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RESEARCH ARTICLE

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Synthesis and electrochemical evaluation of 2-substituted imidazolium salts

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Abstract

Herein, we report the synthesis, electrochemical, and computational evaluation of six 2-substituted imidazolium bromides and six 2-substituted imidazolium triflates. All final compounds were obtained in 2 or fewer synthetic steps from inexpensive starting materials and display a single, irreversible electrochemical reduction. The reduction potentials span a range greater than 1 V depending on the electron withdrawing power of the 2-substituent. Imidazolium bromides such as **Bn_2(H)ImBr** reduce with $E_{1/2} = -2.70$ V vs Fc/Fc^+, whereas the electron-withdrawing Br-containing analog **Bn_2(Br)ImBr** reduces at only −1.58 V vs Fc/Fc^+. The reduction potential of imidazolium bromides obeys a linear free energy relationship to σ_m Hammett constants, whereas imidazolium triflates correlate better with the σ_p Hammett constants. These results indicate that the stabilizing effect of the 2-substituent is anion-sensitive, changing from induction to resonance upon exchanging bromide for triflate. Predicted electron affinities from density functional theory–optimized structures of imidazolium cations and reduced species more closely match experimental data for the triflates, suggesting that a triflate anion does not electronically perturb the imidazolium core as much as a bromide. Taken together, these data highlight the dual modularity of imidazolium salts by changing both 2-substituent and anion.

KEYWORDS

density functional calculations, electrochemistry, linear free energy relationships, nitrogen heterocycles, substituent effects

1 | INTRODUCTION

Renewable resource-based electricity generation—such as wind, solar, and tidal—is poised to contribute an increasingly greater percentage of global energy demand over the coming decades.[1,2] However, these intermittent forms of electricity generation are often geographically and temporally dependent and thus are difficult to synchronize with demand. Grid-scale energy storage can overcome this limitation—of available methods, the technology of redox-flow batteries (RFBs) is gaining momentum as evidenced by the myriad of review articles in this field.[3–8] The solution-phase catholyte and anolyte in RFBs are stored in large tanks, enabling scalability of the system and potential for large-scale energy storage. Early successful RFBs relied on expensive and toxic inorganic active electrolytes such as chromium[9] and vanadium.[10,11] Remaining in tune with the renewable aspect of this technology, research on organic materials has produced many viable active electrolytes. Recent examples include *N,N′*-dialkyl viologens,[12,13] polysulfonated benzo/anthraquinones,[14,15] and Sanford's cyclopropenium salts.[16]

Prototype batteries using these active electrolytes displayed low degradation and >95% coulombic efficiency over at least 100 cycles.

Designing new organic active electrolytes can be a lengthy process when accounting for many technical factors. At minimum, the molecule must exhibit fully reversible redox processes, fast electron-transfer kinetics, be highly soluble in the carrier solvent at all states of charge, and be stable for tens of thousands of charge/discharge cycles.[6,7] We selected the imidazolium core as a building block (Chart 1) to synthesize new organic anolytes because the first reduced species is a neutral radical. Imidazole-type structures have been used for decades to stabilize otherwise reactive classes of compounds[17] such as the *N*-heterocyclic carbenes,[18,19] triphenylimidazolyl radicals,[20,21] and some of Bertrand's cyclic (amino) (carboxy) radicals.[22,23] Our design involves substitution at the 2-position of the imidazole ring to impart extra thermodynamic stability to a radical or anion and the use of bulky *N*-benzyl groups to enhance kinetic persistence (Chart 1). There are few reports on 2-substituted imidazoliums from the *N*-heterocyclic carbenes community because a 2-*H* is commonly required for deprotonation and formation of the carbene.[24–26] *N*-quaternarized imidazoles known as imidazolium salts are a common motif in the field of ionic liquids (ILs) because of their modular core. Recently, some ILs have been used as supporting electrolytes in RFBs because of their high dielectric constant and wide electrochemical potential window.[27,28] However, this application remains uncommon, and there are no reports of any imidazoliums being investigated as active electrolytes in RFBs. Applying 2-substituted imidazoliums in this manner requires rigorous understanding of their electrochemical behavior, which constitutes a gap in current literature. To our knowledge, there has been no electrochemical investigation on a breadth of 2-substituted imidazolium salts.

Electrochemical characterization revealed that all 12 imidazolium salts display a single, irreversible reduction between −2.84 and −1.22 V vs Fc/Fc^+, demonstrating a distinct sensitivity of the reduction potentials towards the nature of each 2-substituent. Furthermore, we found that exchanging anion from bromide to triflate represented a second method for redox property modulation: Magnitude of reduction potential followed a different trend depending on the anion. Hammett analysis of the 2-substituent effect for each anion quantitatively confirmed the observed trends such that reduced imidazolium bromides experience inductive stabilization, whereas reduced triflates are resonance-stabilized. Experimental results are complemented by density functional theory (DFT) calculations, supporting 2-substituent effect on reduction potentials, which correlate best with imidazolium triflates.

2 | RESULTS AND DISCUSSION

2.1 | Synthesis

Synthesis of the imidazolium salts began with double *N*-benzylation of commercially available imidazole (**1a**), 2-methylimidazole (**1b**), and 2-phenylimidazole (**1c**) using a modified literature procedure, shown in Scheme 1.[29] This di-benzylation afforded the first 3 imidazolium bromides to be investigated—**Bn_2(H)ImBr**, **Bn_2(CH_3)ImBr**, and **Bn_2(Ph)ImBr**—with varying 2-substitution in one step. The coordinating nature of the anion for ILs is known to affect the electronic structure of the imidazolium core,[30] because bromides and other halides

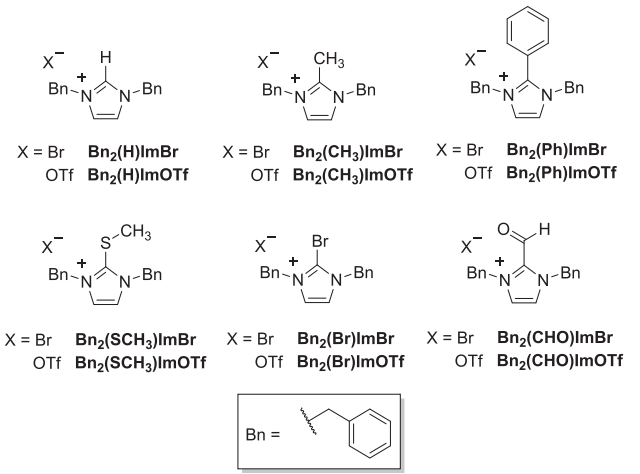
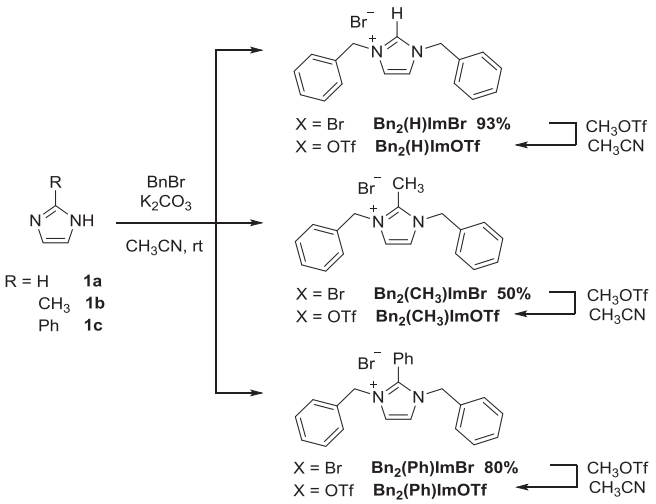


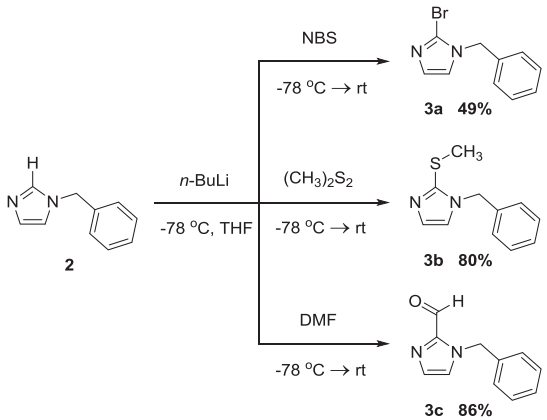
CHART 1 Synthesis of imidazolium salts **Bn_2(SCH_3)ImX**, **Bn_2(Br)ImX**, and **Bn_2(CHO)ImX** with proposed aldehyde-hydrate equilibrium



SCHEME 1 Structures of 2-substituted imidazolium salts investigated in this work

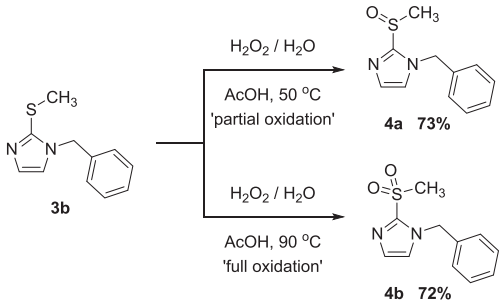
coordinate strongly, whereas bulkier anions such as triflate coordinate only weakly. Stemming from our interest in studying the electronic structure of the imidazolium core, we decided to briefly explore this anion effect. Anion exchange under inert atmosphere with methyl triflate[31] yielded the triflate salts **Bn_2(H)ImOTf**, **Bn_2(CH_3)ImOTf**, and **Bn_2(Ph)ImOTf**. While full purification of the imidazolium triflates by conventional means was unsuccessful (section 2 in Supporting Information), diagnostic shifts in all proton resonances were observed by ^{1}H NMR. Completing ion exchange with AgOTf instead of MeOTf provided NMR-pure materials for analysis (section 2 in Supporting Information). Most notable among the resonances was the 2-*H* proton in **Bn_2(H)ImOTf**, which experienced significantly more shielding (9.3 ppm vs 11.1 ppm) than in its analogous bromide salt, highlighting the weakly coordinating nature of triflate (section 3 in Supporting Information).[30]

Accessing imidazolium salts with more exotic 2-substitution than simple hydrocarbons required a different synthetic strategy than that in Scheme 1, because the required imidazoles were too costly for large-scale synthesis (Scheme 2). Lithiation of commercially available 1-benzylimidazole (**2**), followed by electrophilic quenching of the anion is a well-documented strategy that has been successful for introducing a variety of groups at the 2-position.[32–35] For synthetic versatility, we targeted 2-bromo **3a**, 2-(methylsulfanyl) **3b**, and 2-formyl **3c** derivatives, which could serve as platforms for further functionalization. Successful lithiation of 1-benzylimidazole was confirmed by observing a brilliant red solution upon adding *n*-BuLi, whereas addition of the electrophilic reagent (either NBS, $(CH_3)_2S_2$ or DMF) caused the red color of the anion to dissipate. After chromatographic purification, three 2-substituted imidazoles **3a**-**c** were isolated in 49%, 80%, and 86% yields, respectively.

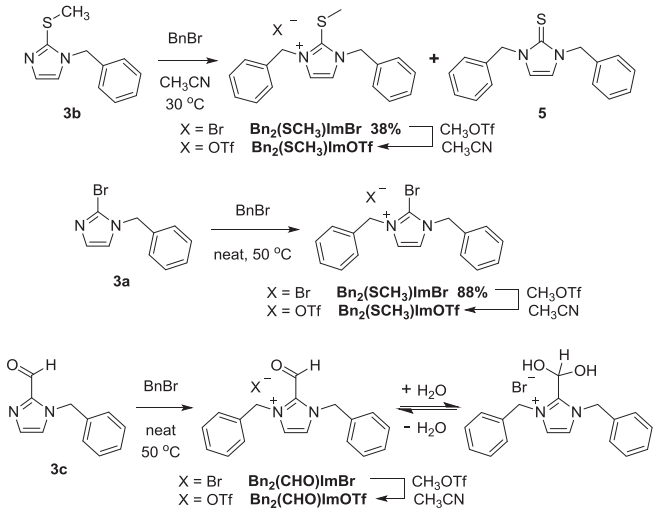


SCHEME 2 Synthesis of **Bn_2(H)ImX**, **Bn_2(CH_3)ImX**, and **Bn_2(Ph)ImX** from commercially available 2-substituted imidazoles

Oxidation of 1-benzyl-2-(methylsulfanyl)imidazole (**3b**) was used to access higher oxidation states of the sulfur atom, as shown in Scheme 3. Treatment with hydrogen peroxide in acetic acid at slightly elevated temperature selectively formed the partially oxidized 2-sulfoxide **4a**, whereas increased temperature caused full oxidation to the 2-sulfone **4b**. The ability to obtain 2 products in good yields with only slight modification of conditions reveals the utility of this mild oxidation protocol reported by Vampa and coworkers.[36] With five 2-substituted imidazoles in hand, benzylation of the remaining imidazole *N* to form the desired imidazolium salts was investigated, as shown in Scheme 4. Gentle treatment of 2-(methylsulfanyl) **3b** with 1 equivalent of benzyl bromide led to selective alkylation of the imidazole *N*, forming the salt **Bn_2(SCH_3)ImBr** in 38% yield. A byproduct of this reaction was identified as imidazol-2-thione **5**. We propose that the thione formation resulted from demethylation by the noninnocent bromide anion, releasing methyl bromide. Both selective *N*-alkylation



SCHEME 3 Divergent synthesis of 2-substituted imidazoles from 1-benzylimidazole **2**



SCHEME 4 Selective oxidation of 2-(methylsulfanyl) **3b** to 2-sulfoxide **4a** and 2-sulfone **4b**

and demethylation behaviors have been observed by Metzger and coworkers with similar imidazoliums.[37] **$Bn_2(SCH_3)ImBr$** was susceptible to demethylation even at room temperature in solution but was indefinitely stable in the solid state. Anion exchange with methyl triflate afforded triflate salt **$Bn_2(SCH_3)ImOTf$**, as determined by diagnostic proton resonance shifts in the ^{1}H NMR (section 3 in Supporting Information). *N*-benzylations of 2-sulfoxide **4a** and 2-sulfone **4b** in CH_3CN resulted in only trace conversion as observed by thin layer chromatography (TLC) even after 2 weeks at 80°C. The decreased reactivity could be ascribed to the presence of strong electron withdrawing groups near the nucleophilic *N*. Forcing conditions in neat benzyl bromide at 50°C resulted in the complete conversion of 2-sulfoxide **4b** in 1 day (TLC), but the resulting imidazolium salt could not be isolated with acceptable purity. Under the same forcing conditions, only trace conversion of 2-sulfone **4b** was observed after 2 weeks at 50°C, so the *N*-benzylation of **4a** and **4b** were abandoned. Conversion of 2-bromoimidazole **3a** into its respective imidazolium salt **$Bn_2(Br)ImBr$** proceeded smoothly in 88% in 1 day using neat benzyl bromide, followed by anion exchange with methyl triflate to form **$Bn_2(Br)ImOTf$** (Scheme 4). *N*-benzylation of 2-formylimidazole **3c** produced the salt **$Bn_2(CHO)ImBr$** as determined by HR MS and ^{1}H NMR; however, further analysis indicated H_2O-sensitivity through hydrate formation (section 3 in Supporting Information). The imidazolium bromide was still converted to its triflate salt **$Bn_2(CHO)ImOTf$** by anion exchange (Scheme 4).

2.2 | Electrochemistry

With the 12 imidazolium bromides and triflates in hand, we next evaluated the redox properties of the salts. The electrochemical behavior of the imidazolium bromides was investigated using cyclic voltammetry (CV) and differential pulse voltammetry (DPV). Figure 1 shows the electrochemical evaluation of **$Bn_2(Ph)ImBr$** using both CV and DPV, whereas voltammograms for remaining imidazoliums can be found in section 4 of the Supporting Information. The $E_{1/2}$ values were taken from the apex of the DPV traces, once corrected for the internal standard. Representatively, the DPV (top trace) and CV (bottom trace) of **$Bn_2(Ph)ImBr$** is shown in Figure 1. The DPV trace clearly shows 2 peaks as the potential is swept from positive to negative, demonstrative of reduction of the internal ferrocene standard and **$Bn_2(Ph)ImBr$** at −2.34 V. The CV of **$Bn_2(Ph)ImBr$** mirrors the same peaks as DPV, but the technique highlights the irreversibility of the electrochemical reduction reaction. All of the imidazoliums investigated undergo irreversible electrochemical reduction reactions within the solvent

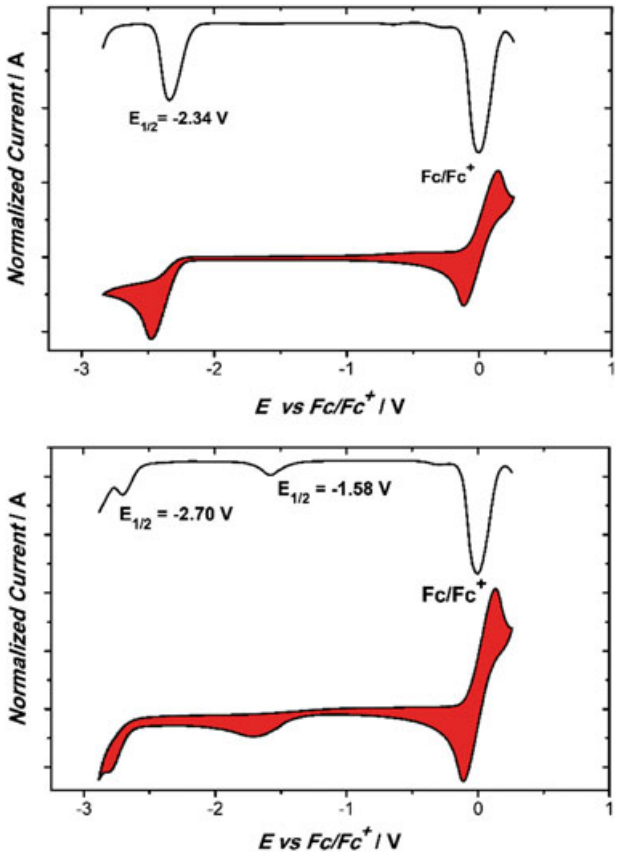


FIGURE 1 Differential pulse voltammetry (black) and cyclic voltammetry (red) of approximately 1-mM **$Bn_2(Ph)ImBr$** (top) and **$Bn_2(Br)ImBr$** (bottom) in dry DMF with approximately 0.5-M $(n\text{-Bu})_4NBF_4$ as supporting electrolyte

stability window at potentials between −2.9 and −1.3 V vs Fc/Fc^+, which are summarized in Table 1. **$Bn_2(Br)ImX$** and **$Bn_2(CHO)ImX$** are unique among the imidazolium salts in that the electron withdrawing groups permit 2 irreversible reductions in the solvent window (Figure 1). Upon switching solvent to CH_3CN, the same irreversible behavior is observed in all cases. The irreversible electrochemical response of imidazoliums bearing an *H*

TABLE 1 Reduction half-wave potentials of synthesized imidazolium bromides and triflates

Compound Code	$E_{1/2}$ (V)[a] X = Br	$E_{1/2}$ (V)[a] X = OTf
$Bn_2(H)ImX$	−2.70	−2.77
$Bn_2(CH_3)ImX$	−2.84	−2.72
$Bn_2(Ph)ImX$	−2.34	−2.32
$Bn_2(SCH_3)ImX$	−2.16	−2.22
$Bn_2(Br)ImX$	−1.58/−2.70	−1.74/−2.68
$Bn_2(CHO)ImX$	−1.73/−2.70	−1.22/−1.90

[a]$E_{1/2}$ referenced against Fc/Fc^+ measured by differential pulse voltammetry in approximately 1-mM dry DMF solutions.

atom at the 2-position has been previously studied by NMR and MS analysis of the decomposition products,[38] and it has been postulated that one-electron reduction forms the imidazol-2-yl radical, which undergoes bimolecular disproportionation into the imidazol-2-ylidene and the 2,3-dihydroimidazole. Clyburne and coworkers supported this claim with CV studies of 1,3-bis(mesityl) imidazolium chloride where intermediacy of the radical was followed by decomposition to the carbene.[39,40]

The reduction potentials in Table 1 of imidazolium bromides and triflates demonstrates the remarkable tunability of this system—simply by exchanging H for Br, the electrochemical reduction potential shifts over 1 V. Given the variety of imidazoliums studied, a trend in the reduction potentials became apparent.

More rigorously, the reduction potentials were evaluated by using the Hammett equation to identify a linear free energy relationship between 2-substituent on the imidazolium and the Hammett substituent constant.[41,42] This approach has been successful for a broad array of studies including fulleroid electrochemistry,[43] rates of benzylic radical dimerization,[44] and photochromic spiropyran isomerization.[45] The imidazolium bromide and triflate reduction half-wave potentials were plotted against both *meta* and *para* Hammett substituent constants, and linear fits were applied, as shown in Figure 2. Note that only the most linear relationships are shown in Figure 2, and the comparison of linear fits can be seen in Figure S12a-b. For the bromide series, both σ_m and σ_p produced linear fits with slopes greater than 1, suggesting that the imidazolium system is more sensitive to substituent effects than benzoic acid.[46] However, a superior correlation is observed using σ_m, which suggests that the substituent at the 2-position contributes more induction than resonance to stabilizing the reduced imidazolium.[42] For the triflate series, there is a marked change in the half-wave potentials compared to the bromides, again supporting the notion of a tighter ion-pairing interaction between the imidazolium and bromide. This ion pairing effect occurs despite electrochemical investigation being performed in 0.5-M $(n\text{-Bu})_4NBF_4$, in which a loosely bound counterion would exchange readily in solution. The most significant difference between the reduction potentials for the imidazolium bromides and triflates is the reversal between **Bn_2(Br)ImX** and **Bn_2(CHO)ImX**: **Bn_2(Br)ImBr** is easier to reduce than **Bn_2(CHO)ImBr**, but for the triflates, the opposite is observed, by over 500 mV. This observation suggests that the imidazolium salt anion influences the electronic properties of the core. To probe this effect, the triflate series' reduction half-wave potentials were plotted against Hammett substituent constants, to identify a free energy relationship, as shown in Figure 2.[42,46] Strikingly, the imidazolium triflates correlate more closely with σ_p than σ_m, which is opposite to the behavior of the bromides. Although the preference for σ_p is slight, it indicates that the nature of the 2-substituent stabilizing effect on the reduced species is in part dependent on the anion, which is supported by the conclusions of Maier and coworkers' detailed spectroscopic work on the effect of imidazolium anions.[30]

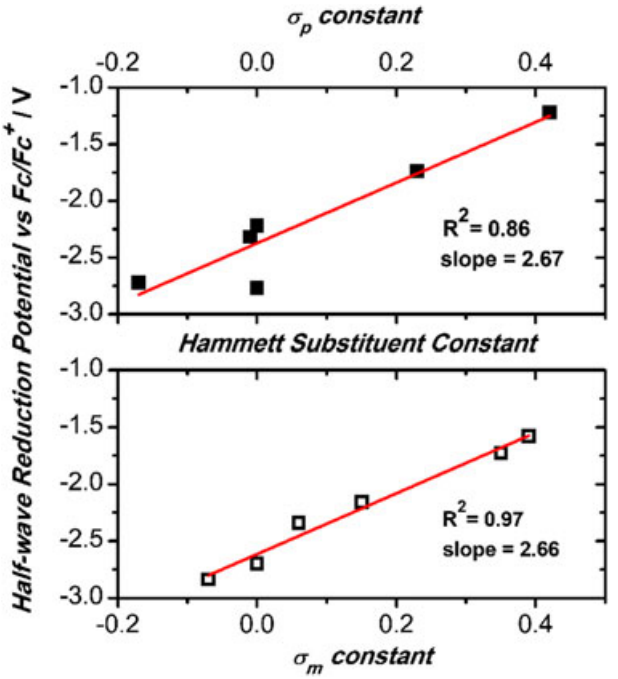


FIGURE 2 Free energy relationship diagram of imidazolium triflates using σ_p constants (top); imidazolium bromides using σ_m constants (bottom). The red lines are linear fits of the data

While the stabilizing effect of the chosen 2-substituents has a marked influence on the ease of reduction, that stabilization appears to have little effect on the reversibility of the electron transfer. The chemical irreversibility of **Bn_2(H)ImBr** is attributable to disproportionation of the nascent radical because of transfer of the 2-*H* atom, but the other 5 imidazolium bromides do not share this trait. Electrochemical investigations of **Bn_2(SCH_3)ImBr** probed the nature of this irreversibility. To discount slow electron transfer kinetics, variable scan rate CV was done between 10 and 1000 $mV{\cdot}s^{-1}$ (Figures S7a and S8a) and no trace of an anodic current is observable, suggesting instead an ensuing chemical reaction after reduction. Coulombic analysis was then conducted to determine the number of electrons accepted during reduction, the diffusion coefficients of **Bn_2(SCH_3)ImBr**, and ferrocene being comparable (Figures S7a-b and S8a-d). Linear scan voltammetry from +1.0 V to −1.9 V on an equimolar DMF solution of **Bn_2(SCH_3)ImBr** and ferrocene produced a voltammogram with 2 peaks of near-equal

area (approximately 0.97:1) (Figure S11). Because ferrocene oxidation is a 1-electron process, this close match in integrated charge of equimolar solutions suggests that **$Bn_2(SCH_3)ImBr$** reduction is also 1-electron, forming an imidazolyl radical. These radicals are well documented in the literature, most notably as the photochromic hexaarylbisimidazole systems, composed of dimerized imidazolyl radicals.[20,21,47,48] Given their propensity towards dimerization, we propose that the nascent radicals of imidazolium bromides and triflates readily dimerize after single electron reduction, which would be the origin of their irreversible CV behavior.

2.3 | Theoretical calculations

To gain further insight into the reduction of the imidazolium core, we conducted DFT calculations using the Gaussian 09 package.[49] Structures of the imidazolium cations and their single electron reduced radicals were optimized with the B3LYP functional[50,51] using the 6-31G+(d) basis set, solvated in DMF using the polarizable continuum model.[52] Expectedly, the imidazolium core of all cations is planar and bears large LUMO coefficients (section 5 in Supporting Information). In particular, the LUMO of **$Bn_2(H)Im^+$** cation, shown in Figure 3, has a large lobe on C2, which is also common between **$Bn_2(CH_3)Im^+$** and **$Bn_2(SCH_3)Im^+$** (section 5 in Supporting Information). This DFT result is in agreement with both a resonance understanding of the structure and PM3 QM calculations of Kroon et al.[38] The localization of the LUMOs also justifies our design of these molecules—placing electron-withdrawing groups at the imidazolium 2-position would have the greatest effect. The LUMOs of **$Bn_2(Ph)Im^+$** and **$Bn_2(CHO)Im^+$** differ slightly from the rest because they exhibit coefficients over the phenyl ring and the carbonyl group. Upon in silico reduction to the imidazolyl radicals, the calculated spin densities largely correlate with the LUMO coefficients of the cations, with one general exception: There is no spin-density on the benzyl Ph rings (section 5 in Supporting Information). This effect is demonstrated with **$Bn_2(H)Im^{\bullet}$** in Figure 3. The large spin density on C2 of the radicals may suggest that dimerization involves that position, which has been observed previously for imidazolyl radicals.[21,53] Such literature precedents further support the proposal for a chemical reaction following the electrochemical reduction of the imidazolium salts. In addition, after in silico reduction followed by reoptimization at the same level of theory, there are notable structural changes due to electronic perturbation of the system. In all cases, the N—C2 and N—backbone C4 and C5 bonds lengthen and backbone C=C bonds contract. The new bond lengths are more reminiscent of C, N single and C,C double bonds. Interestingly, the C2—2-substituent bond lengthens for all radicals save **$Bn_2(Ph)Im^{\bullet}$** and **$Bn_2(CHO)Im^{\bullet}$**, because these 2 radicals have significant spin delocalization onto the phenyl ring and carbonyl group, which explains the observed contraction.

In the literature, there are several methods of varying accuracy for calculating reduction potentials. The most rigorous involves a thermodynamic cycle for the initial and reduced species to compute free energies for reduction and solvation, which was not undertaken here.[54–57] However, a modest approximation of the reduction potential—or more accurately the electron affinity (EA)—used in this work involves optimizing the initial and reduced species in a continuum solvent to account for reorganization and perturbation energy upon adding an electron.[54] This method is advantageous over assuming that the LUMO energy alone is a good measure of electron affinity. The electron affinity of the imidazolium cations was calculated as suggested by Banerjee and coworkers, and the results are shown in Table 2.[54] The results were then compared to experimental LUMO energies for imidazolium bromides and triflates in Figure 4 obtained from DPV apex peaks with ferrocene as internal standard ($E_{HOMO} = -4.8$ eV).[58] The correlation between experiment and theory here is acceptable and highlights the utility of this simple computational method, given the poor fitting observable between experimental and calculated LUMO energies alone, which does not account for molecular reorganization (Figures S13a-b). Imidazolium triflates correlate slightly better to the ideal cationic core, which could reveal the nature of this anion. Triflate is a weakly coordinating anion and likely does not associate

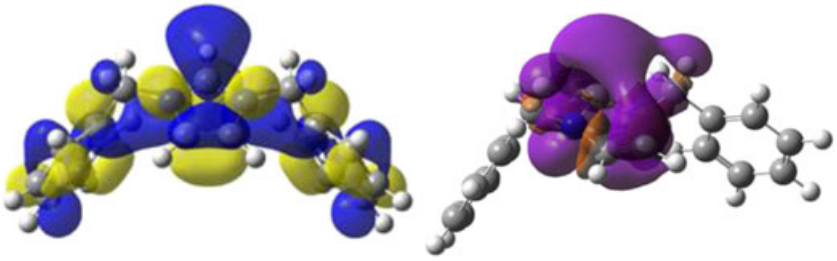


FIGURE 3 Density functional theory–optimized structures of **$Bn_2(H)Im^+$** with LUMO surface (left) and **$Bn_2(H)Im^{\bullet}$** with spin density surface (right), using B3LYP functional and 6-31G+(d) basis set

TABLE 2 Calculated electron affinities for imidazolium cations $Bn_2(R)Im^+$

Cation Code	*EA*[a] (eV)
$Bn_2(H)Im^+$	2.07
$Bn_2(CH_3)Im^+$	2.00
$Bn_2(Ph)Im^+$	2.40
$Bn_2(SCH_3)Im^+$	2.48
$Bn_2(Br)Im^+$	3.47
$Bn_2(CHO)Im^+$	3.65

[a]EA calculated by subtracting optimized radical UB3LYP energy from cation RB3LYP energy and converting to eV. Calculations completed using B3LYP, 6-31G+(d) basis set and PCM DMF solvent model.

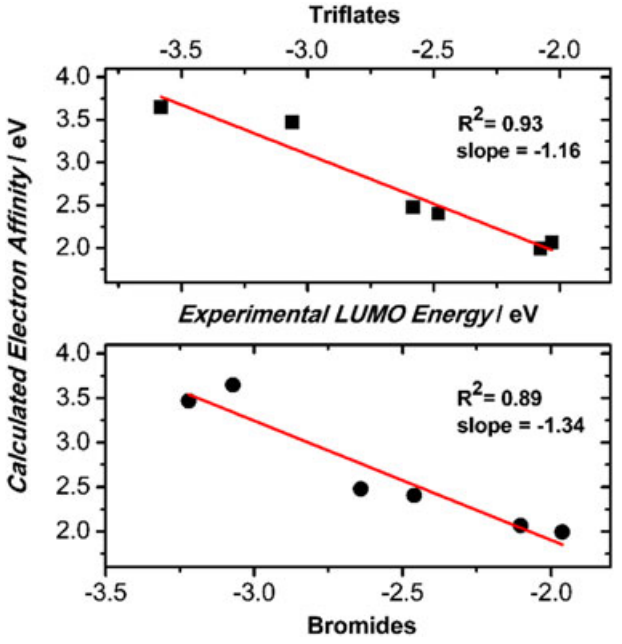


FIGURE 4 Correlation diagram of calculated EA vs experimental $E_{(LUMO)}$ for imidazolium triflates (top) and bromides (bottom)

strongly with the imidazolium, whereas bromide coordinates more strongly and would have a greater influence on the electronics of the imidazolium. These electrochemical and computational data support the spectroscopic observations of Cremer et al on imidazolium anion effects.[30]

3 | CONCLUSIONS

To summarize, we have shown that electrochemical reduction is facilitated by over 1 V through incorporation of electron withdrawing groups at the 2-position of imidazolium salts. The electrochemical modularity is even more pronounced given how few synthetic steps were needed to acquire each system. Furthermore, we observed that using a bromide or triflate anion influences, both the reduction potential and the dominant stabilizing effect of the 2-substituent on the electrochemically reduced species. Namely, reduced imidazolium bromides are stabilized through induction, whereas reduced triflates are stabilized by resonance. DFT-calculated EAs provided theoretical support for the differentiation of anions, indicating that the core of imidazolium bromides is more electronically perturbed than in the analogous imidazolium triflates. Electronic effects from altering 2-substituent and anion highlight the dual modularity of imidazolium salts, paving the way for further comprehensive investigations into 2-substituted imidazolium systems.

4 | EXPERIMENTAL

4.1 | General information

All ^1H NMR spectra were collected at 400 MHz and $^{13}C\{^1H\}$ NMR spectra at 100 MHz on a Bruker DRY400 spectrometer at 298 K. ^1H NMR and $^{13}C\{^1H\}$ NMR spectra were referenced against the residual solvent signals from $CHCl_3$ in $CDCl_3$ (^1H $\delta = 7.26$, ^{13}C $\delta = 77.2$), $(CD_2H)(CD_3)SO$ in $(CD_3)SO$ (^1H $\delta = 2.50$, ^{13}C $\delta = 39.5$), or CD_2HCN in CD_3CN (^1H $\delta = 1.94$, ^{13}C $\delta = 1.3$).[59] High-resolution mass spectra (HR MS) were collected using either EI on a Waters GCT Premier mass spectrometer or ESI on an Agilent Q-TOF mass spectrometer. All chemical formula confirmations were made with less than 5 ppm difference between calculated and observed masses. Purity determination by elemental analysis (EA) was performed in duplicate on a Perkin Elmer 2400 CHN analyzer. Cyclic voltammetry experiments were performed using an Autolab PGSTAT302 potentiostat in a temperature controlled, 3-electrode 15-mL cell. The working electrode was planar glassy carbon, the quasi-reference electrode was a silver wire, and the counter electrode was a platinum wire. All experiments were conducted under argon in approximately 1-mM dried DMF solutions with approximately 0.5-M $(n\text{-}Bu)_4NBF_4$ supporting electrolyte internally referenced against the ferrocene/ferrocenium redox couple. A scan rate of 0.05 $V{\cdot}s^{-1}$ was used unless otherwise stated. The charge integration experiment of **$Bn_2(SCH_3)ImBr$** was conducted using linear sweep voltammetry between 1 and −1.9 V vs Ag/Ag^+ in 2.5 mL of dried DMF having equal moles of both analyte and ferrocene (6.51×10^{-6} mol). The working electrode was equilibrated at 0 V for 20 seconds before the start of the sweep. Multiple scan rate experiments on **$Bn_2(SCH_3)ImBr$** used the same stock solutions as for

charge integration (both analyte and ferrocene being present in 6.51 × 10^{-6} mol), and working electrode was equilibrated at 0 V for 10 seconds before measurement. Full scans from 1.05 to −1.75 V vs Ag/Ag^+ using scan rates of 10, 20, 50, 100, 200, 500, and 1000 $mV{\cdot}s^{-1}$ were collected. Differential pulse voltammetry was performed using the same experimental setup as for CV (above). The working electrode was conditioned at 1 V for 20 seconds, and the experiment was performed from 1 to −1.9 V vs Ag/Ag^+ with 1-second intervals between 0.05-V steps. Tetrahydrofuran, DMF for lithiations, and CH_3CN were purchased from Sigma-Aldrich and dried over flame-dried 3 Å molecular sieves 24 hours prior to use. Benzyl bromide was purchased from Sigma-Aldrich, purified by redistillation under reduced pressures, and stored away from light. NBS was purchased from Sigma-Aldrich, purified by recrystallization from boiling water, and stored in a vacuum desiccator. 35% hydrogen peroxide and 1-benzylimidazole **3a** were purchased from Oakwood Chemical. All other chemicals were purchased from Sigma-Aldrich and used as received. All round-bottomed flasks for reactions were oven-dried for a minimum of 24 hours prior to use. Technical grade silica gel for flash column chromatography (40-63 μm size) was purchased from Sigma-Aldrich and used without modification.

4.2 | Synthesis

4.2.1 | 1-Benzyl-2-(methylsulfanyl)-imidazole 3b

This experimental was adapted from a literature procedure.[60] Into an oven-dried 250-mL RBF, 1-benzyl-imidazole (1.0058 g, 0.0063574 mol, 1 eq.) and an oven-dried magnetic stir bar were added. THF (100 mL) was added and the flask was capped with a rubber septum. The mixture was stirred to dissolution while the flask headspace was flushed with N_2. The flask was submerged into an acetone/$CO_{2(s)}$ bath and thermalized to −78°C. *n*-BuLi (1.54 M, 4.14 mL, 0.00638 mol, 1 eq.) was added dropwise by syringe over 10 minutes. The resulting intense cherry-red and clear solution was allowed to stir for 30 minutes at −78°C. After this time, $(CH_3)_2S_2$ (1.13 mL, 0.0127 mol, 2 eq.) was added at −78°C over 5 minutes. The solution turned light peach-yellow and was allowed to warm to room temperature, then stirred for a further 2 hours. The resulting cloudy deep-yellow solution was diluted with saturated aqueous $NaHCO_3$ (50 mL) and EtOAc (30 mL). The biphase was transferred to a separatory funnel, and the layers were separated. The aqueous layer was extracted with EtOAc (3 × 30 mL), and the combined organics were washed with brine and then dried over anhydrous Na_2SO_4. Concentration under reduced pressures yielded a viscous, clear yellow oil. This was adsorbed to silica and loaded onto a 16-cm-tall × 4.5-cm-wide silica column packed in 25% Et_2O/hexanes. Gradient elution first with 25% Et_2O/hexanes (approximately 400 mL) eluted excess $(CH_3)_2S_2$, then with 50% Et_2O/hexanes (approximately 2 L) eluted 1-benzyl-2-(methylsulfanyl)-imidazole as a clear, light-yellow liquid (1.043 g, 80% yield): R_f (70% EtOAc/hexanes) = 0.40; ^1H NMR (400 MHz, CD_3Cl) δ = 7.38-7.27 (m, 3H), 7.16-7.13 (m, 2H), 7.10 (d, J = 1.4 Hz, 1H), 6.93 (d, J = 1.4 Hz, 1H), 5.11 (s, 2H), 2.57 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 143.2, 136.4, 129.7, 129.0,128.2, 127.4, 121.3, 50.1, 16.6; HRMS (EI, positive) calculated m/z = 204.0721 $[M]^+$, found m/z = 204.0725 $[M]^+$; EA calculated for $C_{11}H_{12}N_2S$ = 64.67% C, 5.92% H, 13.71% N found = 64.29% C, 6.11% H, 13.99% N.

4.2.2 | 1-Benzyl-2-(methylsulfinyl)-imidazole 4a

This experimental was adapted from a literature procedure.[36] Into a 100-mL RBF, a magnetic stir bar and 1-benzyl-2-(methylsulfanyl)-imidazole (0.5223 g, 0.002557 mol, 1 eq.) were added. Glacial acetic acid (50 mL) was added, and the mixture was stirred to dissolution at room temperature. The flask was capped with a rubber septum pierced by a needle for pressure relief, then thermalized to 50°C on an oil bath. Aqueous H_2O_2 (35%, 0.88 mL, 0.010 mol, 4 eq.) was added by syringe, dropwise over 1 minute. The resulting clear light-yellow solution was allowed to stir for 4.5 hours. After this time, the solution had become clear and colorless. Saturated aqueous Na_2SO_3 (5 mL) was added to quench excess H_2O_2, and the solution was allowed to cool to room temperature. It was transferred to a separatory funnel and brought to pH 9 to 10 (by pH indicator paper) by portion-wise addition of 5 M NaOH. Over the course of addition, the solution became slightly cloudy yellow and it was then allowed to cool to room temperature. The basic solution was extracted with EtOAc (8 × 15 mL); the organic extracts were brine washed then dried over anhydrous Na_2SO_4. Concentration under reduced pressures yielded a viscous, light-yellow oil. This was adsorbed to silica and loaded onto a 5-cm-tall × 2.5-cm-wide silica column packed in 50% EtOAc/hexanes. Gradient elution first with 50% EtOAc/hexanes (approximately 200 mL), then with 70% EtOAc/hexanes (approximately 600 mL) eluted 1-benzyl-2-(methylsulfinyl)-imidazole as a clear, colorless oil, which solidified on standing to a white, waxy solid (0.4112 g, 73%): *Rf* (70% EtOAc/hexanes) = 0.10; mp (70% EtOAc/hexanes) = 73-76°C; ^1H NMR (400 MHz,

CD_3CN) δ = 7.40-7.30 (m, 3H), 7.28-7.24 (m, 2H), 7.23 (d, J = 1.0 Hz, 1H), 7.15 (d, J = 1.0 Hz, 1H), 5.46 (s, 1H), 2.95 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, CD_3CN) δ = 147.7, 137.7, 130.5, 129.9, 129.2, 128.5, 125.2, 50.8, 39.1; HRMS (EI, positive) calculated m/z = 220.0670 $[M]^+$, found m/z = 220.0671 $[M]^+$; EA calculated for $C_{11}H_{12}ON_2S$ = 59.98% C, 5.49% H, 12.72% N found = 59.96% C, 5.39% H, 12.70% N.

4.2.3 | 1-Benzyl-2-(methylsulfonyl)-imidazole 4b

This experimental was adapted from a literature procedure.[36] Into a 100 mL RBF, 1-benzyl-(2-methylsulfanyl)-imidazole (0.5250 g, 0.002570 mol, 1 eq.) and a magnetic stir bar were added. Glacial acetic acid (50 mL) was added, and the mixture was stirred to dissolution at room temperature. The flask was capped with a rubber septum pierced with a needle for pressure relief, then it was allowed to thermalize to 90°C on an oil bath. Aqueous H_2O_2 (35%, 0.88 mL, 0.010 mol, 4 eq.) was added by syringe, dropwise over 1 minute. The resulting clear light-yellow solution was allowed to stir for 5 hours. After this time, the solution had become clear and colorless. Saturated aqueous Na_2SO_3 (5 mL) was added to quench excess H_2O_2, and the solution was allowed to cool to room temperature. It was transferred to a separatory funnel and brought to pH 9 to 10 (by pH indicator paper) by portionwise addition of 5 M NaOH. Over the course of addition, the solution became increasingly dull, milky yellow, and it was then allowed to cool to room temperature. The basic solution was extracted with EtOAc (8 × 15 mL); the organic extracts were brine washed then dried over anhydrous Na_2SO_4. Concentration under reduced pressured yielded a viscous, light-yellow oil. This was adsorbed to silica and loaded onto a 5-cm-tall × 2.5-cm-wide silica column packed in 30% EtOAc/hexanes. Gradient elution first with 30% EtOAc/hexanes (approximately 120 mL), then with 50% EtOAc/hexanes (approximately 200 mL) eluted 1-benzyl-2-(methylsulfonyl)-imidazole as a clear, colorless oil, which solidified on standing to an off-white waxy solid (0.4344 g, 72% yield): R_f (70% EtOAc/hexanes) = 0.50; mp (50% EtOAc/hexanes) = 36-39°C; ^1H NMR (400 MHz, CD_3CN) δ = 7.40-7.30 (m, 3H), 7.27 (d, J = 1.1 Hz, 1H), 7.26-7.22 (m, 2H), 7.15 (d, J = 1.1 Hz, 1H), 5.55 (s, 2H), 3.16(s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, CD_3CN) δ = 143.5, 137.6, 130.0, 129.8, 129.2, 128.4, 126.3, 51.9, 43.9; HRMS (EI, positive) calculated m/z = 236.0619 $[M]^+$, found m/z = 236.0616 $[M]^+$; EA calculated for $C_{11}H_{12}O_2N_2S$ = 55.92% C, 5.12% H, 11.86% N found = 55.79% C, 5.07% H, 12.46% N.

4.2.4 | 1-Benzyl-2-bromo-imidazole 3a

This experimental was adapted from a literature procedure.[34] Into an oven-dried 100-mL RBF, 1-benzyl-imidazole (0.5004 g, 0.003182 mol, 1 eq.) and an oven-dried magnetic stir bar were added. THF (50 mL) was added, and the flask was capped with a rubber septum. The mixture was stirred to dissolution while the flask headspace was flushed with N_2. The flask was submerged into an acetone/$CO_{2(s)}$ bath and thermalized to −78°C. n-BuLi (1.31 M, 2.43 mL, 0.00318 mol, 1 eq.) was added dropwise by syringe over 10 minutes. The resulting intense cherry-red and clear solution was allowed to stir for 30 minutes at −78°C. Separately, an NBS/THF solution was prepared under N_2 by adding THF (10 mL) to NBS (0.5289 g, 0.002972 mol, 0.95 eq.) and agitating to dissolution. This solution was added dropwise to the lithiated solution at −78°C over 5 minutes. The solution turned blood-red, dark green-black, then orange-brown. It was allowed to warm to room temperature, then stirred for a further 2 hours, over which time the solution turned red-brown and opaque. The mixture was diluted with saturated aqueous $NaHCO_3$ (15 mL) and EtOAc (15 mL). The biphase was transferred to a separatory funnel, and the layers were separated. The aqueous layer was extracted with EtOAc (3 × 15 mL), and the combined organics were washed with brine and then dried over anhydrous Na_2SO_4. Concentration under reduced pressures yielded a viscous, red-brown oil. This was adsorbed to silica and loaded onto a 15-cm-tall × 4.5-cm-wide silica column packed in 20% EtOAc/hexanes. Elution with 20% EtOAc/hexanes (approximately 1.1 L) eluted 1-benzyl-2-bromo-imidazole as a clear, light-yellow liquid (0.3467 g, 49% yield): R_f (50% EtOAc/hexanes) = 0.73; ^1H NMR (400 MHz, $CDCl_3$) δ = 7.39-7.30 (m, 3H), 7.18-7.14 (m, 2H), 7.04 (d, J = 1.3 Hz, 1H), 6.95 (d, J = 1.3 Hz, 1H), 5.11 (s, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 135.6, 130.4, 129.1, 128.4, 127.4, 122.3, 120.1, 51.4; HRMS (EI, positive) calculated m/z = 235.9949 $[M]^+$, 237.9929 $[M + 2]^+$ found m/z = 235.9957 $[M]^+$, 237.9939 $[M + 2]^+$; EA calculated for $C_{10}H_9N_2Br$ = 50.66% C, 3.83% H, 11.82% N found = 50.33% C, 3.70 % H, 11.83% N.

4.2.5 | 1-Benzyl-2-formyl-imidazole 3c

This experimental was adapted from a literature procedure.[32] Into an oven-dried 100-mL RBF, 1-benzyl-imidazole (0.5028 g, 0.003178 mol, 1 eq.) and an oven-dried magnetic stir bar were added. THF (50 mL) was added, and the flask was capped with a rubber septum. The mixture was stirred to dissolution while the flask headspace was flushed with N_2. The flask was submerged into an acetone/$CO_{2(s)}$ bath and thermalized to −78°C.

n-BuLi (1.31 M, 2.43 mL, 0.00318 mol, 1 eq.) was added dropwise by syringe over 10 minutes. The resulting intense cherry-red and clear solution was allowed to stir for 30 minutes at −78°C. After this time, DMF (0.49 mL, 0.0063 mol, 2 eq.) was added at −78°C over 5 minutes. The solution turned cherry pink and was allowed to warm to room temperature, then stirred for a further 2 hours. The resulting light-yellow solution was diluted with saturated aqueous NH_4Cl (15 mL) and EtOAc (15 mL). The biphase was transferred to a separatory funnel and the layers were separated. The aqueous layer was extracted with EtOAc (3 × 15 mL), and the combined organics were washed with brine and then dried over anhydrous Na_2SO_4. Concentration under reduced pressures yielded a viscous, clear yellow oil. This was adsorbed to silica and loaded onto a 6-cm-tall × 2.5-cm-wide silica column packed in 30% EtOAc/hexanes. Elution with 30% EtOAc/hexanes (approximately 500 mL) eluted 1-benzyl-2-formyl-imidazole as a clear, light-yellow liquid (0.5074 g, 86% yield): R_f (50% EtOAc/hexanes) = 0.72; δ = ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.97 ("apparent d," 1H), 7.49-7.43 (m, 3H), 7.39 (s, 1H), 7.34-7.31 (m, 2H), 5.74 (s, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 182.4, 143.5, 135.9, 132.0, 129.1, 128.5, 127.9, 126.4, 51.1; HRMS (EI, positive) calculated m/z = 186.0793 $[M]^+$, found m/z = 186.0795 $[M]^+$.

4.2.6 | 1,3-(Dibenzyl)imidazolium bromide Bn_2(H)ImBr

This experimental was adapted from a literature procedure.[29] Into an oven-dried 500-mL RBF, imidazole (2.6698 g, 0.039216 mol, 1 eq.), oven-dried anhydrous K_2CO_3 (8.1389 g, 0.058888 mol, 1.5 eq.), and a large oven-dried magnetic stir bar were added. CH_3CN (200 mL) were added, a Drierite drying tube was connected to the mouth of the flask and the resulting mixture was stirred for 15 minutes at room temperature to effect dissolution of the imidazole. Benzyl bromide (9.32 mL, 0.0785 mol, 2 eq.) was added dropwise by syringe over 10 minutes, and the cloudy white mixture was stirred at room temperature for 48 hours. After this time, the resulting light yellow and turbid mixture was gravity filtered through filter paper, and the filter cake was washed with several small portions of CH_3CN. The collected filtrate was concentrated under reduced pressures, yielding a viscous, clear light-yellow oil, which solidified upon standing for several days in the fridge. The solid was transferred to a Büchner funnel and washed with diethyl ether (approximately 10 mL) to remove remaining benzyl bromide, then dried in vacuo. This process was repeated a total of 7 times to yield 1,3-dibenzylimidazolium bromide as a waxy light-yellow solid (12.011 g, 93% yield). It can be recrystallized as an off-white crystalline solid from boiling 1:1 THF:acetone; mp (1:1 THF:acetone) softens at 73°C to 75°C, melts at 82°C to 85°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 11.05 (s, 1H), 7.47-7.44 (m, 4H), 7.43-7.38 (m, 6H), 7.13 (d, J = 1.6 Hz, 2H), 5.56 (s, 4H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 137.7, 132.7, 129.8, 129.7, 129.2, 121.7, 53.8; HRMS (ESI, positive) calculated m/z = 249.1386 $[M\text{-}Br]^+$, found m/z = 249.1388 $[M\text{-}Br]^+$.

4.3 | General procedure for small-scale preparation of imidazolium triflates

This procedure is suitable for preparing small-scale samples of imidazolium triflates, concentrated enough for ^{1}H NMR and ^{13}C NMR analysis. The desired imidazolium bromide (approximately 3×10^{-5} mol, 1 eq.) was weighed into a ½ dram screw-cap glass vial. $CDCl_3$ (0.75 mL) was added by syringe, and the mixture was sonicated to dissolution/dispersion. AgOTf (approximately 3.3×10^{-5} mol) was added in one portion; the cap was tightened and the mixture was sonicated at room temperature for 10 minutes. The resulting milky pale-yellow suspension was filtered through a Pasteur pipette tightly stuffed with a small plug of cotton/glass wool, and the clear colorless filtrate was eluted directly into an NMR tube for analysis.

4.3.1 | 1,3-(Dibenzyl)imidazolium triflate Bn_2(H)ImOTf

This procedure is suitable for preparing macroscopic quantities of imidazolium triflates because of the ease of work-up and scalability. Into an oven-dried 5-mL RBF, 1,3-(dibenzyl)imidazolium bromide (0.3224 g, 9.789×10^{-4} mol, 1 eq.) and a small oven-dried magnetic stir bar were added. CH_3CN (3 mL) was added, and the flask was capped with a rubber septum. The flask headspace was flushed with N_2 and the mixture was stirred to dissolution at room temperature. Methyl triflate (0.11 mL, 0.0010 mol, 1 eq.) was added by syringe causing the solution to change from colorless to golden-yellow. The solution was stirred at room temperature for 18 hours. After this time, the solution was concentrated under reduced pressures, reconstituted with CH_2Cl_2 (10 mL), and partially decolorized by boiling with type-A activated carbon. Removal of the solvent yielded 1,3-(dibenzyl) imidazolium triflate as a viscous yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.60 (t, J = 1.6 Hz, 1H), 7.41-7.32 (m, 10H), 7.16 (d, J = 1.6 Hz, 2H), 5.36 (s, 4H); DEPT-Q $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 136.64

(+), 132.66 (−), 129.75 (+), 129.65 (+), 129.12 (+), 122.11 (+), 53.73 (−).

4.3.2 | 1,3-(Dibenzyl)-2-methylimidazolium bromide $Bn_2(CH_3)ImBr$

This experimental was adapted from a literature procedure.[29] Into an oven-dried 50-mL RBF, 2-methylimidazole (0.3226 g, 0.003929 mol, 1 eq.), oven-dried anhydrous K_2CO_3 (0.8167 g, 0.005909 mol, 1.5 eq.), and a small oven-dried magnetic stir bar were added. CH_3CN (20 mL) were added; a Drierite drying tube was connected to the mouth of the flask and the resulting mixture was stirred for 15 minutes at room temperature to effect dissolution of the 2-methylimidazole. Benzyl bromide (0.93 mL, 0.0078 mol, 2 eq.) was added dropwise by syringe over 3 minutes, and the cloudy white mixture was stirred at room temperature for 48 hours. After this time, the resulting light yellow and turbid mixture was concentrated under reduced pressures to yield a caked white solid, which was then reconstituted with CH_2Cl_2 (20 mL) and H_2O (50 mL). The layers were separated in a separatory funnel, the aqueous layer was extracted with CH_2Cl_2 (3 × 0 mL), and the combined extracts were dried over anhydrous Na_2SO_4. Concentration under reduced pressures produced a white powder, which was suction filtered on filter paper, washed with excess diethyl ether, and dried in vacuo to yield 1,3-(dibenzyl)-2-methylimidazolium bromide as a white granulated solid (0.6697 g, 50% yield). It can be recrystallized as a white crystalline solid from boiling 1:3 acetone: CH_3CN: mp (1:3 acetone:CH_3CN) = 222-226°C; ^1H NMR (400 MHz, $CDCl_3$) δ = 7.44-7.37 (m, 5H), 7.36-7.33 (m, 5H), 5.50 (s, 4H), 2.85 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $(CD_3)_2SO$) δ = 144.5, 134.4, 129.0, 128.5, 127.8, 122.0, 50.8, 9.8; HRMS (ESI, positive) calculated m/z = 263.1543 $[M\text{-}Br]^+$, found m/z = 263.1545 $[M\text{-}Br]^+$.

4.3.3 | 1,3-(Dibenzyl)-2-methylimidazolium triflate $Bn_2(CH_3)ImOTf$

This procedure is suitable for preparing macroscopic quantities of imidazolium triflates because of the ease of work-up and scalability. Into an oven-dried 25-mL RBF, 1,3-(dibenzyl)-2-methylimidazolium bromide (0.3467 g, 0.001010 mol, 1 eq.) and a small oven-dried magnetic stir bar were added. CH_3CN (15 mL) was added, and the flask was capped with a rubber septum. The flask headspace was flushed with N_2, and the suspension was stirred at room temperature. Methyl triflate (0.11 mL, 0.0010 mol, 1 eq.) was added by syringe forming a clear light-yellow solution, which was stirred at room temperature for 18 hours. After this time, the solution was concentrated under reduced pressures, reconstituted with CH_2Cl_2 (10 mL) and partially decolorized by boiling with type-A activated carbon. Removal of the solvent yielded 1,3-(dibenzyl)-2-methylimidazolium triflate as a viscous amber-yellow liquid. ^1H NMR (400 MHz, $CDCl_3$) δ = 7.43-7.34 (m, 6H), 7.26-7.23 (m, 4H), 7.14 (s, 2H), 5.29 (s, 4H), 2.64 (s, 3H); DEPT-Q $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 144.72 (−), 132.56 (−), 129.57 (+), 129.37 (+), 128.29 (+), 121.54 (+), 52.45 (−), 10.69 (+).

4.3.4 | 1,3-(Dibenzyl)-2-phenylimidazolium bromide $Bn_2(Ph)ImBr$

This experimental was adapted from a literature procedure.[29] Into an oven-dried 50-mL RBF, 2-phenylimidazole (0.5631 g, 0.003906 mol, 1 eq.) and an oven-dried magnetic stir bar were added. Oven-dried anhydrous K_2CO_3 (0.8112 g, 0.005869 mol, 1.5 eq.) was added followed by CH_3CN, and the mixture was stirred at room temperature to dissolve all 2-phenylimidazole. Benzyl bromide (0.93 mL, 0.0078 mol, 2 eq.) was added by syringe and the flask was equipped with a Drierite drying tube. The light-yellow mixture was stirred at room temperature for 72 hours. The resulting cloudy white mixture was concentrated under reduced pressures to yield a solid yellow residue. This was reconstituted with deionized H_2O (50 mL) and CH_2Cl_2 (30 mL). The mixture was transferred to a separatory funnel, and the layers were separated. The aqueous layer was extracted with CH_2Cl_2 (3 × 10 mL); the combined organics were dried over anhydrous Na_2SO_4 and concentrated under reduced pressures to yield a viscous yellow oil. This was purified by boiling a CH_2Cl_2 solution with type-A activated carbon and again concentrating the solution producing 1,3-(dibenzyl) imidazolium bromide as a light-yellow viscous liquid (1.3773 g, 88% yield). Spectroscopic characterization matched literature reports.[24]

4.3.5 | 1,3-(Dibenzyl)-2-phenylimidazolium triflate $Bn_2(Ph)ImOTf$

This procedure is suitable for preparing macroscopic quantities of imidazolium triflates because of the ease of work-up and scalability. Into an oven-dried 10-mL RBF, 1,3-(dibenzyl)-2-methylimidazolium bromide (0.5665 g, 0.001398 mol, 1 eq.) and a small oven-dried magnetic stir bar were added. CH_3CN (4 mL) was added, and the flask was capped with a rubber septum. The flask headspace was flushed with N_2, and the mixture was stirred to dissolution at room temperature. Methyl triflate (0.14 mL, 0.0014 mol, 1 eq.) was added by syringe forming a clear golden-orange solution, which was stirred at room temperature for 18 hours. After this time, the solution was

concentrated under reduced pressures, reconstituted with CH_2Cl_2 (10 mL), and partially decolorized by boiling with type-A activated carbon. Removal of the solvent yielded 1,3-(dibenzyl)-2-phenylimidazolium triflate as a viscous dark amber liquid, which formed clear light-brown crystals on standing. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.69 (m, 1H), 7.61 (m, 2H), 7.56-7.51 (m, 2H), 7.46 (s, 2H), 7.37-7.30 (m, 6H), 7.14-7.07 (m, 4H), 5.18 (s, 4H); DEPT-Q ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ = 145.05 (−), 133.21 (−), 133.08 (+), 130.71 (+), 130.09 (+), 129.17 (+), 129.10 (+), 128.30 (+), 122.69 (+), 121.03 (−), 52.78 (−).

4.3.6 | 1,3-(Dibenzyl)-2-(methylsulfanyl) imidazolium bromide $Bn_2(SCH_3)ImBr$

Into an oven-dried 25-mL RBF, 1-benzyl-2-(methylsulfanyl)imidazole (0.2518 g, 0.001175 mol, 1 eq.) and a small oven-dried magnetic stir bar were added. CH_3CN (12.5 mL) was added, and the flask was capped with a rubber septum. The mixture was stirred to dissolution at room temperature while the flask headspace was flushed with N_2 to prevent aerial oxidation of the starting material. The solution was thermalized to 30°C on an oil bath, and benzyl bromide (0.14 mL, 0.0012 mol, 1 eq.) was added by syringe. The solution was allowed to heat and stir for 18 days. After this time, the light-yellow and clear reaction mixture was concentrated under reduced pressures to yield a yellow oil. This was put under high-vacuum for 16 hours to produce a fluffy light-yellow residue. Diethyl ether (25 mL) was added to fill the flask; the residue was manually agitated with a spatula and allowed to settle overnight in the fridge. The mixture was rapidly suction filtered over filter paper, and the isolated solid was quickly transferred to a small Erlenmeyer flask (if the filtration is not completed quickly then the product acquires a caramel-like consistency which is difficult to handle). Trituration with boiling 1:1 EtOAc:acetone (5 mL), suction filtration over filter paper, and drying in vacuo yielded 1,3-(dibenzyl)-2-(methylsulfanyl) imidazolium bromide as an off-white powder (0.1685 g, 38% yield): mp (1:1 EtOAc:acetone) = 124-128°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.76 (s, 2H), 7.44-7.38 (m, 10H), 5.69 (s, 4H), 2.45 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ = 140.4, 133.1, 129.7, 129.6, 128.7, 125.1, 53.9, 19.2; HRMS (ESI, positive) calculated *m/z* = 295.1263 $[M\text{-}Br]^+$, found *m/z* = 295.1276 $[M\text{-}Br]^+$.

4.3.7 | 1,3-(Dibenzyl)-2-(methylsulfanyl) imidazolium triflate $Bn_2(SCH_3)ImOTf$

This procedure is suitable for preparing macroscopic quantities of imidazolium triflates because of the ease of work-up and scalability. Into an oven-dried 10 mL RBF, 1,3-(dibenzyl)-2-(methylsulfanyl)imidazolium bromide (0.4158 g, 0.001108 mol, 1 eq.) and a small oven-dried magnetic stir bar were added. CH_3CN (3 mL) was added, and the flask was capped with a rubber septum. The flask headspace was flushed with N_2, and the mixture was stirred to dissolution at room temperature. Methyl triflate (0.12 mL, 0.0011 mol, 1 eq.) was added by syringe forming a clear light-yellow solution, which was stirred at room temperature for 18 hours. After this time, the solution was concentrated under reduced pressures, reconstituted with CH_2Cl_2 (10 mL), and partially decolorized by boiling with type-A activated carbon. Removal of the solvent yielded 1,3-(dibenzyl)-2-(methylsulfanyl)imidazolium triflate as a viscous amber liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.49 (s, 2H), 7.44-7.30 (m, 10H), 5.53 (s, 4H), 2.34 (s, 3H); DEPT-Q ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ = 131.71 (−), 129.77 (+), 129.61 (+), 128.94 (+), 124.67 (+), 54.64 (−); uDEFT ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ = 131.71, 129.78, 129.63, 128.94, 124.68, 120.60, 54.66.

4.3.8 | 1,3-(Dibenzyl)-2-formylimidazolium bromide $Bn_2(CHO)ImBr$

Into an oven-dried 35 mL RBF, a small oven-dried magnetic stir bar and 1-benzyl-2-formylimidazole (0.5143 g, 0.002762 g, 1 eq.) were added. A rubber septum was attached to the flask, and the headspace was purged with N_2 to prevent aerial oxidation. Benzyl bromide (6.6 mL, 0.056 mol, 20 eq.) was added by syringe; the clear colorless solution was thermalized to 50°C on an oil bath and then stirred for 24 hours. The resulting cloudy off-white mixture was allowed to cool to room temperature then diluted with Et_2O (15 mL) to precipitate a fluffy white solid. The mixture was suction filtered over filter paper, washed with excess Et_2O and dried in vacuo to yield 1,3-(dibenzyl)-2-formylimidazolium bromide as a moisture-sensitive, light-beige chalky solid (0.7585 g, 77% yield). It can be recrystallized as fine, off-white needles from boiling CH_3CN: mp (CH_3CN) = 180-182°C (decomp and gas evolved); ^{1}H NMR (400 MHz, CD_3CN) δ = 10.14 (s, 1H), 7.61 (s, 2H), 7.49-7.39 (m, 10H), 5.76 (s, 4H); DEPT-Q ^{13}C{^{1}H} NMR (100 MHz, CD_3CN) δ = 176.0 (−), 134.2 (+), 130.2 (−), 130.2 (−), 130.0 (−), 129.8 (−), 129.6 (−), 129.4 (−), 126.2 (−), 123.1 (−), 53.9 (+), 53.1 (+); HRMS (ESI, positive) calculated for aldehyde *m/z* = 277.1335 $[M\text{-}Br]^+$, found for aldehyde *m/z* = 277.1337 $[M\text{-}Br]^+$; HRMS (ESI, positive) calculated for hydrate *m/z* = 295.1447 $[M\text{-}Br]^+$, found for hydrate *m/z* = 295.1438 $[M\text{-}Br]^+$. *A ^{13}C NMR spectrum could not be obtained showing all carbons in the compound, even DEPT-Q with 14 000 scans over 16 hours. UDEFT ^{13}C{^{1}H} NMR with 1000 scans revealed 2 more signals at δ = 135.3

and 83.6. This difficulty is likely due to formation of the hydrate, which slowly consumed the aldehyde over the duration of the acquisitions. It is likely that the signals at δ = 135.3, 130.0, 129.8, 129.4, 123.1, 83.6, and 53.1 belong to the hydrate due to their proportionally lower intensities. However, the C-2 carbons for both aldehyde and hydrate were never observed. When ^{1}H NMR was acquired in CD_3CN containing H_2O and the tube was allowed to sit for 4 days, a new set of proton resonances grew at the expense of an old set (Supporting Information). Hydrate formation is supported by recording ^{1}H NMR in CD_3CN before and after adding D_2O and observing the growth/disappearance of the same 2 sets of resonances (Supporting Information). HR MS observations of a peak with *m/z* corresponding to the hydrate further solidified this assignment.

4.3.9 | 1,3-(Dibenzyl)-2-formylimidazolium triflate Bn_2(CHO)ImOTf

This procedure is suitable for preparing macroscopic quantities of imidazolium triflates because of the ease of work-up and scalability. Into an oven-dried 10-mL RBF, 1,3-(dibenzyl)-2-formylimidazolium bromide (0.3907 g, 0.001094 mol, 1 eq.) and a small oven-dried magnetic stir bar were added. CH_3CN (6 mL) was added, and the flask was capped with a rubber septum. The flask headspace was flushed with N_2, and the mixture was stirred to dissolution at room temperature. Methyl triflate (0.12 mL, 0.0011 mol, 1 eq.) was added by syringe forming a clear light-yellow solution, which was stirred at room temperature for 18 hours. After this time, the solution was concentrated under reduced pressures, reconstituted with CH_2Cl_2 (10 mL) and partially decolorized by boiling with type-A activated carbon. Removal of the solvent yielded 1,3-(dibenzyl)-2-formylimidazolium triflate as a viscous amber-orange liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 10.13 (s, 1H), 7.37 (m, 24H), 6.87 (s, 2H), 6.79 (s, 1H), 6.59 (s, 2H), 5.74 (s, 4H), 5.53 (s, 4H). This spectrum contains 1:1 of the aldehyde and its hydrate, by analogy to the spectrum of 1,3-(dibenzyl)-2-formylimidazolium bromide; DEPT-Q ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ = 174.58 (+), 132.69 (−), 132.18 (−), 129.83 (+), 129.65 (+), 129.55 (+), 129.49 (+), 129.15 (+), 129.11 (+), 128.80 (+), 124.90 (+), 121.38 (+), 83.60 (+), 53.81 (−), 53.03 (−). *A ^{13} C NMR spectrum containing all carbons could not be collected, again because of hydrate formation. The missing carbons likely are C-2 of both aldehyde and hydrate.

4.3.10 | 1,3-(Dibenzyl)-2-bromoimidazolium bromide Bn_2(Br)ImBr

Into an oven-dried 25-mL RBF, 1-benzyl-2-bromoimidazole (0.5513 g, 0.002325 mol, 1 eq.) and a small oven-dried magnetic stir bar were added. A rubber septum was attached and benzyl bromide (5.5 mL, 0.046 mol, 20 eq.) was added by syringe. The clear colorless solution was thermalized to 50°C on an oil bath and stirred for 24 hours. After this time, the cloudy off-white mixture was allowed to cool to room temperature, and Et_2O (15 mL) were added to precipitate a fluffy white solid. The mixture was suction filtered through filter paper, washed with excess Et_2O, and dried in vacuo to yield 1,3-dibenzyl-2-bromoimidazolium bromide as a white chalky powder (0.8288 g, 88% yield). It can be recrystallized as fine white needles from boiling CH_3CN: mp (CH_3CN) = 175-180°C; ^{1}H NMR (400 MHz, CD_3CN) δ = 7.63 (s, 2H), 7.47-7.40 (m, 6H), 7.40-7.34 (m, 4H), 5.38 (s, 4H); ^{13}C{^{1}H} NMR (100 MHz, CD_3CN) δ = 133.9, 130.2, 130.2, 129.4, 125.4, 123.8, 54.7; HRMS (ESI, positive) calculated *m/z* = 327.0491 [M-Br]$^+$, found *m/z* = 327.0506 [M-Br]$^+$.

4.3.11 | 1,3-(Dibenzyl)-2-bromoimidazolium triflate Bn_2(Br)ImOTf

This procedure is suitable for preparing macroscopic quantities of imidazolium triflates because of the ease of work-up and scalability. Into an oven-dried 10-mL RBF, 1,3-(dibenzyl)-2-bromoimidazolium bromide (0.4475 g, 0.001096 mol, 1 eq.) and a small oven-dried magnetic stir bar were added. CH_3CN (6 mL) was added, and the flask was capped with a rubber septum. The flask headspace was flushed with N_2 and the suspension was stirred at room temperature. Methyl triflate (0.12 mL, 0.0011 mol, 1 eq.) was added by syringe forming a clear light-yellow solution, which was stirred at room temperature for 18 hours. After this time, the solution was concentrated under reduced pressures, reconstituted in CH_2Cl_2 (10 mL) and partially decolorized by boiling with type-A activated carbon. Removal of the solvent yielded 1,3-(dibenzyl)-2-bromoimidazolium triflate as a viscous amber-orange liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.51 (s, 2H), 7.44-7.32 (m, 10H), 5.37 (s, 4H); DEPT-Q ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ = 131.71 (−), 129.77 (+), 129.61 (+), 128.94 (+), 124.67 (+), 54.64 (−); uDEFT ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ = 131.71, 129.78, 129.63, 128.94, 124.68, 120.60, 54.66.

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REFERENCES

[1] O. Edenhoffer, K. Seyboth, F. Creutzig, S. Schlomer, *Annu. Rev. Environ. Resour.* **2013**, *38*, 169.

[2] S. Weitemeyer, D. Kleinhans, T. Vogt, C. Agert, *Renew. Energy* **2015**, *75*, 14.

[3] G. L. Soloveichik, *Chem. Rev.* **2015**, *115*, 11533.

[4] M. Skyllas-Kazacos, L. Cao, M. Kazacos, N. Kausar, A. Mousa, *ChemSusChem* **2016**, *9*, 1521.

[5] F. Pan, Q. Wang, *Molecules* **2015**, *20*, 20499.

[6] J. Noack, N. Roznyatovskaya, T. Herr, P. Fischer, *Angew. Chemie - Int. Ed.* **2015**, *54*, 9776.

[7] J. Winsberg, T. Hagemann, T. Janoschka, M. D. Hager, U. S. Schubert, *Angew. Chemie - Int. Ed.* **2017**, *56*, 686.

[8] Y. Zhao, Y. Ding, Y. Li, L. Peng, H. R. Byon, J. B. Goodenough, G. Yu, *Chem. Soc. Rev.* **2015**, *44*, 7968.

[9] W. Kangro, H. Pieper, *Electrochim. Acta* **1962**, *7*, 435.

[10] M. Skyllas-Kazacos, M. Rychik, R. G. Robins, A. G. Fane, M. A. Green, *J. Electrochem. Soc.* **1986**, *133*, 1057.

[11] M. Rychik, M. Skyllas-Kazacos, *J. Power Sci.* **1988**, *22*, 59.

[12] B. Hu, C. Debruler, Z. Rhodes, T. Liu, *J. Am. Chem. Soc.* **2017**, *139*, 1207.

[13] T. Liu, X. Wei, Z. Nie, V. Sprenkle, W. Wang, *Adv. Energy Mater.* **2016**, 6, https://doi.org/10.1002/aenm.201501449.

[14] Y. Xu, Y. Wen, J. Cheng, Y. Yanga, Z. Xie, G. Cao, *IEEE* **2009**, *978*, 4244.

[15] B. Huskinson, M. P. Marshak, C. Suh, S. Er, M. R. Gerhardt, C. J. Galvin, X. Chen, A. Aspuru-Guzik, R. G. Gordon, M. J. Aziz, *Nature* **2014**, *505*, 195.

[16] C. S. Sevov, S. K. Samaroo, M. S. Sanford, *Adv. Energy Mater.* **2017**, 7, https://doi.org/10.1002/aenm.201602027.

[17] A. J. Arduengo III, R. Krafczyk, *Org. Chemie* **1998**, *1*, 6.

[18] A. J. Arduengo III, R. L. Harlow, M. Kline, *J. Am. Chem. Soc.* **1991**, *113*, 361.

[19] A. J. Arduengo III, H. V. R. Dias, R. L. Harlow, M. Kline, *J. Am. Chem. Soc.* **1992**, *114*, 5530.

[20] B. S. Tanaseichuk, *Chem. Heterocycl. Compd.* **1974**, *8*, 1173.

[21] T. Hayashi, K. Maeda, *Bull. Chem. Soc. Jpn.* **1960**, *33*, 565.

[22] J. K. Mahoney, D. Martin, F. Thomas, C. E. Moore, A. L. Rheingold, G. Bertrand, *J. Am. Chem. Soc.* **2015**, *137*, 7519.

[23] J. K. Mahoney, D. Martin, F. Thomas, C. E. Moore, A. L. Rheingold, G. Bertrand, *J. Am. Chem. Soc.* **2013**, *135*, 18766.

[24] H. V. Huynh, Y. Han, R. Jothibasu, J. A. Yang, *Organometallics* **2009**, *28*, 5395.

[25] S. T. Handy, M. Okello, *J. Org. Chem.* **2005**, *70*, 1915.

[26] N. Kumar, R. Jain, *J. Heterocycl. Chem.* **2012**, *49*, 370.

[27] K. Periyapperuma, Y. Zhang, D. R. Macfarlane, M. Forsyth, C. Pozo-Gonzalo, P. C. Howlett, *ChemElectroChem* **2017**, 1051.

[28] D. Zhang, Q. Liu, X. Shi, Y. Li, *J. Power Sources* **2012**, *203*, 201.

[29] S. Patil, J. Claffey, A. Deally, M. Hogan, B. Gleeson, L. M. M. Méndez, H. Müller-Bunz, F. Paradisi, M. Tacke, *Eur. J. Inorg. Chem.* **2010**, 1020.

[30] T. Cremer, C. Kolbeck, K. R. J. Lovelock, N. Paape, R. Wölfel, P. S. Schulz, P. Wasserscheid, H. Weber, J. Thar, B. Kirchner, et al., *Chem. - A Eur. J.* **2010**, *16*, 9018.

[31] N. V. Ignat'ev, P. Barthen, A. Kucheryna, H. Willner, P. Sartori, *Molecules* **2012**, *17*, 5319.

[32] L. I. Kruse, C. Kaiser, W. W. De, J. A. Finkelstein, J. S. Frazee, E. L. Hilbert, S. T. Ross, K. E. Flaim, J. L. Sawyer, *J. Med. Chem.* **1990**, *33*, 781.

[33] A. R. Katritzky, G. W. Rewcastle, W.-Q. Fan, *J. Org. Chem.* **1988**, *53*, 5685.

[34] K. Kirk, *J. Org. Chem.* **1978**, *43*, 42.

[35] C. Bakhtiar, E. H. Smith, *J. Chem. Soc. Perkin Trans. 1* **1994**, 239.

[36] F. Zani, P. Mazza, S. Benvenuti, F. Severi, L. Malmusi, G. Vampa, L. Antolini, *Eur. J. Med. Chem.* **1995**, *30*, 729.

[37] J. Kister, G. Assef, G. Mille, J. Metzger, *Can. J. Chem.* **1979**, *57*, 813.

[38] M. C. Kroon, W. Buijs, C. J. Peters, G.-J. Witkamp, *Green Chem.* **2006**, *8*, 241.

[39] B. Gorodetsky, T. Ramnial, N. R. Branda, J. A. C. Clyburne, *Chem. Commun.* **2004**, *1*, 1972.

[40] I. McKenzie, J.-C. Brodovitch, P. W. Percival, T. Ramnial, J. A. C. Clyburne, *J. Am. Chem. Soc.* **2003**, *125*, 11565.

[41] L. P. Hammett, *Chem. Rev.* **1935**, *17*, 125.

[42] C. Hansch, A. Leo, R. W. Taft, *Chem. Rev.* **1991**, *91*, 165.

[43] X. Zhang, L.-X. Ma, X.-D. Li, *Synth. Met.* **2014**, *198*, 357.

[44] J. P. Peterson, M. R. Geraskina, R. Zhang, A. H. Winter, *J. Org. Chem.* **2017**, *82*, 6497.

[45] O. Brugner, T. Reichenbach, M. Sommer, M. Walter, *J. Phys. Chem. A* **2017**, *121*, 2683.

[46] L. P. Hammett, *J. Am. Chem. Soc.* **1937**, *59*, 96.

[47] I. Fumiyasu, S. Hatano, J. Abe, *J. Phys. Org. Chem.* **2007**, *20*, 857.

[48] T. Yamaguchi, M. F. Hilbers, P. P. Reinders, Y. Kobayashi, A. M. Brouwer, J. Abe, *Chem. Commun.* **2015**, *51*, 1375.

[49] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, et al. (Eds), *Gaussian 09, Revision C. 01*, Gaussian, Inc., Wallingford CT **2009**.

[50] C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785.

[51] A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648.

[52] B. Mennucci, E. Cances, J. Tomasi, *J. Phys. Chem. B* **1997**, *101*, 10506.

[53] D. White, J. Sonnenberg, *J. Am. Chem. Soc.* **1966**, *16*, 3825.

[54] S. Kazemiabnavi, Z. Zhang, K. Thornton, S. Banerjee, *J. Phys. Chem. B* **2016**, *120*, 5691.

[55] T. Tugsuz, *Int. J. Quantum Chem.* **2013**, *113*, 715.

[56] N. Shao, X. G. Sun, S. Dai, D. E. Jiang, *J. Phys. Chem. B* **2011**, *115*, 12120.

[57] V. D. Parker, *J. Am. Chem. Soc.* **1976**, *98*, 98.

[58] J. Pommerehne, H. Vestweber, W. Guss, R. F. Mahrt, H. Bassler, M. Porsch, J. Daub, *Adv. Mater.* **1995**, 7.

[59] G. R. Fulmer, A. J. Miller, N. H. Sherden, A. Nudelman, B. M. Stoltz, J. E. Bercaw, K. I. Goldberg, *Organometallics* **2010**, *29*, 2176.

[60] G. Chauvière, B. Bouteille, B. Enanga, C. De Albuquerque, S. L. Croft, M. Dumas, J. Périé, *J. Med. Chem.* **2003**, *46*, 427.

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