl\(_3\)) \( \delta =14.42, 24.29, 34.34, 54.13, 126.94, 128.67, 128.96, 137.40, 192.81; IR (KBr) 2981.1, 2916.8, 2823.4, 1713.3, 1641.4, 1598.5, 1454.6, 1361.2, 1139.2, 759.4, 695.1; GC-MS (EI): m/z 194.0 (M\(^+\)); HRMS calcd for C\(_{11}\)H\(_{14}\)OS (EI): 194.0765; Found: 194.0766.

2,2-bis(ethylthio)-3-phenylpropanal (3s)
Purified with ethyl acetate/petroleum ether (1/100), yielding 79 mg (83%) of 3s as a colorless oil. \( R_f = 0.41 \) (1/50 ethyl acetate/petroleum ether) ; \(^1\)H NMR (400 MHz CDCl\(_3\)) \( \delta =1.20 \) (t, \( J=7.52 \) Hz, 6H), 2.46-2.55 (m, 4H), 3.22 (s, 2H), 7.23-7.26 (m, 1H), 7.26-7.29 (m, 4H), 9.21 (s, 1H), \(^{13}\)C NMR (100 MHz CDCl\(_3\)) \( \delta = 13.88, 23.26, 39.58, 68.54, 127.27, 128.22, 130.44, 135.09, 188.89; IR (KBr) 3035.8, 2969.3, 2929.7, 2870.2, 1703.4, 1498.1, 1458.4, 1372.1, 1265.9, 1033.7, 974.2, 756.1, 696.7, 576.3 cm\(^{-1}\); GC-MS (EI): m/z 254.0 (M\(^+\)); HRMS calcd for C\(_{13}\)H\(_{18}\)OS\(_2\) (EI): 254.0799; Found: 254.0800.

(Z)-2-((2-(2-hydroxyethoxy)ethyl)thio)-3-phenylacrylaldehyde(3t)
Purified with ethyl acetate/petroleum ether (1/1), yielding 94 mg (76%) of 3t as a yellow oil. \( R_f = 0.47 \) (1/4 ethyl acetate/petroleum ether) ; \(^1\)H NMR (400 MHz CDCl\(_3\)) \( \delta = 2.58 \) (s, 1H), 3.14 (t, \( J = 6.24 \) Hz, 2H), 3.45-3.47 (m, 2H), 3.58-3.61 (m, 2H), 3.61-3.65 (m, 2H), 7.43-7.48 (m, 3H), 7.61 (s, 1H), 7.93-7.98 (m, 2H), 9.57 (s, 1H); \(^{13}\)C NMR (100 MHz CDCl\(_3\)) \( \delta = 31.98, 61.64, 70.30, 72.02, 128.62, 130.87, 131.34, 134.03, 135.42, 152.54, 191.79; IR (KBr) 3415.7, 2944.8, 2860.5, 1692.9, 1585.9, 1548.6, 1457.8, 1274.6, 1123.8, 1062.2, 758.9, 690.8, 538.4; GC-MS (EI): m/z 252.0 (M\(^+\)); HRMS calcd for C\(_{13}\)H\(_{16}\)O\(_3\)S (EI): 252.0820 ; Found: 252.0816
2,3-bis(ethylthio)-3-phenylpropanal

Purified with diethyl ether/petroleum ether (1/30), yielding 33 mg (26%) of IV as a yellow oil. R_f = 0.40 (1/20 ethyl acetate/petroleum ether); ^1^H NMR (400 MHz CDCl_3) δ = 9.2034 (d, J = 5.72Hz, 1H), 7.2569-7.3764 (m, 5H), 3.9101 (d, J = 11.48Hz, 1H), 3.4625 (dd, J_1 = 11.52Hz, J_2 = 5.76Hz), 1.0789-1.2624 (m, 6H); ^13^C NMR (100 MHz CDCl_3) δ = 189.18, 138.68, 128.81, 128.29, 127.94, 56.97, 47.09, 25.61, 25.10, 14.26, 14.05; GC-MS (EI): m/z 254.0 (M+)  

References
1H and 13C NMR Spectra of Products
ROESY of 3a