Supporting Information for

Surfactant-Type Asymmetric Organocatalyst: Organocatalytic Asymmetric Michael Addition to Nitrostyrenes in Water

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General Information: Commercial reagents were used as received, unless otherwise stated. $^1$H and $^{13}$C NMR were recorded on either a Bruker-DPX 300 or AV-400 spectrometer. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard. The following abbreviations were used to designate chemical shift mutiplicities: s = singlet, d= doublet, t = triplet, q = quartet, h = heptet, m = multiplet, br = broad. All first-order splitting patterns were assigned on the basis of the appearance of the multiplet. Splitting patterns that could not be easily interpreted are designated as multiplet (m) or broad (br). Mass spectra were obtained using fast-atom bombard (FAB) spectrometer or electrospray ionization (ESI) mass spectrometer. Optical rotations were measured using a 1 mL cell with a 1 dm path length on a Perkin-Elmer 341 digital polarimeter and are reported as follows: $[\alpha]_D^T$ (c in g per 100 mL of solvent). HPLC analysis was performed on Shimadzu CTO-10AS using ChiralPak columns purchased from Daicel Chemical Industries, LTD.
Dodecylbenzenesulfonic acid (>95% content for the alkylbenzesulfonic acids) was commercially available in the form of a mixture of linear alkyl (C_{11}-C_{13}) benzenesulfonic acids. Its molecular weight is regarded as 326.50.

**Synthesis of Surfactant-Type Asymmetric Organocatalyst by anion metathesis (Procedure a):**

Chiral ionic-liquid bromide (0.5 g, 1.73 mmol) and SDS (0.42 g, 1.45 mmol) were mixed in 10 mL of distilled water. The mixture was heated to ca. 60 °C till a clear solution was obtained. The solution was then concentrated under vacuum to dryness. The residue was dissolved in 100 mL of CH\textsubscript{2}Cl\textsubscript{2} and the organic solution was filtered to remove the insoluble salts. The filtrate was washed with distilled water (10 mL×6). The organic layer was dried over anhydrous Na\textsubscript{2}SO\textsubscript{4} and concentrated under vacuum to afford the desired product 1b as pale yellow syrup (0.48 g, 70%).

[\alpha]_{D}^{20} = +16.5^\circ\ (c=1.0, \text{CHCl}_3); ^1\text{H} NMR (300 MHz, CDCl\textsubscript{3}): \delta 0.84 (3H, t, J= 6.6 Hz), 0.92 (3H, t, J= 7.2 Hz), 1.14-1.37 (20H, m br), 1.42-1.52 (1H, m), 1.56-1.66 (2H, m), 1.71-1.89 (3H, m), 1.98-2.09 (1H, m), 2.97 (2H, t, J= 6.6 Hz), 3.66 (2H, br s), 3.96 (2H, t, J= 6.9 Hz), 4.18-4.38 (3H, m), 4.39-4.43 (1H, m), 7.30 (1H, s), 7.61 (1H, s), 9.40 (1H, s); ^13\text{C} NMR (CDCl\textsubscript{3}, 75 MHz): \delta 12.4, 13.1, 18.5, 21.7, 24.3, 24.9, 27.9, 28.3, 28.4, 28.5, 28.6, 28.7, 30.9, 31.0, 31.1, 45.5, 48.8, 52.2, 57.3, 66.8, 120.5, 122.3, 136.2; HRMS for C\textsubscript{12}H\textsubscript{22}N\textsubscript{3}\textsuperscript{+} (M\textsuperscript{+}), calcd. 208.1808, found 208.1807; HRMS for C\textsubscript{12}H\textsubscript{25}O\textsubscript{4}S\textsuperscript{−} (M\textsuperscript{−}), calcd. 265.1479, found 265.1478.

**Synthesis of Surfactant-Type Asymmetric Organocatalyst by neutralization (Procedure b):**
Chiral Ionic-liquid hydroxide was obtained by treatment of the corresponding bromide (0.5 g, 1.73 mmol) with strong basic anion-exchange resin. The hydroxide (100 mL solution in water) was treated with p-dodecyl benzenesulfonic acid (0.47 g, 1.44 mmol) and the solution was stirred overnight at room temperature. Water was removed under vacuum and the residue was dissolved in 100 mL of dichloromethane. The organic layer was washed with distilled water (10 mL×6) and was dried over anhydrous Na₂SO₄. Organic solvent was removed under vacuum to afford the desired product 1c as pale yellow syrup (0.42 g, 55%). \([\alpha]_{D}^{20} = +11.5^\circ\) (c=1.0, CHCl₃); ¹H NMR (300 MHz, CDCl₃): δ (for mixtures of C₁₁-C₁₃ isomers) 0.78-0.92 (6H, m), 1.16-1.34 (20H, m), 1.43-1.58 (6H, m), 1.69-1.86 (4H, m), 1.94-2.04 (1H, m), 2.39-2.50 (1H, m), 2.95 (2H, t, \(J = 6.9\) Hz), 3.72-3.82 (1H, m), 4.19 (2H, t, \(J = 7.5\) Hz), 4.29-4.47 (2H, m), 4.54 (1H, br), 7.10 (2H, d, \(J = 8.1\) Hz), 7.21 (1H, s), 7.62 (1H, s), 7.76 (2H, d, \(J = 8.1\) Hz), 9.81 (1H, s); ¹³C NMR (CDCl₃, 75 MHz): δ (for mixtures of C₁₁-C₁₃ isomers) 12.4, 12.9, 13.1, 18.5, 21.5, 21.6, 21.7, 24.2, 26.5, 26.6, 27.8, 28.3, 28.7, 30.7, 30.8, 30.9, 31.0, 35.8, 35.9, 44.5, 44.8, 45.2, 48.8, 52.1, 57.2, 120.1, 122.2, 124.8, 124.9, 125.7, 126.4, 136.8, 142.6, 147.1; HRMS for C₁₂H₂₂N₃⁺ (M⁺), calced. 208.1808, found 208.1806; HRMS for C₁₇₋₁₉H₂₇₋₃₁O₄S⁻ (M⁻), calced. 311.1686, 325.1843, 339.1999, found 311.1682, 325.1837, 339.2013.

**STAO 2** was synthesized following procedure A. \([\alpha]_{D}^{20} = +14.6^\circ\) (c=1.0, CHCl₃); ¹H NMR (300 MHz, CDCl₃): δ 0.83-0.88 (3H, m), 1.20-1.30 (20H, br), 1.61-1.78 (4H, m), 2.94-2.98 (2H, m), 3.23 (1H, br), 3.68 (1H, br), 3.98 (3H, s), 4.01-4.13 (3H, m), 4.32-4.36 (1H, m), 7.31 (1H, s), 7.54 (1H, s), 9.43 (1H, s); ¹³C NMR (CDCl₃, 75 MHz): δ 14.1, 14.2, 21.0, 22.6, 25.6, 25.9, 29.0, 29.3, 29.4, 29.6, 31.9, 36.5, 46.5, 53.8,
57.9, 60.3, 67.8, 122.7, 123.1, 137.9; HRMS for C₉H₁₆N₃⁺ (M⁺), calcd. 166.1339, found 166.1338; HRMS for C₁₂H₂₅O₄S⁻ (M⁻), calcd. 265.1479, found 265.1478.

3a was synthesized following published procedure.[¹] [α]₀²⁰⁺ = +25.7° (c=1.0, CHCl₃); ¹H NMR (300 MHz, CDCl₃): δ 0.97 (3H, J= 7.2 Hz), 1.41-1.48 (3H, m), 1.70-1.84 (2H, m), 2.00-2.05 (4H, m), 2.91-2.96 (2H, m), 3.84-3.93 (1H, m), 4.46-4.49 (1H, m), 4.53-4.60 (3H, m), 7.60-7.80 (4H, m), 11.19 (1H, s); ¹³C NMR (CDCl₃, 75 MHz): δ13.5, 19.8, 26.0, 29.6, 31.3, 46.6, 47.4, 51.5, 56.7, 112.8, 113.5, 126.9, 131.0, 131.9, 143.2; HRMS for C₁₆H₂₄N₃⁺ (M⁺), calcd. 258.1965, found 258.1964.

STAO 3b was synthesized following procedure A. [α]₀²⁰⁺ = +14.9° (c=1.0, CHCl₃); ¹H NMR (300 MHz, CDCl₃): δ 0.87 (3H, J= 6.6 Hz), 0.98 (3H, J= 7.2 Hz), 1.23 (18H, br), 1.41-1.56 (3 H, m), 1.62-1.83 (4H, m), 1.97-2.13 (3H, m), 2.97 (3H, t, J= 6.6 Hz), 3.86 (1H, br), 4.01 (2H, t, J= 6.9 Hz), 4.48-4.58 (4H, m), 7.59-7.69 (3H, m), 7.79-7.81 (1H, m), 10.47 (1H, s); ¹³C NMR (CDCl₃, 75 MHz): δ 13.4, 14.1, 14.2, 19.7, 22.6, 25.6, 25.9, 29.3, 29.4, 29.5, 29.6, 31.2, 31.9, 46.4, 47.4, 51.2, 57.0, 60.3, 67.8, 112.8, 113.6, 126.8, 126.9, 131.1, 132.0, 143.4; HRMS for C₁₆H₂₄N₃⁺ (M⁺), calcd. 258.1965, found 258.1960; HRMS for C₁₂H₂₅O₄S⁻ (M⁻), calcd. 265.1479, found 265.1472.

STAO 3c was synthesized following procedure A or B. [α]₀²⁰⁺ = +12.9° (c=1.0, CHCl₃); ¹H NMR (300 MHz, CDCl₃): δ (for mixtures of C₁₁-C₁₃ isomers) 0.78-0.85 (6H, m), 0.94-1.18 (20H, m), 1.34-1.65 (6H, m), 1.86-2.14 (4H, m), 2.47 (1H, br), 2.96-3.01 (2H, m), 3.89-3.98 (1H, m), 4.19 (1H, br), 4.46-4.51 (2H, m), 4.65-4.68 (2H, m), 7.08 (2H, d, J= 8.1 Hz), 7.55-7.64 (3H, m), 7.75 (2H, d, J=8.1 Hz), 7.83-7.85 (1H, m), 10.54 (1H, s); ¹³C NMR (CDCl₃, 75 MHz): δ (for mixtures of C₁₁-C₁₃ isomers) 13.4, 14.0, 19.7, 22.5, 22.6, 22.7, 25.2, 27.2, 27.5, 29.2, 29.3, 29.7, 31.1, 31.7, 31.8, 31.9, 36.6,
36.9, 45.5, 45.8, 46.3, 47.4, 50.4, 57.5, 112.7, 113.5, 125.9, 126.7, 126.8, 127.3, 131.2, 132.0, 143.4, 143.8, 148.0; HRMS for C_{16}H_{24}N_{3}^+ (M^+), calcd. 258.1965, found 258.1964; HRMS for C_{17-19}H_{27-31}O_4S^- (M^-), calcd. 311.1686, 325.1843, 339.1999, found 311.1686, 325.1844, 339.2001.

Chiral ionic liquid 4 was synthesized following our published procedure.  \[ \text{[1]} \quad \alpha_D^{20} = +7.2^\circ \ (c=1.0, \text{EtOH}); \quad ^1\text{H NMR (300 MHz, CDCl}_3\text{):} \quad \delta 0.71-0.75 (3\text{H, m}), 1.11-1.18 (12\text{H, br m}), 1.55-1.61 (2\text{H, m}), 1.79-1.86 (3\text{H, m}), 2.36 (1\text{H, br}), 2.74-2.81 (2\text{H, m}), 3.54 (1\text{H, br}), 4.06-4.34 (4\text{H, m}), 7.33 (1\text{H, s}), 7.64 (1\text{H, s}), 10.10 (1\text{H, s}); \quad ^{13}\text{C NMR (CDCl}_3\text{, 75 MHz):} \quad \delta 13.9, 22.4, 25.8, 26.1, 28.8, 28.9, 29.1, 30.2, 31.5, 46.5, 49.9, 54.2, 57.4, 121.2, 123.3, 137.0; \quad \text{HRMS for C}_{16}\text{H}_{30}\text{N}_{3}^+ (M^+), \text{calcd. 264.2434, found 264.2435.}

\begin{equation}
\begin{array}{c}
\text{N} \\
\text{H} \\
\text{N} \\
\text{C}_8\text{H}_{17}
\end{array}
\end{equation}

\begin{equation}
\begin{array}{c}
\text{Br}^-
\end{array}
\end{equation}

Chiral ionic liquid 5 was synthesized following our published procedure.  \[ \text{[1]} \quad \alpha_D^{20} = -1.30^\circ \ (c=1.0, \text{EtOH}); \quad ^1\text{H NMR (300 MHz, DMSO):} \quad \delta 1.24 (14\text{H, br}), 1.56-1.60 (4\text{H, m}), 1.78-1.81 (6\text{H, br}), 2.64-2.83 (3\text{H, br m}), 2.95 (1\text{H, br}), 3.39-3.42 (2\text{H, m}), 3.93-4.00 (2\text{H, m}), 4.13-4.30 (7\text{H, br m}), 7.84 (4\text{H, br}), 9.33-9.59 (2\text{H, br m}); \quad ^{13}\text{C NMR (DMSO, 75 MHz):} \quad \delta 23.9, 25.9, 28.7, 29.0, 29.2, 29.8, 46.3, 49.1, 53.8, 57.5, 122.3, 123.4, 136.8; \quad \text{HRMS for C}_{26}\text{H}_{46}\text{N}_{6}\text{Br}^+ (M^{2+}+\text{Br}^-), \text{calcd. 521.2967 and 523.2947, found 521.2958 and 523.2927.}

\begin{equation}
\begin{array}{c}
\text{N} \\
\text{H} \\
\text{N} \\
\text{Br}^-
\end{array}
\end{equation}

\begin{equation}
\begin{array}{c}
\text{N} \\
\text{C}_{12}\text{H}_{25}
\end{array}
\end{equation}

Chiral ionic liquid 6 was synthesized following our published procedure.  \[ \text{[1]} \quad \alpha_D^{20} = +20.5^\circ \ (\text{as hydrochloride salt, } c=1.0, \text{EtOH}); \quad ^1\text{H NMR (300 MHz, CDCl}_3\text{):} \quad \delta 0.80-0.85 (3\text{H, m}), 1.20 (18\text{H, br}), 1.51-1.94 (5\text{H, m}), 2.84-3.12 (2\text{H, m}), 3.60 (1\text{H, br}), 4.06-4.54 (4\text{H, m}), 7.28 (1\text{H, br}), 7.37 (1\text{H, s}), 10.34 (1\text{H, br}); \quad ^{13}\text{C NMR (CDCl}_3\text{, 75 MHz):} \quad \delta 14.0, 22.6, 23.5, 26.4, 28.1, 29.0, 29.3, 29.4, 29.5, 29.6, 29.8, 31.8, 45.4, 49.0, 50.2, 50.5, 60.2, 122.6, 123.7, 136.4; \quad \text{HRMS for C}_{20}\text{H}_{38}\text{N}_3^+ (M^+), \text{calcd. 320.3060, found 320.3061.}

\begin{equation}
\begin{array}{c}
\text{N} \\
\text{C}_{12}\text{H}_{25}
\end{array}
\end{equation}
General procedure: To a solution of 3c (29 mg, 0.05 mmol) in water (0.5 mL) in a vial, was added nitrostyrene (37 mg, 0.25 mmol) at room temperature. The mixture was stirred vigorously for 5 minutes, and then cyclohexanone was added (130 μL, 1.25 mmol). The reaction mixture was stirred for 12 h. The water was decanted after centrifuge at 6000rpm for 3 minutes. The residue was purified by Flash chromatograph on silica gel to afford the Michael adduct (58 mg, 93%) as white solid. In cases organic extraction is necessary; the aqueous layer was extracted with ether (1mL ×3). The organic extraction was concentrated and purified by flash chromatograph to afford the desired product. Products 7-13, 15-16 are known compounds. [1-4]

White solid. [α]D = -32° (91% ee, c=1.0, CHCl3); 1H NMR (300 MHz, CDCl3): δ 1.17-1.29 (1H, m), 1.61-1.84 (4H, m), 2.02-2.13 (1H, m), 2.32-2.43 (2H, m), 2.90-2.95 (1H, m), 3.75 (3H, s), 3.78 (3H, s), 3.83-3.87 (1H, m), 4.73-4.82 (2H, m), 6.36-6.42 (2H, m), 6.95 (1H, d, J=8.4 Hz); 13C NMR (CDCl3, 75 MHz): δ 25.2, 28.6, 33.3, 40.9, 42.7, 50.7, 53.5, 55.4, 99.1, 104.4, 117.6, 131.5, 158.6, 160.4, 212.7. The enantiomeric excess was determined by HPLC with a AD-H column at 254 nm (2-propanol: hexane=10:90), 0.5 mL/min; tR = 26.8 min (minor), 40.9 min (major).

![Figure](attachment:image.png) Pictures showing 3c catalyzed reaction of 2-chloro-nitrostyrene at the beginning (a) and in the end (b).
Reference:


NMR spectra for STAOs and new compounds

- 8 -
2b

C_{12}H_{25}SO_{4}N\text{CH}_3

**Supplementary Material (ESI) for Chemical Communications**

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\begin{align*}
\text{N} & \text{H} \\
\text{N} & \text{N} \\
\text{C}_4\text{H}_9 & \text{C}_{12}\text{H}_{25}\text{SO}_4
\end{align*}

3b

\begin{align*}
\text{N} & \text{H} \\
\text{N} & \text{N} \\
\text{C}_4\text{H}_9 & \text{C}_{12}\text{H}_{25}\text{SO}_4
\end{align*}

3b
OCH$_3$

\[
\begin{align*}
\text{OCH}_3 & \\
\text{NO}_2 & \\
\end{align*}
\]

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**Supplementary Material (ESI) for Chemical Communications**  
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