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

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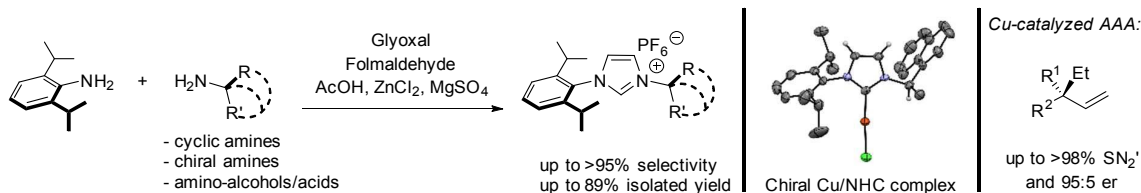
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## Graphical Abstract:

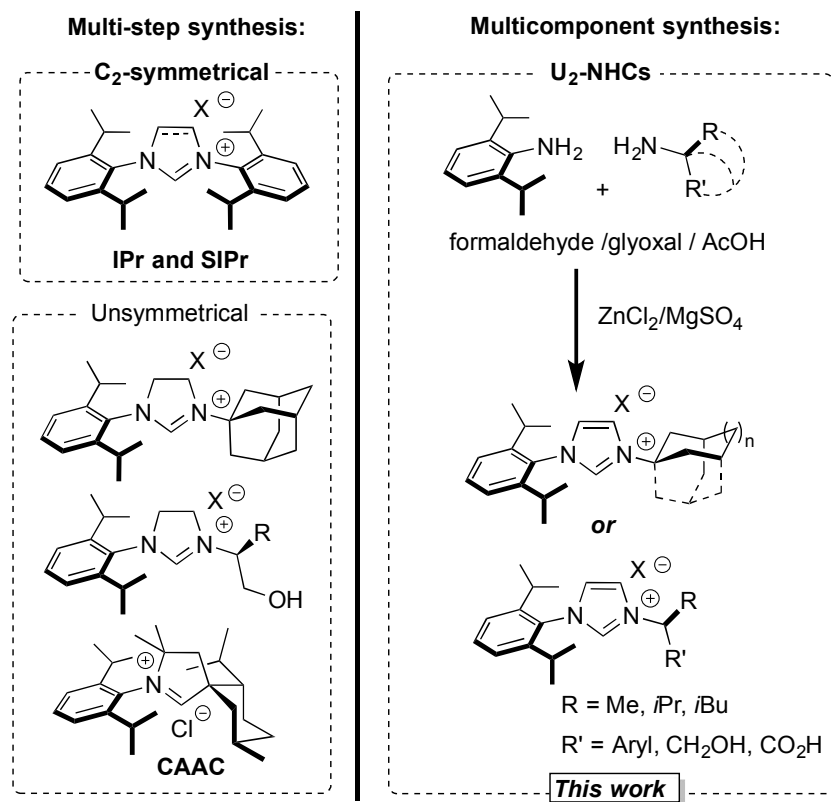


**Abstract:** A new multicomponent procedure was applied to the synthesis of (a)chiral bulky unsymmetrical unsaturated 2,6-diisopropylphenyl-*N*-heterocyclic carbene (NHC) precursors with excellent selectivity (up to 95%) and good yields. This approach offers access to new chiral NHCs ligands, which 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.<sup>1</sup> These species have been used as ligands to kinetically stabilize highly reactive, low-valent transition metals complexes and enable high catalytic activity to be achieved.<sup>2</sup> Among the large variety of NHCs described in the literature, C<sub>2</sub>-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.<sup>3</sup> On the other hand, unsymmetrical NHCs with increased steric discrimination and distinctive electronic properties have witnessed growing interest in the recent years.<sup>4</sup> Indeed, transition metal bearing Dipp-based unsymmetrical NHC have found considerable advantages in terms of reactivity and selectivity towards challenging processes.<sup>5,6</sup> 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.<sup>7</sup> However, the strategies to construct unsymmetrical NHC precursors require multiple steps syntheses that, due to time consumption and cost, may limit their industrial applications.<sup>8</sup> Recently, we described an elegant and practical multicomponent strategy, providing access to various unsymmetrical unsaturated (a)chiral N-heterocyclic carbene (U<sub>2</sub>-NHC) ligands precursors with high selectivity and good yield.<sup>9</sup> 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<sub>2</sub>-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 stereinduction from the chiral center to the metal.<sup>10</sup> Despite the efficiency and flexibility of this multicomponent procedure, the introduction of highly hindered pattern such as the Dipp fragment appeared as a major limitation, affording the desired bulky U<sub>2</sub>-NHC precursors with poor yields and selectivities.<sup>9,10</sup> Herein, we disclose a novel multicomponent procedure leading to a wide range of (a)chiral unsymmetrical unsaturated 1-(2,6-diisopropylphenyl)-3-alkyl-imidazolium 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.



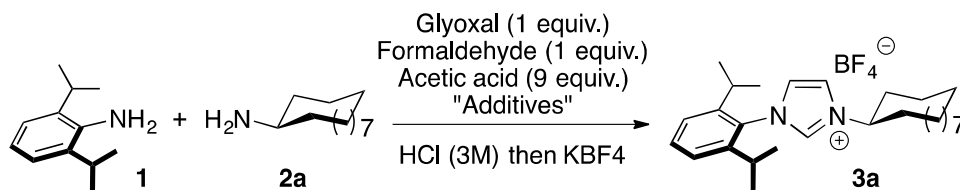
**Figure 1.** Examples of Dipp-based NHC ligands (left) and new synthetic route to Dipp-based U<sub>2</sub>-NHC ligands (right)

## Results and Discussion

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With the objective to reach the exclusive formation of the unsymmetrical 1-(2,6-diisopropylphenyl)-3-cycloalkyl-imidazolium salts **3**, we decided to re-investigate 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 approach, is the inherent low reactivity of this sterically congested amine under typical operational conditions for the synthesis of imidazolium salts.<sup>11</sup> 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 1-2). 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).<sup>12</sup> During the screening of Lewis acids, the addition of zinc chloride (1 equiv.) in diethylether appeared highly beneficial affording the unsymmetrical NHC precursors with very high selectivity (>95%) and excellent NMR yield (Table 1, entry 7).<sup>13</sup> Interestingly, without affecting selectivity, the addition of magnesium sulfate (MgSO<sub>4</sub>) could improve the NMR yield to >95% and allowed isolation of the 1-(2,6-diisopropylphenyl)-3-cyclododecyl-imidazolium salt **3a** in 76% yield (table 1, entry 9). Finally, replacement of the BF<sub>4</sub><sup>-</sup> anion by PF<sub>6</sub><sup>-</sup> facilitated the purification procedure and afforded the corresponding imidazolium.PF<sub>6</sub> salts with high 89% isolated yield (table 1, entry 10).

**Table 1.** Optimization of the conditions for the multicomponent process.



Entry	Additives	T (°C)	Selectivity (%) <sup>a</sup>	Yield (%) <sup>b</sup>
1	NA <sup>c</sup>	40	57	35
2	NA <sup>c</sup>	60	69	51
3	HCl (1 mol%) <sup>d</sup>	60	73	57
4	HCl (1 equiv.) <sup>d</sup>	60	89	89
5	MgCl <sub>2</sub> (s) (1 equiv.)	60	88	73
6	ZnCl <sub>2</sub> (s) (1 equiv.)	60	93	83
7	ZnCl <sub>2</sub> (1 equiv.) <sup>d</sup>	60	>95	88
8	ZnCl <sub>2</sub> (1.2 equiv.) <sup>d</sup>	60	>95	94
9	MgSO <sub>4</sub> (2 equiv.), ZnCl <sub>2</sub> (1.2 equiv.) <sup>d</sup>	60	>95	>95 (76)
10 <sup>e</sup>	MgSO <sub>4</sub> (2 equiv.), ZnCl <sub>2</sub> (1.2 equiv.) <sup>d</sup>	60	<b>&gt;95</b>	<b>&gt;95 (89)</b>
11	MgSO <sub>4</sub> (2 equiv.)	60	65	46
12	Et <sub>2</sub> O	60	45	30

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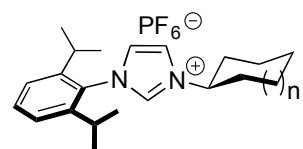
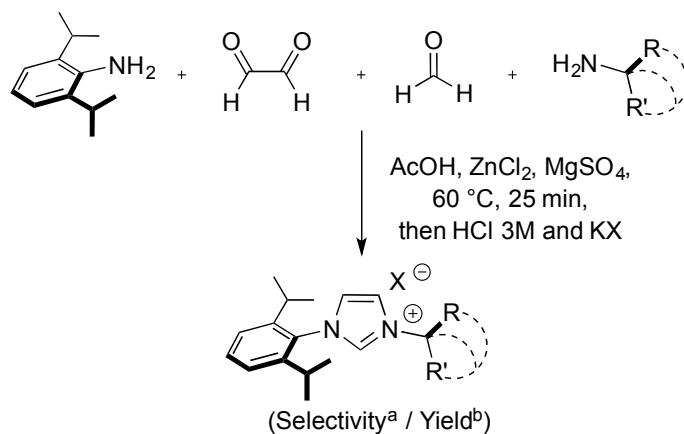
<sup>a</sup>Determined by <sup>1</sup>H NMR using tetrachloroethane as an internal standard. <sup>b</sup>NMR yields using tetrachloroethane as an internal standard; Isolated yields presented in parentheses. <sup>c</sup>Not applicable. <sup>d</sup>1M in Et<sub>2</sub>O. <sup>e</sup>KPF<sub>6</sub> was used instead of KBF<sub>4</sub>.

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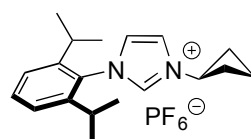
Under the optimized reaction conditions, we extended the scope of the reaction using first a variety of cycloalkylamines (Scheme 1). Similarly to the results

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3 obtained with cyclododecanamine, the desired U<sub>2</sub>-NHC precursors bearing the  
4 cyclooctyl-, cyclopentyl- fragments were obtained with excellent selectivity and good  
5 isolated yields. Interestingly, the polycyclic adamantylamine could be efficiently  
6 employed in this strategy and afforded perfect selectivity in the preparation of **3e**; the  
7 unsaturated analogue of the most effective NHC ligand precursor employed in  
8 ruthenium-catalyzed Z-selective metathesis.<sup>5</sup> Moreover, while cyclobutylamine  
9 reacted quite smoothly (86% selectivity and 66% isolated yield), a noticeable  
10 decrease of selectivity was observed with cyclopropylamine leading to a modest 42%  
11 isolated yield of the corresponding imidazolium salt **3f**. Importantly, this approach  
12 was also applicable to the use of alpha substituted chiral amines such as (*S*)- $\alpha$ -  
13 methylbenzylamine, (*R*)-1-(1-naphthyl)ethylamine, (1*R*, 2*R*, 3*R*, 5*S*)-  
14 isopinocampheylamine and (*R*)-indanamine allowing for a simple and efficient access  
15 to bulky chiral NHC precursors with strong propensity for new applications in  
16 selective catalysis (figure 2).<sup>14,5g</sup> In effort to further extend the synthetic utility of this  
17 multicomponent procedure, the synthesis of chiral bidentate NHC ligand precursors  
18 was investigated. Pleasantly, the bulky chiral imidazolium salts **3k** and **3l** derived  
19 from (L)-leucinol and (L)-valinol were formed with excellent selectivity and isolated in  
20 reasonable yields. Under the same conditions, modest selectivity and isolated yield  
21 could be obtained with (L)-leucine.  
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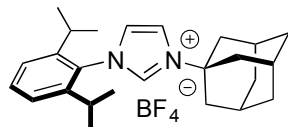
54 **Scheme 1.** Scope of the multicomponent procedure.  
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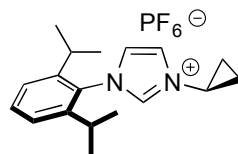
n = 7 **3a** (> 95% / 89%)  
n = 3 **3b** (91% / 70%)  
n = 0 **3c** (> 95% / 78%)



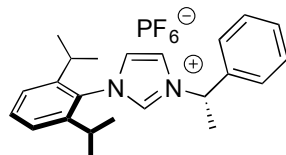
**3d** (86% / 66%)



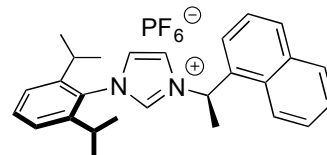
**3e-BF<sub>4</sub>** (94% / 75%)<sup>c</sup>



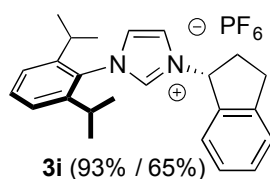
**3f** (70% / 42%)



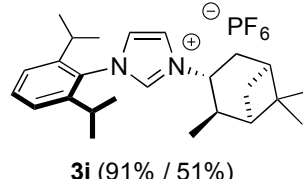
**3g** (94% / 71%)



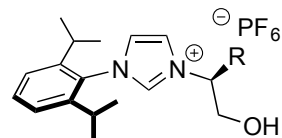
**3h** (83% / 65%)



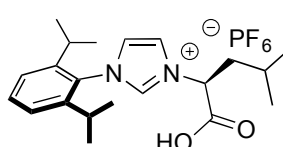
**3i** (93% / 65%)



**3j** (91% / 51%)



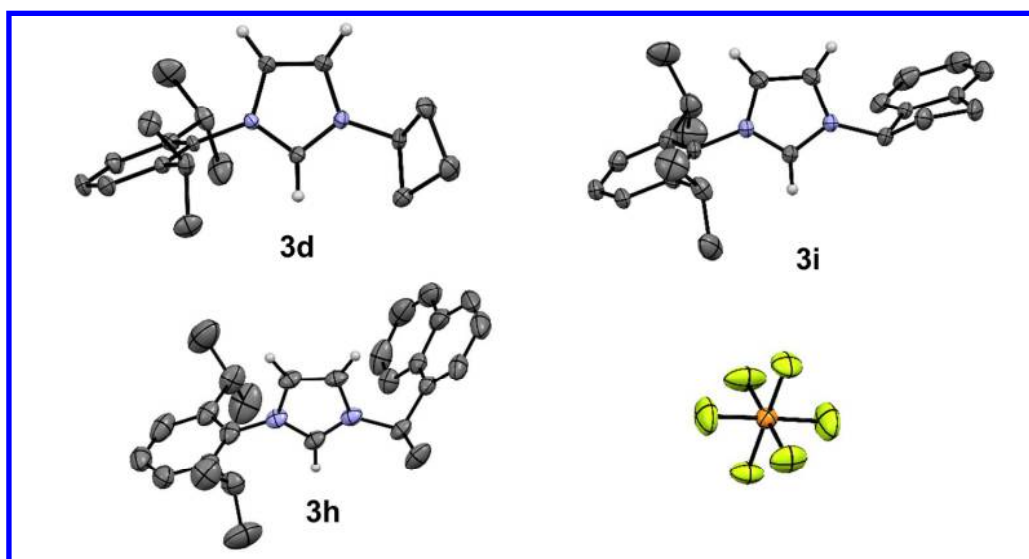
**3k**: R = i-Bu (91% / 65%)  
**3l**: R = i-Pr (93% / 46%)



**3m** (66% / 37%)

<sup>a</sup> Determined by <sup>1</sup>H NMR analysis. <sup>b</sup> Isolated Yields. <sup>c</sup> The purification procedure is facilitated with BF<sub>4</sub><sup>-</sup> instead of PF<sub>6</sub><sup>-</sup>.



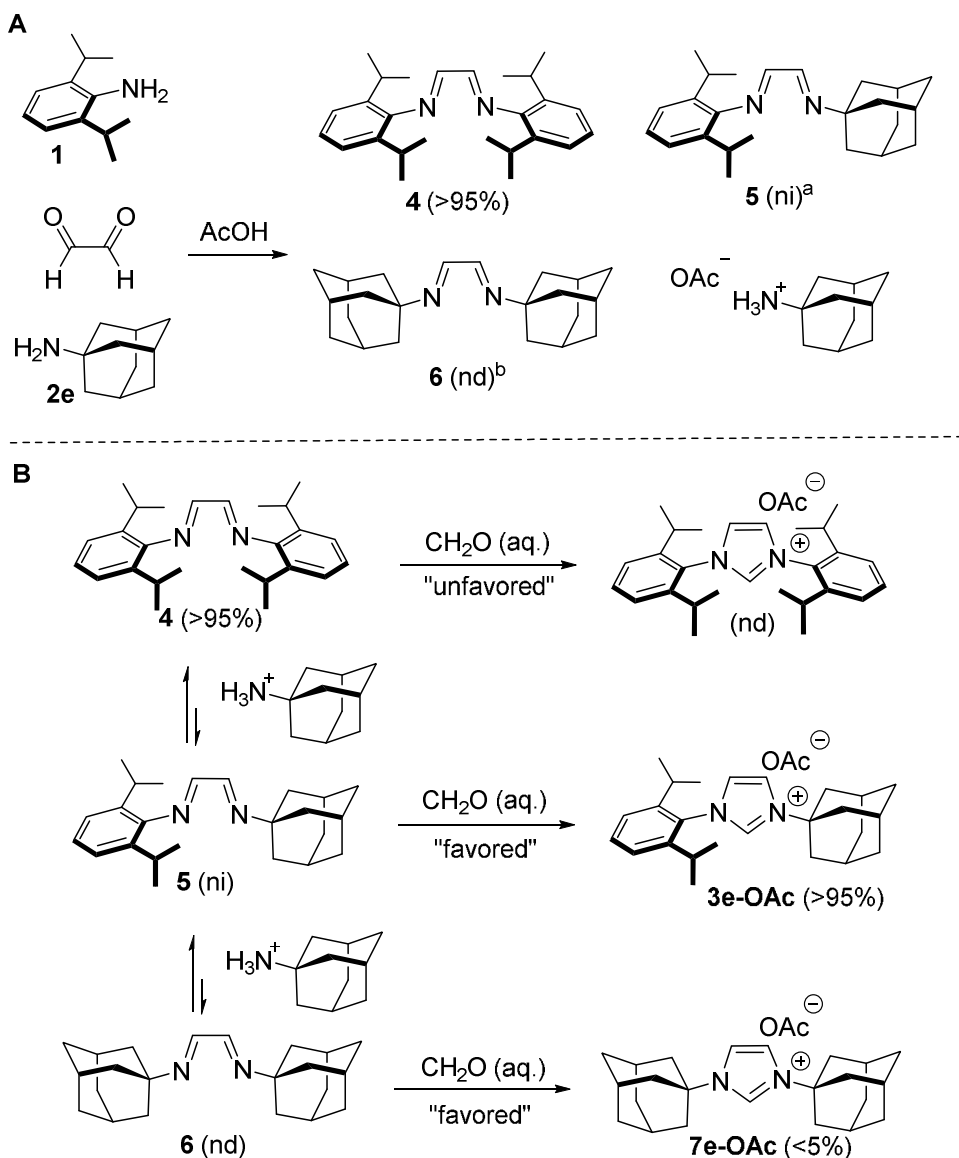


**Figure 2.** Solid-state structure of a selection of imidazolium salts from single crystal X-ray diffraction. Displacement ellipsoids are drawn at 50% probability. Most hydrogen atoms and PF<sub>6</sub> anions have been omitted for clarity (N in blue, C in grey, P in orange, F in yellow, H in white).

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<sub>2</sub> **1** and adamantylamine **2a** could be greatly simplified, since ZnCl<sub>2</sub> and MgSO<sub>4</sub> additives had no significant impact on the outcomes of this specific reaction.<sup>15</sup> Therefore, this simplified protocol was selected as a model for the following mechanistic study. First, a stoichiometric amount of DippNH<sub>2</sub> **1**, AdNH<sub>2</sub> **2a** and aqueous glyoxal were reacted in presence of an excess of acetic acid (9 equiv.). The <sup>1</sup>H NMR analysis of the resulting crude mixture (< 5 min reaction) showed the preferential formation of the diaryl-diimine **4** (>95%) without unequivocal identification

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3 of diimine **5** and no detectable amount of dialkyl-diimine **6** (Scheme 2, A).<sup>16</sup> The  
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5 subsequent addition of 1 equivalent of aqueous formaldehyde afforded the desired  
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7 unsymmetrical imidazolium salt **3e-OAc** with high >95% selectivity along with <5% of  
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9 the symmetrical dialkyl imidazolium salt **7e-OAc** and no detectable amount of the IPr  
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11 imidazolium salt precursors (scheme 2, B). Besides, it was observed that the  
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13 sterically congested diaryl-diimine **4** was poorly reactive towards cyclisation under  
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15 our reactions conditions, whereas the dialkyl-diimine **6** was able to afford easily the  
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17 corresponding cyclized imidazolium salt **7e-OAc**.<sup>16</sup> Nevertheless, when the  
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19 cyclisation of the dialkyl-diimine **6** was performed in the presence of DippNH<sub>2</sub> **1** (2  
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21 equiv.), the major product was the unsymmetrical salt **3e-OAc** (**3e-OAc/7e-OAc** ratio  
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23 = 94:6).<sup>16</sup> Consequently, the high selectivity in favor of the unsymmetrical salt **3e-**  
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25 **OAc** may be explained by the fact that the cyclizations of the symmetrical diimines  
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27 are slower than i) the equilibration reactions between the three diimines<sup>17</sup> and ii) than  
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29 the cyclisation of the unsymmetrical diimine **5**.<sup>18</sup>  
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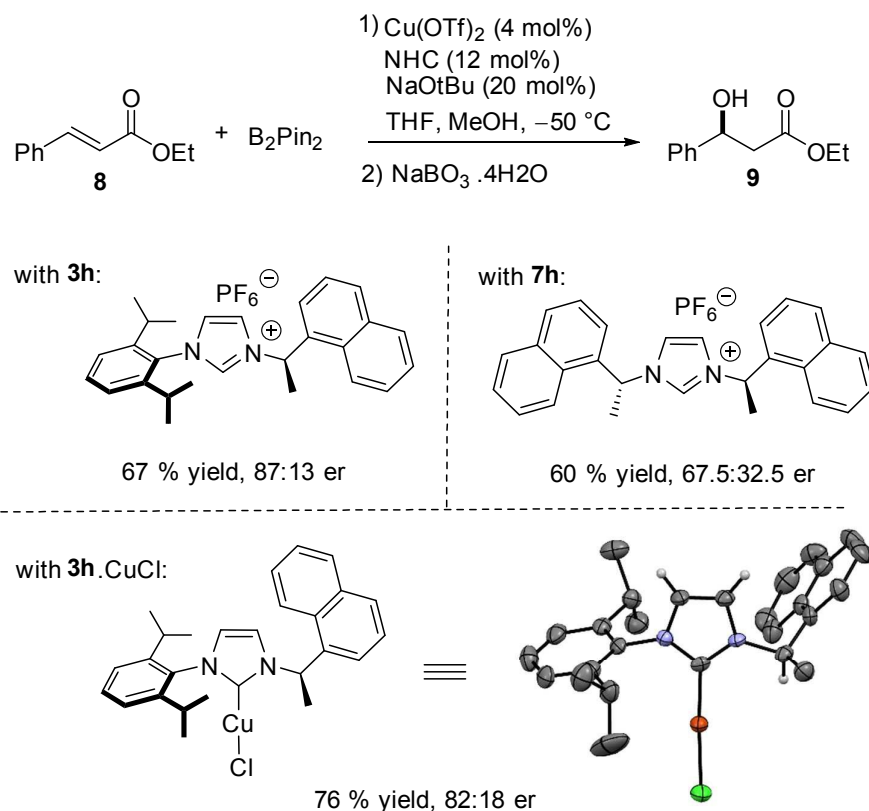
36 **Scheme 2.** Mechanistic investigation of unsymmetrical salts synthesis. (A) Ratio in  
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38 diimines after condensation with aqueous glyoxal and excess acetic acid (< 5 min  
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40 reaction). (B) Selectivity of the cyclization procedure in presence of aqueous  
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42 formaldehyde. <sup>a</sup> Not identified <sup>b</sup> not detected  
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The asymmetric conjugate addition of nucleophiles to electron deficient alkenes represents one of the most powerful methods to form C-C and C-heteroelement bond.<sup>19</sup> In the recent years, enantioselective conjugate addition of diboron reagents to  $\alpha,\beta$ -unsaturated carbonyl compounds catalyzed by Cu-based NHC/complexes has attracted considerable interest.<sup>20</sup> 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 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<sub>2</sub> symmetrical ligand precursor analogue **7h** allowed for 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 82:18 enantiomeric ratio.<sup>21</sup>

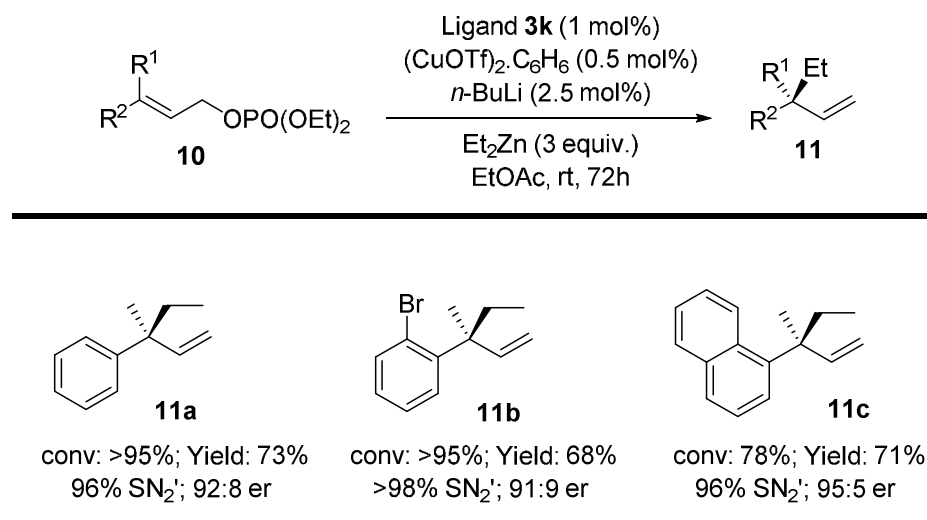
**Scheme 3.** Copper/NHC-Catalyzed asymmetric borylation.<sup>a</sup>



<sup>a</sup>Enantiomeric ratios were obtained from chiral HPLC analysis.

To further demonstrate the potential of newly developed ligand family, the chiral bidentate hydroxyalkyl ligand precursor **3k** was evaluated in copper-catalyzed asymmetric allylic alkylation to form all-carbon quaternary centers.<sup>6c,10</sup> Interestingly the catalytic system prepared in situ by deprotonation of the imidazolium salt **3k** with *n*-butyllithium in 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<sub>2</sub>') and high enantio-selectivity (up to 95:5 er) (Scheme 4).

**Scheme 4.** Copper-catalyzed AAA with allylphosphates.<sup>a,b</sup>



<sup>a</sup> Conversions and SN<sub>2</sub>' ratios were determined by <sup>1</sup>H NMR analysis of the crude mixture. <sup>b</sup>Enantiomeric ratios were obtained from GC and HPLC analysis of the substitution product.

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

## 38 Experimental section

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40 **General Experimental Procedures.** All commercial chemicals were used as  
41 received unless otherwise noted. 1,4-Bis(2,6-diisopropylphenyl)-1,4-diaza-1,3-  
42 butadiene<sup>11a</sup> **4** and N,N'-Bis(1-adamantyl)ethanediimine<sup>22</sup> **6** were obtained following  
43 already described procedures. Reactions were monitored by thin-layer  
44 chromatography (TLC) carried out on silica gel plates (60F254) using UV light as  
45 visualizing agent, KMnO<sub>4</sub>/K<sub>2</sub>CO<sub>3</sub>/NaOH in water for staining. Column  
46 chromatography was performed with Silica Gel (spherical, particle size 40 μm,  
47 neutral). The eluents employed are reported as volume (volume percentages).  
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3 Melting points were measured on a standard melting point apparatus in open  
4 capillary tubes and are uncorrected. Optical rotations were recorded on a polarimeter  
5 and are uncorrected.  $^1\text{H}$  (400 MHz),  $^{13}\text{C}$  (101 MHz),  $^{19}\text{F}$  (376 MHz),  $^{31}\text{P}$  (162 MHz)  
6 and  $^{11}\text{B}$  (128 MHz) NMR spectra were recorded on a NMR spectrometer with  
7 complete proton decoupling for nucleus other than  $^1\text{H}$ . Chemical shifts are reported in  
8 parts per million with the solvent resonance as the internal standard ( $\text{CDCl}_3$ ,  $^1\text{H}$ :  $\delta$   
9 7.26 ppm,  $^{13}\text{C}$ :  $\delta$  77.16 ppm;  $\text{CD}_3\text{OD}$ ,  $^1\text{H}$ :  $\delta$  3.31 ppm,  $^{13}\text{C}$ :  $\delta$  49.00 ppm);  $^{19}\text{F}$   
10 chemical shifts are reported with  $\text{CFCl}_3$  ( $\delta = 0.0$  ppm) as the internal standard;  $^{31}\text{P}$   
11 chemical shifts are reported with  $\text{H}_3\text{PO}_4$  ( $\delta = 0.0$  ppm) as the internal standard;  $^{11}\text{B}$   
12 chemical shifts are reported with  $\text{BF}_3\cdot\text{Et}_2\text{O}$  ( $\delta = 0.0$  ppm) as the internal standard.  
13  
14 Coupling constants ( $J$ ) are reported in Hertz (Hz). Multiplicities are reported using  
15 following abbreviations: s = singlet, br. s = broad singlet, d = doublet, dd = double  
16 doublet, ddd = double double doublet, dt = double triplet, t = triplet, q = quartet, quint  
17 = quintet, sept = septet, m = multiplet. High-resolution mass spectroscopy (HMRS)  
18 were recorded on a Q-TOF .  
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36 **General Procedure for the Multicomponent Synthesis of Unsymmetrical**  
37 **Imidazolium Salts 3.** The reaction was performed in open vessel under air  
38 atmosphere. In a round-bottomed flask were placed 2,6-diisopropylaniline (1 mmol,  
39 1.0 equiv.), alkylamine (1 mmol, 1.0 equiv.) and acetic acid (4.5 mmol, 4.5 equiv.),  
40 then the mixture was heated at 60 °C for 5 minutes and  $\text{MgSO}_4$  (2 mmol, 2 equiv.)  
41 was added (mixture A). In another round-bottomed flask were placed glyoxal (1  
42 mmol, 1.0 equiv., 40 % weight in aqueous solution), formaldehyde (1 mmol, 1.0  
43 equiv., 37 % weight in aqueous solution) and acetic acid (4.5 mmol, 4.5 equiv.), then  
44 the mixture was heated at 60 °C for 5 minutes and  $\text{ZnCl}_2$  (1.2 mmol, 1.2 equiv., 1M in  
45  $\text{Et}_2\text{O}$ ) was added (mixture B). At 60 °C mixture B was added to mixture A and the  
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3 resulting mixture was stirred at 60 °C for 25 minutes then cooled down to room  
4  
5 temperature. An aliquot of the crude reaction mixture was taken and a <sup>1</sup>H NMR was  
6  
7 recorded to determine the selectivity of the reaction, which was calculated by  
8  
9 integration of characteristic signals of the different compounds. Dichloromethane (25  
10  
11 mL) and 3M aqueous solution of HCl (50 mL) were added and the resulting mixture  
12  
13 was stirred at room temperature for 1 hour. Then the organic layer was separated.  
14  
15 Water (50 mL) and potassium hexafluorophosphate or potassium tetrafluoroborate  
16  
17 (1.0 mmol, 1.0 equiv.) was added and the mixture was stirred at room temperature  
18  
19 for 1 hour. The organic layer was separated, dried over magnesium sulfate, filtered  
20  
21 and the solvents were evaporated under reduced pressure. The desired imidazolium  
22  
23 salt was isolated either by flash chromatography on silica gel or recrystallization.  
24  
25  
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27

28 **General Procedure for the Multicomponent Synthesis of Unsymmetrical**  
29  
30 **Imidazolium Salts 7.** In a round-bottomed flask were placed alkylamine (0.53 mmol,  
31  
32 1 equiv.) and acetic acid (1.20 mmol, 2.25 equiv.) then the mixture was heated at  
33  
34 40 °C for 5 min (mixture A). In another round-bottomed flask were placed glyoxal  
35  
36 (0.26 mmol, 0.5 equiv., 40 % wt in aqueous solution), formaldehyde (0.026 mmol, 0.5  
37  
38 equiv., 37 % wt in aqueous solution) and acetic acid (1.20 mmol, 2.25 equiv.)  
39  
40 then the mixture was heated at 40 °C for 5 min (mixture B). At 40 °C mixture B was  
41  
42 added to mixture A and the resulting mixture was stirred at 40 °C for 25 min then  
43  
44 cooled down to room temperature. Dichloromethane (25 mL) was added and the  
45  
46 organic layer was washed with brine (3 x 10 mL). The organic layer was separated,  
47  
48 then water (5 mL) and potassium hexafluorophosphate (48 mg, 0.26 mmol) were  
49  
50 added and the mixture was stirred at room temperature for 1 hour. The organic layer  
51  
52 was separated, dried over magnesium sulfate, filtered and the solvents were  
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3 evaporated under reduced pressure. The desired imidazolium salt **7** was isolated  
4  
5 without further purification.  
6  
7

### 8 **General Procedure for the Synthesis of Copper Complexes 3.CuCl.**

9  
10 Hexafluorophosphate salt **3** (0.24 mmol, 1 equiv.) was loaded on an anion exchange  
11 resin Dowex® 1x2 chloride form (2.4 ml of resin for 0.24 mmol of  
12 hexafluorophosphate salt) with milli-Q water / acetone (1/1) as an eluent. After  
13 removal of solvents under reduced pressure, the residue was dissolved in  
14 dichloromethane, dried over MgSO<sub>4</sub>, filtered and concentrated under reduced  
15 pressure to give the corresponding chloride salt. In a dry Schlenk, under argon  
16 atmosphere, were placed Ag<sub>2</sub>O (0.24 mmol, 1 equiv.), chloride imidazolium salt (0.24  
17 mmol, 1 equiv.), dichloromethane (25 mL) and 4Å molecular sieves. The mixture was  
18 stirred at room temperature overnight in darkness (alumina foil) then CuCl (0.24  
19 mmol, 1 equiv.) was added and the resulting mixture was stirred at room temperature  
20 for 4 h in darkness. The mixture was then filtered on a celite bed with  
21 dichloromethane and the solvent was removed under reduced pressure. The crude  
22 solid was precipitated in dichloromethane/pentane (1/5) to afford the desired copper  
23 complex **3.CuCl**.  
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42 **General Procedure for Copper-Catalyzed Asymmetric Borylation. Starting**  
43 *from the imidazolium salts (3h and 7h):* In the glove box, Cu(OTf)<sub>2</sub> (4 mol%), ligand  
44 (12 mol%), NaOtBu (20 mol%) and THF (1 mL) were added in a flame-dried  
45 microwave flask. The resulting mixture was stirred at room temperature for 10  
46 minutes and bis(pinacolato)diboron (0.55 mmol, 1.1 equiv.) was added. The mixture  
47 was stirred for an extra 10 minutes and the solution was cooled down to -50 °C.  
48 Then, a solution containing MeOH (1.0 mmol, 2 equiv.), ethyl cinnamate (0.5 mmol, 1  
49 equiv.) and THF (1 mL) was slowly added and the mixture was stirred 3 hours at -  
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3 50 °C. Then, the oxidation step was carried out with the successive addition of  
4  
5 NaBO<sub>3</sub>·4H<sub>2</sub>O (2.5 mmol, 5 equiv.) and water (2 mL), after which the mixture was  
6  
7 stirred at room temperature for 3 hours. Water (10 mL) was added and the aqueous  
8  
9 layer was extracted with ethyl acetate (3x20 mL). The organics layers were  
10  
11 combined, washed with brine (20 mL), dried over MgSO<sub>4</sub>, filtered and concentrated  
12  
13 under reduced pressure. The crude product was purified by silica gel  
14  
15 chromatography (pentane/diethyl ether, 8/2) to give the corresponding product **9** as a  
16  
17 colorless oil.  
18  
19

20  
21 *Starting from the isolated copper complex (3h.CuCl):* In the glove box, **3h.CuCl** (4  
22  
23 mol%), Cs<sub>2</sub>CO<sub>3</sub> (8 mol%), bis(pinacolato)diboron (0.55 mmol, 1.1 equiv.) and THF (1  
24  
25 mL) were added in a microwave flask. The resulting mixture was stirred at room  
26  
27 temperature for 10 minutes and the solution was cooled down to -50 °C. Then, a  
28  
29 solution containing MeOH (1.0 mmol, 2 equiv.), ethyl cinnamate (0.5 mmol, 1 equiv.)  
30  
31 and THF (1 mL) was slowly added at -50 °C and the mixture was stirred 3 hours at -  
32  
33 50 °C. Then, the oxidation step was carried out with the successive addition of  
34  
35 NaBO<sub>3</sub>·4H<sub>2</sub>O (1 mmol, 5 equiv.) and water (1 mL), after which the mixture was stirred  
36  
37 at room temperature for 3 hours. Water (5 mL) was added and the aqueous layer  
38  
39 was extracted with ethyl acetate (3x10 mL). The organics layers were combined,  
40  
41 washed with brine (10 mL), dried over MgSO<sub>4</sub>, filtered and concentrated under  
42  
43 reduced pressure. The crude product was purified by silica gel chromatography  
44  
45 (pentane /diethyl ether: 8/2) to give the corresponding product **9** as a colorless oil.  
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#### 51 **General Procedure for Copper-Catalyzed Asymmetric Allylic Alkylation.**

52  
53 A flame-dried Schlenk tube, under an argon atmosphere, was charged with  
54  
55 [Cu(OTf)<sub>2</sub>].C<sub>6</sub>H<sub>6</sub> (0.5 mol%) and **3k** (1 mol%). Freshly distilled ethyl acetate (0.25  
56  
57 mL) was then added and the reaction mixture was stirred 10 minutes at room  
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3 temperature followed by the addition of n-BuLi (1.6M in hexanes, 2.5 mol%). The  
4  
5 reaction was stirred 10 minutes at room temperature and Et<sub>2</sub>Zn (1.5 mmol, 3 equiv.)  
6  
7 was added. After cooling the reaction vessel to 0 °C, the phosphate (0.5 mmol, 1  
8  
9 equiv.) was added. As soon as the addition of the substrate was completed, the ice  
10  
11 bath was removed. The reaction mixture was stirred at room temperature until total  
12  
13 consumption of the phosphate. Upon completion of the reaction, a 1M aqueous  
14  
15 solution of HCl was added and the compound was extracted with diethyl ether. The  
16  
17 combined organic layers were then washed with a saturated aqueous solution of  
18  
19 NaHCO<sub>3</sub>, brine and dried over MgSO<sub>4</sub>. The solvents were carefully removed under  
20  
21 vacuum. The crude product was purified by silica gel chromatography (pentane) to  
22  
23 isolate the corresponding product **11** as a colorless oil.  
24  
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28 **Characterization Data of Isolated Compounds.** *3-cyclododecyl-1-(2,6-*  
29  
30 *diisopropylphenyl)imidazolium hexafluorophosphate (3a)*: Selectivity 3a-OAc/bis<sub>C12-</sub>  
31  
32 OAc/IPr-OAc = >95/traces/traces. Purification over silica gel (dichloromethane then  
33  
34 dichloromethane/ethyl acetate: 9/1). Pale brown solid (481 mg, 89%). m. p.: 173 °C.  
35  
36 <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 8.61 (dd, *J* = 1.7, 1.7 Hz, 1H), 7.66 (dd, *J* = 1.8,  
37  
38 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  
39  
40 (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* =  
41  
42 7.6 Hz, 6H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 145.4, 135.7, 132.0, 130.15, 125.4,  
43  
44 124.7, 121.7, 59.7, 30.2, 28.9, 24.3, 24.0, 23.8, 23.5, 23.3, 23.3, 21.3. <sup>19</sup>F NMR (376  
45  
46 MHz, Chloroform-*d*) δ -72.16 (d, *J* = 713 Hz). <sup>31</sup>P NMR (162 MHz, Chloroform-*d*) δ -  
47  
48 144.32 (sept, *J* = 713 Hz). HRMS (ESI) calcd. for C<sub>27</sub>H<sub>43</sub>N<sub>2</sub><sup>+</sup> (M-PF<sub>6</sub>): *m/z* 395.34207,  
49  
50 found: 395.3422 (0 ppm). Anal. Calcd. for C<sub>27</sub>H<sub>43</sub>F<sub>6</sub>N<sub>2</sub>P: C, 59.99%; H, 8.02%; N,  
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52 5.18%; found: C, 59.85%; H, 7.77%; N, 4.99%  
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3 *3-cyclooctyl-1-(2,6-diisopropylphenyl)imidazolium hexafluorophosphate (3b):*

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5 Selectivity 3b-OAc/bis<sub>C8</sub>-OAc/IPr-OAc = 91/9/0. Purification over silica gel  
6  
7 (dichloromethane) followed by recrystallization in dichloromethane/cyclohexane.  
8  
9 White solid (339 mg, 70%). m. p.: 196 °C. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 8.63  
10 (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  
11 (s, 1H), 7.28 (s, 1H), 7.25 (dd, *J* = 1.5, 1.5 Hz, 1H), 4.82 (quint., *J* = 7.3 Hz, 1H),  
12 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,  
13 6H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 145.5, 135.3, 132.0, 130.2, 125.3, 124.7,  
14 121.3, 62.4, 33.9, 28.9, 26.4, 25.4, 24.4, 24.0, 23.8. <sup>19</sup>F NMR (376 MHz, Chloroform-  
15 *d*) δ -72.20 (d, *J* = 713 Hz). <sup>31</sup>P NMR (162 MHz, Chloroform-*d*) δ -144.29 (sept, *J* =  
16 713 Hz). HRMS (ESI) calcd. for C<sub>23</sub>H<sub>35</sub>N<sub>2</sub><sup>+</sup> (M-PF<sub>6</sub>): *m/z* 339.27947, found: 339.2798  
17 (1 ppm). Anal. Calcd. for C<sub>23</sub>H<sub>35</sub>F<sub>6</sub>N<sub>2</sub>P: C, 57.02%; H, 7.28%; N, 5.78%; found: C,  
18 57.05%; H, 6.87%; N, 5.68%  
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34 *3-cyclopentyl-1-(2,6-diisopropylphenyl)imidazolium hexafluorophosphate (3c):*

35  
36 Selectivity 3c-OAc/bis<sub>C5</sub>-OAc/IPr-OAc = 96/4/0. Purification over silica gel  
37  
38 (dichloromethane). Pale brown solid (345 mg, 78%). m. p.: 172 °C. <sup>1</sup>H NMR (400  
39 MHz, Chloroform-*d*) δ 8.55 (dd, *J* = 1.7, 1.7 Hz, 1H), 7.68 (dd, *J* = 1.9, 1.9 Hz, 1H),  
40 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  
41 (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  
42 (d, *J* = 6.8 Hz, 6H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 145.4, 135.5, 132.0, 130.1,  
43 125.5, 124.7, 121.5, 62.1, 33.5, 28.8, 24.3, 23.9, 23.8. <sup>19</sup>F NMR (376 MHz,  
44 Chloroform-*d*) δ -72.44 (d, *J* = 713 Hz). <sup>31</sup>P NMR (162 MHz, Chloroform-*d*) δ -144.37  
45 (sept, *J* = 713 Hz). HRMS (ESI) calcd. for C<sub>20</sub>H<sub>29</sub>N<sub>2</sub><sup>+</sup> (M-PF<sub>6</sub>): *m/z* 297.23307, found:  
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3 297.2331 (0 ppm). Anal. Calcd. for  $C_{20}H_{29}F_6N_2P$ : C, 54.30%; H, 6.61%; N, 6.33%;  
4  
5 found: C, 54.72%; H, 6.77%; N, 6.39%  
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8  
9 *3-cyclobutyl-1-(2,6-diisopropylphenyl)imidazolium hexafluorophosphate (3d):*

10 Selectivity 3d-OAc/bis $C_4$ -OAc/IPr-OAc = 86/14/0. Purification over silica gel  
11 (dichloromethane/pentane: 8/2 then dichloromethane). Pale brown solid (283 mg,  
12 66%). Single-crystals of **3d** were obtained by slow evaporation of a saturated  
13 solution in dichloromethane/pentane. m. p.: 161 °C.  $^1H$  NMR (400 MHz, Chloroform-*d*)  
14  $\delta$  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,  
15 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 –  
16 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  
17 (d,  $J = 6.8$  Hz, 6H), 1.12 (d,  $J = 6.8$  Hz, 6H).  $^{13}C$  NMR (101 MHz, Chloroform-*d*)  $\delta$   
18 145.5, 135.1, 132.0, 130.1, 125.4, 124.7, 121.4, 54.0, 30.7, 28.7, 24.4, 23.9, 14.6.  $^{19}F$   
19 NMR (376 MHz, Chloroform-*d*)  $\delta$  -72.47 (d,  $J = 713$  Hz).  $^{31}P$  NMR (162 MHz,  
20 Chloroform-*d*)  $\delta$  -144.35 (sept,  $J = 713$  Hz). HRMS (ESI) calcd. for  $C_{19}H_{27}N_2^+$  (M-  
21  $PF_6$ ):  $m/z$  283.21687, found: 283.2169 (0 ppm). Anal. Calcd. for  $C_{19}H_{27}F_6N_2P$ : C,  
22 53.27%; H, 6.35%; N, 6.54%; found: C, 53.75%; H, 6.38%; N, 6.29%  
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43 *3-adamantyl-1-(2,6-diisopropylphenyl)imidazolium tetrafluoroborate (3e-BF<sub>4</sub>):*

44 Selectivity 3e-OAc/7e-OAc/IPr-OAc = 94/6/0. Purification over silica gel  
45 (dichloromethane then dichloromethane/ethyl acetate: 9/1) following by  
46 recrystallization in ethyl acetate. White solid (1.9 g, 75% from 5.6 mmol of  
47 corresponding alkylamine). m. p.: 218 °C.  $^1H$  NMR (400 MHz, Chloroform-*d*)  $\delta$  8.83  
48 (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  
49 (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,  $J =$   
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3 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).  $^{13}\text{C}$   
4 NMR (101 MHz, Chloroform- $d$ )  $\delta$  145.4, 134.5, 131.8, 130.54, 125.1, 124.6, 120.4,  
5 61.6, 42.6, 35.2, 29.6, 28.8, 24.3, 24.0.  $^{19}\text{F}$  NMR (376 MHz, Chloroform- $d$ )  $\delta$  -151.57.  
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9  $^{11}\text{B}$  NMR (128 MHz, Chloroform- $d$ )  $\delta$  -1.02. HRMS (ESI) calcd. for  $\text{C}_{25}\text{H}_{35}\text{N}_2^+$  (M-  
10  $\text{BF}_4$ ):  $m/z$  363.28002, found: 363.2799 (0 ppm)  
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16 *3-cyclopropyl-1-(2,6-diisopropylphenyl)imidazolium hexafluorophosphate (3f)*:

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18 Selectivity 3f-OAc/bis $\text{C}_3$ -OAc/IPr-OAc = 70/26/4. Purification over silica gel  
19 (dichloromethane/pentane: 8/2 then dichloromethane). Pale brown solid (174 mg,  
20 42%). m. p.: 69 °C.  $^1\text{H}$  NMR (400 MHz, Chloroform- $d$ )  $\delta$  8.62 (dd,  $J = 1.6, 1.6$  Hz,  
21 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),  
22 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–  
23 1.22 (m, 4H), 1.17 (d,  $J = 6.8$  Hz, 6H), 1.13 (d,  $J = 6.8$  Hz, 6H).  $^{13}\text{C}$  NMR (101 MHz,  
24 Chloroform- $d$ )  $\delta$  145.5, 137.2, 132.1, 130.0, 125.0, 124.7, 123.7, 32.1, 28.7, 24.4,  
25 23.9, 7.4.  $^{19}\text{F}$  NMR (376 MHz, Chloroform- $d$ )  $\delta$  -72.58 (d,  $J = 714$  Hz).  $^{31}\text{P}$  NMR (162  
26 MHz, Chloroform- $d$ )  $\delta$  -144.42 (sept,  $J = 713$  Hz). HRMS (ESI) calcd. for  $\text{C}_{18}\text{H}_{25}\text{N}_2^+$   
27 (M- $\text{PF}_6$ ):  $m/z$  269.20177, found: 269.2018 (0 ppm)  
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43 *(S)-1-(2,6-diisopropylphenyl)-3-(1-phenylethyl)imidazolium hexafluorophosphate (3g)*:

44  
45 Selectivity 3g-OAc/bis $\text{PhEt}$ -OAc/IPr-OAc = 94/6/0. Purification over silica gel  
46 (dichloromethane). Pale brown solid (341 mg, 71%). m. p.: 178 °C.  $[\alpha]_D^{20}$ : -25.4 (c =  
47 1, chloroform).  $^1\text{H}$  NMR (400 MHz, Chloroform- $d$ )  $\delta$  8.53 (dd,  $J = 1.7, 1.7$  Hz, 1H),  
48 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 –  
49 7.23 (m, 3H), 5.98 (q,  $J = 7.0$  Hz, 1H), 2.26 (sept,  $J = 6.8$  Hz, 1H), 2.11 (sept,  $J = 6.8$   
50 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),  
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3 1.11 (d,  $J = 6.8$  Hz, 3H), 1.06 (d,  $J = 6.8$  Hz, 3H).  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  
4  
5  $\delta$  145.5, 145.3, 137.9, 132.1, 130.1, 129.8, 126.9, 125.2, 124.8, 124.7, 121.8, 60.6,  
6  
7 28.8, 28.8, 24.4, 24.1, 23.9, 20.7.  $^{19}\text{F}$  NMR (376 MHz, Chloroform-*d*)  $\delta$  -72.28 (d,  $J =$   
8  
9 713 Hz).  $^{31}\text{P}$  NMR (162 MHz, Chloroform-*d*)  $\delta$  -144.27 (sept,  $J = 713$  Hz). HRMS  
10  
11 (ESI) calcd. for  $\text{C}_{23}\text{H}_{29}\text{N}_2^+$  (M-PF<sub>6</sub>):  $m/z$  333.23252, found: 333.2330 (1 ppm)  
12  
13

14  
15  
16 *(R)*-1-(2,6-diisopropylphenyl)-3-((1-(naphthalen-1-yl)ethyl)imidazolium

17  
18 *hexafluorophosphate (3h)*: Selectivity 3h-OAc/7h-OAc/IPr-OAc = 83/17/0. Purification  
19  
20 over silica gel (diethyl ether/dichloromethane: 9/1). Pale brown solid (346 mg, 65%).  
21  
22 Single-crystals of **3h** were obtained by slow evaporation of a saturated solution in  
23  
24 dichloromethane/pentane. m. p.: 214 °C.  $[\alpha]_D^{20}$ : -36.2 ( $c = 1$ , chloroform).  $^1\text{H}$  NMR  
25  
26 (400 MHz, Chloroform-*d*)  $\delta$  8.43 (dd,  $J = 1.7, 1.7$  Hz, 1H), 7.94 – 7.87 (m, 3H), 7.74–  
27  
28 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,  
29  
30 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  
31  
32 (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),  
33  
34 0.91 (d,  $J = 6.8$  Hz, 3H).  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  145.4, 145.2, 135.7,  
35  
36 134.2, 132.1, 131.9, 131.0, 130.4, 129.9, 129.6, 127.8, 126.6, 125.6, 125.2, 125.2,  
37  
38 124.7, 124.7, 122.3, 121.8, 57.0, 28.7, 28.7, 24.1, 24.1, 24.1, 23.8, 20.8.  $^{19}\text{F}$  NMR  
39  
40 (376 MHz, Chloroform-*d*)  $\delta$  -72.11 (d,  $J = 713$  Hz).  $^{31}\text{P}$  NMR (162 MHz, Chloroform-*d*)  
41  
42  $\delta$  -144.16 (sept,  $J = 713$  Hz). HRMS (ESI) calcd. for  $\text{C}_{27}\text{H}_{31}\text{N}_2^+$  (M-PF<sub>6</sub>):  $m/z$   
43  
44 383.24817, found: 383.2485 (1 ppm). Anal. Calcd. for  $\text{C}_{27}\text{H}_{31}\text{F}_6\text{N}_2\text{P}$ : C, 61.36%; H,  
45  
46 5.91%; N, 5.30%; found: C, 61.74%; H, 5.91%; N, 5.24%  
47  
48  
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50  
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52  
53  
54 *(R)*-3-(2,3-dihydro-inden-1-yl)-1-(2,6-diisopropylphenyl)imidazolium

55  
56 *hexafluorophosphate (3i)*: Selectivity 3i-OAc/bis<sub>Ind</sub>-OAc/IPr-OAc = 93/7/0. Purification  
57  
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59  
60

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3 over silica gel (dichloromethane) followed by recrystallization in  
4  
5 dichloromethane/cyclohexane. White solid (320 mg, 65%). Single-crystals of **3i** were  
6  
7 obtained by slow evaporation of a saturated solution in dichloromethane/pentane. m.  
8  
9 p.: 205 °C.  $[\alpha]_D^{20}$ : +13.3 (c = 1, chloroform).  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  8.54  
10  
11 (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,  
12  
13 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,  $J$   
14  
15 = 6.8 Hz, 3H), 1.16 (d,  $J$  = 6.8 Hz, 3H), 1.15 (d,  $J$  = 6.8 Hz, 6H).  $^{13}\text{C}$  NMR (101 MHz,  
16  
17 Chloroform-*d*)  $\delta$  145.6, 145.3, 144.5, 137.8, 135.7, 132.2, 130.6, 130.0, 128.2, 125.9,  
18  
19 125.6, 125.0, 124.9, 124.8, 121.7, 66.0, 34.5, 30.4, 28.9, 28.8, 24.3, 24.1.  $^{19}\text{F}$  NMR  
20  
21 (376 MHz, Chloroform-*d*)  $\delta$  -72.30 (d,  $J$  = 713 Hz).  $^{31}\text{P}$  NMR (162 MHz, Chloroform-*d*)  
22  
23  $\delta$  -144.27 (sept,  $J$  = 713 Hz). HRMS (ESI) calcd. for  $\text{C}_{24}\text{H}_{29}\text{N}_2^+$  (M-PF<sub>6</sub>): *m/z*  
24  
25 345.23252, found: 345.2327 (0 ppm). Anal. Calcd. for  $\text{C}_{24}\text{H}_{29}\text{F}_6\text{N}_2\text{P}$ : C, 58.77%; H,  
26  
27 5.96%; N, 5.71%; found: C, 58.64%; H, 6.24%; N, 5.50%

31  
32  
33  
34 *(1R,2R,3R,5S)-1-(2,6-diisopropylphenyl)-3-(isopinocampheyl)imidazolium*

35  
36 *hexafluorophosphate (3j)*: Selectivity 3j-OAc/bisC<sub>Camph</sub>-OAc/IPr-OAc = 91/9/0.  
37  
38 Purification over silica gel (diethyl ether/dichloromethane: 9/1). White solid (260 mg,  
39  
40 51%). m. p.: 177 °C.  $[\alpha]_D^{20}$ : - 3.5 (c = 1, chloroform).  $^1\text{H}$  NMR (400 MHz, Chloroform-  
41  
42 *d*)  $\delta$  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,  
43  
44 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,  
45  
46 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),  
47  
48 2.03–1.94 (m, 2H), 1.29 (s, 3H), 1.20–1.11 (m, 15H), 1.09 (s, 3H).  $^{13}\text{C}$  NMR (101  
49  
50 MHz, CDCl<sub>3</sub>)  $\delta$  145.7, 145.3, 136.9, 132.1, 130.0, 126.3, 124.9, 124.6, 120.6, 60.8,  
51  
52 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.  
53  
54  
55  
56  $^{19}\text{F}$  NMR (376 MHz, Chloroform-*d*)  $\delta$  -72.05 (d,  $J$  = 713 Hz).  $^{31}\text{P}$  NMR (162 MHz,  
57  
58  
59  
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3 Chloroform-*d*)  $\delta$  -144.28 (sept,  $J = 714$  Hz). HRMS (ESI) calcd. for  $C_{25}H_{37}N_2^+$  (M-  
4 PF<sub>6</sub>):  $m/z$  365.29512, found: 365.2953 (0 ppm). Anal. Calcd. for  $C_{25}H_{37}F_6N_2P$ : C,  
5 58.81%; H, 7.31%; N, 5.49%; found: C, 58.94%; H, 7.57%; N, 5.79%  
6  
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11  
12 *(S)*-1-(2,6-diisopropylphenyl)-3-(1-hydroxy-4-methylpentan-2-yl)-imidazolium

13  
14 hexafluorophosphate (**3k**): Selectivity 3k-OAc/bis<sub>Leu</sub>OH<sup>-</sup>-OAc/IPr-OAc = 91/4.5/4.5.  
15  
16 Purification over silica gel (dichloromethane/acetone: 9/1). Brown glassy solid (309  
17 mg, 65%).  $[a]_D^{20}$ : - 4.8 ( $c = 1$ , chloroform). <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  8.52  
18 (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–  
19 7.24 (m, 3H), 4.77–4.65 (m, 1H), 3.95 (dd,  $J = 12.2, 3.4$  Hz, 1H), 3.71 (dd,  $J = 12.2,$   
20 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,  
21 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,  $J =$   
22 6.7 Hz, 6H), 0.94 (d,  $J = 6.5$  Hz, 3H), 0.93 (d,  $J = 6.7$  Hz, 3H). <sup>13</sup>C NMR (101 MHz,  
23 Chloroform-*d*)  $\delta$  145.7, 145.3, 136.6, 132.1, 130.0, 125.1, 124.8, 124.6, 121.4, 64.2,  
24 62.0, 38.5, 28.8, 28.6, 25.0, 24.2, 24.0, 24.0, 23.9, 22.5, 21.7. <sup>31</sup>P NMR (162 MHz,  
25 Chloroform-*d*)  $\delta$  -144.32 (sept,  $J = 713$  Hz). <sup>19</sup>F NMR (376 MHz, Chloroform-*d*)  $\delta$  -  
26 71.83 (d,  $J = 713$  Hz). HRMS (ESI) calcd. for  $C_{21}H_{33}N_2O^+$  (M-PF<sub>6</sub>):  $m/z$  329.25929,  
27 found: 329.2596 (0 ppm). Anal. Calcd. for  $C_{21}H_{33}F_6N_2OP$ : C, 53.16%; H, 7.01%; N,  
28 5.90%; found: C, 53.40%; H, 7.11%; N, 5.98%  
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48 *(S)*-1-(2,6-diisopropylphenyl)-3-(1-hydroxy-4-methylpentan-2-yl)-imidazolium

49  
50 hexafluorophosphate (**3l**): Selectivity 3l-OAc/bis<sub>Val</sub>OH<sup>-</sup>-OAc/IPr-OAc = 92/4/4.  
51  
52 Purification over silica gel (dichloromethane/acetone: 95/5) then washing with Et<sub>2</sub>O.  
53  
54 Brown glassy solid (1.05 g, 46% from 5.0 mmol of corresponding alkylamine).  $[a]_D^{20}$ :  
55 -10.2 ( $c = 0.5$ , chloroform). <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  8.51 (dd,  $J = 1.5, 1.5$   
56  
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3 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  
5 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,  $J =$   
6  
7 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,  $J =$   
8  
9 = 6.7 Hz, 3H), 0.85 (d,  $J = 6.7$  Hz, 3H).  $^{13}\text{C}$  NMR (101 MHz, Chloroform- $d$ )  $\delta$  145.7,  
10  
11 145.3, 136.6, 132.1, 130.0, 125.0, 124.8, 124.7, 122.1, 77.5, 69.4, 61.7, 29.3, 28.8,  
12  
13 28.7, 24.2, 24.1, 23.9, 19.1.  $^{31}\text{P}$  NMR (162 MHz, Chloroform- $d$ )  $\delta$  -144.32 (sept,  $J =$   
14  
15 713 Hz).  $^{19}\text{F}$  NMR (376 MHz, Chloroform- $d$ )  $\delta$  -71.90 (d,  $J = 713$  Hz). HRMS (ESI)  
16  
17 calcd. for  $\text{C}_{20}\text{H}_{31}\text{N}_2\text{O}^+$  (M-PF $_6$ ):  $m/z$  315.24309, found: 315.2431 (0 ppm)  
18  
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21  
22

23 *(S)*-3-(1-carboxy-3-methylbutyl)-1-(2,6-diisopropylphenyl)imidazolium

24  
25 *hexafluorophosphate (3m)*: Selectivity 3m-OAc/bis<sub>Leu</sub>COOH-OAc/IPr-OAc = 79/3/18.  
26  
27 Purification: Chromatography on silica gel (dichloromethane/MeOH: 95/5) and  
28  
29 extraction with a saturated aqueous solution of NaHCO $_3$ . The aqueous solution was  
30  
31 neutralized with 1M aqueous solution of HCl and extracted with dichloromethane.  
32  
33 Orange glassy solid (181 mg, 37%).  $[\alpha]_D^{20}$ : +31.5 ( $c = 1$ , chloroform).  $^1\text{H}$  NMR (400  
34  
35 MHz, Chloroform- $d$ )  $\delta$  9.20 (dd,  $J = 1.5, 1.5$  Hz, 1H), 7.95 (dd,  $J = 1.6, 1.6$  Hz, 1H),  
36  
37 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,  $J$   
38  
39 = 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  
40  
41 (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,  $J =$   
42  
43 6.6 Hz, 3H), 0.92 (d,  $J = 6.6$  Hz, 3H).  $^{13}\text{C}$  NMR (101 MHz, chloroform- $d$ )  $\delta$  170.6,  
44  
45 145.8, 145.4, 137.1, 131.8, 130.6, 124.7, 124.6, 123.8, 123.1, 122.8, 65.5, 43.8,  
46  
47 28.7, 28.7, 24.4, 24.3, 24.2, 24.1, 23.1, 21.7.  $^{31}\text{P}$  NMR (162 MHz, Chloroform- $d$ )  $\delta$  -  
48  
49 144.33 (sept,  $J = 713$  Hz).  $^{19}\text{F}$  NMR (376 MHz, Chloroform- $d$ )  $\delta$  -72.20 (d,  $J = 713$   
50  
51 Hz). HRMS (ESI) calcd. for  $\text{C}_{21}\text{H}_{31}\text{N}_2\text{O}_2^+$  (M-PF $_6$ ):  $m/z$  343.238, found: 343.2376 (1  
52  
53 ppm)  
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5 *1,3-bis((R)-1-(naphthalen-1-yl)ethyl)imidazol-3-ium hexafluorophosphate (7h)*: Yellow  
6 powder (492 mg, 97%). m.p.: 103 °C.  $[\alpha]_D^{20}$  : -118.0 (c = 0.1, chloroform).  $^1\text{H}$  NMR  
7 (400 MHz, Chloroform-*d*)  $\delta$  8.90 (dd,  $J$  = 1.7, 1.7 Hz, 1H), 8.02–7.68 (m, 6H), 7.58 –  
8 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,  
9 6H).  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  134.5, 134.1, 132.5, 130.6, 130.3, 129.4,  
10 127.9, 126.6, 125.5, 124.7, 121.7, 121.3, 56.7, 21.0.  $^{31}\text{P}$  NMR (162 MHz, Chloroform-  
11 *d*)  $\delta$  -144.03 (sept,  $J$  = 713 Hz).  $^{19}\text{F}$  NMR (376 MHz, Chloroform-*d*)  $\delta$  -71.78 (d,  $J$  =  
12 713 Hz). HRMS (ESI) calcd. for  $\text{C}_{27}\text{H}_{25}\text{N}_2^+$  (M- $\text{PF}_6$ ): 377.20122 m/z, found: 377.2013  
13 (0 ppm)

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27 *(R)-1-(2,6-diisopropylphenyl)-3-((1-(naphthalen-1-yl)ethyl)imidazol-2-ylidene)copper*  
28 *chloride complex (3h.CuCl)*: White solid (99 mg, 86%). m.p.: 214 °C.  $[\alpha]_D^{20}$  : +85.4 (c  
29 = 1, chloroform).  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  8.13–8.07 (m, 1H), 7.96–7.87  
30 (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,  
31 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),  
32 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,  $J$  =  
33 6.9 Hz, 3H), 0.99 (d,  $J$  = 6.9 Hz, 3H).  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  178.4,  
34 145.8, 145.7, 134.8, 134.2, 133.9, 131.3, 130.5, 130.2, 129.2, 127.0, 126.4, 125.2,  
35 124.6, 124.2, 124.2, 123.3, 123.2, 118.5, 56.9, 28.6, 28.4, 25.0, 24.7, 24.3, 24.0,  
36 22.5. HRMS (ESI) calcd. for  $\text{C}_{27}\text{H}_{30}\text{N}_2^{35}\text{ClNa}^{63}\text{Cu}^+$  (M+Na) : 503.12857 m/z , found :  
37 503.1291 (1 ppm)

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54 *Ethyl (S)-3-hydroxy-3-phenylpropanoate (9)*: With **3h**: Colorless oil (65 mg, 67%), e.r  
55 = 87 : 13.  $[\alpha]_D^{20}$  : -35.8 (c = 1, chloroform),  $[\text{Litt}]^{19\text{f}}$  :  $[\alpha]_D^{20}$  = -49.2 (c = 0.1, chloroform),  
56  
57  
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3 e.r.= 98:2]. With **7h**: Colorless oil (58 mg, 60%), e.r = 67.5 : 32.5. With **3h.CuCl**:  
4  
5 Colorless oil (74 mg, 76%), e.r.= 82 : 18. Enantiomeric excess was measured by  
6  
7 chiral HPLC:<sup>23</sup> OD-H column, Hexane / 2-propanol (90% / 10%) – 1 mL/min,  $\lambda$ =254  
8  
9 nm, T=25°C, R<sub>t1</sub> = 7.8 min, R<sub>t2</sub> = 10.1 min. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$   
10  
11 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* =  
12  
13 3.4 Hz, 1H), 2.88–2.59 (m, 2H), 1.27 (t, *J* = 7.1 Hz, 3H), <sup>13</sup>C NMR (101 MHz,  
14  
15 Chloroform-*d*)  $\delta$  172.6, 142.6, 128.7, 127.9, 125.8, 70.4, 61.0, 43.5, 14.3.  
16  
17  
18  
19

20  
21 (*S*)-(3-methylpent-1-en-3-yl)benzene (**11a**): Colorless oil (58 mg, 73%, conversion  
22  
23 >95%). S<sub>N</sub>2'/S<sub>N</sub>2 selectivity: 96/4. e.r = 92:8 (*S*).  $[\alpha]_D^{20}$  : +10.5 (c = 1, chloroform)  
24  
25 [Litt<sup>10</sup> :  $[\alpha]_D^{20}$  = +10.1 (c = 1, chloroform), e.r.= 91:9]. Enantiomeric excess was  
26  
27 measured by chiral GC: Beta-dex column, helium (30.9 cm/sec), 80°C-55min-  
28  
29 10°C/min-160°C-10 min, R<sub>t1</sub> = 43.7 min (*R*), R<sub>t2</sub> = 44.3 min (*S*). <sup>1</sup>H NMR (400 MHz,  
30  
31 Chloroform-*d*):  $\delta$  = 7.37–7.16 (m, 5H), 6.04 (dd, *J* = 17.4, 10.8 Hz, 1H), 5.10 (dd, *J* =  
32  
33 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,  
34  
35 CH<sub>3</sub>), 0.80 (t, *J* = 7.6 Hz, 3H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*):  $\delta$  = 147.6, 147.0,  
36  
37 128.1, 126.8, 125.8, 111.9, 44.7, 33.5, 24.5, 9.0.  
38  
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43  
44 1-bromo-2-(3-methylpent-1-en-3-yl)benzene (**11b**): Colorless oil (81 mg, 68%,  
45  
46 conversion >95%). S<sub>N</sub>2'/S<sub>N</sub>2 selectivity: >98/<2. e.r = 91:9 (*S*).  $[\alpha]_D^{20}$  : +1.7 (c = 1,  
47  
48 chloroform). [Litt<sup>10</sup> :  $[\alpha]_D^{20}$  = +2.4 (c = 1, chloroform), e.r. = 95:5]. Enantiomeric excess  
49  
50 was measured by chiral GC: GTA column, helium (33.2 cm/sec), 80°C-60min-110°C-  
51  
52 15min-1°C/min-160°C-10min-10°C/min, R<sub>t1</sub>(major) = 94.7 min (*R*), R<sub>t2</sub>(minor) = 96.7  
53  
54 min (*S*). <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  7.57 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.40 (dd,  
55  
56 *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,  
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59  
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3  $J = 17.6, 10.7$  Hz, 1H), 5.10 (dd,  $J = 10.7, 1.1$  Hz, 1H), 4.93 (dd,  $J = 17.6, 1.1$  Hz,  
4 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).  $^{13}\text{C}$   
5  
6  
7 NMR (101 MHz, Chloroform- $d$ )  $\delta$  146.5, 145.1, 135.6, 129.9, 127.8, 127.0, 123.5,  
8  
9 112.6, 46.4, 31.3, 25.8, 9.1.  
10

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13  
14 *1-(3-methylpent-1-en-3-yl)naphthalene (11c)*: Colorless oil (74 mg, 71%, conversion  
15 78%).  $\text{S}_{\text{N}}2'/\text{S}_{\text{N}}2$  selectivity: 96/4. e.r = 95 : 5.  $[\alpha]_{\text{D}}^{20}$  : -6.5 (c = 1, chloroform). [Litt<sup>10</sup>  
16  
17  $[\alpha]_{\text{D}}^{20}$  = -8.0 (c = 1, chloroform), e.r. = 96:4]. Enantiomeric excess was measured by  
18  
19 chiral HPLC: OJ-H column, hexane (100%) – 0.3 mL/min,  $\lambda=254$  nm, T=25°C,  
20  
21  $R_{\text{t}1}$ (minor) = 17.9 min,  $R_{\text{t}2}$ (major) = 18.5 min.  $^1\text{H}$  NMR (400 MHz, Chloroform- $d$ ):  $\delta$  =  
22  
23 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,  
24  
25 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,  
26  
27 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).  $^{13}\text{C}$   
28  
29 NMR (101 MHz, Chloroform- $d$ )  $\delta$  149.0, 142.5, 135.0, 131.8, 129.2, 127.8, 127.7,  
30  
31 125.2, 125.1, 124.9, 124.4, 112.1, 45.7, 32.9, 27.5, 9.1.  
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3 **Supporting Information:** Detailed spectral data for products, crystallographic data  
4 (CIF files) and supplementary experiments, this material is available free of charge  
5 via the Internet at <http://pubs.acs.org>.  
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43 (17) Preliminary results tend to demonstrate that the equilibration reactions between  
44  
45 the three diimines are accelerated in the presence of ZnCl<sub>2</sub>.

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