JOC The Journal of Organic Chemistry

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Readily Accessible Unsymmetrical Unsaturated 2,6-Diisopropylphenyl N-Heterocyclic Carbene Ligands. Applications in Enantioselective Catalysis

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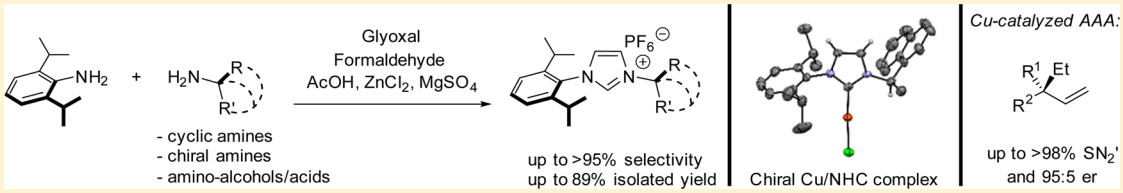
Supporting Information



ABSTRACT: A new multicomponent procedure was applied to the synthesis of (a)chiral bulky unsymmetrical unsaturated 2,6-diisopropylphenyl N-heterocyclic carbene (NHC) precursors with excellent selectivity (up to 95%) and good yields. This approach offers access to new chiral NHC ligands, which have found successful applications in both copper-catalyzed asymmetric allylic alkylation and copper-catalyzed asymmetric borylation.

INTRODUCTION

During the past two decades, N-heterocyclic carbenes (NHCs) have broken through in the field of coordination chemistry.[1] These species have been used as ligands to kinetically stabilize highly reactive, low-valent transition metal complexes and enable high catalytic activity to be achieved.[2] Among the large variety of NHCs described in the literature, C_2-symmetrical ligands bearing the sterically encumbered 2,6-diisopropylphenyl (Dipp) nitrogen substituent, i.e., bis(2,6-diisopropylphenyl)-imidazol-2-ylidene (IPr) and bis(2,6-diisopropylphenyl)-imidazolidin-2-ylidene (SiPr), have on numerous occasions demonstrated significant benefits in multiple modern chemistry applications.[3] On the other hand, unsymmetrical NHCs with increased steric discrimination and distinctive electronic properties have witnessed growing interest in the recent years.[4] Indeed, transition-metal-bearing Dipp-based unsymmetrical NHC have found considerable advantages in terms of reactivity and selectivity toward challenging processes.[5,6] A related type of carbene ligand, the family of cyclic(alkyl)(amino)carbenes (CAACs) developed by Bertrand and coworkers, has allowed important achievements by stabilizing unusual both transition-metal and main group element complexes.[7] However, the strategies to construct unsymmetrical NHC precursors require multiple-step syntheses that, due to time consumption and cost, may limit their industrial applications.[8] Recently, we described an elegant and practical multicomponent strategy that provides access to various unsymmetrical unsaturated (a)chiral N-heterocyclic carbene (U_2-NHC) ligands precursors with high selectivities and good yields.[9] Indeed, by simply mixing an arylamine, an alkylamine, formaldehyde, and glyoxal in acetic acid for few minutes, a wide range of imidazolium salts were obtained with high selectivity (up to 93%). The corresponding U_2-NHC ligands were evaluated and evidenced strong electron donor ability, high steric discrimination, and modular steric demand. This methodology was also successfully applied for the construction of chiral bidentate hydroxyalkyl- and carboxyalkyl-NHC ligands, which demonstrated excellent transfer of the stereoinduction from the chiral center to the metal.[10] Despite the efficiency and flexibility of this multicomponent procedure, the introduction of highly hindered patterns such as the Dipp fragment appeared as a major limitation, affording the desired bulky U_2-NHC precursors with poor yields and selectivities.[9,10] Herein, we disclose a novel multicomponent procedure leading to a wide range of (a)chiral unsymmetrical unsaturated 1-(2,6-diisopropylphenyl)-3-alkylimidazolium salts with high selectivities (up to 95%) and good yields (Figure 1). Moreover, evaluation of this ligand family in copper catalysis demonstrated utility in asymmetric C−B and C−C bond formation.

RESULTS AND DISCUSSION

With the objective of reaching the exclusive formation of the unsymmetrical 1-(2,6-diisopropylphenyl)-3-cycloalkyimidazo-

Received: December 2, 2016
Published: January 18, 2017

DOI: 10.1021/acs.joc.6b02888
J. Org. Chem. 2017, 82, 1880−1887

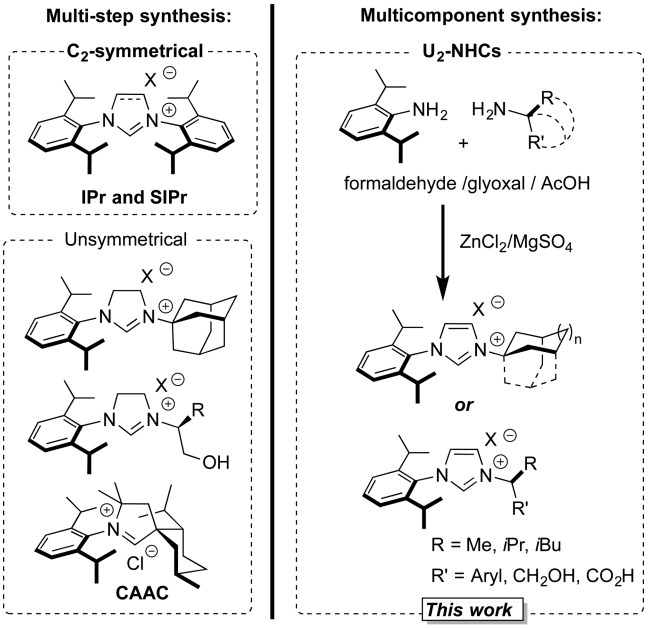
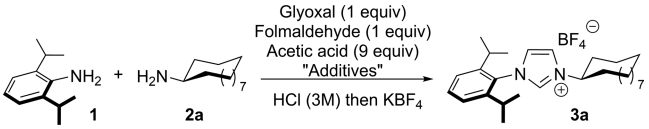


Figure 1. Examples of Dipp-based NHC ligands (left) and a new synthetic route to Dipp-based U_2-NHC ligands (right).

lium salts **3**, we decided to reinvestigate our initial multicomponent procedure by probing various reaction conditions (Table 1). An important point to be taken into consideration when using 2,6-diisopropylaniline (**1**) in such an approach is the inherent low reactivity of this sterically congested amine under typical operational conditions for the synthesis of imidazolium salts.[11] First, using cyclododecanamine as the second partner of the reaction, the modest selectivity and poor yield observed at 40 °C were improved with a slight increase of the temperature to 60 °C (Table 1, entries 1 and 2).

Table 1. Optimization of the Conditions for the Multicomponent Process



entry	additives	T (°C)	selectivity[a] (%)	yield[b] (%)
1	NA[c]	40	57	35
2	NA[c]	60	69	51
3	HCl (1 mol %)[d]	60	73	57
4	HCl (1 equiv)[d]	60	89	89
5	$MgCl_2$(s) (1 equiv)	60	88	73
6	$ZnCl_2$(s) (1 equiv)	60	93	83
7	$ZnCl_2$ (1 equiv)[d]	60	>95	88
8	$ZnCl_2$ (1.2 equiv)[d]	60	>95	94
9	$MgSO_4$ (2 equiv), $ZnCl_2$ (1.2 equiv)[d]	60	>95	>95 (76)
10[e]	$MgSO_4$ (2 equiv), $ZnCl_2$ (1.2 equiv)[d]	60	**>95**	**>95 (89)**
11	$MgSO_4$ (2 equiv)	60	65	46
12	Et_2O	60	45	30

[a]Determined by ^{1}H NMR using tetrachloroethane as an internal standard. [b]NMR yields using tetrachloroethane as an internal standard. Isolated yields presented in parentheses. [c]Not applicable. [d]1 M in Et_2O. [e]KPF_6 was used instead of KBF_4.

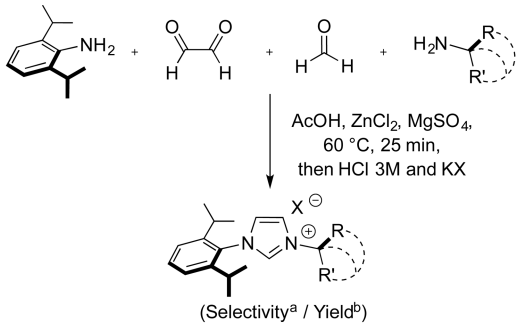
Importantly, a major improvement in both selectivity and yield could be obtained after addition of a stoichiometric amount of hydrochloric acid (Table 1, entry 4).[12] During the screening of Lewis acids, the addition of zinc chloride (1 equiv) in diethyl ether appeared highly beneficial, affording the unsymmetrical NHC precursor with very high selectivity (>95%) and excellent NMR yield (Table 1, entry 7).[13] Interestingly, without affecting selectivity, the addition of magnesium sulfate ($MgSO_4$) could improve the NMR yield to >95% and allowed isolation of the 1-(2,6-diisopropylphenyl)-3-cyclododecylimidazolium salt **3a** in 76% yield (Table 1, entry 9). Finally, replacement of the BF_4^- anion by PF_6^- facilitated the purification procedure and afforded the corresponding imidazolium.PF_6 salts with high 89% isolated yield (Table 1, entry 10).

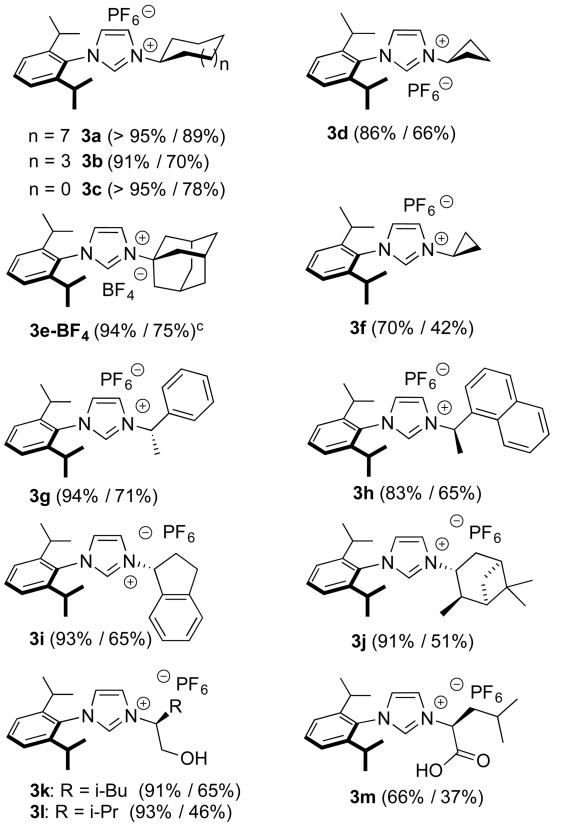
Under the optimized reaction conditions, we extended the scope of the reaction using first a variety of cycloalkylamines (Scheme 1). Similar to the results obtained with cyclododecanamine, the desired U_2-NHC precursors bearing the cyclooctyl and cyclopentyl fragments were obtained with excellent selectivities and good isolated yields. Interestingly, the polycyclic adamantylamine could be efficiently employed in this strategy and afforded perfect selectivity in the preparation of **3e**, the unsaturated analogue of the most effective NHC ligand precursor employed in ruthenium-catalyzed *Z*-selective metathesis.[5] Moreover, while cyclobutylamine reacted quite smoothly (86% selectivity and 66% isolated yield), a noticeable decrease of selectivity was observed with cyclopropylamine leading to a modest 42% isolated yield of the corresponding imidazolium salt **3f**. Importantly, this approach was also applicable to the use of α-substituted chiral amines such as (*S*)-α-methylbenzylamine, (*R*)-1-(1-naphthyl)ethylamine, (1*R*,2*R*,3*R*,5*S*)-isopinocampheylamine, and (*R*)-indanamine allowing for a simple and efficient access to bulky chiral NHC precursors with strong propensity for new applications in selective catalysis (Figure 2).[14,5g] In an effort to further extend the synthetic utility of this multicomponent procedure, the synthesis of chiral bidentate NHC ligand precursors was investigated. Pleasantly, the bulky chiral imidazolium salts **3k** and **3l** derived from L-leucinol and L-valinol were formed with excellent selectivities and isolated in reasonable yields. Under the same conditions, modest selectivity and isolated yield could be obtained with L-leucine.

In order to get a better understanding of the reaction mechanism and to provide insight into the factors governing the selectivity of the multicomponent procedure, we decided to adopt a two-step approach. Importantly, preliminary experiments demonstrated that the procedure involving the combination of $DippNH_2$ **1** and adamantylamine **2e** could be greatly simplified since $ZnCl_2$ and $MgSO_4$ additives had no significant impact on the outcomes of this specific reaction.[15] Therefore, this simplified protocol was selected as a model for the following mechanistic study. First, a stoichiometric amount of $DippNH_2$ **1**, $AdNH_2$ **2e**, and aqueous glyoxal were reacted in the presence of an excess of acetic acid (9 equiv). The ^{1}H NMR analysis of the resulting crude mixture (<5 min reaction) showed preferential formation of the diaryldiimine **4** (>95%) without unequivocal identification of diimine **5** and no detectable amount of dialkyldiimine **6** (Scheme 2, A).[16] The subsequent addition of 1 equiv of aqueous formaldehyde afforded the desired unsymmetrical imidazolium salt **3e-OAc** with high >95% selectivity along with <5% of the symmetrical dialkyl imidazolium salt **7e-OAc** and no detectable amount of

DOI: 10.1021/acs.joc.6b02888
J. Org. Chem. 2017, 82, 1880−1887

Scheme 1. Scope of the Multicomponent Procedure





[a]Determined by ^{1}H NMR analysis. [b]Isolated yields. [c]The purification procedure was facilitated with BF_4^- instead of PF_6^-.

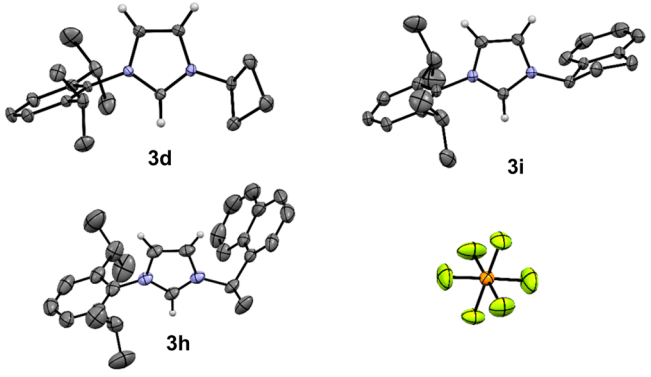
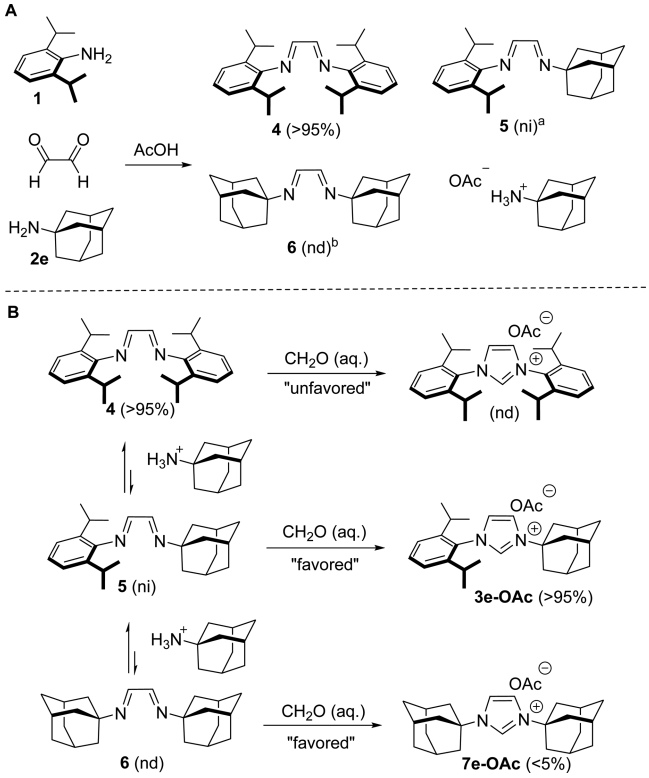


Figure 2. Solid-state structure of a selection of imidazolium salts from single-crystal X-ray diffraction. Displacement ellipsoids are drawn at 50% probability. Most hydrogen atoms and PF_6 anions have been omitted for clarity (N, blue; C, gray; P, orange; F, yellow; H, white.

Scheme 2. Mechanistic Investigation of Unsymmetrical Salt Synthesis. (A) Ratio in Diimines after Condensation with Aqueous Glyoxal and Excess Acetic Acid (<5 min Reaction). (B) Selectivity of the Cyclization Procedure in the Presence of Aqueous Formaldehyde



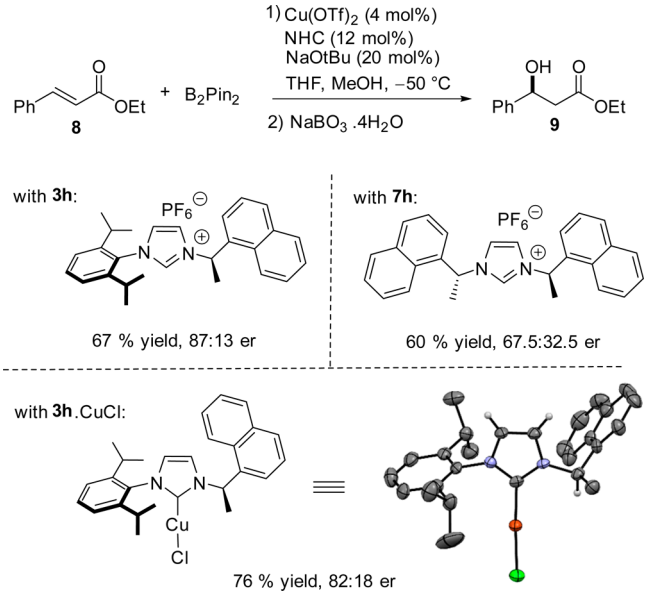
[a]Not identified. [b]Not detected.

the imidazolium salt precursor of IPr (Scheme 2, B). In addition, it was observed that the sterically congested diaryldiimine **4** was poorly reactive toward cyclization under our reaction conditions, whereas the dialkyldiimine **6** was able to afford easily the corresponding cyclized imidazolium salt **7e-OAc**.[16] Nevertheless, when the cyclization of the dialkyldiimine **6** was performed in the presence of $DippNH_2$ **1** (2 equiv), the major product was the unsymmetrical salt **3e-OAc** (**3e-OAc**/**7e-OAc** ratio = 94:6).[16] Consequently, the high selectivity in favor of the unsymmetrical salt **3e-OAc** may be explained by the fact that the cyclizations of the symmetrical diimines are slower than (i) the equilibration reactions between the three diimines[17] and (ii) the cyclization of the unsymmetrical diimine **5**.[18]

The asymmetric conjugate addition of nucleophiles to electron-deficient alkenes represents one of the most powerful methods to form C−C and C-heteroelement bonds.[19] In the recent years, enantioselective conjugate addition of diboron reagents to α,β-unsaturated carbonyl compounds catalyzed by Cu-based NHC/complexes has attracted considerable interest.[20] With our new series of unsymmetrical chiral imidazolium salts in hand, we decided to evaluate their potential as chiral ligands in copper-catalyzed borate addition to ethyl cinnamate (**8**). The chiral NHC precursor **3h** displaying a demanding steric environment was initially selected, and the in situ generated Cu/NHC complex afforded the desired product **9** in good 67% isolated yield and 87:13 enantiomeric ratio (Scheme 3). On the other hand, the use of the C_2-symmetrical ligand

DOI: 10.1021/acs.joc.6b02888
J. Org. Chem. 2017, 82, 1880−1887

Scheme 3. Copper/NHC-Catalyzed Asymmetric Borylation[a]



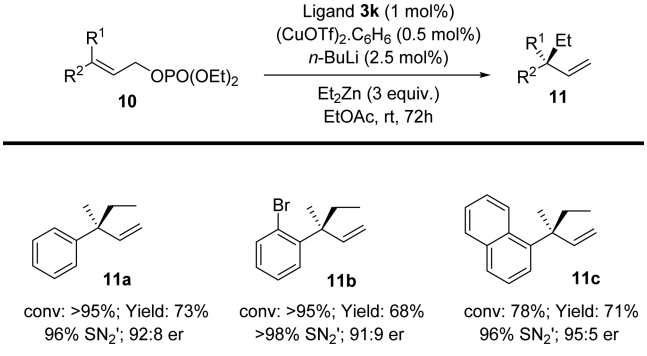
[a]Enantiomeric ratios were obtained from chiral HPLC analysis.

precursor analogue **7h** resulted in poor enantiocontrol (67.5:32.5 er), which demonstrates unambiguously the advantage provided by the sterically congested unsymmetrical chiral ligand. Moreover, it should be noted that the isolated and fully characterized, including X-ray diffraction analysis, Cu/NHC complex **3h**.CuCl catalyzed efficiently the transformation to form product **9** with an 82:18 enantiomeric ratio.[21]

To further demonstrate the potential of the newly developed ligand family, the chiral bidentate hydroxyalkyl ligand precursor **3k** was evaluated via copper-catalyzed asymmetric allylic alkylation to form all-carbon quaternary centers.[6c,10] Interestingly, the catalytic system prepared in situ by deprotonation of the imidazolium salt **3k** with *n*-butyllithium in the presence of copper(I) triflate promoted efficiently the reaction between diethylzinc and allylphosphates **10** to form the desired quaternary carbon centers with excellent regio- (>96% SN_2') and high enantioselectivities (up to 95:5 er) (Scheme 4).

In conclusion, a multicomponent synthesis of sterically congested unsymmetrical unsaturated imidazolium salts has been developed. This practical, low-cost, and efficient methodology allows for the preparation in high yields and high selectivities of a large variety of NHC ligand precursors bearing the sterically hindered 2,6-diisopropylphenyl moieties. The new chiral monodentate ligands have found application in copper-catalyzed asymmetric boronate conjugate addition to unsaturated esters. Significantly, with unsymmetrical chiral monodentate ligand, the chirality transfer is enhanced by the presence of the 2,6-diisopropylphenyl fragment. Moreover, the multicomponent procedure was also successfully applied to the construction of chiral bidentate ligands, which demonstrated excellent control in copper-catalyzed allylic substitution with allyl phosphates to form all-carbon quaternary centers with high regio- and enantioselectivities. The use of this ligand family to construct new transition-metal catalysts along with their applications in asymmetric transformations is currently under intensive investigation in our laboratory and will be reported in due course.

Scheme 4. Copper-Catalyzed AAA with Allylphosphates[a,b]



[a]Conversions and SN_2' ratios were determined by ^1H NMR analysis of the crude mixture. [b]Enantiomeric ratios were obtained from GC and HPLC analysis of the substitution product.

EXPERIMENTAL SECTION

General Experimental Procedures. All commercial chemicals were used as received unless otherwise noted. 1,4-Bis(2,6-diisopropylphenyl)-1,4-diaza-1,3-butadiene[11a] (**4**) and *N*,*N*′-bis(1-adamantyl)-ethanediimine[22] (**6**) were obtained following already described procedures. Reactions were monitored by thin-layer chromatography (TLC) carried out on silica gel plates (60F254) using UV light as visualizing agent and $KMnO_4/K_2CO_3$/NaOH in water for staining. Column chromatography was performed with silica gel (spherical, particle size 40 μm, neutral). The eluents employed are reported as volume (volume percentages). Melting points were measured on a standard melting point apparatus in open capillary tubes and are uncorrected. Optical rotations were recorded on a polarimeter and are uncorrected. ^1H (400 MHz), ^{13}C (101 MHz), ^{19}F (376 MHz), ^{31}P (162 MHz), and ^{11}B (128 MHz) NMR spectra were recorded on a NMR spectrometer with complete proton decoupling for nucleus other than ^1H. Chemical shifts are reported in parts per million with the solvent resonance as the internal standard ($CDCl_3$: ^1H, δ 7.26 ppm; ^{13}C, δ 77.16 ppm; CD_3OD: ^1H, δ 3.31 ppm; ^{13}C, δ 49.00 ppm); ^{19}F chemical shifts are reported with $CFCl_3$ (δ = 0.0 ppm) as the external standard; ^{31}P chemical shifts are reported with H_3PO_4 (δ = 0.0 ppm) as the external standard; ^{11}B chemical shifts are reported with $BF_3.Et_2O$ (δ = 0.0 ppm) as the external standard. Coupling constants (J) are reported in hertz (Hz). Multiplicities are reported using following abbrevations: s = singlet, br s = broad singlet, d = doublet, dd = double doublet, ddd = double double doublet, dt = double triplet, t = triplet, q = quartet, quint = quintet, sept = septet, m = multiplet. High-resolution mass spectroscopy (HMRS) was recorded on a Q-TOF.

General Procedure for the Multicomponent Synthesis of Unsymmetrical Imidazolium Salts 3. The reaction was performed in an open vessel under air atmosphere. In a round-bottomed flask were placed 2,6-diisopropylaniline (1 mmol, 1.0 equiv), alkylamine (1 mmol, 1.0 equiv), and acetic acid (4.5 mmol, 4.5 equiv), and then the mixture was heated at 60 °C for 5 min and $MgSO_4$ (2 mmol, 2 equiv) was added (mixture A). In another round-bottomed flask were placed glyoxal (1 mmol, 1.0 equiv, 40% weight in aqueous solution), formaldehyde (1 mmol, 1.0 equiv, 37% weight in aqueous solution), and acetic acid (4.5 mmol, 4.5 equiv), and then the mixture was heated at 60 °C for 5 min and $ZnCl_2$ (1.2 mmol, 1.2 equiv, 1 M in Et_2O) was added (mixture B). At 60 °C, mixture B was added to mixture A, and the resulting mixture was stirred at 60 °C for 25 min and then cooled to room temperature. An aliquot of the crude reaction mixture was taken, and ^1H NMR was recorded to determine the selectivity of the reaction, which was calculated by integration of characteristic signals of the different compounds. Dichloromethane (25 mL) and 3 M aqueous solution of HCl (50 mL) were added, and the resulting mixture was stirred at room temperature for 1 h. Then the organic layer was separated. Water (50 mL) and potassium hexafluorophosphate or potassium tetrafluoroborate (1.0 mmol, 1.0 equiv) were added, and the

DOI: 10.1021/acs.joc.6b02888
J. Org. Chem. 2017, 82, 1880−1887

mixture was stirred at room temperature for 1 h. The organic layer was separated, dried over magnesium sulfate, and filtered, and the solvents were evaporated under reduced pressure. The desired imidazolium salt was isolated either by flash chromatography on silica gel or recrystallization.

General Procedure for the Multicomponent Synthesis of Unsymmetrical Imidazolium Salts 7. In a round-bottomed flask were placed alkylamine (0.53 mmol, 1 equiv) and acetic acid (1.20 mmol, 2.25 equiv), and then the mixture was heated at 40 °C for 5 min (mixture A). In another round-bottomed flask were placed glyoxal (0.26 mmol, 0.5 equiv, 40% wt in aqueous solution), formaldehyde (0.026 mmol, 0.5 equiv, 37% wt in aqueous solution), and acetic acid acid (1.20 mmol, 2.25 equiv), and then the mixture was heated at 40 °C for 5 min (mixture B). At 40 °C, mixture B was added to mixture A, and the resulting mixture was stirred at 40 °C for 25 min and then cooled to room temperature. Dichloromethane (25 mL) was added, and the organic layer was washed with brine (3 × 10 mL). The organic layer was separated, water (5 mL) and potassium hexafluorophosphate (48 mg, 0.26 mmol) were added, and the mixture was stirred at room temperature for 1 h. The organic layer was separated, dried over magnesium sulfate, and filtered, and the solvents were evaporated under reduced pressure. The desired imidazolium salt **7** was isolated without further purification.

General Procedure for the Synthesis of Copper Complexes 3·CuCl. Hexafluorophosphate salt **3** (0.24 mmol, 1 equiv) was loaded on an anion-exchange resin Dowex 1 × 2 chloride form (2.4 mL of resin for 0.24 mmol of hexafluorophosphate salt) with milli-Q water/acetone (1/1) as an eluent. After removal of solvents under reduced pressure, the residue was dissolved in dichloromethane, dried over $MgSO_4$, filtered, and concentrated under reduced pressure to give the corresponding chloride salt. In a dry Schlenk tube, under argon atmosphere, were placed Ag_2O (0.24 mmol, 1 equiv), chloride imidazolium salt (0.24 mmol, 1 equiv), dichloromethane (25 mL), and 4 Å molecular sieves. The mixture was stirred at room temperature overnight in darkness (alumina foil), then CuCl (0.24 mmol, 1 equiv) was added, and the resulting mixture was stirred at room temperature for 4 h in darkness. The mixture was then filtered on a Celite bed with dichloromethane, and the solvent was removed under reduced pressure. The crude solid was precipitated in dichloromethane/pentane (1/5) to afford the desired copper complex **3**·CuCl.

General Procedure for Copper-Catalyzed Asymmetric Borylation. *Starting from the Imidazolium Salts (**3h** and **7h**).* In the glovebox, $Cu(OTf)_2$ (4 mol %), ligand (12 mol %), NaOtBu (20 mol %), and THF (1 mL) were added in a flame-dried microwave flask. The resulting mixture was stirred at room temperature for 10 min, and bis(pinacolato)diboron (0.55 mmol, 1.1 equiv) was added. The mixture was stirred for an extra 10 min, and the solution was cooled to −50 °C. Then a solution containing MeOH (1.0 mmol, 2 equiv), ethyl cinnamate (0.5 mmol, 1 equiv), and THF (1 mL) was slowly added, and the mixture was stirred 3 h at −50 °C. Then the oxidation step was carried out with the successive addition of $NaBO_3 \cdot 4H_2O$ (2.5 mmol, 5 equiv) and water (2 mL), after which the mixture was stirred at room temperature for 3 h. Water (10 mL) was added, and the aqueous layer was extracted with ethyl acetate (3 × 20 mL). The organic layers were combined, washed with brine (20 mL), dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was purified by silica gel chromatography (pentane/diethyl ether, 8/2) to give the corresponding product **9** as a colorless oil.

*Starting from the Isolated Copper Complex (**3h**·CuCl).* In the glovebox, **3h**·CuCl (4 mol %), Cs_2CO_3 (8 mol %), bis(pinacolato)-diboron (0.55 mmol, 1.1 equiv), and THF (1 mL) were added in a microwave flask. The resulting mixture was stirred at room temperature for 10 min, and the solution was cooled to −50 °C. Then a solution containing MeOH (1.0 mmol, 2 equiv), ethyl cinnamate (0.5 mmol, 1 equiv), and THF (1 mL) was slowly added at −50 °C, and the mixture was stirred 3 h at −50 °C. Then the oxidation step was carried out with the successive addition of $NaBO_3 \cdot 4H_2O$ (1 mmol, 5 equiv) and water (1 mL), after which the mixture was stirred at room temperature for 3 h. Water (5 mL) was added, and the aqueous layer was extracted with ethyl acetate (3 × 10 mL). The organic layers were combined, washed with brine (10 mL), dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was purified by silica gel chromatography (pentane/diethyl ether 8:2) to give the corresponding product **9** as a colorless oil.

General Procedure for Copper-Catalyzed Asymmetric Allylic Alkylation. A flame-dried Schlenk tube, under an argon atmosphere, was charged with $[Cu(OTf)_2] \cdot C_6H_6$ (0.5 mol %) and **3k** (1 mol %). Freshly distilled ethyl acetate (0.25 mL) was then added, and the reaction mixture was stirred 10 min at room temperature followed by the addition of *n*-BuLi (1.6 M in hexanes, 2.5 mol %). The reaction was stirred 10 min at room temperature, and Et_2Zn (1.5 mmol, 3 equiv) was added. After the reaction vessel was cooled to 0 °C, the phosphate (0.5 mmol, 1 equiv) was added. As soon as the addition of the substrate was completed, the ice bath was removed. The reaction mixture was stirred at room temperature until total consumption of the phosphate. Upon completion of the reaction, a 1 M aqueous solution of HCl was added, and the compound was extracted with diethyl ether. The combined organic layers were then washed with a saturated aqueous solution of $NaHCO_3$ and brine and dried over $MgSO_4$. The solvents were carefully removed under vacuum. The crude product was purified by silica gel chromatography (pentane) to isolate the corresponding product **11** as a colorless oil.

Characterization Data of Isolated Compounds. *3-Cyclododecyl-1-(2,6-diisopropylphenyl)imidazolium Hexafluorophosphate (**3a**).* Selectivity **3a**-OAc/bis$_{C12}$-OAc/IPr-OAc = >95/traces/traces. Purification over silica gel (dichloromethane then dichloromethane/ethyl acetate 9/1). Pale brown solid (481 mg, 89%). Mp: 173 °C. ^{1}H NMR (400 MHz, chloroform-*d*): δ 8.61 (dd, J = 1.7, 1.7 Hz, 1H), 7.66 (dd, J = 1.8, 1.8 Hz, 1H), 7.49 (t, J = 7.8 Hz, 1H), 7.33−7.17 (m, 3H), 4.73−4.67 (m, 1H), 2.21−2.06 (m, 4H), 1.95−1.70 (m, 2H), 1.61−1.18 (m, 18H), 1.13 (d, J = 7.6 Hz, 6H), 1,11 (d, J = 7.6 Hz, 6H). ^{13}C NMR (101 MHz, chloroform-*d*) δ 145.4, 135.7, 132.0, 130.15, 125.4, 124.7, 121.7, 59.7, 30.2, 28.9, 24.3, 24.0, 23.8, 23.5, 23.3, 23.3, 21.3. ^{19}F NMR (376 MHz, chloroform-*d*): δ −72.16 (d, J = 713 Hz). ^{31}P NMR (162 MHz, chloroform-*d*): δ −144.32 (sept, J = 713 Hz). HRMS (ESI) calcd for $C_{27}H_{43}N_2^+$ (M − PF_6): m/z 395.34207, found 395.3422 (0 ppm). Anal. Calcd for $C_{27}H_{43}F_6N_2P$: C, 59.99; H, 8.02; N, 5.18. Found: C, 59.85; H, 7.77; N, 4.99.

*3-Cyclooctyl-1-(2,6-diisopropylphenyl)imidazolium Hexafluorophosphate (**3b**).* Selectivity **3b**-OAc/bis$_{C8}$-OAc/IPr-OAc = 91/9/0. Purification over silica gel (dichloromethane) followed by recrystallization in dichloromethane/cyclohexane. White solid (339 mg, 70%). Mp: 196 °C. ^{1}H NMR (400 MHz, chloroform-*d*): δ 8.63 (dd, J = 1.7, 1.7 Hz, 1H), 7.67 (dd, J = 1.9, 1.9 Hz, 1H), 7.52 (t, J = 7.8 Hz, 1H), 7.30 (s, 1H), 7.28 (s, 1H), 7.25 (dd, J = 1.5, 1.5 Hz, 1H), 4.82 (quint., J = 7.3 Hz, 1H), 2.28−2.01 (m, 6H), 1.91−1.52 (m, 10H), 1.17 (d, J = 6.8 Hz, 6H), 1.14 (d, J = 6.8 Hz, 6H). ^{13}C NMR (101 MHz, chloroform-*d*): δ 145.5, 135.3, 132.0, 130.2, 125.3, 124.7, 121.3, 62.4, 33.9, 28.9, 26.4, 25.4, 24.4, 24.0, 23.8. ^{19}F NMR (376 MHz, chloroform-*d*): δ −72.20 (d, J = 713 Hz). ^{31}P NMR (162 MHz, chloroform-*d*): δ −144.29 (sept, J = 713 Hz). HRMS (ESI) calcd for $C_{23}H_{35}N_2^+$ (M − PF_6) m/z 339.27947, found 339.2798 (1 ppm). Anal. Calcd for $C_{23}H_{35}F_6N_2P$: C, 57.02; H, 7.28; N, 5.78. Found: C, 57.05; H, 6.87; N, 5.68.

*3-Cyclopentyl-1-(2,6-diisopropylphenyl)imidazolium Hexafluorophosphate (**3c**).* Selectivity **3c**-OAc/bis$_{C5}$-OAc/IPr-OAc = 96/4/0. Purification over silica gel (dichloromethane). Pale brown solid (345 mg, 78%). Mp: 172 °C. ^{1}H NMR (400 MHz, chloroform-*d*): δ 8.55 (dd, J = 1.7, 1.7 Hz, 1H), 7.68 (dd, J = 1.9, 1.9 Hz, 1H), 7.51 (t, J = 7.8 Hz, 1H), 7.32−7.24 (m, 3H), 4.98 (quint, J = 7.1 Hz, 1H), 2.55−2.32 (m, 2H), 2.21 (sept, J = 6.7 Hz, 2H), 2.09−1.67 (m, 6H), 1.15 (d, J = 6.8 Hz, 6H), 1.12 (d, J = 6.8 Hz, 6H). ^{13}C NMR (101 MHz, chloroform-*d*): δ 145.4, 135.5, 132.0, 130.1, 125.5, 124.7, 121.5, 62.1, 33.5, 28.8, 24.3, 23.9, 23.8. ^{19}F NMR (376 MHz, chloroform-*d*): δ −72.44 (d, J = 713 Hz). ^{31}P NMR (162 MHz, chloroform-*d*): δ −144.37 (sept, J = 713 Hz). HRMS (ESI) calcd for $C_{20}H_{29}N_2^+$ (M − PF_6) m/z 297.23307, found 297.2331 (0 ppm). Anal. Calcd for $C_{20}H_{29}F_6N_2P$: C, 54.30; H, 6.61; N, 6.33. Found: C, 54.72; H, 6.77; N, 6.39.

DOI: 10.1021/acs.joc.6b02888
J. Org. Chem. 2017, 82, 1880−1887

*3-Cyclobutyl-1-(2,6-diisopropylphenyl)imidazolium Hexafluorophosphate (**3d**).* Selectivity **3d**-OAc/bis$_{C4}$-OAc/IPr-OAc = 86/14/0. Purification over silica gel (dichloromethane/pentane 8/2 then dichloromethane). Pale brown solid (283 mg, 66%). Single crystals of **3d** were obtained by slow evaporation of a saturated solution in dichoromethane/pentane. Mp: 161 °C. ^{1}H NMR (400 MHz, chloroform-*d*): δ 8.55 (dd, J = 1.7, 1.7 Hz, 1H), 7.78 (dd, J = 1.8, 1.8 Hz, 1H), 7.52 (t, J = 7.8 Hz, 1H), 7.30 (s, 1H), 7.28 (s, 1H), 7.27–7.24 (m, 1H), 5.13 (quint, J = 8.5 Hz, 1H), 2.74–2.62 (m, 2H), 2.58–2.44 (m, 2H), 2.22 (sept, J = 6.8 Hz, 2H), 2.06–1.88 (m, 2H), 1.16 (d, J = 6.8 Hz, 6H), 1.12 (d, J = 6.8 Hz, 6H). ^{13}C NMR (101 MHz, chloroform-*d*): δ 145.5, 135.1, 132.0, 130.1, 125.4, 124.7, 121.4, 54.0, 30.7, 28.7, 24.4, 23.9, 14.6. ^{19}F NMR (376 MHz, chloroform-*d*): δ −72.47 (d, J = 713 Hz). ^{31}P NMR (162 MHz, chloroform-*d*): δ −144.35 (sept, J = 713 Hz). HRMS (ESI) calcd for $C_{19}H_{27}N_2^+$ (M − PF_6): m/z 283.21687, found 283.2169 (0 ppm). Anal. Calcd for $C_{19}H_{27}F_6N_2P$: C, 53.27; H, 6.35; N, 6.54. Found: C, 53.75; H, 6.38; N, 6.29.

*3-Adamantyl-1-(2,6-diisopropylphenyl)imidazolium Tetrafluoroborate (**3e-BF$_4$**).* Selectivity **3e**-OAc/7e-OAc/IPr-OAc = 94/6/0. Purification over silica gel (dichloromethane then dichloromethane/ethyl acetate 9/1) following by recrystallization in ethyl acetate. White solid (1.9 g, 75% from 5.6 mmol of corresponding alkylamine). Mp: 218 °C. ^{1}H NMR (400 MHz, chloroform-*d*): δ 8.83 (dd, J = 1.7, 1.7 Hz, 1H), 7.94 (dd, J = 1.9, 1.9 Hz, 1H), 7.51 (t, J = 7.8 Hz, 1H), 7.31 (dd, J = 1.9, 1.9 Hz, 1H), 7.29 (s, 1H), 7.27 (s, 1H), 2.36–2.25 (m, 9H), 2.20 (sept, J = 6.8 Hz, 2H), 1.87–1.74 (m, 6H), 1.18 (d, J = 6.8 Hz, 6H), 1.14 (d, J = 6.8 Hz, 6H). ^{13}C NMR (101 MHz, chloroform-*d*): δ 145.4, 134.5, 131.8, 130.54, 125.1, 124.6, 120.4, 61.6, 42.6, 35.2, 29.6, 28.8, 24.3, 24.0. ^{19}F NMR (376 MHz, chloroform-*d*): δ −151.57. ^{11}B NMR (128 MHz, chloroform-*d*): δ −1.02. HRMS (ESI) calcd for $C_{25}H_{35}N_2^+$ (M − BF_4): m/z 363.28002, found 363.2799 (0 ppm).

*3-Cyclopropyl-1-(2,6-diisopropylphenyl)imidazolium Hexafluorophosphate (**3f**).* Selectivity **3f**-OAc/bis$_{C3}$-OAc/IPr-OAc = 70/26/4. Purification over silica gel (dichloromethane/pentane 8/2 then dichloromethane). Pale brown solid (174 mg, 42%). Mp: 69 °C. ^{1}H NMR (400 MHz, chloroform-*d*): δ 8.62 (dd, J = 1.6, 1.6 Hz, 1H), 7.63 (dd, J = 1.9, 1.9 Hz, 1H), 7.53 (t, J = 7.9 Hz, 1H), 7.31 (s, 1H), 7.29 (s, 1H), 7.21 (dd, J = 1.9, 1.8 Hz, 1H), 4.02–3.94 (m, 1H), 2.23 (sept, J = 6.8 Hz, 2H), 1.33–1.22 (m, 4H), 1.17 (d, J = 6.8 Hz, 6H), 1.13 (d, J = 6.8 Hz, 6H). ^{13}C NMR (101 MHz, chloroform-*d*): δ 145.5, 137.2, 132.1, 130.0, 125.0, 124.7, 123.7, 32.1, 28.7, 24.4, 23.9, 7.4. ^{19}F NMR (376 MHz, chloroform-*d*): δ −72.58 (d, J = 714 Hz). ^{31}P NMR (162 MHz, chloroform-*d*): δ −144.42 (sept, J = 713 Hz). HRMS (ESI) calcd for $C_{18}H_{25}N_2^+$ (M − PF_6): m/z 269.20177, found 269.2018 (0 ppm).

*(S)-1-(2,6-Diisopropylphenyl)-3-(1-phenylethyl)imidazolium Hexafluorophosphate (**3g**).* Selectivity **3g**-OAc/bis$_{PhEt}$-OAc/IPr-OAc = 94/6/0. Purification over silica gel (dichloromethane). Pale brown solid (341 mg, 71%). m. p.: 178 °C. $[\alpha]_D^{20}$: −25.4 (c = 1, chloroform). ^{1}H NMR (400 MHz, chloroform-*d*): δ 8.53 (dd, J = 1.7, 1.7 Hz, 1H), 7.66 (dd, J_1 = 1.9, 1.9 Hz, 1H), 7.51 (t, J = 7.9 Hz, 1H), 7.46–7.35 (m, 5H), 7.32–7.23 (m, 3H), 5.98 (q, J = 7.0 Hz, 1H), 2.26 (sept, J = 6.8 Hz, 1H), 2.11 (sept, J = 6.8 Hz, 1H), 2.02 (d, J = 7.0 Hz, 3H), 1.15 (d, J = 6.8 Hz, 3H), 1.13 (d, J = 6.8 Hz, 3H), 1.11 (d, J = 6.8 Hz, 3H), 1.06 (d, J = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, chloroform-*d*): δ 145.5, 145.3, 137.9, 132.1, 130.1, 129.8, 126.9, 125.2, 124.8, 124.7, 121.8, 60.6, 28.8, 28.8, 24.4, 24.1, 23.9, 20.7. ^{19}F NMR (376 MHz, chloroform-*d*): δ −72.28 (d, J = 713 Hz). ^{31}P NMR (162 MHz, chloroform-*d*): δ −144.27 (sept, J = 713 Hz). HRMS (ESI) calcd for $C_{23}H_{29}N_2^+$ (M − PF_6): m/z 333.23252, found 333.2330 (1 ppm).

*(R)-1-(2,6-Diisopropylphenyl)-3-((1-(naphthalen-1-yl)ethyl)-imidazolium Hexafluorophosphate (**3h**).* Selectivity **3h**-OAc/7h-OAc/IPr-OAc = 83/17/0. Purification over silica gel (diethyl ether/dichloromethane 9/1). Pale brown solid (346 mg, 65%). Single crystals of **3h** were obtained by slow evaporation of a saturated solution in dichloromethane/pentane. Mp: 214 °C. $[\alpha]_D^{20}$: −36.2 (c = 1, chloroform). ^{1}H NMR (400 MHz, chloroform-*d*): δ 8.43 (dd, J = 1.7, 1.7 Hz, 1H), 7.94–7.87 (m, 3H), 7.74–7.71 (m, 1H), 7.63 (dd, J = 1.9, 1.9 Hz, 1H), 7.58–7.49 (m, 3H), 7.45 (t, J = 7.8 Hz, 1H), 7.23–7.19 (m, 3H), 6.71 (q, J = 6.8 Hz, 1H), 2.17 (d, J = 6.9 Hz, 3H), 2.14–2.03 (m, 2H), 1.07 (d, J = 6.8 Hz, 3H), 1.04 (d, J = 6.8 Hz, 3H), 1.03 (d, J = 6.8 Hz, 3H), 0.91 (d, J = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, chloroform-*d*): δ 145.4, 145.2, 135.7, 134.2, 132.1, 131.9, 131.0, 130.4, 129.9, 129.6, 127.8, 126.6, 125.6, 125.2, 125.2, 124.7, 124.7, 122.3, 121.8, 57.0, 28.7, 28.7, 24.1, 24.1, 24.1, 23.8, 20.8. ^{19}F NMR (376 MHz, chloroform-*d*): δ −72.11 (d, J = 713 Hz). ^{31}P NMR (162 MHz, chloroform-*d*): δ −144.16 (sept, J = 713 Hz). HRMS (ESI) calcd for $C_{27}H_{31}N_2^+$ (M − PF_6): m/z 383.24817, found 383.2485 (1 ppm). Anal. Calcd for $C_{27}H_{31}F_6N_2P$: C, 61.36; H, 5.91; N, 5.30. Found: C, 61.74; H, 5.91; N, 5.24.

*(R)-3-(2,3-Dihydroinden-1-yl)-1-(2,6-diisopropylphenyl)-imidazolium Hexafluorophosphate (**3i**).* Selectivity **3i**-OAc/bis$_{Ind}$-OAc/IPr-OAc = 93/7/0. Purification over silica gel (dichloromethane) followed by recrystallization in dichloromethane/cyclohexane. White solid (320 mg, 65%). Single crystals of **3i** were obtained by slow evaporation of a saturated solution in dichloromethane/pentane. Mp: 205 °C. $[\alpha]_D^{20}$: +13.3 (c = 1, chloroform). ^{1}H NMR (400 MHz, chloroform-*d*): δ 8.54 (dd, J = 1.7, 1.7 Hz, 1H), 7.53 (t, J = 7.8 Hz, 1H), 7.45–7.35 (m, 3H), 7.32–7.23 (m, 5H), 6.29 (dd, J = 7.8, 4.2 Hz, 1H), 3.27–2.90 (m, 3H), 2.41–2.17 (m, 3H), 1.18 (d, J = 6.8 Hz, 3H), 1.16 (d, J = 6.8 Hz, 3H), 1.15 (d, J = 6.8 Hz, 6H). ^{13}C NMR (101 MHz, chloroform-*d*): δ 145.6, 145.3, 144.5, 137.8, 135.7, 132.2, 130.6, 130.0, 128.2, 125.9, 125.6, 125.0, 124.9, 124.8, 121.7, 66.0, 34.5, 30.4, 28.9, 28.8, 24.3, 24.1. ^{19}F NMR (376 MHz, chloroform-*d*): δ −72.30 (d, J = 713 Hz). ^{31}P NMR (162 MHz, chloroform-*d*): δ −144.27 (sept, J = 713 Hz). HRMS (ESI) calcd for $C_{24}H_{29}N_2^+$ (M − PF_6): m/z 345.23252, found 345.2327 (0 ppm). Anal. Calcd for $C_{24}H_{29}F_6N_2P$: C, 58.77; H, 5.96; N, 5.71. Found: C, 58.64; H, 6.24; N, 5.50.

*(1R,2R,3R,5S)-1-(2,6-Diisopropylphenyl)-3-(isopinocampheyl)-imidazolium Hexafluorophosphate (**3j**).* Selectivity **3j**-OAc/bis-C$_{Camph}$-OAc/IPr-OAc = 91/9/0. Purification over silica gel (diethyl ether/dichloromethane 9/1). White solid (260 mg, 51%). Mp: 177 °C. $[\alpha]_D^{20}$: −3.5 (c = 1, chloroform). ^{1}H NMR (400 MHz, chloroform-*d*): δ 8.78 (dd, J = 1.7, 1.7 Hz, 1H), 7.74 (dd, J = 1.9, 1.9 Hz, 1H), 7.52 (t, J = 7.8 Hz, 1H), 7.35 (dd, J_1 = 1.9, 1.9 Hz, 1H), 7.34–7.24 (m, 2H), 5.08 (dt, J = 10.2, 7.2 Hz, 1H), 2.97–2.85 (m, 1H), 2.68–2.57 (m, 1H), 2.39–2.20 (m, 2H), 2.19–2.01 (m, 3H), 2.03–1.94 (m, 2H), 1.29 (s, 3H), 1.20–1.11 (m, 15H), 1.09 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.7, 145.3, 136.9, 132.1, 130.0, 126.3, 124.9, 124.6, 120.6, 60.8, 47.4, 45.8, 41.4, 39.1, 36.2, 35.4, 29.0, 28.9, 28.1, 24.5, 24.4, 24.0, 23.7, 23.1, 19.7. ^{19}F NMR (376 MHz, chloroform-*d*): δ −72.05 (d, J = 713 Hz). ^{31}P NMR (162 MHz, chloroform-*d*): δ −144.28 (sept, J = 714 Hz). HRMS (ESI) calcd for $C_{25}H_{37}N_2^+$ (M − PF_6): m/z 365.29512, found 365.2953 (0 ppm). Anal. Calcd for $C_{25}H_{37}F_6N_2P$: C, 58.81; H, 7.31; N, 5.49. Found: C, 58.94; H, 7.57; N, 5.79.

*(S)-1-(2,6-Diisopropylphenyl)-3-(1-hydroxy-4-methylpentan-2-yl)imidazolium Hexafluorophosphate (**3k**).* Selectivity **3k**-OAc/bis$_{LeuOH}$-OAc/IPr-OAc = 91/4.5/4.5. Purification over silica gel (dichloromethane/acetone 9/1). Brown glassy solid (309 mg, 65%). $[\alpha]_D^{20}$: −4.8 (c = 1, chloroform). ^{1}H NMR (400 MHz, chloroform-*d*): δ 8.52 (dd, J = 1.8, 1.8 Hz, 1H), 7.73 (dd, J = 1.8, 1.8 Hz, 1H), 7.53 (t, J = 7.8 Hz, 1H), 7.36–7.24 (m, 3H), 4.77–4.65 (m, 1H), 3.95 (dd, J = 12.2, 3.4 Hz, 1H), 3.71 (dd, J = 12.2, 7.6 Hz, 1H), 2.90 (br s, 1H), 2.34–2.16 (m, 2H), 1.96–1.89 (m, 1H), 1.76–1.64 (m, 1H), 1.52–1.36 (m, 1H), 1.16 (d, J = 6.8 Hz, 3H), 1.14 (d, J = 6.9 Hz, 3H), 1.12 (d, J = 6.7 Hz, 6H), 0.94 (d, J = 6.5 Hz, 3H), 0.93 (d, J = 6.7 Hz, 3H). ^{13}C NMR (101 MHz, chloroform-*d*): δ 145.7, 145.3, 136.6, 132.1, 130.0, 125.1, 124.8, 124.6, 121.4, 64.2, 62.0, 38.5, 28.8, 28.6, 25.0, 24.2, 24.0, 24.0, 23.9, 22.5, 21.7. ^{31}P NMR (162 MHz, chloroform-*d*): δ −144.32 (sept, J = 713 Hz). ^{19}F NMR (376 MHz, chloroform-*d*): δ −71.83 (d, J = 713 Hz). HRMS (ESI) calcd for $C_{21}H_{33}N_2O^+$ (M − PF_6): m/z 329.25929, found 329.2596 (0 ppm). Anal. Calcd for $C_{21}H_{33}F_6N_2OP$: C, 53.16; H, 7.01; N, 5.90. Found: C, 53.40; H, 7.11; N, 5.98.

*(S)-1-(2,6-Diisopropylphenyl)-3-(1-hydroxy-4-methylpentan-2-yl)imidazolium Hexafluorophosphate (**3l**).* Selectivity **3l**-OAc/bis$_{ValOH}$-OAc/IPr-OAc = 92/4/4. Purification over silica gel (dichloromethane/acetone 95/5) then washing with Et_2O. Brown glassy solid (1.05 g, 46% from 5.0 mmol of corresponding alkylamine). $[\alpha]_D^{20}$:

DOI: 10.1021/acs.joc.6b02888
J. Org. Chem. 2017, 82, 1880–1887

−10.2 (*c* = 0.5, chloroform). ^{1}H NMR (400 MHz, chloroform-*d*): δ 8.51 (dd, *J* = 1.5, 1.5 Hz, 1H), 7.75 (dd, *J* = 1.8, 1.8 Hz, 1H), 7.53 (t, *J* = 7.8 Hz, 1H), 7.33−7.28 (m, 3H), 4.31 (ddd, *J* = 10.1, 6.9, 3.2 Hz, 1H), 4.06 (dd, *J* = 12.3, 3.2 Hz, 1H), 3.95 (dd, *J* = 12.3, 7.0 Hz, 1H), 2.77 (br s, 1H), 2.38−2.16 (m, 3H), 1.19−1.11 (m, 12H), 1.09 (d, *J* = 6.7 Hz, 3H), 0.85 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (101 MHz, chloroform-*d*): δ 145.7, 145.3, 136.6, 132.1, 130.0, 125.0, 124.8, 124.7, 122.1, 77.5, 69.4, 61.7, 29.3, 28.8, 28.7, 24.2, 24.1, 23.9, 19.1. ^{31}P NMR (162 MHz, chloroform-*d*): δ −144.32 (sept, *J* = 713 Hz). ^{19}F NMR (376 MHz, chloroform-*d*): δ −71.90 (d, *J* = 713 Hz). HRMS (ESI) calcd for $C_{20}H_{31}N_2O^+$ (M − PF_6): *m*/*z* 315.24309, found 315.2431 (0 ppm)

*(S)-3-(1-Carboxy-3-methylbutyl)-1-(2,6-diisopropylphenyl)-imidazolium Hexafluorophosphate (**3m**).* Selectivity **3m**-OAc/$bis_{LeuCOOH}$-OAc/IPr-OAc = 79/3/18. Purification: chromatography on silica gel (dichloromethane/MeOH 95/5) and extraction with a saturated aqueous solution of $NaHCO_3$. The aqueous solution was neutralized with 1 M aqueous solution of HCl and extracted with dichloromethane. Orange glassy solid (181 mg, 37%). $[a]_D^{20}$: +31.5 (*c* = 1, chloroform). ^{1}H NMR (400 MHz, chloroform-*d*): δ 9.20 (dd, *J* = 1.5, 1.5 Hz, 1H), 7.95 (dd, *J* = 1.6, 1.6 Hz, 1H), 7.51 (t, *J* = 7.8 Hz, 1H), 7.32−7.26 (m, 2H), 7.12 (dd, *J* = 1.9, 1.9 Hz, 1H), 5.19 (dd, *J* = 10.6, 4.7 Hz, 1H), 2.38−2.25 (m, 2H), 2.20 (ddd, *J* = 14.0, 9.0, 4.7 Hz, 1H), 1.97 (ddd, *J* = 14.9, 10.6, 5.0 Hz, 1H), 1.46−1.30 (m, 1H), 1.27−1.06 (m, 12H), 0.98 (d, *J* = 6.6 Hz, 3H), 0.92 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR (101 MHz, chloroform-*d*) δ 170.6, 145.8, 145.4, 137.1, 131.8, 130.6, 124.7, 124.6, 123.8, 123.1, 122.8, 65.5, 43.8, 28.7, 28.7, 24.4, 24.3, 24.2, 24.1, 23.1, 21.7. ^{31}P NMR (162 MHz, chloroform-*d*): δ −144.33 (sept, *J* = 713 Hz). ^{19}F NMR (376 MHz, chloroform-*d*): δ −72.20 (d, *J* = 713 Hz). HRMS (ESI) calcd for $C_{21}H_{31}N_2O_2^+$ (M − PF_6): *m*/*z* 343.238, found 343.2376 (1 ppm).

*1,3-Bis((R)-1-(naphthalen-1-yl)ethyl)imidazol-3-ium Hexafluorophosphate (**7h**).* Yellow powder (492 mg, 97%). Mp: 103 °C. $[\alpha]_D^{20}$: −118.0 (*c* = 0.1, chloroform). ^{1}H NMR (400 MHz, chloroform-*d*) δ 8.90 (dd, *J* = 1.7, 1.7 Hz, 1H), 8.02−7.68 (m, 6H), 7.58−7.35 (m, 8H), 6.98 (d, *J* = 1.7 Hz, 2H), 6.43 (q, *J* = 6.9 Hz, 2H), 2.06 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR (101 MHz, chloroform-*d*): δ 134.5, 134.1, 132.5, 130.6, 130.3, 129.4, 127.9, 126.6, 125.5, 124.7, 121.7, 121.3, 56.7, 21.0. ^{31}P NMR (162 MHz, chloroform-*d*): δ −144.03 (sept, *J* = 713 Hz). ^{19}F NMR (376 MHz, chloroform-*d*): δ −71.78 (d, *J* = 713 Hz). HRMS (ESI) calcd for $C_{27}H_{25}N_2^+$ (M − PF_6): 377.20122 *m*/*z*, found 377.2013 (0 ppm).

*(R)-1-(2,6-Diisopropylphenyl)-3-((1-(naphthalen-1-yl)ethyl)-imidazol-2-ydene)copper Chloride Complex (**3h**·CuCl).* White solid (99 mg, 86%). Mp: 214 °C. $[\alpha]_D^{20}$: +85.4 (*c* = 1, chloroform). ^{1}H NMR (400 MHz, chloroform-*d*): δ 8.13−8.07 (m, 1H), 7.96−7.87 (m, 2H), 7.81−7.73 (m, 1H), 7.63−7.41 (m, 4H), 7.30−7.19 (m, 2H), 6.76−6.71 (m, 2H), 6.68 (q, *J* = 6.9 Hz, 1H), 2.45 (sept, *J* = 6.8 Hz, 1H), 2.27 (sept, *J* = 6.9 Hz, 1H), 2.14 (d, *J* = 6.9 Hz, 3H), 1.32 (d, *J* = 6.9 Hz, 3H), 1.27 (d, *J* = 6.9 Hz, 3H), 1.13 (d, *J* = 6.9 Hz, 3H), 0.99 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, chloroform-*d*): δ 178.4, 145.8, 145.7, 134.8, 134.2, 133.9, 131.3, 130.5, 130.2, 129.2, 127.0, 126.4, 125.2, 124.6, 124.2, 124.2, 123.3, 123.2, 118.5, 56.9, 28.6, 28.4, 25.0, 24.7, 24.3, 24.0, 22.5. HRMS (ESI) calcd for $C_{27}H_{30}N_2{}^{35}ClNa^{63}Cu^+$ (M + Na): 503.12857 *m*/*z*, found 503.1291 (1 ppm).

*Ethyl (S)-3-Hydroxy-3-phenylpropanoate (**9**).* With **3h**: colorless oil (65 mg, 67%), er = 87:13. $[\alpha]_D^{20}$: −35.8 (*c* = 1, chloroform), [lit.[20f] $[\alpha]_D^{20}$= −49.2 (*c* = 0.1, chloroform), er = 98:2]. With **7h**: colorless oil (58 mg, 60%), er = 67.5:32.5. With **3h**·CuCl: colorless oil (74 mg, 76%), er = 82:18. Enantiomeric excess was measured by chiral HPLC:[23] OD-H column, hexane/2-propanol (90%/10%), 1 mL/min, λ = 254 nm, *T* = 25 °C, t_R1 = 7.8 min, t_R2 = 10.1 min. ^{1}H NMR (400 MHz, chloroform-*d*): δ 7.48−7.12 (m, 5H), 5.14 (dt, *J* = 8.5, 3.6 Hz, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 3.26 (d, *J* = 3.4 Hz, 1H), 2.88−2.59 (m, 2H), 1.27 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, chloroform-*d*): δ 172.6, 142.6, 128.7, 127.9, 125.8, 70.4, 61.0, 43.5, 14.3.

*(S)-(3-Methylpent-1-en-3-yl)benzene (**11a**).* Colorless oil (58 mg, 73%, conversion >95%). S_N2'/S_N2 selectivity: 96/4. er = 92:8 (*S*). $[\alpha]_D^{20}$: +10.5 (*c* = 1, chloroform) [lit.[10] $[\alpha]_D^{20}$= +10.1 (*c* = 1, chloroform), er = 91:9]. Enantiomeric excess was measured by chiral GC: Beta-dex column, helium (30.9 cm/sec), 80 °C, 55 min, 10 °C/min, 160 °C, 10 min, t_R1 = 43.7 min (*R*), t_R2 = 44.3 min (*S*). ^{1}H NMR (400 MHz, chloroform-*d*): δ = 7.37−7.16 (m, 5H), 6.04 (dd, *J* = 17.4, 10.8 Hz, 1H), 5.10 (dd, *J* = 10.8, 1.4 Hz, 1H), 5.04 (dd, *J* = 17.4, 1.4 Hz, 1H), 1.90−1.74 (m, 2H), 1.38 (s, 3H, CH_3), 0.80 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (101 MHz, chloroform-*d*): δ = 147.6, 147.0, 128.1, 126.8, 125.8, 111.9, 44.7, 33.5, 24.5, 9.0.

*1-Bromo-2-(3-methylpent-1-en-3-yl)benzene (**11b**).* Colorless oil (81 mg, 68%, conversion >95%). S_N2'/S_N2 selectivity: > 98/<2. er = 91:9 (*S*). $[\alpha]_D^{20}$: +1.7 (*c* = 1, chloroform). [lit.[10] $[\alpha]_D^{20}$ = +2.4 (*c* = 1, chloroform), er = 95:5]. Enantiomeric excess was measured by chiral GC: GTA column, helium (33.2 cm/s), 80 °C, 60 min, 110 °C, 15 min, 1 °C/min, 160 °C, 10 min, 10 °C/min, t_R1(major) = 94.7 min (*R*), t_R2(minor) = 96.7 min (*S*). ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.57 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.40 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.29−7.22 (m, 1H), 7.05 (ddd, *J* = 7.9, 7.2, 1.7 Hz, 1H), 6.20 (dd, *J* = 17.6, 10.7 Hz, 1H), 5.10 (dd, *J* = 10.7, 1.1 Hz, 1H), 4.93 (dd, *J* = 17.6, 1.1 Hz, 1H), 2.41−2.29 (m, 1H), 1.94−1.82 (m, 1H), 1.49 (s, 3H), 0.71 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (101 MHz, chloroform-*d*): δ 146.5, 145.1, 135.6, 129.9, 127.8, 127.0, 123.5, 112.6, 46.4, 31.3, 25.8, 9.1.

*1-(3-Methylpent-1-en-3-yl)naphthalene (**11c**).* Colorless oil (74 mg, 71%, conversion 78%). S_N2'/S_N2 selectivity: 96/4. er = 95:5. $[\alpha]_D^{20}$: −6.5 (*c* = 1, chloroform). [lit.[10] $[\alpha]_D^{20}$ = −8.0 (*c* = 1, chloroform), er = 96:4]. Enantiomeric excess was measured by chiral HPLC: OJ-H column, hexane (100%) 0.3 mL/min, λ = 254 nm, *T* = 25 °C, t_R1(minor) = 17.9 min, t_R2(major) = 18.5 min. ^{1}H NMR (400 MHz, chloroform-*d*): δ = 8.38 (d, *J* = 8.6 Hz, 1H), 7.86−7.83 (m, 1H), 7.74 (d, *J* = 8.0 Hz, 1H), 7.50−7.37 (m, 4H), 6.32 (dd, *J* = 17.7, 10.7 Hz, 1H), 5.13 (d, *J* = 10.8 Hz, 1H), 5.03 (d, *J* = 17.6 Hz, 1H), 2.35−2.26 (m, 1H), 2.04−1.95 (m, 1H), 1.57 (s, 3H), 0.67 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, chloroform-*d*) δ 149.0, 142.5, 135.0, 131.8, 129.2, 127.8, 127.7, 125.2, 125.1, 124.9, 124.4, 112.1, 45.7, 32.9, 27.5, 9.1.

■ ASSOCIATED CONTENT

Supporting Information

Detailed spectral data for products, crystallographic data (CIF files) and supplementary experiments, this material is available free of charge via the Internet at The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b02888.

X-ray data for **3d**, **3i**, **3h**, and **3h**·**CuCl** (CIF)
Detailed spectral data for products, crystallographic data, and supplementary experiments (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We are grateful to the CNRS, Ecole Nationale Supérieure de Chimie de Rennes. This work was supported by Omega Cat System and the Région Bretagne (ARED No. COH14007 "NHC-MET" grant to R.T.) and the Agence Nationale de la Recherche (No. ANR-15-CE07-0012-01 "CHADOC").

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(16) See the Supporting Information for details
(17) Preliminary results tend to demonstrate that the equilibration reactions between the three diimines are accelerated in the presence of $ZnCl_2$.
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