Supporting Information for

N-heterocyclic carbene-catalyzed sulfa-Michael addition of enals

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1. Experimental Section

All reactions were conducted under nitrogen atmosphere in oven-dried glassware with magnetic stirring bar. $^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (100 MHz, CDCl$_3$) spectra were recorded using deuterated chloroform as solvent, with tetramethylsilane as an internal standard and reported in ppm ($\delta$). Melting points was measured on a WRS-1B melting point apparatus and were uncorrected. High-resolution mass spectra (HRMS) were recorded on FTICRMS. Thiols, enals and other chemicals were obtained from Adamas-beta and used without purification. Anhydrous THF, MTBE and toluene were distilled from sodium and benzophenone. DMSO, DMF, CH$_2$Cl$_2$, CHCl$_3$ and CH$_3$CN were distilled from calcium hydride. 1, 2-dichloroethane was distilled from calcium chloride.

2. General procedure A: NHC-catalyzed sulfa-Michael addition of enals in 1, 2-dichloroethane

$$\begin{align*}
R^1-\text{C} &= R^2-\text{SH} & & \text{10 mol\% NHC A} \\
DCE, rt, overnight & & \text{20 mol\% HFIP} & & \text{2. General procedure B: NHC-catalyzed sulfa-Michael addition of enals in DCM/}
\end{align*}$$

IPr A (7.8 mg, 10 mol%) was dissolved in 2.0 mL dry 1,2-dichloroethane. Enal 1 (0.2 mmol), thiol 2 (0.6 mmol,) and 1,1,1,3,3,3-hexafluoro-2-propanol (6.7 mg, 20 mol%) were added subsequently via a syringe at ambient temperature. The reaction mixture was stirred overnight at the same temperature. Then, the mixture was diluted with Et$_2$O (5.0 mL$\times$3) and concentrated under vacuum. The crude product was purified by flash column chromatography on silica gel (PE) to give the desired product 3.
pH 6.8 phosphate aqueous mixture

\[
\text{IPr A (7.8 mg, 10 mol%)} \text{ was dissolved in a mixture of 1.3 mL dry 1,2-dichloroethane and 1.0 mL pH 6.8 phosphate-based buffer solution. Cinnamaldehyde 1a (0.2 mmol), thiol 2 (0.6 mmol), and HFIP (6.7 mg, 20 mol%) were added subsequently via a syringe at ambient temperature. The reaction mixture was stirred overnight at the same temperature. Then, the mixture was extracted with DCM (5.0 mL×3) and dried over anhydrous MgSO}_4, then concentrated under vacuum. The crude product was purified by flash column chromatography on silica gel (PE) to give the desired product 3.}
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4. Procedure for NHC-catalyzed reversible reaction of sulfa-Michael adduct

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\text{To a solution of NHC A (7.8 mg, 10 mol%) in 2.0 mL 1,2-dichloroethane was added 1,1,1,3,3,3-hexafluoro-2-propanol (6.7 mg, 20 mol%) and 3-(isopropylthio)-3-phenylpropanal (3j) (0.2 mmol). The reaction mixture was stirred at room temperature for 12 h, and then, the reaction mixture was filtered through a short silica pad and washed with EtOAc (15.0 mL) and concentrated in vacuum. The ratio of 3j to cinnamaldehyde (2.4 : 1) was determined by }^1\text{H NMR} \text{ analysis of the crude reaction mixture. The crude product was further purified by flash column}
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chromatography on silica gel (PE) to give the product cinnamaldehyde in 29% yield.

![Fig.1 1H NMR (CDCl₃, 400 MHZ) of the crude reaction mixture of 3j](image)

**Fig.1** ¹H NMR (CDCl₃, 400 MHZ) of the crude reaction mixture of 3j

**5. 1 NHC-catalyzed Michael addition between mercaptoisoborneol and cinnamaldehyde**

3ac was prepared according to **General Procedure B**.

![Chemical Structure](image)

**5. 2 Reduction and deprotection of compound 3ac**

To a solution of 3ac (1 mmol) in anhydrous EtOH (10.0 mL) was added NaBH₄ (1.5 mmol) at 0 °C, and after the addition of NaBH₄, the reaction mixture was stirred at room temperature for additional 2.0 hours. The reaction was quenched with water.
(30 ml) at 0 ° and extracted with DCM (3×20 ml), the combined organic layer was washed with brine, and dried over magnesium sulfate, filtered, and concentrated in vacuum to give intermediate 4ac, which was used directly in the next step. Intermediate 4ac was dissolved in CH₂Cl₂ (12.0 mL), and then, BF₃•OEt₂ (1.0 mmol) was added at room temperature. The reaction mixture was stirred at room temperature until full consumption of 4ac (about 3 hours). n-Octadecylmercaptan (20.0 mmol) was then added and the resultant mixture was stirred for 6 h at room temperature. The reaction mixture was poured into water, and extracted with ethyl acetate (3×30 mL). The combined organic layers were washed with brine, and dried over magnesium sulfate, filtered, and concentrated in vacuum. Purification of the residue by silica gel column chromatography (hexane/ethyl acetate = 10:1) gave the product 5ac.
3-((Ethylthio)-3-phenylpropanal (3a) \(^1\)

Pale yellow oil; 37.7 mg, 97% yield; \(R_f\) (PE/DCM = 2/1): 0.35; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 9.69 (t, \(J = 1.8\) Hz, 1H), 7.37 – 7.29 (m, 4H), 7.27 – 7.22 (m, 1H), 4.36 (t, \(J = 7.5\) Hz, 1H), 2.95 (dt, \(J = 7.6, 1.9\) Hz, 2H), 2.42–2.24 (m, 2H), 1.16 (t, \(J = 7.4\) Hz, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 199.50, 141.33, 128.71, 127.64, 127.53, 49.76, 42.89, 25.19, 14.29.

3-Phenyl-3-(propylthio)propanal (3b)

Colorless oil; 37.5 mg, 90% yield; \(R_f\) (PE/EtOAc = 10/1): 0.35; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 9.69 (t, \(J = 1.8\) Hz, 1H), 7.38 – 7.30 (m, 4H), 7.27 – 7.22 (m, 1H), 4.32 (t, \(J = 7.5\) Hz, 1H), 2.95 (dd, \(J = 7.6, 1.8, 1.2\) Hz, 2H), 2.43 – 2.21 (m, 2H), 1.57 – 1.43 (m, 2H), 0.90 (t, \(J = 7.3\) Hz, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 199.55, 141.39, 128.70, 127.65, 127.52, 49.85, 43.16, 33.25, 22.46; FTIR (film) 3430, 3029, 2962, 2727, 1724, 1679, 1491, 1454, 1385, 1293, 1240, 1123, 1051, 751, 700 cm\(^{-1}\); HRMS (ESI) \(m/z\) calcd for C12H17OS\(^+\) (M+H)\(^+\) 209.0995, found 209.0999.

3-(Butylthio)-3-phenylpropanal (3c) \(^2\)

Colorless oil; 36.0 mg, 81% yield; \(R_f\) (PE/EtOAc = 10/1): 0.35; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 9.70 (t, \(J = 1.8\) Hz, 1H), 7.38 – 7.30 (m, 4H), 7.27 – 7.25 (m, 1H), 4.33 (t, \(J = 7.5\) Hz, 1H), 2.95 (dt, \(J = 7.6, 1.7\) Hz, 2H), 2.41 – 2.24 (m, 2H), 1.52 – 1.42 (m, 2H), 1.35 – 1.26 (m, 2H), 0.84 (t, \(J = 7.3\) Hz, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 199.56,
3-(Octadecythio)-3-phenylpropanal (3d)
Colorless oil; 68.5 mg, 82\% yield; $R_f$ (PE/DCM = 3/1): 0.21; $^1$H NMR (400 MHz, CDCl$_3$) δ 9.70 (t, $J$ = 1.8 Hz, 1H), 7.37 – 7.26 (m, 4H), 7.26 – 7.22 (m, 1H), 4.32 (t, $J$ = 7.5 Hz, 1H), 2.95 (dt, $J$ = 7.6, 1.7 Hz, 2H), 2.44 – 2.19 (m, 2H), 1.53 – 1.41 (m, 2H), 1.24 (d, $J$ = 9.2 Hz, 30H), 0.88 (t, $J$ = 6.8 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 199.56, 141.38, 128.69, 127.65, 127.52, 49.83, 43.21, 31.17, 30.90, 21.93, 13.60.

3-(Benzylthio)-3-phenylpropanal (3e)
Pale yellow oil; 46.6 mg, 91\% yield; $R_f$ (PE/DCM = 1/1): 0.35; $^1$H NMR (400 MHz, CDCl$_3$) δ 9.58 (t, $J$ = 1.9 Hz, 1H), 7.38 – 7.27 (m, 7H), 7.25 – 7.19 (m, 3H), 4.18 (t, $J$ = 7.5 Hz, 1H), 3.59 – 3.42 (m, 2H), 2.89 (ddd, $J$ = 7.6, 3.7, 1.9 Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 199.39, 140.88, 128.94, 128.77, 128.52, 128.32, 127.89, 127.67, 127.15, 49.58, 42.75, 35.57.

3-(Allylthio)-3-phenylpropanal (3f)
Pale yellow oil; 36.3 mg, 88\% yield; $R_f$ (PE/EtOAc = 10/1): 0.35; $^1$H NMR (400 MHz, CDCl$_3$) δ 9.70 (t, $J$ = 1.8 Hz, 1H), 7.37 – 7.26 (m, 4H), 7.26 – 7.22 (m, 1H), 4.32 (t, $J$ = 7.5 Hz, 1H), 2.95 (dt, $J$ = 7.6, 1.7 Hz, 2H), 2.44 – 2.19 (m, 2H), 1.53 – 1.41 (m, 2H), 1.24 (d, $J$ = 9.2 Hz, 30H), 0.88 (t, $J$ = 6.8 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 199.56, 141.38, 128.69, 127.65, 127.52, 49.83, 43.21, 31.17, 30.90, 21.93, 13.60.
MHz, CDCl$_3$ $\delta$ 9.67 (t, $J = 1.8$ Hz, 1H), 7.38 – 7.30 (m, 4H), 7.28 – 7.24 (m, 1H), 5.81 – 5.70 (m, 1H), 5.13 – 5.01 (m, 2H), 4.31 (t, $J = 7.5$ Hz, 1H), 3.04 – 2.87 (m, 4H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 199.41, 141.02, 133.92, 128.74, 127.87, 127.61, 117.60, 49.68, 42.10, 34.13. FTIR (film) 3429, 3082, 3029, 2914, 2827, 2727, 1724, 1635, 1453, 1403, 1230, 991, 919, 751, 700 cm$^{-1}$; HRMS (ESI) m/z calcd for C$_{12}$H$_{15}$OS$^+$ (M+H)$^+$ 207.0838, found 207.0838.

![Methyl 3-((3-oxo-1-phenylpropyl)thio)propanoate (3g)](image)

Methyl 3-((3-oxo-1-phenylpropyl)thio)propanoate (3g)

Colorless oil; 42.0 mg, 83% yield; $R_f$ (PE/EtOAc = 5/1): 0.25; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.68 (t, $J = 1.7$ Hz, 1H), 7.39 – 7.30 (m, 4H), 7.30 – 7.26 (m, 1H), 4.38 (t, $J = 7.4$ Hz, 1H), 3.66 (s, 3H), 2.96 (dt, $J = 7.5$, 1.9 Hz, 2H), 2.60 (td, $J = 7.1$, 1.0 Hz, 2H), 2.50 – 2.45 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 199.12, 172.15, 140.89, 128.84, 127.77, 127.67, 51.81, 49.71, 43.35, 34.14, 26.14; FTIR (film) 3441, 2923, 1723, 1436, 1360, 1171, 1055, 751, 700 cm$^{-1}$; HRMS (ESI) m/z calcd for C$_{13}$H$_{16}$O$_3$S$^+$ (M+H)$^+$ 253.0893, found 253.0889.

![3-((Furan-2-ylmethyl)thio)-3-phenylpropanal (3h)](image)

3-((Furan-2-ylmethyl)thio)-3-phenylpropanal (3h)

Colorless oil; 45.3 mg, 92% yield; $R_f$ (PE/EtOAc = 10/1): 0.35; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.62 (t, $J = 1.8$ Hz, 1H), 7.39 – 7.31 (m, 5H), 7.31 – 7.26 (m, 1H), 6.30 (dd, $J = 3.2$, 1.9 Hz, 1H), 6.11 (dd, $J = 3.3$, 0.8 Hz, 1H), 4.33 (t, $J = 7.5$ Hz, 1H), 3.63 – 3.40 (m, 2H), 3.03 – 2.84 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 199.21, 151.16, 142.21, 140.57, 128.78, 127.90, 127.74, 110.44, 107.73, 49.47, 42.88, 27.64; FTIR (film) 3463, 2728, 1723, 1638, 1502, 1384, 1150, 1010, 934, 740, 700 cm$^{-1}$; HRMS
(ESI) $m/z$ calcd for C14H15O2S$^+$ (M+H)$^+$ 247.0787, found 247.0786.

3-((2-Hydroxyethyl)thio)-3-phenylpropanal (3i)
Colorless oil; 36.8 mg, 87%$^b$ yield; $R_f$ (PE/EtOAc = 1/1): 0.15; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.70 (t, $J = 1.5$ Hz, 1H), 7.36 – 7.31 (m, 5H), 4.41 (t, $J = 7.4$ Hz, 1H), 3.74 – 3.55 (m, 3H), 2.99 (dt, $J = 7.3$, 1.5 Hz, 2H), 2.55 (t, $J = 5.9$ Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 199.17, 141.13, 128.88, 127.80, 127.64, 60.64, 49.99, 42.71, 34.37. FTIR (film) 3428, 2919, 1721, 1453, 1384, 1057, 700 cm$^{-1}$; HRMS (ESI) $m/z$ calcd for C$_{11}$H$_{14}$O$_2$S$^+$ (M+H)$^+$ 211.0787, found 211.0779.

3-(Isopropylthio)-3-phenylpropanal (3j)
Colorless oil; 31.7 mg, 76%$^b$ yield; $R_f$ (PE/EtOAc = 10/1): 0.35; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.68 (t, $J = 1.8$ Hz, 1H), 7.42 – 7.29 (m, 4H), 7.26 – 7.21 (m, 1H), 4.40 (t, $J = 7.5$ Hz, 1H), 2.92 (ddd, $J = 7.5$, 3.3, 1.8 Hz, 2H), 2.67 – 2.57 (m, 1H), 1.26 (d, $J = 6.6$ Hz, 3H), 1.11 (d, $J = 6.8$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 199.56, 128.72, 127.60, 127.47, 50.19, 42.36, 34.55, 23.48, 22.90; FTIR (film) 3028, 2960, 2929, 2866, 2725, 2359, 1724, 1679, 1453, 1246, 1055, 752, 700 cm$^{-1}$; HRMS (ESI) $m/z$ calcd for C$_{12}$H$_{17}$OS$^+$ (M+H)$^+$ 209.0995, found 209.0993.
3-(Cyclohexylthio)-3-phenylpropanal (3k)
Pale yellow oil; 38.3 mg, 77% yield; \( R_f \) (PE/EtOAc = 10/1): 0.33; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 9.68 (t, \( J = 1.8 \) Hz, 1H), 7.39 – 7.26 (m, 4H), 7.26 – 7.21 (m, 1H), 4.42 (t, \( J = 7.5 \) Hz, 1H), 2.92 (dt, \( J = 7.6, 2.0 \) Hz, 2H), 2.48 – 2.34 (m, 1H), 1.98 (d, \( J = 13.2 \) Hz, 1H), 1.77 – 1.57 (m, 3H), 1.40 – 1.11 (m, 5H), 0.94 – 0.80 (m, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 199.70, 128.69, 127.55, 127.42, 50.27, 43.06, 41.81, 33.63, 33.14, 25.89, 25.75, 25.68. FTIR (film) 3436, 2929, 1724, 1637, 1449, 1384, 1073, 908, 734 cm\(^{-1}\); HRMS (ESI) \( m/z \) calcd for C\(_{15}\)H\(_{21}\)OS\(^{+}\) (M+H)\(^{+}\) 249.1308, found 249.1307.

![Structure of 3-(Cyclohexylthio)-3-phenylpropanal (3k)](image)

3-Phenyl-3-(phenylthio)propanal (3m)
Pale yellow oil; 26.1 mg, 54% yield; \( R_f \) (PE/EtOAc = 10/1): 0.29; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 9.69 (t, \( J = 1.7 \) Hz, 1H), 7.53 – 7.16 (m, 10H), 4.69 (t, \( J = 7.5 \) Hz, 1H), 3.04 (ddd, \( J = 7.2, 3.5, 1.7 \) Hz, 2H);
\(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 199.45, 140.44, 133.40, 129.06, 128.93, 128.63, 127.99, 127.67, 49.22, 47.26.

![Structure of 3-Phenyl-3-(phenylthio)propanal (3m)](image)

3-(Ethylthio)-3-(4-fluorophenyl)propanal (3n)
Colorless oil; 39.9 mg, 94% yield; \( R_f \) (PE/EtOAc = 10/1): 0.24; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 9.69 (t, \( J = 1.7 \) Hz, 1H), 7.37 – 7.30 (m, 2H), 7.06 – 6.98 (m, 2H), 4.36 (t, \( J = 7.4 \) Hz, 1H), 2.94 (dd, \( J = 7.5, 1.7 \) Hz, 2H), 2.38 – 2.28 (m, 2H), 1.16 (t, \( J = 7.4 \) Hz, 3H); \(^{13}\)C NMR (100 MHz, Chloroform-\(d\)) \( \delta \) 199.14, 161.95 (d, \( J = 246.4 \) Hz), 137.14 (d, \( J = 3.2 \) Hz), 129.22 (d, \( J = 8.0 \) Hz), 115.57 (d, \( J = 21.6 \) Hz), 49.97 (d, \( J = 0.7 \) Hz), 42.09, 25.20, 14.24; \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \( \delta \) -114.73; FTIR (film) 3430, 2969,
3-(4-Chlorophenyl)-3-(ethylthio)propanal (3o)
Yellow oil; 40.1 mg, 88% yield; $R_f$ (PE/EtOAc = 10/1): 0.23; $^1$H NMR (400 MHz, CDCl$_3$) δ 9.69 (t, $J = 1.6$ Hz, 1H), 7.30 (s, 4H), 4.34 (t, $J = 7.4$ Hz, 1H), 2.94 (dd, $J = 7.4$, 1.6 Hz, 2H), 2.38–2.28 (m, 2H), 1.16 (t, $J = 7.4$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 198.94, 139.99, 133.18, 129.02, 128.86, 49.79, 42.14, 25.23, 14.23. FTIR (film) 3431, 2968, 2926, 2851, 2728, 1724, 1682, 1490, 1409, 1265, 1091, 1013, 807 cm$^{-1}$; HRMS (ESI) $m/z$ calced for C$_{11}$H$_{14}$ClOS$^+$ (M+H)$^+$ 229.0448, found 229.0445.

3-(4-Bromophenyl)-3-(ethylthio)propanal (3p)$^5$

Yellow oil; 43.5 mg, 80% yield; $R_f$ (PE/DCM = 1/1): 0.31; $^1$H NMR (400 MHz, CDCl$_3$) δ 9.70 (t, $J = 1.6$ Hz, 1H), 7.50–7.45 (m, 2H), 7.29–7.24 (m, 2H), 4.35 (t, $J = 7.4$ Hz, 1H), 2.95 (dd, $J = 7.4$, 1.6 Hz, 2H), 2.40–2.30 (m, 2H), 1.18 (t, $J = 7.4$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 198.91, 140.54, 131.82, 129.38, 121.25, 49.73, 42.19, 25.23, 14.23.

3-(Ethylthio)-3-(p-tolyl)propanal (3q)
Pale yellow oil; 29.2 mg, 70% yield; $R_f$ (PE/EtOAc = 10/1): 0.41; $^1$H NMR (400 MHz, CDCl$_3$) δ 9.69 (t, $J = 1.9$ Hz, 1H), 7.24 (d, $J = 8.1$ Hz, 2H), 7.13 (d, $J = 7.7$ Hz,
2H), 4.33 (t, $J = 7.5$ Hz, 1H), 2.93 (dt, $J = 7.5$, 1.8 Hz, 2H), 2.39 – 2.30 (m, 5H), 1.16 (t, $J = 7.4$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 199.70, 138.18, 137.24, 127.50, 49.81, 42.63, 25.15, 14.29; FTIR (film) 2966, 1686, 1629, 1488, 1073, 1010, 905, 868, 728, 649 cm$^{-1}$; HRMS (ESI) m/z calcd for C$_{12}$H$_{17}$OS$^+$ (M+H)$^+$ 209.0995, found 209.0997.

3-(Ethylthio)-3-(4-methoxyphenyl)propanal (3r)$^6$
Yellow oil; 31.4 mg, 70% yield; $R_f$ (PE/EtOAc = 5/1): 0.45; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.69 (t, $J = 1.8$ Hz, 1H), 7.29 – 7.26 (m, 2H), 6.88 – 6.84 (m, 2H), 4.34 (t, $J = 7.5$ Hz, 1H), 3.80 (s, 3H), 2.92 (dt, $J = 7.5$, 1.8 Hz, 2H), 2.38 – 2.28 (m, 2H), 1.16 (t, $J = 7.4$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 199.72, 158.88, 128.70, 114.05, 55.28, 49.93, 42.31, 25.12, 14.30.

3-(3-Chlorophenyl)-3-(ethylthio)propanal (3s)
Yellow oil; 36.0 mg, 79% yield; $R_f$ (PE/DCM = 2/1): 0.38; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.70 (t, $J = 1.5$ Hz, 1H), 7.38 – 7.35 (m, 1H), 7.26 – 7.21 (m, 3H), 4.33 (t, $J = 7.4$ Hz, 1H), 2.99 – 2.92 (m, 2H), 2.41 – 2.30 (m, 2H), 1.18 (t, $J = 7.4$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 198.83, 143.65, 134.57, 129.94, 127.75, 125.94, 49.70, 42.35, 25.32, 14.22; FTIR (film) 3434, 2970, 2931, 1724, 1629, 1384, 1079, 786 cm$^{-1}$; HRMS (ESI) m/z calcd for C$_{11}$H$_{14}$ClOS$^+$ (M+H)$^+$ 229.0448, found 229.0446.
3-(2-Chlorophenyl)-3-(ethylthio)propanal (3t)
Yellow oil; 34.7 mg, 76% yield; $R_f$ (PE/DCM = 2/1): 0.38; $^1$H NMR (400 MHz, CDCl$_3$) δ 9.72 (t, $J = 2.0$ Hz, 1H), 7.58 (dd, $J = 7.8$, 1.7 Hz, 1H), 7.36 (dd, $J = 7.9$, 1.4 Hz, 1H), 7.29 (td, $J = 7.6$, 1.5 Hz, 1H), 7.19 (td, $J = 7.6$, 1.7 Hz, 1H), 4.97 (t, $J = 7.5$ Hz, 1H), 2.91 (dd, $J = 7.5$, 2.0 Hz, 2H), 2.51 – 2.35 (m, 2H), 1.20 (t, $J = 7.4$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 199.15, 138.90, 133.32, 129.66, 129.00, 128.56, 127.49, 49.24, 39.02, 25.50, 14.48. FTIR (film) 3432, 2969, 2928, 1725, 1473, 1443, 1268, 1035, 753 cm$^{-1}$; HRMS (ESI) $m/z$ calcd for C$_{11}$H$_{14}$ClOS$^+$ (M+H)$^+$ 229.0448, found 229.0449.

\[ \text{SC}_2\text{H}_5 \text{O} \]

3-(Ethylthio)-3-(2-nitrophenyl)propanal (3u)
Yellow oil; 43.0 mg, 90% yield; $R_f$ (PE/EtOAc = 5/1): 0.23; $^1$H NMR (400 MHz, CDCl$_3$) δ 9.72 (t, $J = 2.1$, 1.3 Hz, 1H), 7.84 (td, $J = 8.0$, 1.4 Hz, 2H), 7.67 – 7.61 (m, 1H), 7.42 (ddd, $J = 8.1$, 7.4, 1.4 Hz, 1H), 5.09 (t, $J = 7.5$ Hz, 1H), 3.08 – 2.92 (m, 2H), 2.54 – 2.36 (m, 2H), 1.18 (t, $J = 7.4$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 198.33, 136.80, 133.21, 129.9, 128.19, 124.24, 50.10, 37.57, 25.95, 14.31. FTIR (film) 3436, 2967, 2927, 1723, 1686, 1526, 1350, 1119, 971, 785, 741 cm$^{-1}$; HRMS (ESI) $m/z$ calcd for C$_{11}$H$_{14}$NO$_3$S$^+$ (M+H)$^+$ 240.0689, found 240.0688.

\[ \text{SC}_2\text{H}_5 \text{O} \]

3-(Ethylthio)-3-(2-methoxyphenyl)propanal (3v)
Yellow oil; 36.8 mg, 82% yield; $R_f$ (PE/EtOAc = 5/1): 0.51; $^1$H NMR (400 MHz, CDCl$_3$) δ 9.70 (t, $J = 2.2$ Hz, 1H), 7.43 (dd, $J = 7.6$, 1.7 Hz, 1H), 7.23 (ddd, $J = 8.2$, 7.4, 1.7 Hz, 1H), 6.96 (td, $J = 7.5$, 1.2 Hz, 1H), 6.88 (dd, $J = 8.2$, 1.1 Hz, 1H), 4.85 (t, $J = 7.5$ Hz, 1H), 3.85 (s, 3H), 2.90 (ddd, $J = 7.4$, 2.2, 0.7 Hz, 2H), 2.47 – 2.37 (m, 2H),

S13
1.19 (t, $J = 7.4$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 200.48, 156.63, 129.33, 128.42, 128.23, 120.95, 110.73, 55.51, 49.06, 36.26, 25.48, 14.45. FTIR (film) 3435, 2970, 2928, 1724, 1631, 1384, 1149, 1069, 1010, 925, 740 cm$^{-1}$; HRMS (ESI) $m/z$ calcd for C12H17O2S$^+$ (M+H)$^+$ 225.0944, found 225.0943.

3-(Ethylthio)-3-(furan-2-yl)propanal (3w)
Pale yellow oil; 23.6 mg, 64% yield; $R_f$ (PE/EtOAc = 5/1): 0.42; $^1$H NMR (400 MHz, CDCl$_3$) δ 9.75 (t, $J = 1.7$ Hz, 1H), 7.37 (dd, $J = 1.9, 0.9$ Hz, 1H), 6.31 (dd, $J = 3.3, 1.8$ Hz, 1H), 6.21 (d, $J = 3.2$ Hz, 1H), 4.44 (t, $J = 7.3$ Hz, 1H), 3.14 – 2.90 (m, 2H), 2.49 (qd, $J = 7.4, 1.0$ Hz, 2H), 1.20 (t, $J = 7.4$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 199.11, 153.24, 142.25, 110.31, 107.06, 46.90, 35.74, 25.20, 14.37. FTIR (film) 3435, 2970, 2928, 1724, 1631, 1384, 1149, 1069, 1010, 925, 740 cm$^{-1}$; HRMS (ESI) $m/z$ calcd for C9H13O2S$^+$ (M+H)$^+$ 185.0631, found 185.0631.

3-(anthracen-9-yl)-3-(ethylthio)propanal (3x)
Yellow oil; 23.6 mg, 78% yield; $R_f$ (PE/DCM = 1/1): 0.53; $^1$H NMR (400 MHz, CDCl$_3$) δ 9.74 (t, $J = 1.2$ Hz, 1H), 8.67 (d, $J = 8.9$ Hz, 1H), 8.51 – 8.36 (m, 2H), 8.05 – 7.96 (m, 2H), 7.59 – 7.51 (m, 2H), 7.50 – 7.43 (m, 2H), 6.11 (t, $J = 6.6$ Hz, 1H), 3.69 (ddd, $J = 18.2, 7.1, 1.5$ Hz, 1H), 3.47 (dd, $J = 18.3, 6.1$ Hz, 1H), 2.73 – 2.46 (m, 2H), 1.20 (t, $J = 7.4$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 199.41, 133.32, 129.77, 129.53, 128.22, 126.70, 126.16, 125.54, 125.16, 124.97, 124.88, 123.05, 51.67, 35.56, 27.82, 14.79; FTIR (film) 3435, 3050, 2924, 2360, 1720, 1681, 1445, 888, 731 cm$^{-1}$; HRMS (ESI) $m/z$ calcd for C19H18OS$^+$ (M+H)$^+$ 295.1151, found 295.1152.
3-(Ethylthio)hexanal (3y)
Colorless oil; 31.1 mg, 97% yield; \( R_f \) (PE/EtOAc = 10/1): 0.49; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 9.79 (t, \( J = 2.1 \) Hz, 1H), 3.18 – 3.10 (m, 1H), 2.68 – 2.63 (m, 2H), 2.56 (q, \( J = 7.4 \) Hz, 2H), 1.65 – 1.56 (m, 2H), 1.52 – 1.42 (m, 2H), 1.25 (t, \( J = 7.4 \) Hz, 3H), 0.93 (t, \( J = 7.2 \) Hz, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 201.15, 48.84, 39.04, 37.48, 24.48, 20.03, 14.74, 13.82.

3-(Ethylthio)-4-methylpentanal (3z)
Colorless oil; 31.1 mg, 97% yield; \( R_f \) (PE/EtOAc = 10/1): 0.53; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 9.83 – 9.76 (m, 1H), 3.03 (ddd, \( J = 8.9, 5.3, 4.4 \) Hz, 1H), 2.69 – 2.54 (m, 4H), 1.98 – 1.90 (m, 1H), 1.25 (t, \( J = 7.4 \) Hz, 3H), 0.99 (dd, \( J = 11.9, 6.7 \) Hz, 6H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 201.40, 46.40, 46.37, 32.37, 26.24, 19.34, 19.27, 14.85.

(R)-3-(((1S,2R,4R)-2-hydroxy-7,7-dimethylbicyclo[2.2.1]heptan-1-yl)methyl)thio)-3-phenylpropanal (syn-3ac)
Colorless oil; 26.0 mg 31% yield. \( R_f \) (PE /EtOAc = 5/1): 0.35, \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 9.71 (t, \( J = 1.8 \) Hz, 1H), 7.40 – 7.32 (m, 4H), 7.32 – 7.26 (m, 1H), 4.28 (t, \( J = 7.5 \) Hz, 1H), 3.75 (dd, \( J = 7.5, 3.7 \) Hz, 1H), 3.00 (dd, \( J = 7.5, 1.8 \) Hz, 2H), 2.54 – 2.44 (m, 2H), 1.75 – 1.59 (m, 6H), 1.51 – 1.44 (m, 1H), 1.18 – 1.11 (m, 1H), 1.05 – 0.98 (m, 1H), 0.89 (s, 3H), 0.77 (s, 3H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 199.30,
141.49, 128.95, 127.93, 127.46, 51.93, 49.65, 47.61, 44.98, 44.06, 38.95, 30.90, 30.21, 27.11, 20.59, 19.75. FTIR (film) 3435, 2931, 1723, 1453, 1388, 1265, 1072, 878, 739, 700 cm$^{-1}$; HRMS (ESI) m/z calcd for C19H27O2S$^+$ (M+H)$^+$ 319.1726, found 319.1722.

(R)-3-(((1S,2R,4R)-2-hydroxy-7,7-dimethylbicyclo[2.2.1]heptan-1-yl)methyl)thio)-3-phenylpropanal(anti-3ac)

Colorless oil; 34.3 mg 54% yield. $R_f$ (PE /EtOAc = 5/1): 0.30, $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.73 (t, $J = 1.6$ Hz, 1H), 7.37 – 7.33 (m, 4H), 7.30 – 7.26 (m, 1H), 4.34 (dd, $J = 8.1, 6.8$ Hz, 1H), 3.82 (dd, $J = 8.0, 3.9$ Hz, 1H), 3.08 – 2.95 (m, 2H), 2.69 (d, $J = 11.0$ Hz, 1H), 2.43 – 2.27 (m, 2H), 1.81 – 1.58 (m, 5H), 1.37 – 1.28 (m, 1H), 1.13 – 1.06 (m, 1H), 1.02 – 0.96 (m, 4H), 0.71 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 199.51, 141.42, 128.79, 127.63, 127.46, 51.90, 49.75, 47.62, 45.13, 44.51, 39.24, 30.93, 30.83, 27.06, 20.55, 19.89. FTIR (film) 3436, 2930, 1723, 1454, 1388, 1264, 1072, 879, 739, 700 cm$^{-1}$; HRMS (ESI) m/z calcd for C19H27O2S$^+$ (M+H)$^+$ 319.1726, found 319.1722.

3-Mercapto-3-phenylpropan-1-ol(5ac)

Colorless oil; 94% yield. $R_f$ (Pet. ether /EtOAc = 3/1): 0.20, $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.36 – 7.30 (m, 4H), 7.27 – 7.22 (m, 1H), 4.21 (td, $J = 7.6, 5.8$ Hz, 1H), 3.80 – 3.61 (m, 2H), 2.28 – 2.08 (m, 2H), 1.96 (d, $J = 5.9$ Hz, 1H), 1.48 (d, $J = 1.9$ Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 144.38, 128.77, 127.34, 126.87, 60.61, 42.04, 40.59.
Reference
