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SUPPLEMENTARY MATERIALS

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Figs. S1 to S12
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BATTERIES

Alkaline quinone flow battery

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Storage of photovoltaic and wind electricity in batteries could solve the mismatch problem between the intermittent supply of these renewable resources and variable demand. Flow batteries permit more economical long-duration discharge than solid-electrode batteries by using liquid electrolytes stored outside of the battery. We report an alkaline flow battery based on redox-active organic molecules that are composed entirely of Earth-abundant elements and are nontoxic, nonflammable, and safe for use in residential and commercial environments. The battery operates efficiently with high power density near room temperature. These results demonstrate the stability and performance of redox-active organic molecules in alkaline flow batteries, potentially enabling cost-effective stationary storage of renewable energy.

The cost of photovoltaic (PV) and wind electricity has dropped so much that one of the largest barriers to getting most of our electricity from these renewable sources is their intermittency (*1*–*3*). Batteries provide a means to store electrical energy; however, traditional, enclosed batteries maintain discharge at peak power for far too short a duration to adequately regulate wind or solar power output (*1*, *2*). In contrast, flow batteries can independently scale the power and energy components of the system by storing the electro-active species outside the battery container itself (*3*–*5*). In a flow battery, the power is generated in a device resembling a fuel cell, which contains electrodes separated by an ion-permeable membrane. Liquid solutions of redox-active species are pumped into the cell, where they can be charged and discharged, before being returned to storage in an external storage tank. Scaling the amount of energy to be stored thus involves simply making larger tanks (Fig. 1A). Existing flow batteries are based on metal ions in acidic solution, but challenges with corrosivity, hydrogen evolution, kinetics, materials cost and abundance, and efficiency thus far have prevented large-scale commercialization. The use of anthraquinones in an acidic aqueous flow battery can dramatically

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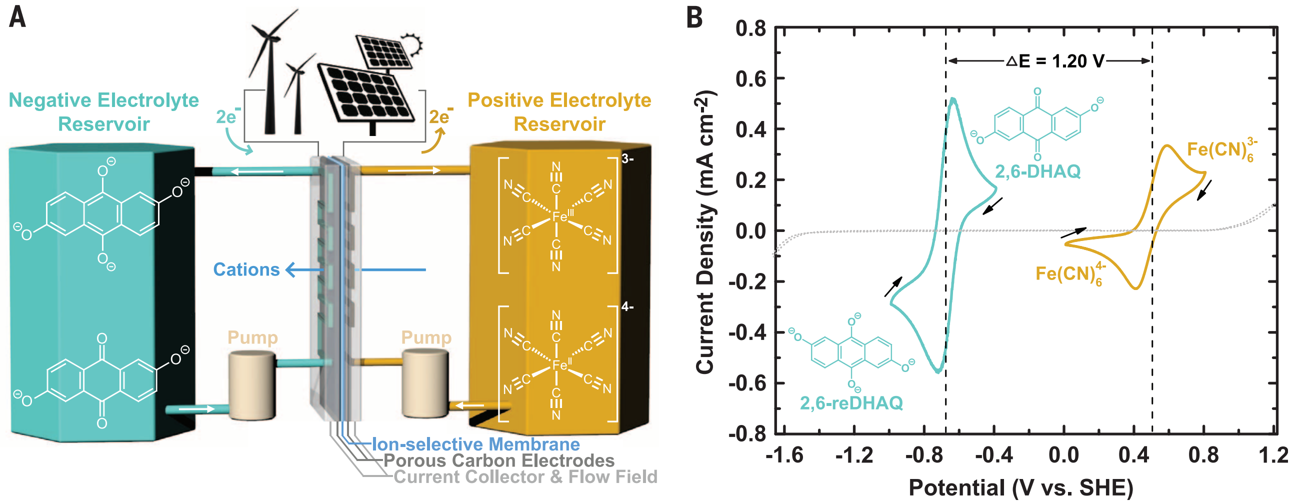

Fig. 1. Cyclic voltammetry of electrolyte and cell schematic. (**A**) Schematic of cell in charge mode. Cartoon on top of the cell represents sources of electrical energy from wind and solar. Curved arrows indicate direction of electron flow, and white arrows indicate electrolyte solution flow. Blue arrow indicates migration of cations across the membrane. Essential components of electrochemical cells are labeled with color-coded lines and text. The molecular structures of oxidized and reduced species are shown on corresponding reservoirs. (**B**) Cyclic voltammogram of 2 mM 2,6-DHAQ (dark cyan curve) and ferrocyanide (gold curve) scanned at 100 mV/s on glassy carbon electrode; arrows indicate scan direction. Dotted line represents CV of 1 M KOH background scanned at 100 mV/s on graphite foil electrode.

reduce battery costs (*6*, *7*); however, the use of bromine in the other half of the system precludes deployment in residential communities owing to toxicity concerns.

We demonstrate that quinone-based flow batteries can be adapted to alkaline solutions, where hydroxylated anthraquinones are highly soluble and bromine can be replaced with the nontoxic ferricyanide ion (*8*, *9*)—a food additive (*10*). Functionalization of 9,10-anthraquinone (AQ) with electron-donating groups such as OH has been shown to lower the reduction potential and expand the battery voltage (*6*). In alkaline solution, these OH groups are deprotonated to provide solubility and greater electron donation capability, which results in an increase in the open-circuit voltage (OCV) of 47% over the previously reported system. Because functionalization away from the ketone group provides molecules with the highest solubility (*11*, *12*), we initially targeted commercially available 2,6-dihydroxyanthraquinone (2,6-DHAQ), which we find exhibits a room-temperature solubility of >0.6 M in 1 M KOH. This system can achieve power densities of >0.45 W cm^{-2} at room temperature and 0.7 W cm^{-2} at 45°C.

The use of alkaline electrolyte exploits pH as a parameter to shift the thermodynamic potentials of proton-dependent reactions to more negative values. In acid solutions, AQ undergoes a two-electron two-proton reduction at a single potential, which shifts to more negative values as the pH increases (*6*). When the pH exceeds 12, the reduction potential of 2,6-DHAQ becomes pH-independent because the reduced species is generated in its fully deprotonated form (fig. S1). In contrast with the pH-dependent electrochemical behavior of quinones (negative terminal), the ferro/ferricyanide redox couple (positive terminal) has a pH-independent redox potential. This contrasting pH dependence can be exploited through the development of low–reduction potential quinones at high pH. The cyclic voltammograms (CVs) of 2,6-DHAQ and ferro/ferricyanide predict an equilibrium cell potential of 1.2 V upon combination of these two half-reactions (Fig. 1B). A quantitative analysis of the CV of 2,6-DHAQ at pH 14 (fig. S2) revealed redox behavior consistent with two one-electron reductions at potentials separated by only 0.06 V, with a rapid kinetic rate similar to that of quinones in acid (*6*). This behavior raises interesting questions about the relationship between quinone redox and hydrogen bonding (*13*).

Cell testing was performed at 20°C with solutions of 0.5 M 2,6-DHAQ dipotassium salt and 0.4 M $K_4Fe(CN)_6$, both dissolved in 1 M KOH. These solutions were pumped through a flow cell constructed from graphite flow plates and carbon paper electrodes, which were separated by a Nafion membrane. A charging current of 0.1 A cm^{-2} was applied to charge the cell, and polarization curves were measured at 10, 50, and 100% states of quinone charge (SOC). The OCV is 1.2 V at 50%

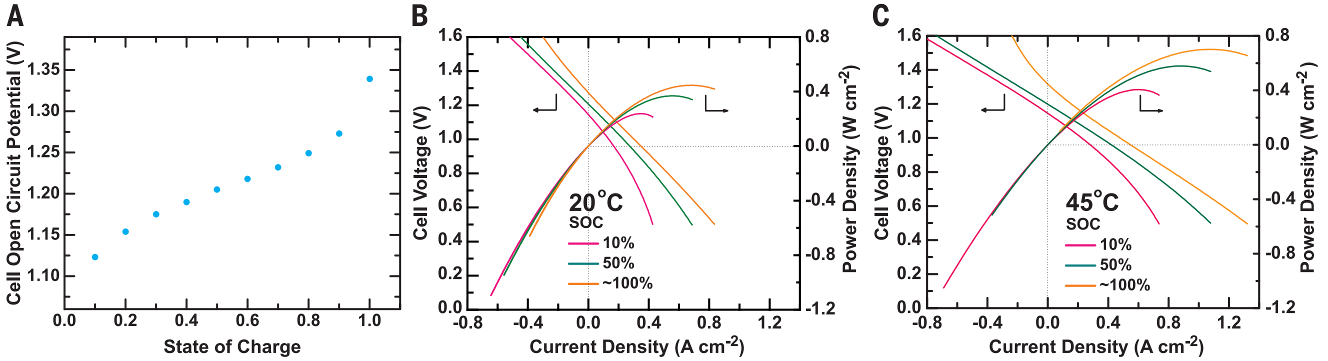

Fig. 2. Cell performance. (**A**) Cell open-circuit voltage versus state of charge. All potentials were taken when cell voltage stabilized to within ±1 mV. One hundred percent SOC was reached by potentiostatic holding at 1.5 V until the current decreased to below 20 mA/cm^2. (**B** and **C**) Cell voltage and power density versus current density at 20° and 45°C, respectively, at 10, 50, and ~100% SOC. Electrolyte composition: At 20°C, 0.5 M 2,6-DHAQ and 0.4 M ferrocyanide were used in negative electrolyte and positive electrolyte, respectively. At 45°C, both concentrations were doubled. In both cases, potassium hydroxide content started at 1 M for both sides in the fully discharged state.

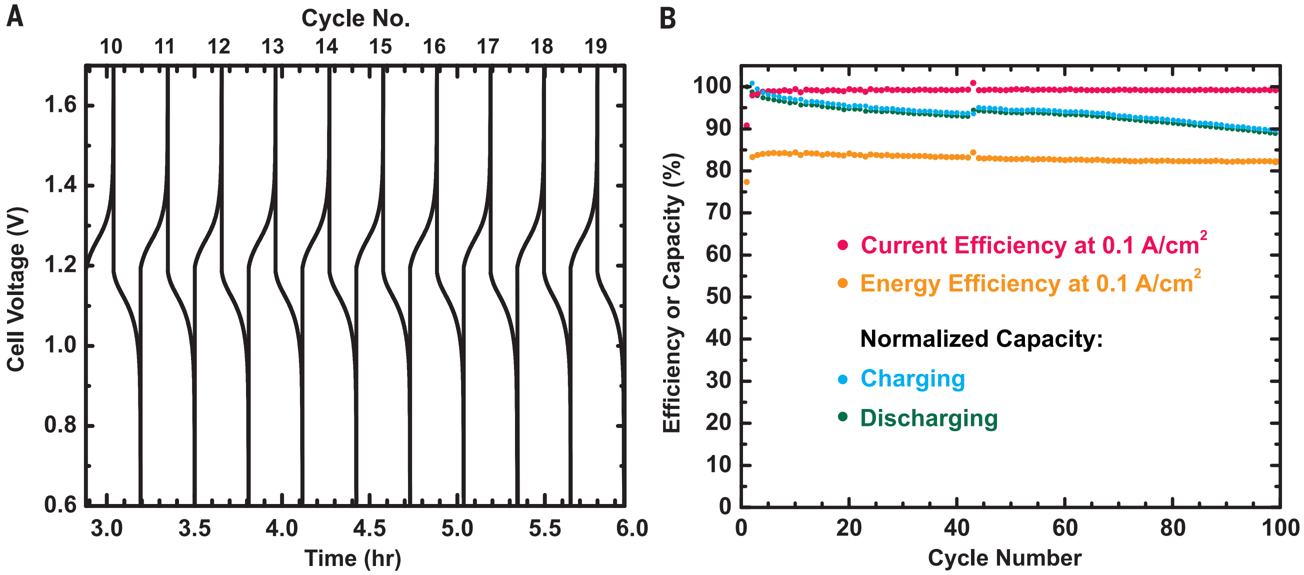

Fig. 3. Cell cycling performance. (**A**) Representative voltage versus time curves during 100 charge-discharge cycles at 0.1 A/cm^2, recorded between the 10th and 19th cycles. (**B**) Capacity retention, current efficiency, and energy efficiency values of 100 cycles. Normalized capacity is evaluated based on the capacity of the first charge and discharge cycle.

SOC; its dependence on SOC is shown in Fig. 2A. The polarization curves (Fig. 2B) show no sign of redox kinetic limitations and exhibit a peak galvanic power density exceeding 0.4 W cm^{-2}.

The cell was cycled at a constant current density of ±0.1 A cm^{-2} for 100 cycles (Fig. 3A). The current efficiency exceeded 99%, with a stable round-trip energy efficiency of 84%. A 0.1% loss in capacity per cycle was observed during cycling, which appears to be a continuous loss of electrolyte over the 100 cycles. Three possible loss mechanisms were explored: chemical decomposition, electrolyte crossover through the membrane, and leakage from the pumping system. Chemical and electrochemical stability studies showed that the negative electrolyte is stable. Ten millimolar 2,6-DHAQ was heated in 5 M KOH solution at 100°C for 30 days and was characterized by proton nuclear magnetic resonance (NMR). Cycled negative electrolyte was also collected and characterized by the same method; both studies showed no degradation product at the sensitivity level of 1% (fig. S3). Membrane crossover contamination has been a common challenge in acid-based redox flow batteries, where most electro-active molecules are either neutral or positive and tend to migrate through proton-conductive membranes (*5*). In this alkaline system, however, all the electro-active molecules remain negatively charged in all charge states, leading to a dramatic decrease in the degree of crossover during cell cycling. Cyclic voltammetry of the ferro/ferricyanide electrolyte collected at the end of cycling showed no evidence of the presence of 2,6-DHAQ. This observation places an upper limit on crossover of 0.8% of the DHAQ, implying a crossover current density of <2.5 μA cm^{-2} (fig. S4). Finally, hydraulic leakage was investigated because an apparent but unquantifiable small decrease in fluid levels was observed in the reservoirs. After cell cycling, the cell was washed with deionized water until no coloration of eluent could be observed. The cell was then disassembled; coloration was found on the gaskets, indicating the likely site of electrolyte leakage (fig. S5). This source of capacity loss—equivalent to roughly eight drops in our system—is expected to become negligible as system size is scaled up.

By increasing the temperature to 45°C, the peak galvanic power density increases from 0.45 to ~0.7 W cm^{-2} (Fig. 2C), as the cell area-specific resistance (ASR) decreases from about 0.878 to 0.560 ohm cm^2, estimated from the linear parts of the polarization curves in Fig. 2. Most of this ASR decrease comes from a change in the high-frequency ASR (r_{hf}) measured by electrochemical impedance spectroscopy (fig. S6). In both cases, the r_{hf} contributes more than 70% of the ASR and is indeed the limiting factor to the cell current and power outputs. The r_{hf} is dominated by the resistance of the membrane, which is an order of magnitude higher than the resistance of the same membrane in a pH 0 acid solution (*14*).

The sluggish kinetics of the hydrogen evolution reaction in alkaline solution on carbon electrodes results in a larger practical stability window in base rather than in acid (fig. S7). Consequently, quinones with substantially more negative reduction potentials are feasible as negative electrolyte materials. Preliminary investigations into the synthesis of different hydroxy-substituted anthraquinones suggest that further increases in cell potential are possible. Self-condensation reactions of substituted benzene yield 2,3,6,7-tetrahydroxy-AQ (THAQ) (*15*) and 1,5-dimethyl-2,6-DHAQ (15-DMAQ) (figs. S8 and S9). The CVs of these species in 1 M KOH suggest cell potentials versus ferri/ferrocyanide approaching 1.35 V (Fig. 4, A and B), which exceeds that of many aqueous rechargeable batteries (Fig. 4C).

The cyanide ions in both ferro- and ferricyanide are bound too tightly to be released under most conditions. Consequently, it is nontoxic in both oxidized and reduced forms and is even

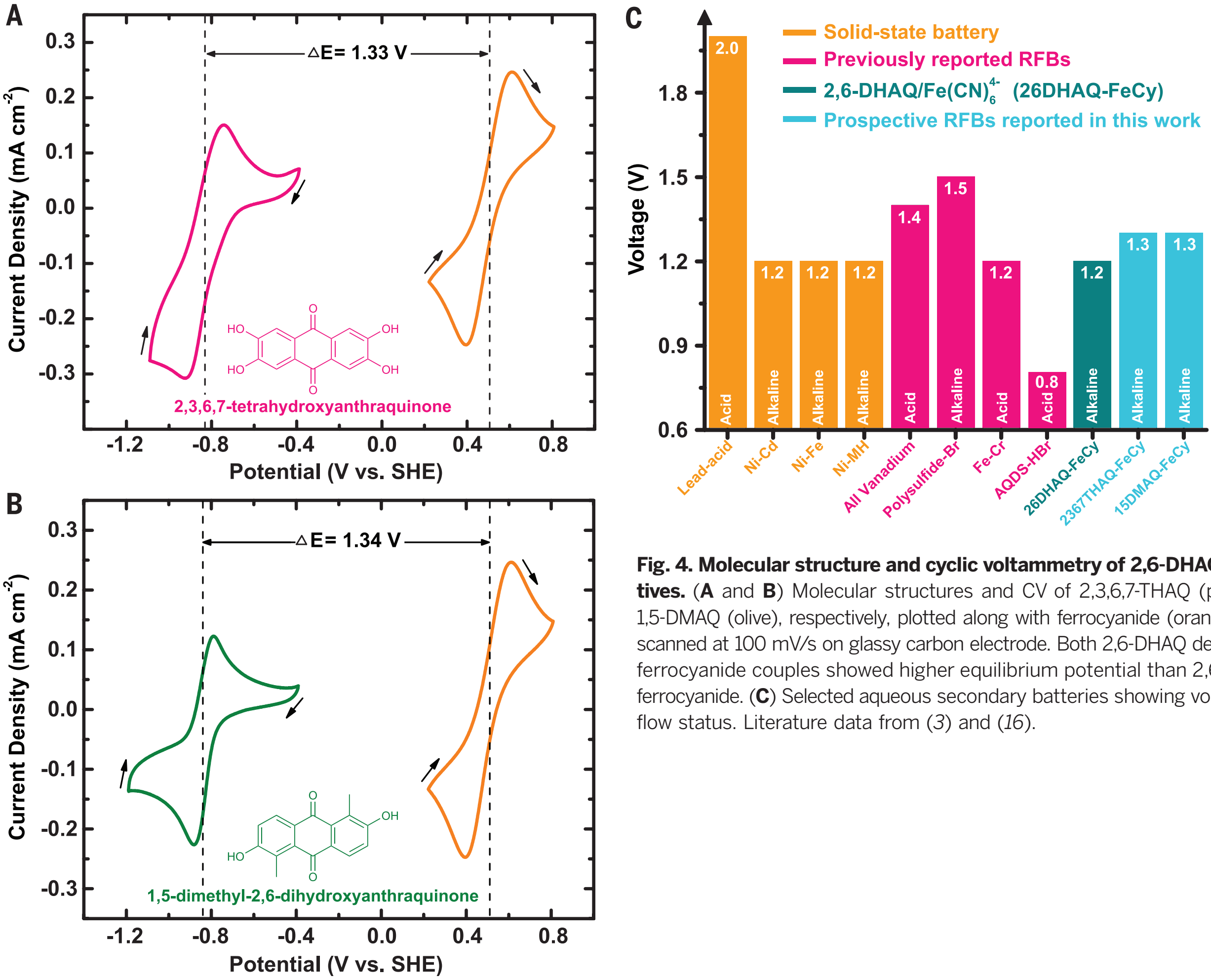

Fig. 4. Molecular structure and cyclic voltammetry of 2,6-DHAQ derivatives. (**A** and **B**) Molecular structures and CV of 2,3,6,7-THAQ (pink) and 1,5-DMAQ (olive), respectively, plotted along with ferrocyanide (orange curve) scanned at 100 mV/s on glassy carbon electrode. Both 2,6-DHAQ derivatives/ferrocyanide couples showed higher equilibrium potential than 2,6-DHAQ/ferrocyanide. (**C**) Selected aqueous secondary batteries showing voltage and flow status. Literature data from (*3*) and (*16*).

permitted for use as a food additive (*10*). The use of ferrocyanide offers notable advantages over bromine because it is nonvolatile and noncorrosive, allowing simpler and less expensive materials of construction. In addition, these tri- and tetra-anionic organometallic molecules exhibit low crossover rates through cation-exchange membranes.

The results reported herein highlight the ability of hydroxy-substituted anthraquinone and ferrocyanide to function as stable flow battery electrolytes in alkaline solution. The use of organic and organometallic coordination complexes in base, rather than aqueous metal ions in acid, resolves serious cost, corrosion, and safety concerns of previous flow battery chemistries. Alkaline flow batteries can compensate for higher membrane resistance with higher voltage, leading to performance similar to that of their acidic counterparts. In addition, quinone-ferrocyanide alkaline chemistry avoids the membrane crossover, corrosivity, toxicity, and regulations associated with bromine. This reduced corrosivity can lead to a substantially lower materials cost because many components can be made of inexpensive polyolefin or poly(vinyl chloride) plastics.

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SUPPLEMENTARY MATERIALS

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Fig. S1 to S9
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H-BONDING CATALYSIS

O–H hydrogen bonding promotes H-atom transfer from α C–H bonds for C-alkylation of alcohols

Jenna L. Jeffrey,* Jack A. Terrett,* David W. C. MacMillan†

The efficiency and selectivity of hydrogen atom transfer from organic molecules are often difficult to control in the presence of multiple potential hydrogen atom donors and acceptors. Here, we describe the mechanistic evaluation of a mode of catalytic activation that accomplishes the highly selective photoredox α-alkylation/lactonization of alcohols with methyl acrylate via a hydrogen atom transfer mechanism. Our studies indicate a particular role of tetra-*n*-butylammonium phosphate in enhancing the selectivity for α C–H bonds in alcohols in the presence of allylic, benzylic, α-C=O, and α-ether C–H bonds.

Complex molecules, such as medicinal agents and natural products, often possess multiple types of C–H bonds, each with a different inherent reactivity. This intrinsic reactivity depends on a multifaceted interplay of steric effects, inductive and conjugative influences, as well as innate strain (*1*, *2*). The intermolecular catalytic functionalization of C(sp^3)–H bonds in a selective manner represents a longstanding challenge that has inspired decades of effort within the synthetic community. Notable early studies by Bergman (*3*), as well as recent advances in selective intermolecular transition metal catalyzed C(sp^3)–H activation—including, among others, Hartwig's rhodium-catalyzed borylation of terminal methyl groups (*4*) and White's iron-catalyzed oxidation of both secondary (2°) and tertiary (3°) aliphatic C–H bonds (*5*)—highlight the importance of catalyst structure on site selectivity.

Catalyst structure has also proven critical to the selectivity of C(sp^3)–H functionalization via hydrogen atom transfer (HAT) catalysis. HAT—the effective movement of a hydrogen atom between two molecular sites—represents a ubiquitous elementary reaction step in organic chemistry (*6–8*). The rate of hydrogen abstraction from a C–H bond depends not only on the C–H bond dissociation enthalpy (BDE) but also on polar effects in the transition state. In 1987, Roberts noted that certain electrophilic radicals (such as *t*-butoxyl) preferentially abstract hydrogen from electron-rich C–H bonds, whereas nucleophilic radicals (such as amine-boryl) selectively cleave electron-deficient C–H bonds (*9*). The generality of this concept was subsequently delineated through the broad application of polarity reversal catalysis (PRC), which takes advantage of favorable polar effects to control the regioselectivity of HAT from multiple C–H groups of similar strength (*10*).

We questioned whether the basic principles of PRC could be integrated into a catalytic system for the selective activation of alcohol α-C–H bonds in the presence of a wide range of other C–H bonds (such as α-C=O, α-ether, or allylic or benzylic C–H) (*11*, *12*). Specifically, we postulated that the selective C-alkylation of alcohols could be achieved via a photoredox-catalyzed, H-bond–assisted bond activation strategy (Fig. 1) (*13–15*), in which the hydroxyalkyl C–H bond is selectively polarized and weakened via O–H hydrogen bonding.

It is well known that the strength of α C–H bonds of alcohols decreases upon deprotonation of the alcohol O–H group. This so-called "oxy anionic substituent effect" (*16*, *17*) leads to the acceleration of a wide range of organic reactions [such as oxyanionic [1,3] and [3,3] sigmatropic rearrangements and HAT from alkoxides (*18*)]. More recently, it has been shown that intermolecular hydrogen bonding between alcohols and various acceptor molecules gives rise to a similar polarization and weakening of the adjacent C–H bond (*19*), the strength of which is reflected in the ^{13}C nuclear magnetic resonance (NMR) chemical shift and the one-bond ^{13}C–^{1}H coupling constant ($^{1}J_{CH}$) (*20*, *21*). In particular, it was found that a 1 kJ/mol increase in the enthalpy of the H-bond resulted in a 0.2-Hz decrease in $^{1}J_{CH}$ for hexafluoroisopropanol complexed to various amines (*20*). On the basis of these studies, we reasoned that the efficiency and selectivity of alcohol C–H activation

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