Published in final edited form as:

J Org Chem. 2007 April 27; 72(9): 3492–3499.

Intramolecular “Hydroiminiumation and –amidiniumation” of Alkenes: A Convenient, Flexible, and Scalable Route to Cyclic Iminium and Imidazolinium Salts

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Abstract

Addition of a stoichiometric amount of HCl to alkenylaldimines, -formamidines, and -amidines results in the protonation of the sp^2 -nitrogen atom. The resulting alkenylaldiminium, -formamidinium, and -amidinium salts can be isolated and fully characterized, including single-crystal X-ray diffraction studies. Heating solutions of these salts induces ring closure cleanly and regioselectively via formal “exo” addition of the nitrogen–hydrogen bond to the pendent carbon–carbon double bond, affording the corresponding cyclic aldiminium, dihydroisoquinolinium, and imidazolinium salts. Of special interest, novel 4,4-disubstituted imidazolinium salts are accessible via this synthetic route. Similarly, addition of phosgene to alkenyl ureas and alkenyl amides, followed by gentle heating, cleanly affords C-chloro imidazolinium, and cyclic C-chloro iminium salts, respectively. Treatment of the latter with tetrakis(triphenylphosphine)-palladium allows for the preparation of the first transition-metal complex bearing a cyclic arylaminocarbene as ligand. Deuterium labeling experiments suggest that the mechanism of the hydroiminiumation and -amidiniumation reactions involves an intramolecular proton transfer to the double bond in the rate-determining step. This novel synthetic methodology gives access to a variety of *N*-heterocyclic carbene (NHC) and cyclic alkyl- and arylaminocarbene (CAAC) precursors.

Introduction

Imidazolinium **A** (Scheme 1) and imidazolium salts have found numerous applications as room-temperature ionic liquids, of particular importance for “Green Chemistry”,¹ but also for dye-sensitized solar cells, electrochemical devices, wet double-layer capacitors, and ion transport systems.² When R = H, they serve as direct precursors for free Arduengo-type carbenes (NHCs)^{3,4} and for the introduction of NHC ligands into transition metal based catalysts;⁵ the chloro analogues (R = Cl) can also be used for the latter application.⁶ As recently noted by Fürstner et al.,⁷ despite a huge number of structural variants, several obvious and seemingly trivial substitution patterns for these dinitrogen-containing heterocyclic salts are as yet unknown or very rare. Among them are the unsymmetrical versions, and particularly 4,4-disubstituted imidazolinium salts **A'**.^{7,8} These limitations stem from the scarcity of viable synthetic routes. Moreover, it is astounding to note that the classical route to imidazolinium salts⁹ involves the use of NaBH₄ as a reducing agent, which turns out to be rather expensive from an industrial point of view, and even more importantly from a “Green Chemistry”

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Supporting Information Available: X-ray crystallographic data for **4b**, **10a**, **11a**, and **18a** (CIF) and spectral data for prepared compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

perspective, poses many environmental and recycling challenges. Among the alternative synthetic methods,¹⁰ the most common relies on *N*-substitution of appropriate imidazoline precursors, which is only possible with a small number of reactive electrophiles.

Because saturated nitrogen-containing heterocycles form the core structures, and are key intermediates, of many natural products,¹¹ several synthetic methods for their preparation have been developed. Among them is the intramolecular hydroamination of alkenes, in which the nitrogen–carbon bond is formed by addition of an amine N–H bond to an olefin.¹² Various catalysts have been used to effect this transformation, and importantly, it has been shown recently that when weakly basic amines are used, the hydroamination can be catalyzed by Brønsted acids.¹³ Recognizing that imines are less basic than amines, we have studied the feasibility of “hydroiminiumation” reactions and recently reported preliminary results.¹⁴ We showed that the addition of a stoichiometric amount of HCl to alkenyl imines resulted in the formation of the *N*-protonated species **B**, which underwent, under gentle heating, a ring closure cleanly and regioselectively, leading to the cyclic iminium salts **C** (Scheme 1). Importantly, salts **C** are the direct precursors of stable cyclic alkylaminocarbenes (CAACs).¹⁵ We have shown that CAACs can compete with NHCs as ligands for transition-metal-based catalysts^{15a} and also allow the preparation of very low coordinate transition-metal centers.^{15b}

We report herein examples of an asymmetric version of the hydroiminiumation reaction and the extension of our approach to the synthesis of dihydroisoquinolinium salts as well as cyclic *C*-chloro iminium salts. We show that the N–H bond of amidinium salts also adds to a pendent carbon–carbon double bond giving a straightforward, atom-economical route to imidazolinium salts, especially those of type **A'**. Last, the mechanism of this ring-closing reaction is discussed on the basis of isotopic labeling experiments.

Results and Discussion

We have already shown that relatively bulky electrophiles (such as the 1,2-epoxy-2-methylpropane) approach the cyclohexane moiety of the aza-allyl anion prepared from the aldimine **1a** [derived from (–)-menthone] exclusively from the equatorial direction.^{15a} Therefore, despite the fact that **1a** exists as a 90/10 mixture of diastereomers, addition of 3-bromo-2-methylpropene to its lithium salt led to the enantiomerically pure alkenylaldimine **2a** in 94% yield (Scheme 2). After addition of HCl to form the alkenylaldiminium salt **3a**, the cyclization occurred readily and was complete after 5 h at 50 °C. The optically pure cyclic iminium salt **4a** was isolated in 92% yield (by the previously reported method, **4a** was obtained in only 41% yield).

The use of 3-bromopropene provided an opportunity to create a new stereogenic center next to nitrogen and to check if the presence of the enantiomerically pure menthyl ring would produce an asymmetric induction. It was pleasing to observe that heating **3b** in acetonitrile at 100 °C for 12 h cleanly afforded the desired heterocyclic salt **4b**, isolated in 86% yield, with an 82% de (according to ¹H NMR spectroscopy) (Scheme 2). The absolute configuration of the major diastereomer was assigned by single-crystal X-ray crystallography (Figure 1).

To demonstrate further the generality of the hydroiminiumation route, we turned our attention to the preparation of 3,4-dihydroisoquinolinium salts. Although several synthetic routes are available for such heterocycles, 6,6-disubstituted derivatives featuring a bulky substituent at nitrogen are attainable only through addition of an electrophile to the nitrogen of the corresponding dihydroisoquinoline, thus placing severe restrictions on the size of the *N*-substituent;¹⁶ they are highly desirable precursors for the preparation of the as yet unknown stable cyclic arylaminocarbenes.¹⁷ Starting from the readily available aldimine **5**, a lithium–halogen exchange with *n*-BuLi, followed by addition of 3-bromo-2-methylpropene

quantitatively led to the desired precursor **6**. Then, addition of HCl and heating at 110 °C for 24 h afforded the 6,6-dimethyldihydroisoquinolinium salt **7**, which was isolated in 95% yield (Scheme 3).

Despite the greater basicity of amidines over imines, it was decided to investigate the possibility of extrapolating this ring-closure protocol to the synthesis of imidazolinium salts **A**. Deprotonation of **8a** with *n*-BuLi followed by addition of allyl chloride afforded the corresponding alkenyl formamidine **9a** in 94% yield (Scheme 4). Addition of a stoichiometric amount of a 2 M solution of HCl/Et₂O to a toluene or ether solution of **9a** resulted in the formation of a precipitate. After filtration and recrystallization from chloroform, a new compound **10a** was isolated as white crystals in 95% yield. A doublet resonance in the ¹H NMR spectrum at 14.0 ppm (*J*_{HH} = 12.0 Hz) suggested the protonation of one nitrogen atom. A single-crystal X-ray diffraction study unambiguously proved the alkenyl formamidinium structure of **10a** (Figure 2, left). We were pleased to observe that heating a toluene or acetonitrile solution of **10a** in a flask sealed by a Teflon stopcock at 135 °C for 36 h afforded the desired imidazolinium salt **11a** as a racemate in 83% yield (Figure 2, right) (Scheme 4). Similarly, alkenylformamidines **9b–d**, prepared from the corresponding formamidines in high yields, were found to be suitable precursors for 4,4-disubstituted imidazolinium salts **11b–d**. The protonation/cyclization sequence was performed in situ. Imidazolinium salt **11b** was isolated in 80% yield after heating for 24 h at 110 °C. When the Dipp substituents of **10b** were replaced by mesityl groups, the cyclization required heating at 135 °C for 12 h, and heterocyclic salt **11c** was isolated in 78% yield. Under the same experimental conditions, imidazolinium salt **11d** featuring 2,6-difluorophenyl groups was also obtained in 79% yield from **9d**, illustrating the broad scope of application of this synthetic route.

Since the *N*-substitution of formamidines by reactive electrophiles is a well-known reaction, it quickly became apparent that the above synthesis of imidazolinium salts could be simplified even further. Indeed, allyl bromide and 3-bromo-2-methylpropene are quite reactive as electrophiles, and in the process of the substitution of formamidine **8a**, one equivalent of HBr is liberated, protonating the remaining nitrogen. Thus, heating an equimolar toluene solution of allyl bromide and formamidine **8a** in a tube sealed by a Teflon stopcock at 135 °C for 36 h afforded imidazolinium salt **11a**, which was isolated in 66% yield. The one-pot procedure appeared to occur at a slightly lower temperature when 3-bromo-2-methylpropene was used. The reaction was complete after 24 h at 110 °C and imidazolinium salt **11b**, featuring two methyl groups in the 4 position, was isolated in 70% yield (Scheme 5).

The cyclization process is not restricted to formamidines. When a phenyl substituent is present at the NCN carbon and given bulky groups at nitrogen, the allylation of **12** may be performed via its corresponding lithium salt. Then, after protonation with HCl, the ring closure leading to **13** is complete after 12 h at 105 °C (Scheme 6).

As mentioned in the introduction, *C*-chloro imidazolinium salts can be used to introduce the corresponding NHCs as ligands for transition-metal centers. Chloro amidines are classically prepared by addition of a strong chlorinating reagent (such as phosgene or oxalyl chloride) to trisubstituted urea derivatives, followed by elimination of HCl; obviously, this transformation proceeds via *C*-chloro amidinium salts.¹⁸ Therefore, we hypothesized that using *N*-allylurea **14** as a starting material, a *C*-chloro amidinium salt would be formed by addition of phosgene and this may undergo a subsequent hydroamidinium reaction, affording the desired *C*-chloro imidazolinium salt **15**. *N*, *N'*-Diaryl-*N*-allylurea **14** is readily available as shown in Scheme 7. Simple heating of a toluene solution of **14** at 80 °C for 24 h in the presence of a stoichiometric amount of phosgene, cleanly leads to **15**, which was isolated in 78% yield.

A very similar methodology can be applied to prepare C-chloro iminium salts **17a,b**. Heating **16a** and **16b** at 80 °C for 24 h gave rise to **17a** and **17b**, which were isolated in 86 and 78% yield, respectively (Scheme 8). Since transition-metal complexes of cyclic aminoarylcarbenes have not yet been reported, and as a proof of principle that this type of C-chloro iminium salts are effective prolignands for transition-metal complexes, **17a** was treated with palladium tetrakis (triphenylphosphine). Indeed, palladium(II) complex **18a** was isolated in 55% yield and fully characterized including a single-crystal X-ray diffraction study (Figure 3).

In order to gain more insight into the mechanism of the cyclization process, deuterium labeling experiments were carried out using **2c** and **9a** as starting materials. In both cases, only one deuterated compound (**4c_D** and **11c_D**, respectively) was obtained (Scheme 9). These observations argue against a reversible protonation of the alkene, since in this case mono- and polydeuterated derivatives would be obtained. Of special importance is the exclusive formation of **4c_D**. If an inter-molecular protonation of the olefin were to occur, we would expect little or no preference for deuteration at either olefinic carbon, and consequently observe scrambling of the deuterium over these two positions, since in both cases a secondary carbocation would be formed. Therefore, it can be concluded that the proton is transferred intramolecularly to the double bond in the rate-determining step.

Conclusion

Simple protonation of the sp²-nitrogen atom of alkenylaldimines, -formamidines, and -amidines and addition of a chlorinating agent to alkenyl amides followed by heating are very convenient synthetic routes to a variety of NHC and CAAC precursors. Deuterium labeling experiments suggest that the mechanism of the cyclization reaction involves an intramolecular proton transfer to the double bond in the rate-determining step. Extension of this novel methodology to related systems is under investigation.

Experimental Section

General Methods

All manipulations were performed under an inert atmosphere of dry argon using standard Schlenk techniques. Dry, oxygen-free solvents were employed. ¹H and ¹³C NMR chemical shifts are reported relative to residual solvent resonances. ³¹P and ¹⁹F NMR chemical shifts are reported relative to 85% H₃PO₄ and CFC₃, respectively.

Synthesis of Aldimine 1a

In a Schlenk tube containing activated molecular sieves (10 g), menthyl 3-carboxaldehyde (90/10 mixture of diastereomers)¹⁹ (33.8 mL, 181 mmol) was added dropwise at room temperature to a solution of 2,6-diisopropylaniline (30.6 g, 173 mmol) in toluene (100 mL). The suspension was stirred for 12 h at 100 °C. After filtration, the molecular sieves were washed with hexane (60 mL). Evaporation of the solvent, and heating under vacuum at 100 °C to remove all volatiles, afforded **1a** (80% de) as an oily yellow solid (52.0 g, 92%). Major diastereomer: ¹H NMR (CDCl₃) δ 7.43 (d, *J*_{HH} = 7.1 Hz, 1H), 7.14–7.05 (m, 3H), 2.98 (sept, *J*_{HH} = 6.9 Hz, 2H), 2.54 (m, 1H), 1.94–1.70 (m, 4H), 1.59–1.38 (m, 5H), 1.17 (2 × overlapping d, *J*_{HH} = 6.9 Hz, 12H), 0.97 (2 × overlapping d, *J*_{HH} = 6.5 Hz, 6H), 0.90 (d, *J*_{HH} = 6.9 Hz, 3H); ¹³C{¹H} NMR (CDCl₃) δ 171.6, 148.9, 138.0, 124.1, 123.1, 48.5, 45.2, 39.2, 35.0, 32.3, 29.5, 27.7, 23.9, 23.7, 22.8, 21.6, 15.5; MS(HR-ESI) *m/z* 328.3004 [M + H]⁺ (calcd 328.3004).

Synthesis of Alkenylaldimine 2a

An Et₂O solution (20 mL) of Me₂NLi (0.467 g, 9.2 mmol) at –78 °C was added to an Et₂O solution (20 mL) of **1a** (3.00 g, 9.2 mmol) at –78 °C. After 15 min, the mixture was warmed

to rt and stirred for an additional 4 h. The volatiles were removed under vacuum, affording an oily yellow/orange residue which was dissolved in Et₂O (30 mL) and cooled to -78 °C. 3-Bromo-2-methylpropene (0.92 mL, 9.2 mmol) was slowly added. After 15 min, the solution was warmed to rt and stirred for an additional 12 h. Removal of the volatiles under vacuum and extraction with hexanes afforded alkenylaldimine **2a** as a light yellow oil (3.11 g, 94%): ¹H NMR (CDCl₃) δ 8.21 (s, 1H), 7.33 (d, *J*_{HH} = 7.2 Hz, 2H), 7.27 (t, *J*_{HH} = 7.2 Hz, 1H), 5.23 and 5.04 (s × 2, 1H), 3.22 (sept, *J*_{HH} = 6.8 Hz, 2H), 2.84 (m, 2H), 2.53 (m, *J*_{HH} = 6.4 Hz, 1H), 2.23 (d, *J*_{HH} = 12.8 Hz, 1H), 2.12 (s, 3H), 2.07 (d, *J*_{HH} = 12.4 Hz, 1H), 1.89 (d, *J*_{HH} = 12.4 Hz, 1H), 1.77–1.55 (m, 4H), 1.42 (m, 12H), 1.22 (d, *J*_{HH} = 6.8 Hz, 3H), 1.16 (d, *J*_{HH} = 6.4 Hz, 3H), 1.02 (d, *J*_{HH} = 6.8 Hz, 3H); ¹³C{¹H} NMR (CDCl₃) δ 172.1, 149.3, 142.8, 137.7, 123.9, 123.1, 116.4, 49.2, 47.7, 45.7, 44.1, 35.8, 29.3, 27.8, 26.5, 26.0, 24.0, 23.9, 23.7, 23.2, 23.1, 19.1; MS(EI) *m/z* 382 [M + H]⁺.

Synthesis of Alkenylaldimine 2b

Following the same procedure used for **2a**, but with 3-bromopropene, **2b** was obtained as a light yellow oil (89%): ¹H NMR (CDCl₃) δ 7.98 (s, 1H), 7.16–7.06 (m, 3H), 6.02–5.88 (m, 1H), 5.20 (s, 1H), 5.16 (s, 1H), 2.97 (sept, *J*_{HH} = 6.8 Hz, 2H), 2.67–2.45 (m, 2H), 2.26–2.15 (m, 1H), 2.00–1.66 (m, 4H), 1.46–1.26 (m, 4H), 1.20 (t, *J*_{HH} = 6.4 Hz, 12H), 1.00 (d, *J*_{HH} = 6.9 Hz, 3H), 1.16 (d, *J*_{HH} = 6.2 Hz, 3H), 1.02 (d, *J*_{HH} = 6.9 Hz, 3H); ¹³C{¹H} NMR (CDCl₃) δ 171.9, 149.3, 137.6, 134.7, 123.9, 123.1, 118.4, 48.4, 48.1, 44.9, 41.8, 35.8, 29.2, 27.7, 25.6, 24.4, 23.8, 23.7, 23.3, 23.0, 19.2; MS(EI) *m/z* 368 [M + H]⁺.

Synthesis of Alkenylaldiminium 3a

To a hexane solution (10 mL) of **2a** (1.00 g, 2.6 mmol) at -78 °C was added a solution of HCl in Et₂O (1.30 mL, 2.0 M, 2.6 mmol). Precipitation of a white powder was immediately observed. After 15 min, the mixture was warmed to rt and stirred for an additional 15 min. Filtration of the precipitate, washing with hexanes (2 × 10 mL), and drying under vacuum afforded the alkenyliminium salt **3a** as a white powder (1.01 g, 92%): mp 60–62 °C dec; ¹H NMR (CDCl₃) δ 14.66 (br s, 1H), 8.31 (s, 1H), 7.24 (m, 3H), 5.08 (s, 1H), 4.93 (s, 1H), 3.07 (d, *J*_{HH} = 13.7 Hz, 1H), 2.95 (sept, *J*_{HH} = 6.8 Hz, 2H), 2.73 (d, *J*_{HH} = 13.7 Hz, 1H), 2.43 (br d, *J*_{HH} = 13.0 Hz, 1H), 2.30 (sept, *J*_{HH} = 6.4 Hz, 2H), 1.95 (s, 2H), 1.86–1.50 (m, 6H), 1.34 (m, 2H), 1.26 (dd, *J*_{HH} = 2.3 Hz, 12H), 0.99 (br t, *J*_{HH} = 7.9 Hz, 6H), 0.79 (d, *J*_{HH} = 6.8 Hz, 3H); ¹³C{¹H} NMR (CDCl₃) δ 189.9, 143.2, 139.2, 134.8, 130.7, 124.7, 119.2, 51.7, 46.6, 45.7, 42.4, 34.8, 30.7, 28.8, 26.1, 26.0, 24.2, 23.9, 23.4, 23.2, 22.5, 18.3.

Synthesis of Alkenylaldiminium Salt 3b

Following the same procedure used for **3a**, but starting from **2b** (1.00 g, 2.7 mmol), **3b** was obtained as a white solid (0.99 g, 90%): mp 60 °C; ¹H NMR (CDCl₃) δ 15.47 (br s, 1H), 8.15 (s, 1H), 7.26 (t, *J*_{HH} = 7.6 Hz, 1H), 7.13 (d, *J*_{HH} = 7.6 Hz, 2H), 5.75 (m, 1H), 5.21 (d, *J*_{HH} = 2.7 Hz, 1H, =CH₂), 5.19 (br d, 1H), 3.08 (dd, *J*_{HH} = 7.1, 13.9 Hz, 1H), 2.84 (sept, *J*_{HH} = 6.7 Hz, 2H), 2.66 (dd, *J*_{HH} = 7.1, 13.9 Hz, 1H), 2.44 (dd, *J*_{HH} = 12.8, 13.9 Hz, 1H), 2.08 (sept, *J*_{HH} = 6.5 Hz, 1H), 1.79 (d, *J*_{HH} = 12.5 Hz, 1H), 1.69 (d, *J*_{HH} = 12.5 Hz, 1H), 1.53 (br s, 1H), 1.45 (d, *J*_{HH} = 13.0 Hz, 2H), 1.22 (br s, 1H), 1.16 (d, *J*_{HH} = 6.7 Hz, 12H), 0.96 (br s, 1H), 0.99 (d, *J*_{HH} = 6.5 Hz, 6H), 0.69 (d, *J*_{HH} = 6.7 Hz, 3H); ¹³C{¹H} NMR (CDCl₃) δ 185.1, 141.5, 138.0, 131.3, 128.8, 124.0, 120.6, 50.0, 47.3, 44.7, 40.5, 34.8, 29.9, 28.3, 25.4, 23.7, 23.5, 22.9, 22.3, 18.3.

Synthesis of CAAC, H⁺ 4a

An oven-dried, argon-flushed, scalable Schlenk tube with a Teflon stopcock was loaded with **3a** (1.00 g, 2.4 mmol) in CHCl₃ (5 mL). The mixture was heated at 55 °C for 6 h. The volatiles

were removed under vacuum to afford **4a** as a white powder (0.92 g, 92%): mp 157 °C; the spectroscopic data are similar to those reported for the trifluoromethane sulfonate salt.^{15a}

Synthesis of CAAC, H⁺ **4b**

Cyclic iminium salt **4b** was prepared in one pot starting from **2b**. An oven-dried, argon-flushed, scalable Schlenk tube with a Teflon stopcock was loaded with **2b** (1.00 g, 2.7 mmol) and toluene (10 mL) and was cooled to −78 °C, at which point a solution of HCl in Et₂O (1.36 mL, 2.0 M, 2.7 mmol) was added. Precipitation of a white powder (**3b**) was immediately observed. After 15 min at −78 °C, the mixture was allowed to warm to rt and stirred for an additional 15 min. The mixture was heated at 110 °C for 24 h, after which time the volatiles were removed under vacuum to afford **4b** as a 91:9 ratio of diastereomers (0.86 g, 86%). The major isomer was obtained optically pure by recrystallization from chloroform at −30 °C: mp 150 °C; ¹H NMR (CD₃CN) δ 10.45 (s, 1H), 7.60 (t, *J*_{HH} = 7.8 Hz, 1H), 7.46–7.42 (m, 2H), 4.87 (sext, *J*_{HH} = 7.1 Hz, 1H), 2.97 (sept, *J*_{HH} = 6.8 Hz, 2H), 2.67–2.45 (m, 2H) 2.26–2.15 (m, 1H), 2.00–1.66 (m, 4H), 1.46–1.26 (m, 4H), 1.20 (t, *J*_{HH} = 6.4 Hz, 12H), 1.00 (d, *J*_{HH} = 6.9 Hz, 3H), 1.16 (d, *J*_{HH} = 6.2 Hz, 3H), 1.02 (d, *J*_{HH} = 6.9 Hz, 3H); ¹³C{¹H} NMR (CD₃CN) δ 194.6, 145.6, 144.3, 133.1, 132.0, 126.7, 126.5, 72.8, 60.2, 50.3, 48.5, 40.6, 35.9, 31.1, 30.3, 29.9, 27.4, 26.6, 25.4, 24.0, 23.7, 23.5, 23.3, 22.6, 19.1, 18.4; MS(ESI) *m/z* 368 [M]⁺.

Synthesis of Alkenylaldimine **6**

A solution of *n*-BuLi in hexanes (3.6 mL, 1.6 M, 5.8 mmol) was added dropwise to an Et₂O solution (20 mL) of **5**²⁰ (2.00 g, 5.8 mmol) at −78 °C. After 15 min, the mixture was warmed to rt and stirred for an additional 1 h. The mixture was then cooled to −78 °C, and 3-bromo-2-methylpropene (0.59 mL, 5.8 mmol) was slowly added. After 15 min, the solution was warmed to rt and stirred for an additional 12 h. Removal of the volatiles under vacuum and extraction with hexanes afforded **6** as a light yellow oil (1.80 g, 97%): ¹H NMR (CDCl₃) δ 8.49 (s, 1H), 8.32–8.28 (m, 1H), 8.32–8.28 (m, 1H), 7.50–7.44 (m, 2H), 7.33–7.30 (m, 1H), 7.26–7.18 (m, 2H), 4.89 (s, 1H), 4.48 (s, 1H), 3.61 (s, 2H), 3.07 (sept, *J*_{HH} = 6.8 Hz, 2H), 1.83 (s, 3H), 1.24 (d, *J*_{HH} = 6.8 Hz, 12H); ¹³C{¹H} NMR (CDCl₃) δ 160.7, 149.8, 145.2, 140.0, 137.8, 134.6, 131.3, 131.1, 127.6, 127.2, 124.2, 123.2, 112.7, 40.9, 28.1, 23.7, 23.3; MS(EI) *m/z* 320 [M + H]⁺.

Synthesis of Dihydroisoquinolinium **7**

Salt **7** was prepared from **6** following the same procedure as for the synthesis of **4b**. Precipitation of the residue from Et₂O afforded **7** as a white powder (95%): mp 118 °C; ¹H NMR (CDCl₃) δ 9.98 (s, 1H), 8.73 (d, *J*_{HH} = 7.6 Hz, 1H), 7.82 (br dd, 1H), 7.80–7.47 (m, 3H), 7.31 (d, *J*_{HH} = 7.9 Hz, 2H), 3.54 (s, 2H), 2.77 (sept, *J*_{HH} = 6.8 Hz, 2H), 1.43 (s, 6H), 1.33 (d, *J*_{HH} = 6.8 Hz, 6H), 1.21 (d, *J*_{HH} = 6.8 Hz, 6H); ¹³C{¹H} NMR (CDCl₃) δ 172.0, 143.8, 139.5, 138.1, 136.7, 135.0, 131.2, 129.0, 125.1, 125.0, 67.8, 40.7, 29.7, 26.2, 25.2, 23.0; MS-(HR-ESI) *m/z* 320.2373 [M]⁺ (calcd 320.2378).

Synthesis of Alkenylformamidines **9a–d**

To a THF solution (40 mL) of the corresponding formamidines **8** (5.5 mmol) at −78 °C was added a solution of *n*-BuLi in hexanes (5.5 mmol). The mixture was stirred for 30 min and then was allowed to warm to rt and stirred for a further 12 h. The mixture was again cooled to −78 °C, and 3-bromopropene (5.5 mmol) or 3-bromo-2-methylpropene (5.5 mmol) was slowly added. The mixture was stirred for 30 min at −78 °C and then heated at 50 °C for 12 h. Removal of the volatiles under vacuum and extraction with hexanes afforded derivatives **9a–d**. Derivative **9a** was obtained as a white solid (94%): mp 62 °C; ¹H NMR (CDCl₃) δ 7.37–6.99 (m, 7H), 6.26–6.13 (m, 1H), 5.19 (d, *J*_{HH} = 5.5 Hz, 1H), 5.15 (br s, 1H), 4.42 (d, *J*_{HH} = 6.8 Hz, 2H), 3.33–3.18 (m, 4H), 1.30 (d, *J*_{HH} = 6.8 Hz, 6H), 1.22 (d, *J*_{HH} = 6.8 Hz, 12H), 1.15 (d,

$J_{\text{HH}} = 6.8 \text{ Hz}$, 6H); $^{13}\text{C}\{^1\text{H}\}$ NMR(CDCl_3) δ 151.1, 148.4, 147.5, 140.1, 138.4, 133.4, 128.9, 124.4, 122.8, 118.3, 53.0, 28.5, 28.0, 25.4, 24.4, 23.8; MS-(EI) m/z 405 $[\text{M} + \text{H}]^+$. Derivative **9b** was obtained as a white solid (89%): mp 73 °C; ^1H NMR (CDCl_3) δ 7.34–6.96 (m, 7H), 4.84 (s, 1H), 4.68 (s, 1H), 4.41 (s, 2H), 3.24 (m, 4H), 1.98 (s, 3H), 1.29 (d, $J_{\text{HH}} = 6.7 \text{ Hz}$, 6H), 1.20 (d, $J_{\text{HH}} = 6.8 \text{ Hz}$, 12H), 1.12 (d, $J_{\text{HH}} = 6.8 \text{ Hz}$, 6H); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3) δ 152.2, 148.4, 147.5, 141.5, 140.0, 138.7, 128.7, 124.4, 122.8, 115.8, 55.3, 28.4, 28.0, 25.6, 24.5, 23.8, 21.9; MS(EI) m/z : 419 $[\text{M} + \text{H}]^+$. Derivative **9c** was obtained as a white solid (91%): mp 72 °C; ^1H NMR (C_6D_6) δ 6.91 (br s, 2H), 6.80 (br s, 1H), 6.69 (br s, 2H), 4.77 (br s, 2H), 4.36 (br s, 2H), 2.28 (s, 10H), 2.09 (s, 8H), 1.98 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6) δ 153.4, 148.8, 143.4, 140.6, 137.6, 137.4, 131.2, 130.0, 129.4, 115.1, 54.2, 22.6, 21.3, 21.2, 19.7, 18.8; MS(EI) m/z 335 $[\text{M} + \text{H}]^+$. Derivative **9d** was obtained as a yellow oil (92%): ^1H NMR (CDCl_3) δ 7.89 (m, 1H), 7.26 (m, 1H), 7.00 (m, 2H), 6.87 (m, 3H), 4.87 (s, 1H), 4.81 (s, 1H), 4.63 (s, 2H), 1.82 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3) δ 159.2 (d, $J_{\text{CF}} = 226.0 \text{ Hz}$), 156.4 (dd, $J_{\text{CF}} = 244.1$, 6.0 Hz), 155.8, 140.6, 128.2 (t, $J_{\text{CF}} = 8.8 \text{ Hz}$), 122.4 (t, $J_{\text{CF}} = 9.6 \text{ Hz}$), 114.1, 112.4 (d, $J_{\text{CF}} = 22.4 \text{ Hz}$), 111.5 (br s), 51.7, 20.0; MS(EI) m/z 323 $[\text{M} + \text{H}]^+$.

Synthesis of Alkenylformamidinium 10a

Following the procedure described for the synthesis of **3a**, derivative **10a** was obtained from **9a** as a white powder (95%). Crystals were grown from chloroform: mp 151 °C dec; ^1H NMR (CDCl_3) δ 14.0 (d, $J_{\text{HH}} = 12.0 \text{ Hz}$, 1H), 7.52–7.40 (m, 1H), 7.36–7.19 (m, 6H), 5.97 (m, 1H), 5.64 (d, $J_{\text{HH}} = 16.9 \text{ Hz}$, 1H), 5.38 (d, $J_{\text{HH}} = 10.0 \text{ Hz}$, 1H), 5.14 (d, $J_{\text{HH}} = 7.1 \text{ Hz}$, 2H), 3.27 (sept, $J_{\text{HH}} = 6.8 \text{ Hz}$, 2H), 3.00 (sept, $J_{\text{HH}} = 6.8 \text{ Hz}$, 2H), 1.40 (br d, $J_{\text{HH}} = 6.8 \text{ Hz}$, 6H), 1.32 (d, $J_{\text{HH}} = 6.8 \text{ Hz}$, 6H), 1.22 (br d, $J_{\text{HH}} = 6.8 \text{ Hz}$, 6H), 1.15 (d, $J_{\text{HH}} = 6.8 \text{ Hz}$, 6H); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3) δ 155.5, 146.0, 145.8, 135.7, 132.2, 131.0, 129.9, 128.0, 125.3, 124.2, 123.8, 57.2, 29.0, 25.5, 24.4, 24.0, 23.6; MS(HR-ESI) m/z 405.3266 $[\text{M}]^+$ (calcd 405.3264).

Synthesis of NHC, H⁺s 11a–d from 9a–d

Following the procedure described for the synthesis of **4b**, but heating at the temperature and during time indicated hereafter, derivatives **11a–d** were isolated as white solids after washing with toluene and ether. **11a**: 36 h at 135 °C; 83% yield; mp 204 °C; ^1H NMR ($\text{CD}_3\text{CN}/\text{CDCl}_3$, 20:1) δ 9.39 (s, 1H), 7.53 (m, 2H), 7.56 (m, 4H), 4.88 (m, 1H), 4.63 (t, $J_{\text{HH}} = 11.8 \text{ Hz}$, 1H), 4.01 (dd, $J_{\text{HH}} = 11.8$, 10.2 Hz, 1H), 3.04 (m, 4H), 1.45 (d, $J_{\text{HH}} = 6.5 \text{ Hz}$, 3H), 1.36 (m, 12H), 1.26–1.21 (m, 12H); $^{13}\text{C}\{^1\text{H}\}$ NMR ($\text{CD}_3\text{CN}/\text{CDCl}_3$, 20:1) δ 161.5, 148.4, 147.7, 147.6, 147.3, 132.4, 130.7, 128.7, 126.2, 126.0, 63.5, 61.2, 30.0, 29.9, 26.2, 25.6, 24.1, 24.0, 23.5, 18.5; MS(FAB) m/z 405 $[\text{M}]^+$. **11b**: 24 h at 110 °C; 80% yield; mp 212 °C; ^1H NMR (CD_3CN) δ 10.45 (s, 1H), 7.58 (m, 2H), 7.43 (t, $J_{\text{HH}} = 7.7 \text{ Hz}$, 4H), 4.23 (s, 2H), 3.16 (m, 4H), 1.59 (s, 6H), 1.46 (d, $J_{\text{HH}} = 6.7 \text{ Hz}$, 12H), 1.40 (d, $J_{\text{HH}} = 6.8 \text{ Hz}$, 6H), 1.30 (d, $J_{\text{HH}} = 6.8 \text{ Hz}$, 6H); $^{13}\text{C}\{^1\text{H}\}$ NMR(CD_3CN) δ 161.9, 149.9, 148.1, 132.8, 131.5, 127.5, 126.6, 126.4, 72.2, 67.0, 31.1, 30.6, 27.8, 27.4, 26.2, 24.4, 23.4; MS(FAB) m/z 419 $[\text{M}]^+$. **11c**: 12 h at 135 °C; 78% yield; mp 166 °C; ^1H NMR (CDCl_3) δ 9.76 (s, 1H), 7.01 (s, 2H), 6.98 (s, 2H), 2.44 (s, 6H), 2.42 (s, 6H), 2.31 (s, 3H), 2.30 (s, 3H), 1.67 (s, 6H); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3) δ 159.4, 140.5, 140.3, 137.0, 135.0, 133.8, 130.6, 130.2, 127.4, 71.5, 64.0, 27.2, 21.2, 21.1, 20.1, 18.3; MS-(FAB) m/z 335 $[\text{M}]^+$. **11d**: 12 h at 135 °C; 79% yield; mp 186 °C; ^1H NMR (CD_3CN) δ 9.54 (s, 1H), 7.70 (m, 1H), 7.59 (m, 1H), 7.30 (m, 4H), 4.45 (s, 2H), 1.60 (s, 6H); $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_3CN) δ 162.1, 160.2 (dd, $J_{\text{CF}} = 249.7$, 6.0 Hz), 158.1 (dd, $J_{\text{CF}} = 248.2$, 6.0 Hz), 134.8 (t, $J_{\text{CF}} = 10.3 \text{ Hz}$), 132.9 (t, $J_{\text{CF}} = 10.1 \text{ Hz}$), 114.0 (dd, $J_{\text{CF}} = 7.4$, 3.2 Hz), 113.8 (dd, $J_{\text{CF}} = 6.8$, 3.3 Hz), 72.9, 64.0, 25.4; MS(HR-ESI) m/z 323.1178 $[\text{M}]^+$ (calcd 323.1171).

Synthesis of NHC, H⁺s 11a,b from 8a

A tube sealed by a Teflon stopcock was loaded with **8a** (2.00 g, 5.5 mmol), toluene (20 mL), and 3-bromopropene (0.474 mL, 5.5 mmol) or 3-bromo-2-methylpropene (0.54 mL, 5.5

mmol). Heating for 36 h at 135 °C or 24 h at 110 °C afforded **11a** and **11b**, respectively, as white solids after removal of the volatiles in vacuo and washing with toluene, **11a**: 1.76g, 66%; mp 200 °C. **11b**: 1.92g, 70%; mp 204 °C.

Synthesis of 13

Following the procedure for **9a**, amidine **12**²¹ (1.17 g, 2.7 mmol) was converted to its corresponding alkenyl derivative using 1 equiv of *n*-BuLi and 3-bromo-2-methylpropene. The alkenylamidine was obtained as a white solid (1.25 g, 95%): mp 90 °C; ¹H NMR (CDCl₃) δ 7.42–6.84 (m, 11H), 5.25 (s, 1H), 4.98 (s, 1H), 4.39 (s, 2H), 3.69 (sept, *J*_{HH} = 6.6 Hz, 2H), 3.17 (sept, *J*_{HH} = 6.6 Hz, 2H), 1.90 (s, 3H), 1.26 (d, *J*_{HH} = 6.6 Hz, 6H), 1.19 (2 x overlapping d, *J*_{HH} = 6.6 Hz, 12H), 0.98 (d, *J*_{HH} = 6.6 Hz, 6H); ¹³C{¹H} NMR (CDCl₃) δ 156.7, 147.5, 145.4, 142.0, 141.4, 138.0, 133.6, 128.9, 128.4, 128.0, 127.0, 124.4, 122.6, 121.7, 110.5, 58.6, 28.5, 28.4, 26.6, 24.8, 23.2, 22.3, 22.0; MS(FAB) *m/z* 495 [M + H]⁺. Following the procedure described for the synthesis of **4b**, **13** was obtained from **12** in 85% yield: mp 181 °C; ¹H NMR (CDCl₃) δ 7.40–7.24 (m, 3H), 7.17–7.03 (m, 6H), 6.92 (m, 2H), 4.45 (s, 2H), 2.83 (sept, *J*_{HH} = 6.6 Hz, 4H), 1.71 (s, 6H), 1.27 (d, *J*_{HH} = 6.6 Hz, 6H), 1.25 (d, *J*_{HH} = 6.6 Hz, 6H), 0.86 (d, *J*_{HH} = 6.6 Hz, 6H), 0.70 (d, *J*_{HH} = 6.6 Hz, 6H); ¹³C{¹H} NMR (CDCl₃) δ 165.8, 147.0, 144.8, 134.3, 131.4, 131.2, 129.5, 128.8, 127.9, 126.2, 125.5, 121.5, 70.9, 66.5, 29.4, 29.1, 26.3, 25.6, 25.1, 24.5, 23.1; MS(FAB) *m/z* 495 [M]⁺.

Synthesis of Alkenylurea 14

To a solution of lithium (2,6-diisopropylphenyl)amide²² (1.5 g, 8.2 mmol) in Et₂O (20 mL) at rt was added dropwise 3-bromo-2-methylpropene (0.91 mL, 1.22 g, 9.0 mmol). The solution was stirred for 2 h, and then the volatiles were removed under vacuum and the residue was extracted with hexanes and filtered. Removal of volatiles from the filtrate under vacuum provided (2,6-diisopropylphenyl)(2-methylallyl)amine as a colorless liquid: yield (1.71 g, 90%); ¹H NMR (CDCl₃) δ 7.12 (m, 3H), 5.15 (s, 1H), 4.94 (s, 1H), 3.42 (d, *J*_{HH} = 7.6 Hz, 2H), 3.29 (sept, *J*_{HH} = 6.8 Hz, 2H), 2.97 (br t, *J*_{HH} = 7.4 Hz, 1H), 1.89 (s, 3H), 1.27 (d, *J*_{HH} = 6.8 Hz, 12H). ¹³C NMR (neat) δ 144.1, 143.3, 142.6, 124.2, 123.4, 110.8, 58.1, 27.7, 24.3, 20.8.

A solution of *n*-BuLi in hexanes (5.4 mL, 1.6M, 8.6 mmol) was added to an Et₂O solution (40 mL) of (2,6-diisopropylphenyl)(2-methylallyl)amine (2.00 g, 8.6 mmol) at –78 °C. After 30 min, the mixture was warmed to rt and stirred for 3 h. The mixture was then cooled to –78 °C, and 2,6-diisopropylphenyl isocyanate (1.85 mL, 8.6 mmol) was added dropwise. The mixture was warmed to rt and stirred for 12 h, over which time a white precipitate formed. The mixture was cooled in an ice bath, and H₂O (40 mL) was added slowly. Extraction with Et₂O, drying over MgSO₄, and removal of the volatiles under vacuum afforded **14** as an off-white crystalline solid (3.34 g, 89%): mp 147 °C; ¹H NMR (CDCl₃) δ 7.38 (t, *J*_{HH} = 7.4 Hz, 1H), 7.27 (d, *J*_{HH} = 7.4 Hz, 2H), 7.21 (t, *J*_{HH} = 7.4 Hz, 1H), 7.12 (d, *J*_{HH} = 7.4 Hz, 2H), 5.40 (s, 1H), 4.81 (s, 1H), 4.70 (s, 1H), 4.22 (s, 2H), 3.30 (sept, *J*_{HH} = 6.8 Hz, 2H), 3.13 (sept, *J*_{HH} = 6.8 Hz, 2H), 1.93 (s, 3H), 1.31 (d, *J*_{HH} = 6.8 Hz, 6H), 1.28 (d, *J*_{HH} = 6.8 Hz, 6H), 1.17 (d, *J*_{HH} = 6.8 Hz, 12H); ¹³C{¹H} NMR (CDCl₃) δ 156.8, 148.5, 146.8, 142.9, 136.8, 132.0, 129.3, 127.8, 125.3, 123.5, 114.2, 57.3, 28.6, 26.2, 24.6, 24.2, 21.2.

Synthesis of C-chloro Imidazolinium Salt 15

To a toluene solution (10 mL) of alkenylurea **14** (1.00 g, 2.3 mmol) in a sealable tube fitted with a Teflon stopcock at –78 °C was added a toluene solution of phosgene (1.26 mL, 2.0 M, 2.5 mmol). After 10 min at –78 °C, the mixture was warmed to rt and stirred for 2 h. The mixture was then sealed and heated at 80 °C for 24 h. After removal of the volatiles in vacuo and precipitation of the product from Et₂O (20 mL), **15** was obtained as a white solid (0.78 g, 78%): mp 142 °C; ¹H NMR (CDCl₃) δ 7.48 (t, *J*_{HH} = 7.7 Hz, 1H), 7.29 (m, 3H), 7.12 (d, *J*_{HH} = 7.7 Hz, 2H), 3.90 (s, 2H), 2.99 (sept, *J*_{HH} = 6.8 Hz, 4H), 1.66 (s, 6H), 1.48 (d, *J*_{HH} =

6.8 Hz, 6H), 1.31 (d, $J_{\text{HH}} = 6.8$ Hz, 6H), 1.20 (d, $J_{\text{HH}} = 6.8$ Hz, 6H), 1.14 (d, $J_{\text{HH}} = 6.8$ Hz, 6H); $^{13}\text{C}\{^1\text{H}\}$ NMR(CDCl_3) δ 158.2, 148.6, 145.8, 132.0, 129.4, 126.6, 125.7, 123.8, 88.7, 64.1, 29.4, 28.8, 27.7, 25.7, 24.2, 23.8; MS-(FAB) m/z 435 [$\text{M} - \text{Cl} + (\text{OH})^+$].

Synthesis of Alkenylamides 16a,b

A solution of *n*-BuLi in hexanes (6.3 mL, 1.6 M, 10.2 mmol) was added to an Et_2O solution (20 mL) of 1-bromo-2-isopropenylbenzene²³ (2.00 g, 10.2 mmol) at -78°C . After 30 min, the mixture was warmed to rt and stirred for an additional 1 h. The mixture was then cooled to -78°C , and 2,6-diisopropylphenylisocyanate (2.17 mL, 10.2 mmol) or *tert*-butyl isocyanate (1.17 mL, 10.2 mmol) was slowly added. The mixture was allowed to warm to rt and stirred for 12 h while a white precipitate formed. After the mixture was cooled with an ice bath, H_2O (20 mL) was added slowly. Extraction with Et_2O , drying over MgSO_4 , and removal of the volatiles under vacuum afforded **16a,b** as off-white crystalline solids. **16a**: 2.66 g, 81% yield; mp 115°C ; ^1H NMR (CDCl_3) δ 7.83 (dd, $J_{\text{HH}} = 1.9, 7.4$ Hz, 1H), 7.48–7.21 (m, 6H), 5.30 (s, 1H), 5.16 (s, 1H), 3.21 (sept, $J_{\text{HH}} = 6.8$ Hz, 2H), 2.24 (s, 3H), 1.25 (d, $J_{\text{HH}} = 6.8$ Hz, 12H); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3) δ 168.5, 146.8, 146.5, 142.5, 134.3, 131.2, 130.6, 129.2, 128.8, 128.6, 127.7, 123.8, 116.1, 29.0, 25.4, 24.0; MS(EI) m/z 322 [$\text{M} + \text{H}]^+$. **16b**: 1.93 g, 87% yield; ^1H NMR (CDCl_3) δ 7.66 (dd, $J_{\text{HH}} = 1.8, 7.2$ Hz, 1H), 7.36 (m, 2H), 7.20 (dd, $J_{\text{HH}} = 1.5, 7.2$ Hz, 1H), 6.00 (bs, 1H), 5.24 (s, 1H), 5.10 (s, 1H), 2.12 (s, 3H), 1.44 (s, 9H); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3) δ 168.0, 146.0, 141.1, 135.0, 130.2, 129.0, 128.7, 127.7, 115.9, 51.8, 28.7, 24.7.

Synthesis of Cyclic C-Chloro Iminium Salt 17a,b

Following the procedure used for **15** and heating as indicated hereafter, **17a,b** were obtained as off-white solids. **17a**: 80°C for 24 h, 86% yield; mp 130°C ; ^1H NMR (CD_3CN) δ 9.49 (d, $J_{\text{HH}} = 7.9$ Hz, 1H), 7.95 (t, $J_{\text{HH}} = 7.6$ Hz, 1H), 7.76 (m, 2H), 7.48 (t, $J_{\text{HH}} = 7.7$ Hz, 1H), 7.36 (d, $J_{\text{HH}} = 7.9$ Hz, 2H), 3.08 (sept, $J_{\text{HH}} = 6.8$ Hz, 2H), 1.72 (s, 6H), 1.24 (d, $J_{\text{HH}} = 6.8$ Hz, 6H), 1.16 (d, $J_{\text{HH}} = 6.8$ Hz, 6H); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3) δ 171.6, 155.2, 145.6, 138.0, 131.2, 130.8, 129.2, 125.2, 123.9, 122.6, 100.4, 29.7, 26.7, 24.3, 23.6. MS-(HR-ESI) m/z 322.2174 [$\text{M} - \text{Cl} + \text{OH}]^+$ (calcd 322.2170). **17b**: 80°C for 24 h, 78% yield; mp 154°C ; ^1H NMR (CDCl_3) δ 9.77 (d, $J_{\text{HH}} = 7.9$ Hz, 1H), 7.76 (t, $J_{\text{HH}} = 7.5$ Hz, 1H), 7.64 (t, $J_{\text{HH}} = 7.7$ Hz, 1H), 7.39 (d, $J_{\text{HH}} = 7.7$ Hz, 1H), 1.79 (s, 6H), 1.67 (s, 9H); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3) δ 170.3, 152.1, 136.2, 130.4, 130.0, 120.4, 120.4, 98.4, 58.3, 28.5, 26.9; MS(HR-ESI) m/z 218.1543 [$\text{M} - \text{Cl} + \text{OH}]^+$ (calcd 218.1539).

Palladium Complex 18a

A CH_2Cl_2 (15 mL) solution of **17a** (0.10 g, 0.27 mmol) and tetrakis(triphenylphosphine) palladium (0.31 g, 0.27 mmol) was heated under reflux for 24 h. The solvent was removed under vacuum, then repeated extraction with boiling hexane to remove the liberated triphenylphosphine provided complex **18a** as a yellow solid (0.11 g, 55%): ^1H NMR (CDCl_3) δ 7.67–7.19 (m, 22H), 3.09 (sept, $J_{\text{HH}} = 6.9$ Hz, 2H), 1.61 (s, 6H), 1.21 (d, $J_{\text{HH}} = 6.5$ Hz, 12H); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3) δ 221.1 (d, $J_{\text{PC}} = 175$ Hz), 149.1 (br), 148.1, 134.8 (d, $J_{\text{PC}} = 11.0$ Hz), 133.7, 132.9, 130.6 (d, $J_{\text{PC}} = 40.5$ Hz), 130.1, 129.7, 128.6, 128.0 (d, $J_{\text{PC}} = 9.9$ Hz), 125.7, 120.0, 84.3 (d, $J_{\text{PC}} = 7.9$ Hz), 29.5, 29.0, 26.5, 24.4; ^{13}C NMR resonances corresponding to the aromatic quaternary carbons of the fused ring system could not be located; ^{31}P NMR (CD_3CN) δ +15.3; MS(HR-ESI) m/z 778.1141 [$\text{M} + \text{Cl}]^+$ (calcd 778.1155).

Labeling Experiment: Synthesis of Cyclic Iminium Salt 4c_D

In a sealable vessel fitted with a Teflon stopcock was bubbled deuterium chloride gas through a solution of alkenyl imine **2c** (0.34 g, 1.0 mmol) in toluene for 1 min. The vessel was then sealed and heated to 110°C for 16 h. After the mixture was cooled to rt, the volatiles were removed under vacuum and the residue was extracted with CD_3CN and transferred to an NMR

tube: ^1H NMR (CD_3CN) δ 9.85 (s, 1H, CH=N), 7.57 (t, $J_{\text{HH}} = 7.79$ Hz, 1H, H_{ar}), 7.43 (m, 2H, H_{ar}), 4.69 (m, 1H, N-CH), 2.81–2.57 (m, 3H, 2H from $\text{CH}_3\text{-Pr}$ plus 1H from endocyclic CH_2), 2.07–1.92 (m, 3H, includes 1H from endocyclic CH_2), 1.81 (m, 4H), 1.67–1.46 (m, 5H, includes CHD_{Et}), 1.30–1.16 (4 overlapping d, 12H, CH_3^{iPr}), 0.85 (d, $J_{\text{HH}} = 6.48$ Hz, 3H, $\text{CH}_3\text{-Et}$); ^2H NMR (CD_3CN) δ 10.49 (br, $\text{DCl}_2\text{-counterion}$), 1.60 (br, CHD_{Et}); $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_3CN) δ 192.8 (N=CH), 144.6, 143.4 ($\text{C}_{\text{ar}}^{\text{OrthO-DIPP}}$), 132.4 ($\text{C}_{\text{ar}}^{\text{Para-DIPP}}$), 131.5 ($\text{C}_{\text{ar}}^{\text{ipso-DIPP}}$), 125.8, 125.7 ($\text{C}_{\text{ar}}^{\text{meta-DIPP}}$), 78.1 (N-CH), 54.4 (C), 38.0 (endocyclic NCHCH₂), 34.2, 31.7, 26.2 (t, $J_{\text{CD}} = 19.3$ Hz, CHD_{Et}), 25.2, 22.1, 21.6 (CH_2), 29.4, 29.3 (CH^{iPr}), 25.6, 25.0, 23.4, 22.6 (CH_3^{iPr}), 10.7 (CH_3^{Et}). Assignments for the aliphatic region of the ^1H and ^{13}C NMR spectrum were made based on ^1H – ^1H and ^1H – ^{13}C coupling correlations of the N-CH and CH_3^{Et} protons from COSY and HMBC spectra, in addition to DEFT-135° and DEPT-90° protocols; MS(FAB) m/z 326 $[\text{M}]^+$.

Crystal Structure Determination of Compounds 4b, 10a, 11a, and 18a

The Bruker X8-APEX X-ray diffraction instrument with Mo radiation was used for data collection. All data frames were collected at low temperature ($T = 100$ K) using an ω, ϕ -scan mode (0.5° ω -scan width, hemisphere of reflections) and integrated using a Bruker SAINTPLUS software package. The intensity data were corrected for Lorentzian polarization. Absorption corrections were performed using the SADABS program. The SIR97 software package was used for direct methods of phase determination and the Bruker SHELXTL software package for structure refinement and difference Fourier maps. Atomic coordinates and isotropic and anisotropic displacement parameters of all of the non-hydrogen atoms of two compounds were refined by means of a full-matrix least-squares procedure on F^2 . All H-atoms were included in the refinement in calculated positions riding on the C atoms. Drawings of molecules were performed using Ortep 3.

Crystal and structure parameters of 4b

size $0.51 \times 0.17 \times 0.12$ mm³, monoclinic, space group $P2(1)2(1)2(1)$, $a = 10.5761(7)$ Å, $b = 16.3822(10)$ Å, $c = 19.6147(12)$ Å, $\alpha = \gamma = \beta = 90.0^\circ$, $V = 3398.4(4)$ Å³, $\rho_{\text{calcd}} = 1.256$ g/cm³, Mo radiation ($\lambda = 0.71073$ Å), $T = 100(2)$ K, reflections collected = 67338, independent reflections = 13087 ($R_{\text{int}} = 0.0797$), absorption coefficient $\mu = 0.602$ mm⁻¹, max/min transmission = 0.9313 and 0.7488, 387 parameters were refined and converged at $R1 = 0.0381$, $wR2 = 0.0744$, with intensity $I > 2\sigma(I)$.

Crystal and structure parameters of 10a

size $0.40 \times 0.15 \times 0.10$ mm³, monoclinic, space group $P2(1)/c$, $a = 20.6299(18)$ Å, $b = 19.1236(17)$ Å, $c = 13.9795(12)$ Å, $\alpha = 90.0^\circ$, $\beta = 108.2590(10)^\circ$, $\gamma = 90.0^\circ$, $V = 5237.5(8)$ Å³, $\rho_{\text{calcd}} = 1.199$ g/cm³, Mo radiation ($\lambda = 0.71073$ Å), $T = 100(2)$ K, reflections collected = 24727, independent reflections = 6333 ($R_{\text{int}} = 0.0322$), absorption coefficient $\mu = 0.163$ mm⁻¹, max/min transmission = 0.9839 and 0.9378, 576 parameters were refined and converged at $R1 = 0.0587$, $wR2 = 0.1462$, with intensity $I > 2\sigma(I)$.

Crystal and structure parameters of 11a

size $0.46 \times 0.14 \times 0.06$ mm³, monoclinic, space group $P2(1)/c$, $a = 17.326(2)$ Å, $b = 8.5078(10)$ Å, $c = 21.213(3)$ Å, $\alpha = \gamma = 90.0^\circ$, $\beta = 101.369(2)^\circ$, $\gamma = 3065.6(6)$ Å³, $\rho_{\text{calcd}} = 1.212$ g/cm³, Mo-radiation ($\lambda = 0.71073$ Å), $T = 100(2)$ K, reflections collected = 17060, independent reflections = 4376 ($R_{\text{int}} = 0.0358$), absorption coefficient $\mu = 0.406$ mm⁻¹, max/min transmission = 0.9780 and 0.8369, 363 parameters were refined and converged at $R1 = 0.0553$, $wR2 = 0.1451$, with intensity $I > 2\sigma(I)$.

Crystal and structure parameters of 18a

size $0.70 \times 0.19 \times 0.13 \text{ mm}^3$, monoclinic, space group $P2(1)/c$, $a = 12.535(3) \text{ \AA}$, $b = 20.342(5) \text{ \AA}$, $c = 27.860(7) \text{ \AA}$, $\alpha = 90.0^\circ$, $\beta = 94.939(6)^\circ$, $\gamma = 90.0^\circ$, $V = 7077(3) \text{ \AA}^3$, $\rho_{\text{calcd}} = 1.398 \text{ g/cm}^3$, Mo radiation ($\lambda = 0.71073 \text{ \AA}$), $T = 100(2) \text{ K}$, reflections collected = 32838, independent reflections = 10046 ($R_{\text{int}} = 0.0754$), absorption coefficient $\mu = 0.750 \text{ mm}^{-1}$, max/min transmission = 0.9088 and 0.6219, 823 parameters were refined and converged at $R1 = 0.0538$, $wR2 = 0.1277$, with intensity $I > 2\sigma(I)$.

Acknowledgements

We are grateful to the NIH (R01 GM 68825) and RHODIA for financial support.

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FIGURE 1.
Molecular structure of the major isomer of the cyclic aldiminium salt **4b** in the solid state.

FIGURE 2.
Molecular structures of alkenyl formamidine salt **10a** (left) and imidazolinium salt **11a** (right) in the solid state.

FIGURE 3.

Molecular structure of the palladium complex **18a** (H atoms are omitted). Selected bond distances (Å) and angles (deg): N1–C1 1.307(7), C1–Pd 1.997(6), Pd–P 2.3514(16), Pd–Cl1 2.3088(15), Pd–Cl2 2.2957(15); C_{ar}–C1–N1 107.8(5), C1–Pd–Cl1 88.41(15), C1–Pd–Cl2 87.18(15), C1–Pd–P 173.87(16).

SCHEME 1.

SCHEME 2.

SCHEME 3.

8a-11a: Ar = Dipp, R = H; **8b-11b:** Ar = Dipp, R = Me; **8c-11c:** Ar = Mes, R = Me;
8d-11d: Ar = 2,6-difluorophenyl, R = Me

SCHEME 4.

SCHEME 5.

SCHEME 6.

SCHEME 7.

SCHEME 8.

SCHEME 9.