Electronic Supplementary Information

for

Ordered nanoporous lyotropic liquid crystal polymer resin for heterogeneous catalytic aerobic oxidation of alcohols

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I. Materials and General Procedures

Methyl gallate, acryloyl chloride, thionyl chloride, triethylamine, 2-hydroxy-2-methylpropiophenone, and L-alanine were obtained from Sigma-Aldrich. 11-Bromoundecanol was obtained from Accela ChemBio, Inc. 4-Amino-TEMPO was obtained from AK Scientific, Inc. Acryloyl chloride, thionyl chloride, and triethylamine were distilled prior to use. Dioxane (Sigma-Aldrich) was distilled from sodium benzophenone ketyl before use. Acetonitrile (Sigma-Aldrich) was distilled from calcium hydride before use. All other chemicals and solvents were purchased from either Sigma-Aldrich, TCI America, or Fisher Scientific and used without further purification. PS-TEMPO and SiO$_2$-TEMPO (i.e., Siliacat®) were purchased from Sigma-Aldrich. Normal-phase column chromatography was performed using 200–400 mesh silica gel purchased from Sorbent Technologies, Inc. All manipulations (except for reaction work-up procedures) were performed under light Ar flush using conventional Schlenk line techniques. Unless otherwise specified, organic extracts were dried over anhydrous sodium sulfate. Solvents were removed using a rotary evaporator, followed by drying on a Schlenk line ($\leq 10^{-4}$ torr). The lyotropic liquid crystal (LLC) mixtures were mixed using a IEC Centra-CL2 centrifuge. A focused-spot UV beam (Lumen Dynamics OmniCure Series 1000 UV lamp at a distance of ca. 3 cm) was used for photopolymerizations. Polymerizations were conducted in an N$_2$-filled glovebox from Coy Lab Products (Rigid Basic Glove Box design). Polymer resins were powdered for catalysis experiments using a steel vial (0.5 inches in diameter x 1.0 inches in length) and ball pestle with a Wig-L-Bug® grinder/amalgamator purchased from Sigma-Aldrich. The wire-mesh sieves used for particle size separation were 3 inches in diameter, made of stainless steel, and purchased from Cole-Parmer. The percent conversion values reported for heterogeneous catalysis reactions are average values with standard deviation error bars from duplicate or triplicate experiments and were determined by quantitatively by $^1$H NMR analysis or semi-quantitatively by gas chromatography-mass spectrometry (GC-MS) analysis.

II. Instrumentation

$^1$H and $^{13}$C NMR spectra were obtained using a Bruker AMX-300 (300 MHz for $^1$H) spectrometer or Varian Inova 500 (500 MHz for $^1$H) and Inova 400 (400 MHz for $^1$H) spectrometers. Chemical shifts are reported in ppm relative to residual nondeuterated solvent. FT-IR measurements were performed using a Thermo Scientific Nicolet 6700 spectrometer equipped with a PIKE MIRacleTM single-reflection horizontal attenuated total reflectance (ATR) accessory with a diamond crystal. Powder X-ray diffraction (PXRD) spectra were obtained with an Inel CPS 120 diffraction system using monochromated Cu K$_\alpha$ radiation. PXRD measurements on samples were all performed at ambient temperature ($21 \pm 1$ °C). Polarized optical microscopy (POM) studies was performed with a Leica DMRXP polarizing light microscope equipped with an Optronics digital camera assembly. High-resolution mass spectral analysis was performed by the Central Analytical Facility in the Dept. of Chemistry and Biochemistry at the University of Colorado Boulder. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN. GC-MS measurements were performed using a Thermo-Finnigan PolarisQ Ion Trap GC-MS system.
III. Monomer Syntheses

3,4,5-Tris(11′-acryloyloxyundecyloxy)benzoic acid (3). This compound was prepared from methyl gallate, 11-bromoundecanol, and acryloyl chloride as described in the literature, with the following modifications to the final step: After the dropwise addition of acryloyl chloride (5 equivalents) to the reaction flask at 60 °C, the reaction was allowed to cool to 50 °C and continued stirring overnight. Methanol (ca. 5 mL) was added to quench excess acryloyl chloride. The solvents were then removed by rotary evaporation. The resulting residue was dissolved in a 80 mL of a 1:1 (v/v) solution of water:pyridine and stirred for 1 h at 80 °C. Subsequently, the solution was acidified with 3 M aq. HCl (ca. 120 mL), causing the formation of a white precipitate. The product was then extracted into EtOAc (3 x 200 mL) and worked up as previously described. Characterization data agreed with those reported in the literature.

Acrylic acid 11-[2,3-bis-(11-acryloyloxy-undecyloxy)-5-(1-carboxy-ethylcarbamoyl)-phenoxy]-undecyl ester (1). Compound 3 (0.750 g, 0.890 mmol), N-(3-Dimethylaminopropyl)-N′-ethylcarbodiimide hydrochloride (EDC-HCl) (0.187 g, 0.979 mmol, 1.1 equiv.), DMAP (0.011 g, 0.089 mmol, 0.1 equiv.), and 4-amino-TEMPO (0.168 g, 0.979 mmol, 1.1 equiv.) were dissolved in anhydrous dichloromethane (10 mL) in a flame-dried, 50-mL Schlenk flask under Ar flush. The clear, red solution was stirred at room temperature under Ar for 18 h. The reaction was then diluted with dichloromethane to a total volume of ca. 80 mL. This solution was washed with 0.5 M aq. HCl (2 x 50 mL), saturated aq. NaHCO$_3$ (2 x 50 mL), and then brine (1 x 50 mL). The clear, red solution was dried over anhydrous sodium sulfate. Evaporation of the solvent gave a red oil, which was loaded onto a silica plug. The product was eluted with 5% (v/v) methanol in dichloromethane to give 3 as a rose-colored oil. (0.880 g, 0.880 mmol, 99% yield). $^1$H NMR (500.37 MHz, acetone-d$_6$): $\delta$ 1.27–1.95 (br m, 60H), 4.03 (m, 6H), 4.15 (m, 6H), 5.89 (d, $J$ = 10 Hz, 3H), 6.16 (dd, $J$ = 11 Hz, 7 Hz, 3H), 6.37 (d, $J$ = 17 Hz, 3H), 7.26 (br s, 2H). $^{13}$C NMR (100.63 MHz, acetone-d$_6$): $\delta$ 25.86, 26.11, 28.61, 29.56, 30.35, 64.21, 64.24, 68.91, 72.85, 105.88, 128.82, 128.86, 130.14, 130.17, 140.71, 152.95, 165.44. IR (neat): 3288, 2974, 2851, 1722, 1630, 1584, 1542, 1500, 1466, 1426, 1405, 1381, 1294, 1269, 1225, 1183, 1111, 1069, 1024, 986, 811. Elemental analysis calculated for C$_{58}$H$_{95}$N$_2$O$_{11}$: 69.92 C, 9.61 H, 2.81 N. Found: 69.82 C, 9.52 H, 3.04 N.

Acrylic acid (S)-11-[2,3-bis-(11-acryloyloxy-undecyloxy)-5-(1-carboxy-ethylcarbamoyl)phenoxy]-undecyl ester (2). An improved, modified procedure for the synthesis of this compound was used instead of that reported in the literature: Compound 3 (2.49 g, 2.97 mmol)
was loaded under Ar flush into a flame-dried, 50-mL round-bottom flask. Thionyl chloride (2.60 mL, 35.6 mmol) was added dropwise using a syringe. An oil bubbler was connected to the reaction flask; and the clear, yellow solution stirred at room temperature under Ar for 24 h. The flask was then placed in an ice-water bath. Anhydrous dioxane (5 mL) was then added by syringe. L-Alanine (0.530 g, 5.94 mmol) and K$_2$CO$_3$ (2.05 g, 14.9 mmol) were dissolved in a minimum amount (ca. 5 mL) of deionized water and added to the reaction flask in one portion with vigorous stirring. (Caution: This step is highly exothermic and produces corrosive, toxic gases and should be performed in a functioning fume hood with adequate air flow.) The resulting suspension was stirred at room temperature for an additional 12 h, after which time 1.2 M aq. HCl (ca. 50 mL) was added. The reaction was then worked up and purified as previously described.$^2$ Characterization data agreed with those reported in the literature.$^2$

**Oxoammonium and hydroxylammonium salts of 1 (1a[BF$_4$] + 1b[BF$_4$]).** Monomer 1 (1.0 equiv.) was dissolved in a minimum volume of anhydrous diethyl ether in a 1.5-dram glass vial with a magnetic stir bar. HBF$_4$•Et$_2$O (2.0 equiv.) was added, which immediately precipitated the products. The suspension was stirred for an additional 10 min at room temperature, then the solvent was removed by rotary evaporation to give an oil containing a mixture of 1a[BF$_4$] + 1b[BF$_4$], which was used immediately without further purification for LLC phase blending.

This salt mixture was analyzed by $^1$H and $^{13}$C NMR spectroscopies, but further purification/isolation of these salts was not extensively pursued. This is because of the difficulty of isolating these salts in pure form (in part due to the complex equilibria that can exist between the nitroxide, oxoammonium, and hydroxylammonium forms in solution at neutral pH). Furthermore, 1a[BF$_4$] and 1b[BF$_4$] are both, in principle, catalytic under the reaction conditions (based on published mechanisms for this oxidation).$^{3,4}$ Also, the acid-induced disproportionation of TEMPO, especially with HBF$_4$, to give a 1:1 (mol/mol) mixture of the oxoammonium and hydroxylammonium tetrafluoroborate salts is a well-known reaction.$^{5-9}$ $^1$H NMR (500.37 MHz, CDCl$_3$): $\delta$ 1.24–1.51 (br m, 51H), 1.57-1.86 (br m, 17H), 1.95 (s, 3H), 2.05 (s, 0.5H), 2.17-2.40 (br m, 2H), 5.30-5.55 (br s, 0.5H), 5.82 (dd, $J = 10$ Hz, 1.4 Hz, 3H), 6.10 (dd, $J = 17$ Hz, 10 Hz, 3H), 6.38 (dd, $J = 17$ Hz, 1.4 Hz, 3H), 7.-02 (s, 1H), 7.06 (s, 1H), 8.13 (s, 0.5H), 8.31 (s, 0.5H), 8.83 (s, 1H), 9.54 (br s, 3H). $^{13}$C NMR (100.63 MHz, CDCl$_3$): 19.59, 25.80, 25.87, 25.93, 25.96, 28.15, 28.47, 28.52, 28.62, 29.14, 29.19, 29.22, 29.31, 29.41, 29.44, 29.49, 29.51, 29.59, 30.25, 31.71, 64.94, 64.97, 65.02, 65.04, 69.23, 69.82, 73.65, 103.02, 128.34, 128.36, 128.40, 130.88, 130.92, 130.98, 131.03, 153.32, 166.86, 166.95, 166.99.
IV. Preparation and Physical Characterization of New Catalytic LLC Polymer Resins

General procedure for preparation of the TEMPO-based H$_{II}$-phase resin from a mixture of (1a[BF$_4$] + 1b[BF$_4$])/2/H$_2$O

The (1a[BF$_4$] + 1b[BF$_4$]) monomer mixture (20 wt %) and 2 (80 wt %) were dissolved in a minimum of CH$_2$Cl$_2$ to give a clear, light orange solution. The solvent was removed by evaporation to give an orange paste, which was dried under high vacuum for 1 h. To this paste was added deionized water (5 wt %), and the mixture was mixed by hand with a spatula. The mixture was then centrifuged for 5 min at 3800 rpm, heated in an 85 °C hot-water bath for 30 s, and hand-mixed again. This procedure was repeated (typically one to three additional times) until the mixture appeared homogeneous to the eye. The mixture was sandwiched between glass slides and photopolymerized in an N$_2$-filled glovebox for 1 h. The degree of polymerization was monitored by the disappearance of the acrylate C=C band at 812 cm$^{-1}$ (see Figs. S1 and S2, below). The formation of the H$_{II}$ phase by the monomeric mixture and its retention after photopolymerization was confirmed by birefringence under POM and by PXRD signals corresponding to the characteristic $d$-spacing ratio (1:1/$\sqrt{3}$:1/$\sqrt{7}$:1:3...) for the H$_{II}$ phase (Fig. S1).$^1$

Note that radical photo-initiator was not used in these LLC mixtures because acrylates can be polymerized by powerful UV light alone.$^{10}$ Also, including radical photo-initiator reduces the shelf life of the unpolymerized LLC blends because it renders them more prone to autopolymerization.

For the heterogeneous catalysis experiments, the resulting TEMPO-based H$_{II}$ polymer resin films were powdered using a Wig-L-Bug amalgamator and sieved to a 75–150 m particle size using wire-mesh sieves.

Fig. S1 (a) PXRD spectra of the TEMPO-based H$_{II}$ LLC mixture prior to UV cross-linking and (b) PXRD spectrum of the TEMPO-based H$_{II}$ resin after UV cross-linking, showing retention of the H$_{II}$ nanostructure.
Fig. S2 Sample FT-IR spectrum of an LLC mixture of \((1a[BF_4] + 1b[BF_4])/2/H_2O\) before photopolymerization. Inset: Zoomed-in region of interest for monitoring the polymerization reaction. Note the presence of an acrylate C=C stretching band at 812 cm\(^{-1}\).

Fig. S3 Sample FT-IR spectrum of an LLC mixture of \((1a[BF_4] + 1b[BF_4])/2/H_2O\) after photopolymerization. Inset: Zoomed-in region of interest for monitoring the polymerization reaction. Note the absence of an acrylate C=C stretching band at 812 cm\(^{-1}\).
Preparation of isotropic TEMPO-based catalytic resin for the substrate size-selectivity control experiments

The amorphous/isotropic TEMPO-based control resin was prepared by following the same general procedure described above for mixing but was polymerized on a hot plate at 85 °C, above the LLC phase clearing point of ca. 75 °C. The lack of nanostructure in this sample was verified by a black optical texture under POM and the lack of any PXRD peaks.

![PXRD spectrum and POM image (inset, 5x mag.) of the amorphous/isotropic TEMPO-based control catalyst resin.](image)

**Fig. S4** PXRD spectrum and POM image (inset, 5x mag.) of the amorphous/isotropic TEMPO-based control catalyst resin.

Determination of percent of accessible catalytic sites in the TEMPO-based $H_{II}$ resin by anion exchange

**Procedure:** The procedure used to determine the amount of accessible catalytic sites in the TEMPO-based $H_{II}$ resin is based on a procedure previously used for other types of catalytic $H_{II}$ resins. In a 1.5-dram glass vial, 27.0 mg of TEMPO-based $H_{II}$ resin (75–150 μm particle size) was suspended in excess 1.0 M aq. HNO$_3$ (ca. 5 mL). The suspension was vigorously stirred for 24 h at room temperature. Subsequently, acetonitrile (5 mL) was added to the suspension to decrease the density of the liquid phase such that the resin particles could be separated by centrifugation. The suspension was centrifuged for 2 min at 4000 rpm. The supernatant solution was removed and the solid particles were re-suspended in acetonitrile (5 mL). The suspension was vigorously stirred at room temperature for 1 h. Then, the suspension was again centrifuged for 2 min at 4000 rpm, and the supernatant was removed. This process was repeated twice more to ensure that no ions were adsorbed onto the surface of the resin particles. Finally, the solid resin was dried under high dynamic vacuum for 12 h to remove excess solvent and sent for elemental analysis to determine the amount of residual fluorine left in the solid.
Calculation: Fluorine-to-carbon mass ratio before ion exchange: 0.02714. Fluorine-to-carbon mass ratio after ion exchange: 0.0081254.

\[
\% \text{BF}_4 \text{ anions remaining after anion exchange} = 100 \times \frac{0.0081254}{0.02714} = 30\%
\]

This indicates that 70% of the BF\(_4^-\) anions in the resin had been removed, indicating that 70% of the theoretical TEMPO catalytic sites are accessible.

Issues with gas-adsorption-based BET surface area analysis of the TEMPO-based H\(_{11}\) resin

Prior work in our group has shown that surface area measurements using standard BET gas adsorption techniques are not effective at providing an accurate estimate of the actual pore area or pore structure of LLC polymer resins (see the Supp. Info associated with Ref. 11).\(^\text{11}\) The reason for this is that it is not possible to completely remove the solvent molecules in the LLC resin nanopores: There are very high capillary forces in the nanopores, and the ionic headgroups in these pores coordinate with solvent molecules remain partially solvated even after rigorous drying under vacuum at elevated temperatures. The residual solvent molecules restrict the entry of gas molecules into the pores and occupy pore volume that would otherwise adsorb gas molecules, leading to a significant underestimation of the actual nanopore area in BET analysis is used.

We attempted a BET surface area measurement on the new TEMPO-based H\(_{11}\) resin using an Autosorb-1 system manufactured by Quantachrome Instruments and N\(_2\) gas. This experiment gave only a measured surface area of 5.5 m\(^2\)/g for this material, which is far below typical values for microporous materials (i.e., >100 m\(^2\)/g). This observed value is consistent with what has previously been observed for similar LLC resin systems,\(^\text{11}\) in terms of residual solvent molecules filling the nanopore void spaces and rendering standard gas sorption techniques for surface area measurement ineffective.

V. Setup and Monitoring of Heterogeneous Catalytic Aerobic Oxidation Reactions

General procedure for aerobic alcohol oxidation reactions catalyzed by the TEMPO-based polymer resins

A powdered sample of the TEMPO-based polymer resin (0.05 equiv. catalytic sites based on the number of oxoammonium and hydroxylammonium groups available in the sample by mass) and a freshly prepared stock solution containing NaNO\(_2\) (0.15 equiv.) and I\(_2\) (0.15 equiv.) in glacial AcOH were loaded into a 1.5-dram glass vial containing a magnetic stir bar. The alcohol substrate (1.00 equiv.) was then added. The vial was sealed with a rubber septum and placed in an oil or sand bath that was held at a constant 50 °C by a hot plate fitted with a temperature probe. A needle connected to PVC tubing was used to puncture the rubber septum and connect the vial to an O\(_2\) gas manifold that was maintained at a constant pressure of 1 atm.
Determination of percent conversion by $^1$H NMR analysis.

**Procedure:** For the catalytic conditions experiments and size selectivity experiments (Figure 4 in main manuscript) using benzyl alcohol (BA) and 3,5-bis(tert-butyldiphenylsilyloxy)benzyl alcohol (BTBA), the percent conversion after 3 h was determined by $^1$H NMR spectroscopy. The reaction vial was removed from the setup described above, and the suspension was filtered through a short Celite plug to remove solid catalyst particles. The resulting clear, pink/purple solutions were then diluted approximately three-fold by the addition of AcOH-$d_4$ and immediately subjected to NMR analysis.

**Calculation:** Percent conversion was calculated using the integration values for the characteristic $CH_2OH$ and $C(O)H$ signals. A sample calculation is shown below using the $^1$H NMR spectrum of a reaction in progress as an example.
Screening of TEMPO-based H_{II} resin catalyst to oxidize different types of alcohol substrates

To test the versatility of the TEMPO-based H_{II} resin catalyst to oxidize alcohols, a series of preliminary experiments were performed using different types of alcohol substrates (Table S4). Reactions were performed as described above (see: General procedure for the aerobic alcohol oxidation reactions catalyzed by the TEMPO-based polymer resins) and monitored by GC-MS as described below.

Determination of percent alcohol substrate oxidation conversion by GC-MS analysis

For the substrate scope screening experiments (Table S4) using various benzylic and aliphatic alcohols other than BA and BTBA, percent conversion was determined semi-quantitatively by GC-MS analysis according to the following general procedure: After 3 h, a 5-µL aliquot of the reaction mixture was removed and diluted with dichloromethane (ca. 5 mL). 1 µL of this solution

\[
\% \text{ conversion} = 100 \times \frac{\text{benzaldehyde (δ = 10.08 ppm) integral}}{\text{benzaldehyde integral} + 0.5 \times \text{benzyl alcohol (δ = 4.80 ppm) integral}} = 100 \times \frac{1.00}{1.00 + 0.5 \times 5.34} = 38\%
\]
was then immediately injected into the GC-MS instrument. The GC methods used (oven temperatures, times, and ramp rates) are summarized in Table S2. Peaks were identified by comparison of mass spectra against known, pure samples or against NIST library data.

**Calculation:** Percent conversion was calculated using the peak areas of the starting alcohol and product carbonyl compound. A sample calculation for the catalytic oxidation of phenylethanol is shown below as an example. Note: rt = retention time

\[
\text{% conversion} = 100 \times \frac{\text{area of acetophenone peak (rt = 5.79 min)}}{\text{areas of phenylethanol (rt = 5.94 min)} + \text{acetophenone peaks}}
\]

\[
= 100 \times \frac{3537831}{3537831 + 13474064} = 79\%
\]
Table S1 Summary of the GC methods, experimental boiling points, and retention times of each substrate alcohol and oxidation product for the compounds screened in the alcohol substrate scope experiments.

<table>
<thead>
<tr>
<th>GC Method</th>
<th>Substrate</th>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>A</strong></td>
<td>OH</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>163 °C, 7.29 min</td>
</tr>
<tr>
<td><strong>A</strong></td>
<td>OH</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>162 °C, 6.80 min</td>
</tr>
<tr>
<td><strong>B</strong></td>
<td>OH</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>195 °C, 6.03 min</td>
</tr>
<tr>
<td><strong>B</strong></td>
<td>OH</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>180 °C, 4.98 min</td>
</tr>
<tr>
<td><strong>C</strong></td>
<td>OH</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>112 °C, 7.99 min</td>
</tr>
<tr>
<td><strong>D</strong></td>
<td>OH</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>185 °C, 6.54 min</td>
</tr>
<tr>
<td><strong>E</strong></td>
<td>OH</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>260 °C, 4.26 min</td>
</tr>
<tr>
<td><strong>F</strong></td>
<td>OH</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>204 °C, 5.95 min</td>
</tr>
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Table S2 Parameters for GC methods used in the alcohol substrate screening experiments.

<table>
<thead>
<tr>
<th>GC method</th>
<th>( T_0 ) (°C)</th>
<th>Hold time (min)</th>
<th>Ramp rate (°C/min)</th>
<th>( T_f ) (° C)</th>
<th>Hold time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>50</td>
<td>2</td>
<td>5</td>
<td>95</td>
<td>5</td>
</tr>
<tr>
<td>B</td>
<td>80</td>
<td>2</td>
<td>10</td>
<td>160</td>
<td>0</td>
</tr>
<tr>
<td>C</td>
<td>50</td>
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<td>20</td>
<td>280</td>
<td>0</td>
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<tr>
<td>D</td>
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<td>20</td>
<td>280</td>
<td>2</td>
</tr>
<tr>
<td>E</td>
<td>120</td>
<td>0</td>
<td>10</td>
<td>250</td>
<td>0</td>
</tr>
<tr>
<td>F</td>
<td>80</td>
<td>0</td>
<td>5</td>
<td>140</td>
<td>0</td>
</tr>
</tbody>
</table>

Table S3 Testing various reported conditions for catalytic activity with the TEMPO-based \( \text{H}_{\text{II}} \) resin.

\(^{a}\)NMR yields.

Proceure for heterogeneous catalyst resin recycling and reuse experiments

For the catalyst recycling experiment described in the main manuscript (see Fig. 3), run 1 was set up as described above (see: General procedure for the LLC polymer resin-catalyzed aerobic alcohol oxidation reactions.). After 3 h, the reaction vial was centrifuged for 2 min at 4000 rpm. A small aliquot for NMR analysis was prepared as described above (see: Determination of percent conversion by \(^1\text{H} \) NMR analysis.). The rest of the supernatant was removed and discarded. The TEMPO-containing \( \text{H}_{\text{II}} \) polymer residue in the reaction vial was then stirred in 5 mL glacial AcOH for 2 min at 50 °C. The vial was then centrifuged again for 2 min at 4000 rpm. The supernatant was discarded. This washing process was repeated once more. The solid residue was then used immediately for the subsequent run(s).
Table S4 The percent conversion (by GC-MS) for each alcohol tested during the substrate screening experiments. In all cases, the substrate alcohols and products shown here were the only organic components detected in the reaction mixture. *NMR yields.

![Chemical reaction diagram]

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Product</th>
<th>Conversion (%)</th>
</tr>
</thead>
</table>
| [Chemical structure of alcohol] | [Chemical structure of aldehyde] | 93 ± 3*
| [Chemical structure of iodohydroxy alcohol] | [Chemical structure of benzaldehyde] | 90 ± 20
| [Chemical structure of 4-hydroxy-3-methoxyphenol] | [Chemical structure of 4-methoxybenzaldehyde] | 90 ± 20
| [Chemical structure of 4-hydroxy-3-nitrophenol] | [Chemical structure of 4-nitrobenzaldehyde] | 90 ± 10
| [Chemical structure of 4-hydroxyphenol] | [Chemical structure of 4-methoxybenzaldehyde] | 99 ± 2
| [Chemical structure of benzyl alcohol] | [Chemical structure of benzaldehyde] | 70 ± 10
| [Chemical structure of cyclopentanol] | [Chemical structure of cyclopentanone] | 80 ± 30
VI. Calculation of Molecular Diameters of BA and BTBA

To determine the approximate molecular diameters of the alcohols tested, we drew their fully atomistic structures in 2D using MarvinSketch 17.13 and then geometry-optimized the structures in 3D based on parameters from the Dreiding forcefield using the 'Clean in 3D' function built into MarvinSketch. Using the optimized structure, we calculated the linear distance between all atom pairs and defined the longest distance between pairs as the molecular diameter.

VII. PXRD Spectra of Commercial SiO$_2$-TEMPO and PS-TEMPO Solid-State Catalysts

Fig. S7 PXRD spectra of (a) SiO$_2$-TEMPO and (b) PS-TEMPO.

VIII. References for the ESI


