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# Tunable Oleo-Furan Surfactants by Acylation of Renewable Furans

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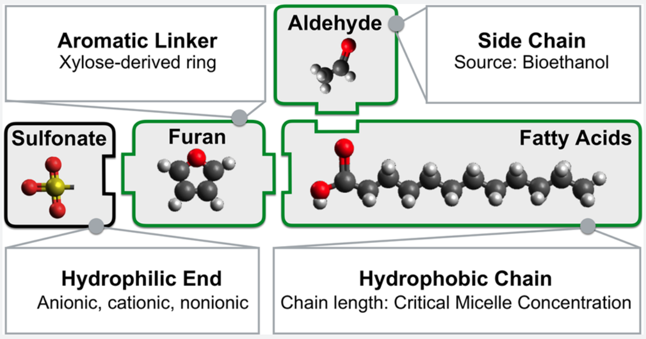
*Supporting Information*

**ABSTRACT:** An important advance in fluid surface control was the amphiphilic surfactant composed of coupled molecular structures (i.e., hydrophilic and hydrophobic) to reduce surface tension between two distinct fluid phases. However, implementation of simple surfactants has been hindered by the broad range of applications in water containing alkaline earth metals (i.e., hard water), which disrupt surfactant function and require extensive use of undesirable and expensive chelating additives. Here we show that sugar-derived furans can be linked with triglyceride-derived fatty acid chains via Friedel−Crafts acylation within single layer (SPP) zeolite catalysts. These alkylfuran surfactants independently suppress the effects of hard water while simultaneously permitting broad tunability of size, structure, and function, which can be optimized for superior capability for forming micelles and solubilizing in water.



## INTRODUCTION

The surface energy of droplets, bubbles, and foams determines the efficacy of applications in food,[1] agriculture, cleaning,[2] and drug delivery[3,4] and can be optimized for each use by chemical surfactants. Many approaches to surfactant design have utilized commodity chemicals to provide both hydrophilic (water engaging) and hydrophobic (oil engaging) functionality from low-cost feedstocks. The use of surfactants with eight to 18 saturated carbon atoms combined with a polar function has been particularly useful within aqueous systems,[2] as the carbon chains aggregate into micelles that can trap oils or stabilize active ingredients within water. This approach has worked in soap and detergent technologies for over a century, but modern variations of these surfactants based on fossil fuel precursors exhibit performance limitations inherent to their molecular structure.[5,6] In addition to modifying interfacial surface energy, surfactants are characterized by their ability to make and stabilize foams, to wet porous materials such as fibers and particles, and to operate in aggressive conditions such as high temperature or hard water.[7] The breadth of performance targets is sufficiently large that modern surfactant structures cannot be independently optimized for all properties, requiring the use of substantial additives for effective application.[2,8] Here, we report the use of heterogeneous catalysts for the efficient synthesis of surfactants from renewable furans and fatty acids with tunable structures that are optimized to form micelles in hard water (e.g., $Ca^{2+}$) at low temperatures.

The largest volume surfactant for aqueous applications such as detergency remains linear alkylbenzenesulfonate (LAS). As depicted in Figure 1A, LAS chemicals are composed of a benzene ring connecting polar functionality (e.g., $Na^+SO_3^-$) with branched alkyl chains (eight to 14 carbons). These surfactants are produced by alkylation of benzene with alpha-olefins such as 1-dodecene; by this method, acid catalysts protonate the olefin leading to double bond migration and various alkylbenzene isomers such as 2-phenyl- to 6-phenyl-dodecane.[9−12] The surfactant is then prepared by reacting alkylbenzene precursors with $SO_3$−air or $SO_3$ in sulfuric acid mixtures.[13]

The limited opportunity for tuning the LAS class of surfactants to further enhance its properties has necessitated incorporation of chemical agents such as metal chelants as depicted in Figure 1A. For example, LAS surfactants in hard

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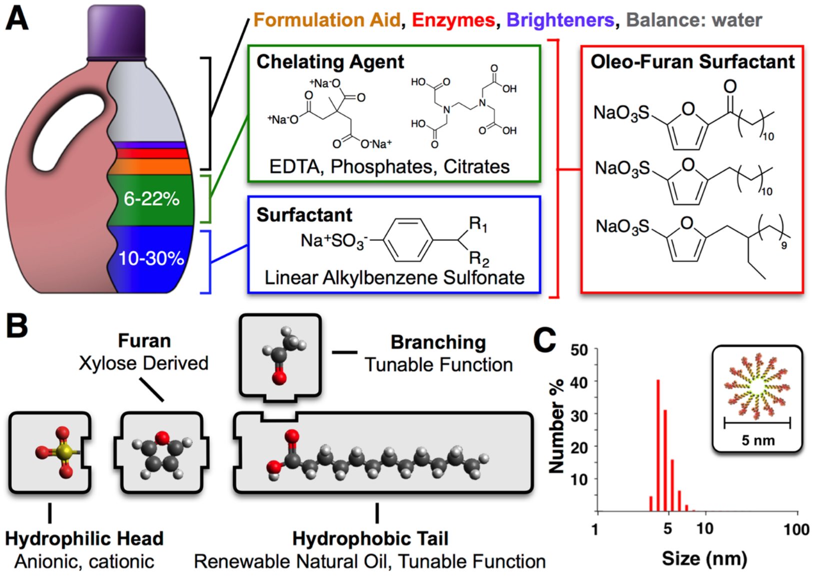


Figure 1. Oleo-furansulfonate surfactant structure and function. (A) Water-based linear alkylbenzenesulfonate (LAS, blue) surfactants require metal chelating agents (green), both of which are replaced by a single oleo-furansulfonate surfactant (OFS, red). (B) Preparation of OFS utilizes selective addition of hydrophobic alkyl-chain tails with or without added branching to furan linkers connected to hydrophilic heads such as sulfonates. (C) Oleo-furansulfonate (OFS-12) forms micelles characterized by dynamic light scattering at 1.4 wt % in water (20 × CMC).

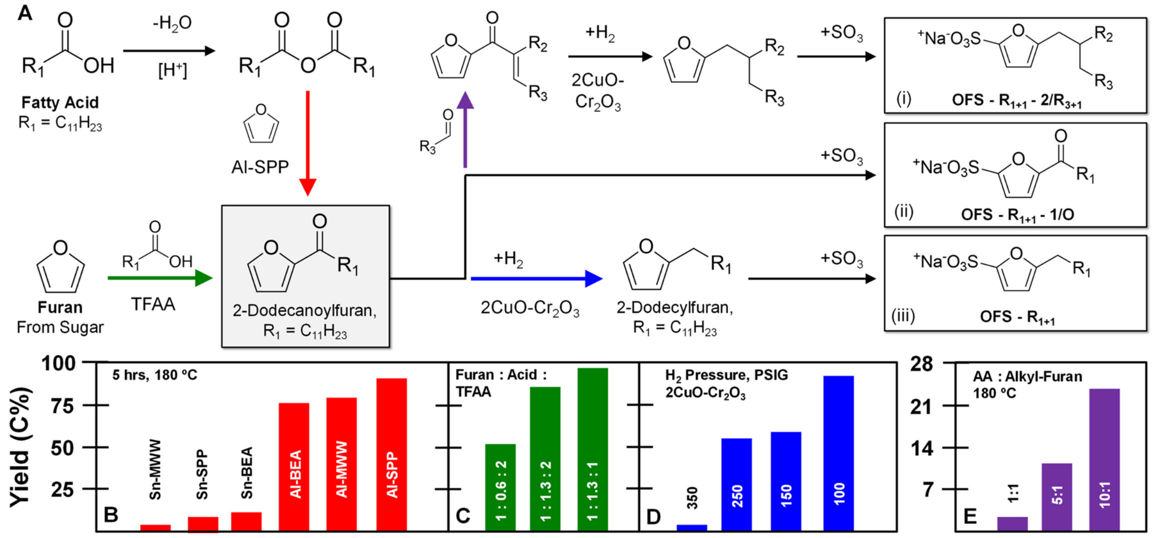
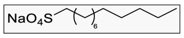
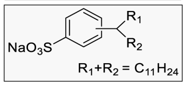
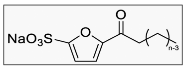
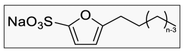
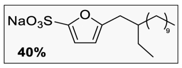


Figure 2. Furan acylation to renewable oleo-furansulfonate (OFS) surfactants. (A) Reaction of furan with the anhydride form of fatty acids ($R_1$) with a solid acid such as Al-SPP zeolite produces acylated furan ketone at ∼90% yield. Alternatively, direct acylation of fatty acids ($R_1$) occurs in two integrated steps via trifluoroacetic anhydride (TFAA). Three classes of OFS include (i) aldol condensation, reduction, and sulfonation to branched surfactants (OFS-$R_{1+1}$-2/$R_{3+1}$), (ii) direct sulfonation (OFS-$R_{1+1}$-1/O), or (iii) reduction to a linear chain and sulfonation (OFS-$R_{1+1}$). (B) Furan acylation with solid acid catalysts for 5 h, 180 °C. (C) Combined anhydride formation and furan acylation with varying ratios of furan, fatty acid, and TFAA. (D) Hydrogenation of 2-dodecanoylfuran on copper chromite at 220 °C with varying hydrogen pressure. (E) Aldol condensation with varying ratios of acetaldehyde (AA) and 2-dodecanoylfuran at 180 °C.

water (with $Mg^{2+}$ and $Ca^{2+}$) require additives such as ethylenediaminetetraacetic acid (EDTA), which preferentially bind to and suspend hard water ions, preventing the ions from forming inactive precipitates or multilamellar vesicles with surfactants.[14,15] Hard water conditions, which often exceed 200 ppm of $Ca^{2+}$,[16] require coformulation of chelating agents with surfactants in equal parts,[15] increasing cost and complexity. Moreover, incorporation of chelating agents is region and application specific, with many compounds such as EDTA and phosphates banned due to their environmental impact.[15,17,18] Despite development of a large variety of alternative chelating agents including zeolites,[19] citrates, and polycarboxylates,[17] sodium tripolyphosphate remains the standard by which all other chelants are measured.[14]

In this work, we replace the benzene moiety of LAS with biomass-derived furans[20] to link polar and hydrophobic alkyl chains from the fatty acids of natural oils[21] to form new oleo-furansulfonate (OFS) surfactants, shown in Figure 1B, that can retain detergency without the need for additives such as chelants. We hypothesize that substitution of benzene with furan will increase overall solubility in water and alter the balance of polar and nonpolar groups, thereby allowing for OFS surfactants with straight (unbranched) alkyl chains derived from fatty acids. Surfactant synthesis occurs by precise furan

Table 1. Oleo-Furan and Commercial Surfactant Structure and Property Characteristics

| Surfactant | Structure | CMC[a] [ppm] | Krafft Point[b] [°C] | Draves Wetting[c] [s] | Foam Growth Rate[d] $r_i / r_{SLS}$ [-] | Foam Height$_{60}$[e] $h_{i\text{-}60} / h_{SLS\text{-}60}$ [-] | Micelle Stability[f] [ppm $Ca^{2+}$] |
|---|---|---|---|---|---|---|---|
| **Commercial** | | | | | | | |
| SLS, Sodium Lauryl Sulfate |  | 2010 | 15 | 6.3 | 1.00 | 1.00 | 33 |
| MES, Methyl Ester Sulfonate | | 130 | < 0 | 15.1 | 0.79 | 0.54 | 500 |
| LAS, Linear Alkylbenzene Sulfonate |  | 460 | 20 | 4.9 | 1.36 | 2.20 | 100 |
| SLES, Sodium Lauryl Ether Sulfate | | 380 | < 0 | 15.4 | 1.60 | 2.94 | > 50,000 |
| **OFS, Oleo-Furan Sulfonates** | | | | | | | |
| *OFS-n-1/O* | | | | | | | |
| n=12 |  | 11520 | < 0 | > 3600 | 0 | 0 | 230 |
| n=14 | | 3127 | < 0 | > 3600 | 0 | 0 | 33 |
| n=18 | | 1156 | < 0 | > 3600 | 0 | 0 | > 50,000 |
| Cocinic, n = 8-18 | | 4890 | < 0 | > 3600 | 0 | 0 | 6600 |
| *OFS-n* | | | | | | | |
| n=7 |  | 2669 | < 0 | > 3600 | 1.04 | 0.12 | 120 |
| n=12 | | 720 | 30 | 48.9 | 1.83 | 2.11 | > 50,000 |
| n=14 | | 267 | 41.5 | 39.4 | 2.34 | 0.75 | > 50,000 |
| n=18 | | 316 | > 50 | - | - | - | 33,000 |
| Cocinic, n = 8-18 | | 512 | 18.5 | 58.0 | 2.06 | 2.19 | > 50,000 |
| 40:60 mol% OFS-12-2/C2H5:OFS-12 |  | 510 | 25.7 | 18.5 | 1.96 | 2.37 | 2000 |
| 85:15 mol% OFS-12-1/O:OFS-12 | | 2445 | < 0 | - | - | - | - |

[a] Critical micelle concentration, measured above Krafft point. [b] Measured at 1.0 wt % surfactant in water. [c] Measured at 0.25 wt % in water. [d] Measured at 0.5 wt % in water. [e] At 60 min. [f] Measured at twice CMC.

acylation using heterogeneous catalysts and systematic tuning of the molecular structure via incorporation of branching, polarity, and variable chain length. For each variation of molecular design, surfactant performance is characterized to elucidate the structure−property relationships accounting for solvation in water, capability for forming micelles, and stability in hard water; this insight is then used to identify an ideal OFS molecule.

## ■ RESULTS AND DISCUSSION

Preparation of OFS surfactants utilizes furan as a linker connecting alkyl chains and sulfonate. As depicted in Figure 2, long (>C10) alkyl chains are obtained from hydrolysis of triglycerides to fatty acids such as lauric acid (C12), myristic acid (C14), or stearic acid (C18) and can be converted to anhydrides by numerous existing methods including dehydration in the presence of water sorbents or other short-chain recyclable anhydrides.[22,23] Here, we demonstrate the coupling of these long alkyl chain anhydrides with furans by Friedel−Crafts acylation with heterogeneous catalysts. As shown in Figure 2B, the reaction of lauric anhydride with furan on either Lewis acid zeolites (such as Sn-BEA, Sn-MWW, or Sn-SPP) or Brønsted acid zeolites (such as Al-BEA or Al-SPP) exhibited significant activity for acylation (see Supporting Information for details). Acylation of furan occurs with varying activity on Sn and $H^+$ sites as well as large and small pore structures (Figure 2B); yield of acylated furan was only 11% with Sn-BEA but was 89% with hierarchical porous Al-SPP after 5 h of reaction at 180 °C.

Alternatively, the two-step process of long-alkyl chain conversion to an anhydride and Friedel−Crafts acylation can occur simultaneously with the use of small anhydrides with strongly electron withdrawing groups. As shown in Figure 2C, the reaction of furan, lauric acid, and trifluoroacetic anhydride (TFAA) produces high yields of acylated furans. By varying the reaction temperature and ratio of the three components, yield of 2-dodecanoylfuran can be increased from about 50% to over 95% in only a few minutes. At lower concentrations, the time-resolved conversion of the three components was measured (see Figure S4 for details); lauric acid rapidly reacts with TFAA to form lauric anhydride and the mixed anhydride, which are consumed as acylation of the furan proceeds. By this method 2-dodecanoylfuran was recovered by evaporating any remaining furan, solvent, or trifluoroacetic acid, which can be recycled to TFAA.[22]

Long chain furan ketones such as 2-dodecanoylfuran (gray in Figure 2) prepared by acylation provide the key capability for producing tunable surfactant chemicals. As shown in Figure 2D, the ketone functionality can be eliminated by catalytic reduction with copper chromite ($2CuO-Cr_2O_3$) catalyst without hydrogenation of the furan ring. Variation of the reaction temperature and hydrogen pressure resulted in varying yield of the reduced 2-dodecylfuran from less than 1% (350 psi of $H_2$, 220 °C) to over 91% (100 psi of $H_2$, 220 °C). Additionally, a third class of branched alkylfurans was prepared by aldol condensation of C12 alkyl chain furan ketones with acetaldehyde. As depicted in Figure 2E, aldol condensation preferentially occurred at the second carbon, resulting in a best yield of 23%, which was enhanced to a 40:60 mol ratio of branched versus straight chain OFS surfactants after hydrogenation with copper chromite and purification (see Supporting Information for details).

A single acylation occurred overwhelmingly at the furan $\alpha$ carbon by either solid acid or TFAA methods as confirmed by NMR spectroscopy, and multiple acylation additions to furan were not observed. The remaining furan $\alpha$ carbon could then be sulfonated by existing commercial methods of sulfur trioxide sulfonation or the laboratory method with a sulfur trioxide−pyridine complex,[24,25] which yielded high purity alkylfuransulfonate. As listed in Table 1, sulfonation of three acylated furans including C12, C14, and C18 yielded three oleo-furansulfonate surfactants identified as OFS-*n*-1/O to denote the ketone functionality on the alkyl chain at the first carbon position. A fourth ketone surfactant was prepared from cocinic acid, a mixture of C8 to C18 fatty acids. Linear (OFS-*n*) surfactants prepared by hydrogenation and branched (OFS-12-2/C2H5) surfactants prepared by aldol condensation were sulfonated by the same method.

Preparation of precise oleo-furan surfactant molecules permitted evaluation of colloidal properties relative to

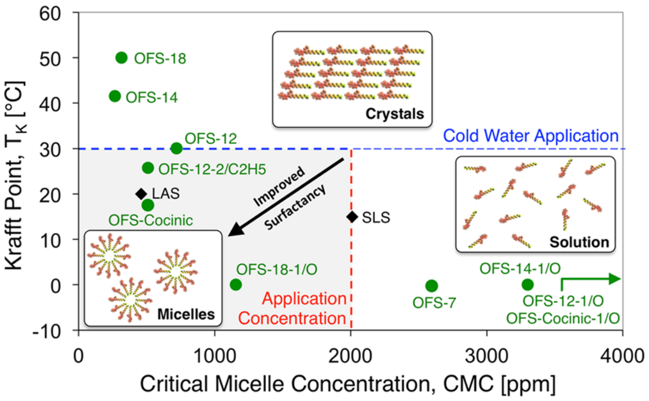


**Figure 3.** Oleo-furan surfactant performance. Comparison of the surfactant critical micelle concentration (CMC) above which micelles form and the Krafft temperature ($T_K$) below which surfactants crystallize as a separate solid phase. Optimal conditions for aqueous applications (gray box) require a Krafft point below 30 °C and a critical micelle concentration below about 2000 ppm. Linear chain oleo-furansulfonate surfactants (OFS-12 and OFS-cocinic) and branched OFS-12-2/C2H5 exhibit comparable or better properties when compared with linear alkylbenzenesulfonates (LAS).

surfactant structure. As shown in Figure 3, surfactant performance was evaluated by measuring the critical micelle concentration (CMC), defined as the minimum concentration for which dissolved surfactants spontaneously self-assemble to micelles. Surfactants were also characterized by their Krafft temperature ($T_K$), defined as the temperature below which surfactants form solid crystals. Dashed lines denoting the requirements of common aqueous application concentration (2000 ppm, red) and cold water detergency (30 °C, blue) form the bounds of the lower left region of Figure 3, at which the surfactant has desirable properties in cold water and dilute conditions.

Direct comparison of OFS and LAS reveals that the oleo-furan structure exhibits superior detergency. As depicted in Figure 3 and listed in Table 1, OFS-12 with a linear alkyl chain achieves feasible performance (CMC of 720 ppm, $T_K$ of 30 °C) while the analogous LAS-12 linear alkyl chain has a higher Krafft temperature of 58 °C;[5] the furan linker moiety can therefore be interpreted as improving surfactant solubility relative to benzene. Introduction of moderate two-carbon branching in a 40:60 ratio of OFS-12-2/C2H5:OFS-12 also lowers the CMC and Krafft temperature, further improving surfactancy. However, the most dramatic performance enhancement was derived from the mixture of linear alkyl chains found in OFS-cocinic (CMC of 512 ppm, $T_K$ of 18 °C): the variation of linear alkyl chain lengths in OFS-cocinic with a furan linker is comparable to that of branched LAS (CMC of 460 ppm, $T_K$ = 20 °C).

Performance of OFS in hard water conditions indicates dramatically enhanced surfactant stability of furan-based OFS molecules compared with conventional benzene-based and linear surfactants. Figure 4 depicts the concentration [ppm] of hard water ions, $Ca^{2+}$, with two surfactant performance descriptors. Solution turbidity [ppm] was defined as the $Ca^{2+}$ concentration for which the aqueous surfactant solution visually lost its clarity due to formation of crystals. Micelle stability was identified as the $Ca^{2+}$ concentration [ppm] at which the solution surface tension began increasing associated with loss in surfactant performance. Comparison of OFS stability overlaid with $Ca^{2+}$ concentrations common to soft and hard water applications[16] demonstrates a two-order-of-magnitude increase in stability of OFS molecules when compared with conventional surfactants. OFS-*n* surfactants exhibit $Ca^{2+}$ turbidity and stability concentrations in the range of 10,000 ppm, while conventional LAS and SLS surfactants are in the 10−100 ppm range. Thus, OFS surfactants retain surfactancy in extreme hard water conditions without the need for coformulation of chelating agents.

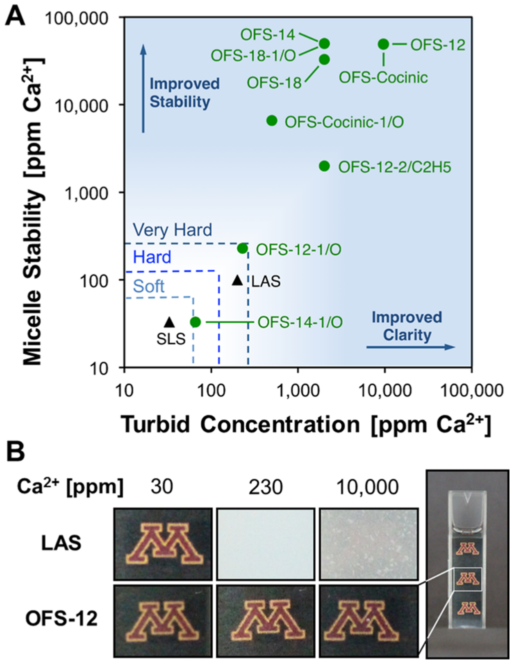


**Figure 4.** Hard water performance of oleo-furansulfonate surfactants. Comparison of sulfonated surfactants for micelle stability and solution turbidity (A) for a range of soft to moderately hard (0−120 ppm), hard (121−150 ppm), and very hard (>251 ppm) water reveals that most oleo-furan surfactants remain clear and functional in hard water conditions when viewed through a cuvette (B), while conventional surfactants such as LAS become cloudy (230 ppm) and precipitate (10,000 ppm). Details of individual experiments are provided in Figures S31−S35.

Additional performance metrics indicate that OFS surfactants exhibit sufficiently fast wetting kinetics and foaming behavior (see Figures S17−S30 for details). Surfactant wetting kinetics, as measured by the Draves test, determines the rate at which an aqueous surfactant solution wets hydrophobic surfaces. The time ($T_D$) required for surfactant wetting of a cotton skein (i.e., Draves wetting test) in Table 1 indicates desirable wetting characteristics for all OFS-*n* structures ($T_D$ less than 1 min), suitable for applications requiring fast-acting surfactants.[15] Additionally, aqueous surfactant solutions were characterized for their ability to grow foams and stabilize a height of foam at steady state (Table 1).[2] By bubbling air through a graduated cylinder of surfactant solution, the foam growth rate ($r$) and steady state foam heights ($h$) were measured. Comparison of foam growth rate and foam height, as shown in Table 1 (see Figures S28 and S29 for details), shows that OFS-*n* molecules have similar foaming performance to conventional LAS surfactants.

Facile assembly of xylose-derived furan molecules with triglyceride-derived fatty acids into oleo-furan surfactants demonstrates a highly tunable method for renewable surfactant synthesis. The ability to precisely select and assemble with heterogeneous catalysts amenable to chemical processing allows for the chemical targeting of specific surfactant performance. By this approach, the optimal OFS molecules such as OFS-12 or OFS-cocinic demonstrate strong surfactant performance in minimal concentrations and low temperatures compared with current large volume surfactants. These surfactants utilize straight alkyl chains that are optimal for biodegradation.[26−28] More importantly, enhanced hard water stability of the OFS platform of molecules permits surfactant function in extremely hard water. This lack of sensitivity to metal ions enables formulation of surfactant systems free of chelating agents, capturing a broad range of applications in hard water and simplifying formulation of application specific surfactant systems.

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscentsci.6b00208.

> Materials and methods, screening of reaction conditions, reaction results, product characterization via NMR spectroscopy, SAXS, and GC−MS, and evaluation of surfactant performance (PDF)

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### Author Contributions

$^{\S}$D.S.P. and K.E.J. contributed equally.

### Notes

The authors declare no competing financial interest.

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