On new N-heterocyclic carbene derived alkylidene imidazolines†‡

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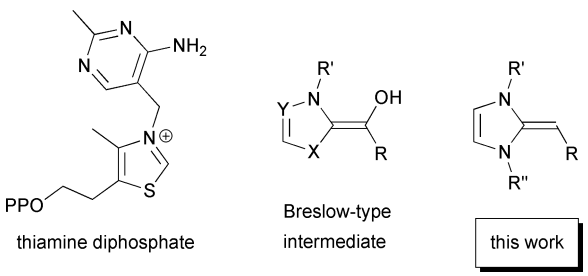
A series of novel 2-alkylidene imidazolines has been synthesized from imidazolium halides and substituted alkyl halides in the presence of base. The resultant exocyclic enediamines have been characterized and their nucleophilicity has been evaluated upon NMR spectroscopic data and substitution reactions.

Introduction

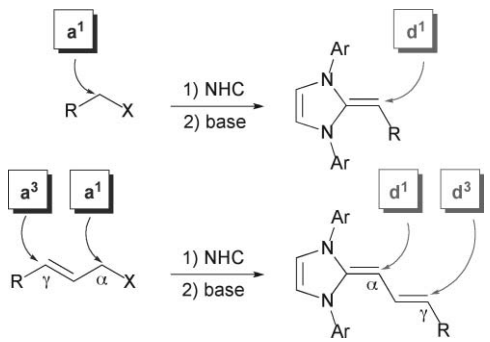
Since the isolation of the first stable N-heterocyclic carbene (NHC)[1] several applications of this interesting class of heterocycles to organic synthesis and catalysis have been reported.[2,3] Over the past decade, NHCs established themselves as ligands for transition metal-catalyzed reactions.[4] Their potential to act as nucleophilic catalysts in umpolung reactions was initially harnessed with the development of carbene-catalyzed benzoin and Stetter reactions.[5] These biomimetic reactions are synthetic copies of acylation reactions catalyzed by thiamine-dependent transketolases.[6] The cofactor thiamine (Vitamin B_1) is embedded within the enzyme center and bears a reactive thiazolium ion as precursor for a nucleophilic carbene (Scheme 1, left).[7] Breslow postulated a mechanistic model that involves umpolung of an electrophilic formyl moiety into an acyl anion equivalent.[8] Various applications of this general reactivity pattern have demonstrated the use of carbenes for umpolung addition reactions. While a vast majority of research effort has been devoted to carbonyl compounds for the generation of intermediate nucleophiles *via* umpolung,[9] alternative reaction modes have received only little attention.



Scheme 1 Biological archetype and carbene-derived umpolung intermediates.

We were particularly attracted by the property of imidazolium cations to act as electron-withdrawing auxiliaries. Due to their electron-deficient aromaticity, imidazolium salts are rather stable compounds that induce a high acidity of the proton in the 2-position.[10] The preparation of the corresponding N-heterocyclic carbenes *via* deprotonation at C2 can be effected with strong bases.[11] Obviously, the electronic pull of the cationic imidazolium moiety also enhances the acidity of 2-alkyl substituents.

There are only a few examples of selective reactions between alkyl halides and NHCs. Interestingly, these precedents are limited to simple saturated alkyl halides.[12,15] Intermediate alkylazolium species are susceptible to deprotonation to afford the corresponding azolylidenes[12,13,14a,15] which are competent nucleophiles for further alkylation.[12,13a] The underlying a^1-d^1 umpolung[16] relates to the formation of Breslow-type intermediates from aldehydes.[8] We were interested to expand the scope of 2-substituted imidazolylidenes to also include unsaturated substituents that could permit further manipulation. A vinylogous approach would result in formal a-d-umpolung at the α- and γ-carbons upon reaction of an allyl halide with an NHC and subsequent deprotonation (Scheme 2). The latter reaction mode relates to the umpolung of α,β-unsaturated aldehydes and thus affords the deoxy-analogue of carbene-derived homoenolates.[9] It is important to note that the resultant exocyclic enediamines constitute an under-utilized class of nucleophiles with little literature precedents,[12,14,17,18] but offer new avenues for untapped umpolung reactions. This work represents the first comprehensive study of the synthesis and characterization of a series of novel alkylidene imidazolines demonstrating a novel entry into NHC-mediated umpolung chemistry.



Scheme 2 Umpolung of alkyl halides.

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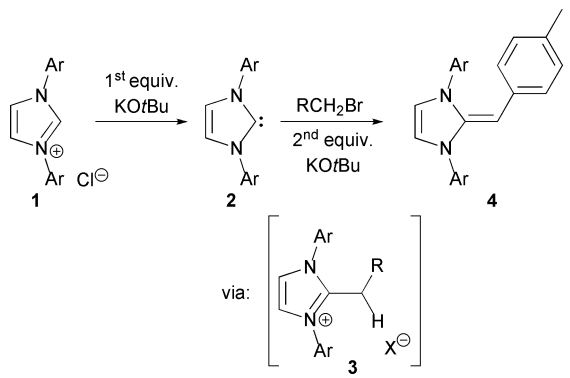
‡ Electronic supplementary information (ESI) available: NMR and UV/Vis spectra, proposed mechanism for reaction of carbene **2** with epibromohydrin, crystal structures. CCDC reference numbers 751976–751978. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b921655c

Results and discussion

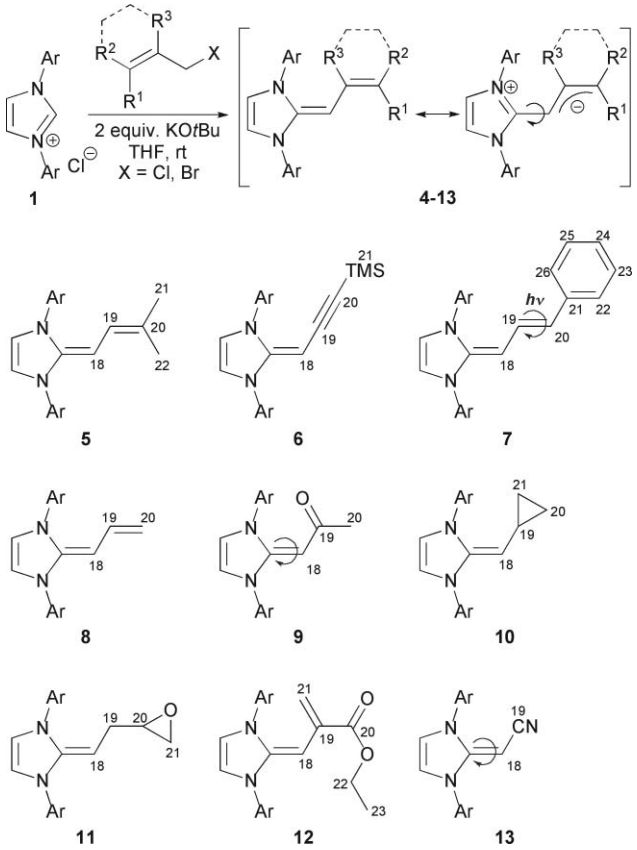
NMR studies

Our initial studies were performed in sealed NMR tubes with 1,3-bis-(2,6-diisopropylphenyl)imidazolium chloride (**1**)[19] as NHC precursor in THF-d_8 under anaerobic conditions and monitored by ^{1}H NMR. Reaction of **1** with equimolar KO*t*Bu resulted in the complete conversion to carbene **2** after 2 min at room temperature applying ultra-sonification. Carbene **2** proved to be stable under these conditions for > 20 days. ^{1}H NMR monitoring of the subsequent addition of stoichiometric amounts of *p*-methylbenzyl bromide exhibited only 50% conversion to **4** but complete disappearance of carbene **2**. The identity of ene-1,1-diamine **4** was established by NMR and ESI-MS. **4** is presumably formed by rapid deprotonation of intermediate alkyl imidazolium **3** with carbene **2** as base.§ This observation is a consequence of the high acidity in the α-position of the 2-alkyl substituent (stabilization by vicinal azolium and aryl moieties). Generally, the electron-withdrawing effect of the imidazolium moiety alone is not sufficient to trigger deprotonation at the exocyclic α-position by the imidazol-2-ylidene in contrast to analogous reactions with the more basic benzimidazol-2-ylidenes and imidazolin-2-ylidenes.[12,13a,14] Upon employment of 2 equiv. of base (KO*t*Bu), the conversion was increased to > 80% (Scheme 3).



Scheme 3 Reaction of *in situ* generated carbene **2** with *p*-methylbenzyl bromide (Ar = 2,6-diisopropylphenyl, R = *p*-tolyl).

We then pursued studies into the reactivity of alternative electrophiles with imidazolium chloride **1** in the presence of two equiv. of KO*t*Bu in order to extend the scope of this enediamine synthesis. Reaction with *p*-methylbenzyl chloride under identical conditions proved much slower. A series of nine further alkylidene imidazolines (**5–13**) was synthesized at room temperature (with mostly 50–90% conversion) from prenyl bromide, 3-trimethylsilylpropargyl bromide, cinnamyl chloride, allyl chloride, chloroacetone, bromomethyl-cyclopropane, 3,4-epoxybutyl bromide, ethyl 2-bromomethyl-acrylate, and chloroacetonitrile, respectively (Scheme 4). Syntheses of **7** and **8** from the organobromides were less selective and led to the formation of oligomeric by-products which could be suppressed by running the reactions at lower temperature (−78 °C). Enediamine **9** was also obtained from **2** and epibromohydrin under identical conditions.[20]



Scheme 4 Synthesis of enediamines (Ar = 2,6-diisopropylphenyl).

Reaction progress and carbene consumption were best monitored by ^{1}H NMR resonance shifting of the imidazoline and peripheral *i*Pr moieties. Fig. 1 shows the ^{1}H spectra of the synthesis of benzylidene **4** from carbene **2** and *p*-methylbenzyl bromide. In comparison with carbene **2**, the signals of the imidazoline ring protons (at C4 and C5) of enediamines **4–13** were shifted significantly up-field ($\Delta\delta$ = 0.48–1.05 ppm). The *i*Pr septets, however, experienced a down-field shift ($\Delta\delta$ = 0.07–0.62). Resonances of other protons were only slightly affected by the transformations of **2** to enediamines. Compounds **4–8** and **10–13** each showed two *i*Pr septets. This asymmetry arises from a locked configuration of the exocyclic double bond at room temperature which entails the presence of a *syn* and an *anti* diisopropylphenyl substituent (NOESY). Ketone **9** gave only one signal set for both *N*-substituents, as facile keto-enol tautomerism results in rapid interconversion of both double bond isomers on the NMR time scale.[21]

The electron-donating character of the five-membered 6π electron heterocycle renders the exocyclic alkene moiety of the synthesized enediamines strongly nucleophilic. The degree of

§ Cationic species **1** and **3** were poorly soluble in THF under the reaction conditions and not detected by ^{1}H NMR. **3** was independently prepared from **4** and HI. Reaction of **1** with equimolar KO*t*Bu and 50 mol% of *p*-methylbenzylbromide cleanly gave **4** while no ^{1}H resonances of carbene **2** could be detected. After addition of another equiv. of base, ^{1}H NMR signals of carbene **2** appeared. We thus postulate the intermediacy of imidazolium salt **3** and its deprotonation by **2** (to give **1**) when no additional base is present. UV/Vis spectroscopic monitoring of the reaction sequence was not enlightening since *p*-methylbenzyl bromide, carbene **2**, and imidazolium salt **3** showed nearly the same absorption maxima (230-238 nm), while only enediamine **4** exhibited a strong red-shifted band at 350 nm (see also Supporting Information‡).

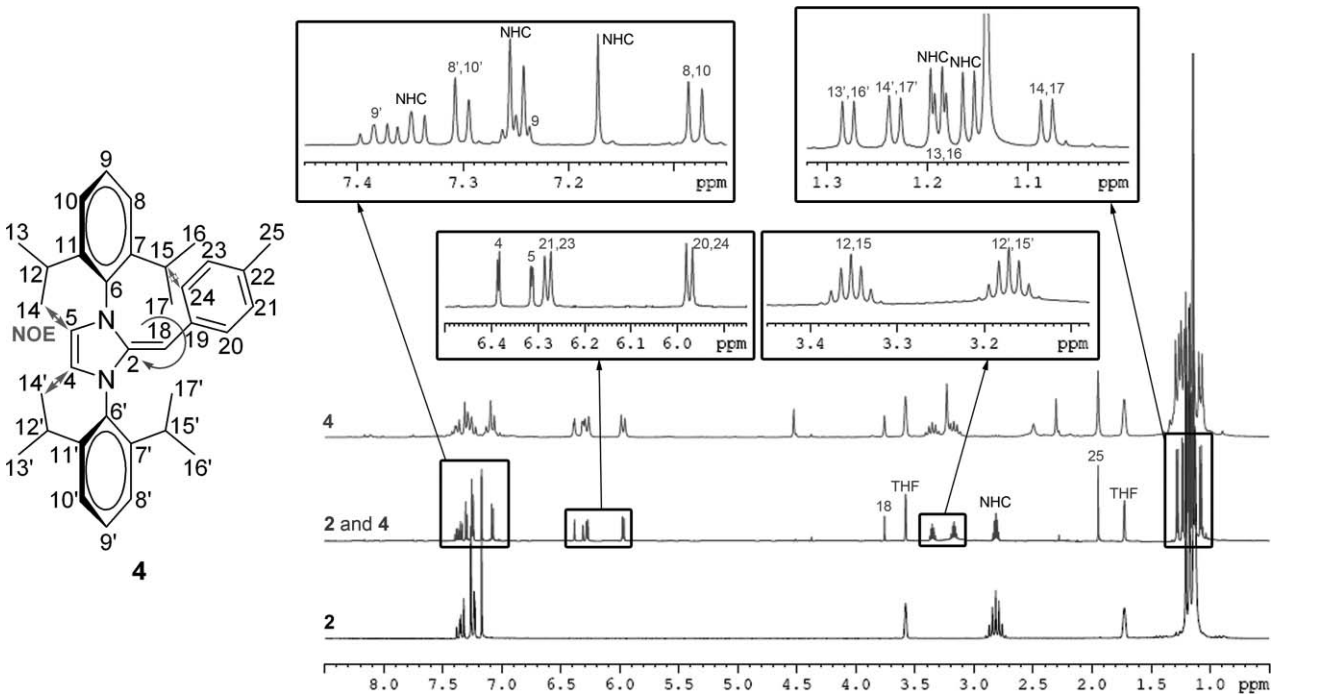


Fig. 1 ^{1}H NMR monitoring of conversion from **2** to **4** (slight excess of electrophile in upper spectrum).

Table 1 ^{13}C and ^{1}H chemical shifts of exocyclic double bonds (δ in ppm)

Enediamine	N*C*N	α-*C*H	α-C*H*
4	145.8	70.2	3.76
5	145.4	67.9	3.43
6	152.0	46.2	2.76
7	147.1	73.0	3.86
8	146.5	72.2	3.67
9	151.8	74.1	3.97
10	147.1	68.0	1.99
11	147.0	56.9 or 53.6[a]	2.33–2.27
12	148.0	66.4	3.76
13	153.5	33.2	2.38

[a] Undetermined assignment.

exocyclic double bond polarization is considered to be most significant for the evaluation of its nucleophilic reactivity. As a first approximation, the electronic nature of the double bond correlates with the ^{13}C NMR resonances. Table 1 displays the chemical shifts of the quaternary C2 carbons (N*C*N) and the vicinal sp^2-hybridized α-*CH* moieties. Consistent with literature observations on related compounds,[12,14,17] the exocyclic double bonds are highly polarized in **4–13**. The transformations of carbene **2** (^{13}C: δ = 220.9 ppm) to alkylidene imidazolines **4–13** (^{13}C: δ = 145–152) exert a large shielding effect onto the endocyclic N*C*N moieties as a consequence of the umpolung of C2 from the nucleophilic carbene **2** to the electrophilic aminals **4–13**. The strong electron-donating property of the imidazoline ring can also be deduced from the ^{13}C resonances of the conjugated γ-position in the alkylidene substituents *vs.* the organohalide. The effect is quite significant for prenyl derivative **5** (^{13}C(γ-*C*H): δ = 111.6 ppm (**5**) *vs.* 140.3 (prenyl bromide)), cinnamyl derivative **7** (111.4 (**7**) *vs.* 135.0 (cinnamyl chloride)), and allyl derivative **8** (95.1 (**8**) *vs.* 118.4 (allyl bromide))

NMR spectroscopy was also utilized to monitor chemical exchange phenomena in **4**, **7**, and **13**. EXSY NMR spectra of **4** and **13** displayed a chemical exchange between the two diisopropylphenyl groups as a result of conjugative stabilization of the zwitterionic resonance structure and free rotation about the exocyclic double bond. Compounds **5–12** showed no such behaviour. Synthesis of **7** from *trans*-cinnamyl chloride was accompanied by the formation of minor amounts of the *cis*-isomer (*E*/*Z* appr. 2/1). We observed a facile light-driven isomerization (with a maximum *E*/*Z* of 1/1 at daylight). The *trans*-isomer spontaneously regenerated in the dark (*E*/*Z* 10/1 after 6 h at r.t.) or could be exclusively afforded from a dark reaction. Electron donation from the imidazoline ring and benzylic stabilization favour rotation about the styryl double bond. The regioisomeric product which would arise from an S_N' attack of the NHC onto cinnamyl chloride was not observed.

Trapping reactions

Based upon literature precedents by Kuhn,[12,17a,b,22] Bourson,[23] Begtrup,[13a,24] and Alt[25] we set out to probe the nucleophilicity of enediamines **4** and **5** in selected reactions with electrophiles. We observed protonation of benzylidene **4** at the exocyclic α-carbon. Treatment of **4** with non-aqueous hydrogen iodide at room temperature gave imidazolium iodide **3**. (HI was generated stoichiometrically from reaction of TMSI with the *t*-butanol containing reaction mixture. Protonation of **4** with gaseous HCl also afforded compound **3**, with X=Cl.) The crystal structure of the resultant square, slightly yellow prisms is depicted in Fig. 2. It shows the expected planarity of the five-membered heterocycle; the bond lengths confirm its aromatic delocalization. All three carbon-based substituents are slightly tilted out of the heterocycle plane. The aryl substituents are perpendicular to the imidazolium ring,

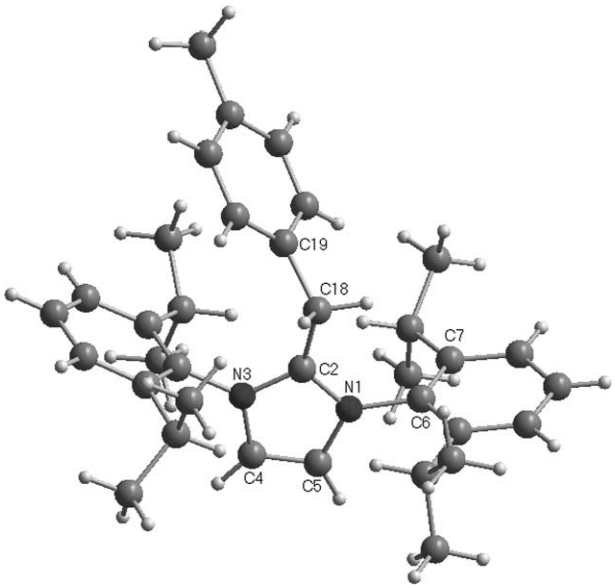
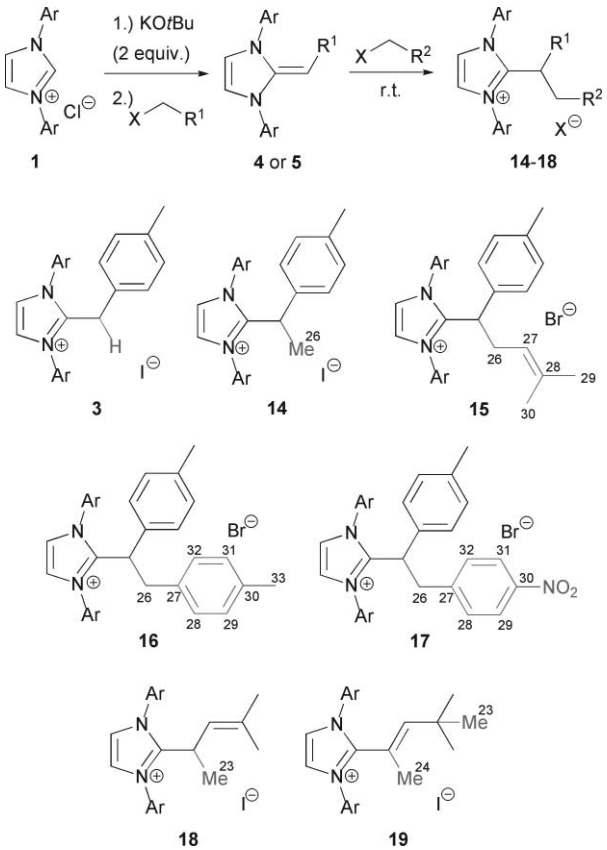


Fig. 2 Crystal structure of **3** (iodide is omitted for clarity). Selected bond lengths [Å] and angles [°]:C2-N1 1.349(2), C2-N3 1.346(2), N1-C5 1.391(3), N3-C4 1.390(2), C4-C5 1.335(3), N1-C6 1.452(2), C2-C18 1.493(3), C18-C19 1.537(3), C2-C18-C19 117.3(2), N1-C2-C18 124.2(2), N3-C2-C18 128.4(2), C2-N1-C6 126.6(2), C2-N1-C5 109.1(2), C2-N3-C4 109.1(2), N1-C5-C4 107.2(2), N3-C4-C5 107.6(2), N1-C2-N3 107.0(2), N1-C2-C18-C19 130.3(2), C5-N1-C2-C18 172.4(2), C4-N3-C2-C18 –172.0 (2), C2-N1-C6-C7 –87.8(2), N1-C5-C4-N3 –0.1(2), C5-N1-C2-N3 1.1(2), N3-C2-N1-C6 –178.6(2).

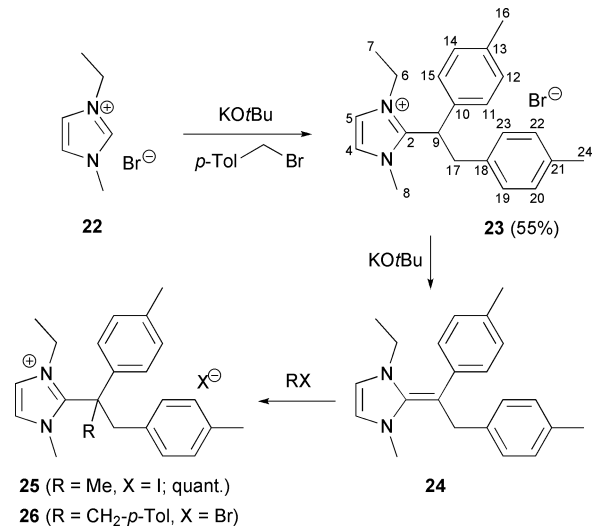
while the tolyl moiety spans an angle of 74° with the heterocycle. The unit cell contains two molecules with an inversion centre.

2-(*p*-Methylbenzyl)imidazolium iodide **3** crystallized in the same space group ($P\bar{1}$) as the structurally related 2-iodomethyl-1,3,4,5-tetramethylimidazolium triiodide.[17b]

Upon employment of carbon-based electrophiles, new imidazolium derivatives with exocyclic α,α-di-substitution were prepared. Reactions of **2** with methyl iodide, prenyl bromide, *p*-methylbenzyl bromide, and *p*-nitrobenzyl bromide at room temperature afforded the desired 2-alkyl imidazolium halides **14**–**17**, respectively (Scheme 5). Prenylidene **5** was methylated in the α-position by reaction with methyl iodide to afford **18**. When NaH (instead of KO*t*Bu) was employed for the formation of **5**, further methylation in γ-position was observed as side reaction *via* deprotonation of **18** by excess NaH and subsequent second methylation to give 2-alkenylimidazolium **19**. In the presence of excess KO*t*Bu, citenzyl imidazolium **16** was converted into its conjugated base **20**. NMR spectra indicated the presence of a polarized tetra-substituted double bond with a ^{13}C NMR resonance of the α-carbon at $\delta = 80.1$ ppm. Analogous deprotonation of mixed prenyl-benzyl derivative **15** gave enediamine **21** which showed a similar ^{13}C NMR resonance at $\delta = 79.8$ ppm.



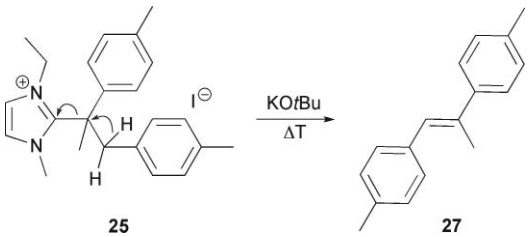
Scheme 5 Secondary substitution products (Ar = 2,6-diisopropylphenyl).



Scheme 6 Synthesis and benzylation of *N*,*N*-dialkyl enediamine **24**.

Variation of *N*-substituents

In order to investigate the influence of the *N*-substituents of the NHC on the reactivity, analogous substitution reactions were performed with 1-ethyl-3-methylimidazolium bromide **22** (Scheme 6). Benzylation of **22** proceeded under identical conditions as shown for **1**. Bibenzyl derivative **23** was synthesized in 55% yield and its deprotonation to the corresponding base **24** effected with KO*t*Bu **24** was subjected to further alkylation with methyl iodide and *p*-methylbenzyl bromide to give imidazolium **25** (quant.) and **26**, respectively, with quaternary exocyclic α-carbons. Treatment of **25** with base at elevated temperature resulted in the formation of stilbene **27** with 80% yield by formal elimination of 1-ethyl-3-methylimidazolium iodide (Scheme 7).



Scheme 7 Stilbene synthesis by base-mediated NHC elimination.

Conclusions

We have developed an operationally simple protocol for the synthesis of conjugated 2-alkylidene imidazolines from imidazolium halides and unsaturated alkyl halides in the presence of 2 equivalents of base. This work constitutes the first systematic study of the synthesis and stereo-electronic properties of such enediamines that contain exocyclic alkene, diene, enyne, and styryl moieties and further unsaturation in the side chain (keto, cyclopropyl, epoxy, ester, nitrile functions). The general structural motif bears a close conceptual relationship to the Breslow-type homoenolates and can be viewed as their deoxy-counterpart. Detailed NMR experiments document the presence of polarized exocyclic double bonds that render the α- and γ-positions highly nucleophilic as a consequence of an overall base-mediated umpolung process. Initial model studies proved their ability to engage in facile substitution reactions with electrophiles (H^+, methyl, prenyl, benzyl) to give access to new imidazolium cations with branched side chains. Imidazolium salts with quaternary substitution of the exocyclic α-carbon are subject to base-mediated carbene elimination to give tri-substituted olefins. Further investigations into the reactivity of alkylidene imidazolines toward other electrophiles and the development of umpolung processes for carbene-mediated carbon-carbon bond-forming reactions are currently being undertaken.

Experimental section

General

All chemicals were purchased from commercial suppliers and used without further purification unless otherwise noted. THF was distilled over sodium and benzophenone under an argon atmosphere. THF-d_8 was dried over molecular sieve (4 Å). ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance II 600 (600.20 and 150.94 MHz), a Bruker DRX 500 (500.13 and 125.77 MHz) and a Bruker Avance 300 (300.13 and 75.48 MHz) at 298 K unless otherwise stated. TopSpin (Version 1.3, 2.0 and 2.1) was used. Chemical shifts (δ in ppm) are referenced to tetramethylsilane (TMS) or solvent residual peaks (THF-d_8 at δ_H 3.58, δ_C 67.4; CD_3OD at δ_H 3.35, δ_C 49.3; $CDCl_3$ at δ_H 7.24, δ_C 77.0; DMSO-d_6 at δ_H 2.49, δ_C 39.7). Abbreviations for ^{1}H-NMR data: s = singlet, d = doublet, t = triplet, sep = septet, m = multiplet, "t" = pseudo triplet. Abbreviations for ^{13}C-APT/DEPTQ-NMR[26] data: u = up (CH_3 or CH), d = down (CH_2 or C_q). Peaks were assigned based on H,H-COSY, H,C-HMQC, H,C-HMBC, and H,H-NOESY/EXSY (mixing time d8 = 500 ms) correlation spectra. For atom numbering, please see Schemes 4–6 and Fig. 1. Conversions of *in situ* NMR experiments were determined relative to carbene *via* peak integration against TMS. 99.998% argon from Linde was used for manipulations under inert atmosphere. IR-ATR spectroscopy was performed on a Perkin-Elmer 100 Paragon FT-IR. ESI-MS were measured with a Finnigan MAT 900S and an Agilent LC/MSD VL G1956A, respectively. Exact masses (HRMS) were determined by peak matching method. GC-MS were run on an Agilent 6890 N Network GC system with Agilent 7683B series injector and Agilent 5975 inert mass-selective detector; stationary phase HP-5MS (L = 30 m, Ø = 0.25 mm) from Macherey-Nagel, mobile phase H_2, temperature program: 50 °C (2 min), 25 °C min^{-1} (10 min), final temperature 300 °C (5 min). UV/Vis absorptions were recorded on an OceanOptics USB2000 Fiber Optic. Crystal structure data were collected on a Nonius KappaCCD diffractometer using monochromated Mo-Kα radiation, and the structures refined by shelxs97 and shelxl97.[27]

In situ NMR studies of enediamines

General procedure. Under anaerobic conditions, an NMR tube was charged with 1,3-bis-(2,6-diisopropyl-phenyl)-imidazolium chloride (**1**) (recrystallized from $CHCl_3$ and azeotropized with CH_2Cl_2), sealed with a rubber septum, and transferred to a glove box where KO*t*Bu was added. Alternatively, KO*t*Bu was dissolved in THF-d_8 under anaerobic conditions and the solution added to **1**. Addition of THF-d_8 and ultrasonification gave a colourless solution after 5 min to which the electrophile was added.

1,3-Bis-(2,6-diisopropylphenyl)-2-(4-methylbenzylidene)-2,3-dihydro-1*H*-imidazole (4). **1** (1.5 mg, 0.0059 mmol) and KO*t*Bu (0.012 mmol) were dissolved in THF-d_8 (0.6 mL with TMS). A solution of *p*-methylbenzyl bromide (0.0059 mmol) in THF-d_8 was added. The colour of the solution turned yellow and a yellow precipitate formed. Conversion: 80%. ^{1}H-NMR (600 MHz, THF-d_8): δ = 7.38 (t; 1H, $^3J_{HH}$ = 7.8 Hz, H-9′), 7.30 (d; 2H, $^3J_{HH}$ = 7.8 Hz, H-8′, H-10′), 7.25 (t; 1H, $^3J_{HH}$ = 7.8 Hz, H-9), 7.08 (d; 2H, $^3J_{HH}$ = 7.8 Hz, H-8, H-10), 6.38 (d; 1H, $^3J_{HH}$ = 2.4 Hz, H-4), 6.31 (d; 1H, $^3J_{HH}$ = 2.4 Hz, H-5), 6.28 (d; 2H, $^3J_{HH}$ = 8.2 Hz, H-21, H-23), 5.97 (d; 2H, $^3J_{HH}$ = 8.2 Hz, H-20, H-24), 3.76 (s; 1H, H-18), 3.35 (sep; 2H, $^3J_{HH}$ = 6.7 Hz, H-12, H-15), 3.17 (sep; 2H, $^3J_{HH}$ = 6.7 Hz, H-12′, H-15′), 1.95 (s; 3H, H-25), 1.28 (d; 6H, $^3J_{HH}$ = 6.8 Hz, H-13′, H-16′), 1.23 (d; 6H, $^3J_{HH}$ = 6.8 Hz, H-14′, H-17′), 1.19 (d; 6H, $^3J_{HH}$ = 6.8 Hz, H-13, H-16), 1.08 (d; 6H, $^3J_{HH}$ = 6.8 Hz, H-14, H-17); ^{13}C-APT-NMR (151 MHz, THF-d_8): δ = 149.5 (d; 2C, C7′, C11′), 147.8 (d; 2C, C7, C11), 145.8 (d; 1C, C2), 137.7 (d; 1C, C6), 136.3 (d; 1C, C19), 135.3 (d; 1C, C6′), 130.0 (u; 1C, C9′), 129.4 (u; 1C, C9), 128.4 (d; 1C, C22), 127.8 (u; 2C, C21, C23), 126.2 (u; 2C, C20, C24), 125.2 (u; 2C, C8′, C10′), 124.3 (u; 2C, C8, C10), 118.0 (u; 1C, C5), 116.2 (u; 1C, C4), 70.2 (u; 1C, C18), 29.4 (u; 2C, C12′, C15′), 29.2 (u; 2C, C12, C15), 25.0 (u; 2C, C13, C16), 24.4 (u; 2C, C13′, C16′), 23.9 (u; 2C, C14′, C17′), 22.7 (u; 2C, C14, C17), 20.8 (u; 1C, C25); ESI-MS: m/z 493 [M+H$^+$]; UV/Vis λ_{max}(THF)/nm = 350.

1,3-Bis-(2,6-diisopropylphenyl)-2-(3-methylbut-2-enylid-ene)-2,3-dihydro-1*H*-imidazole (5). **1** (12.3 mg, 0.029 mmol) and KO*t*Bu (6 mg, 0.05 mmol) were dissolved in THF-d_8 (0.6 mL). Distilled 1-bromo-3-methylbut-2-ene (3.3 μL, 0.029 mmol) in THF-d_8 was added. The colour of the solution turned yellow and cloudy. ^{1}H-NMR (600 MHz, THF-d_8): δ = 7.36–7.33 (m; 2H, H-9, H-9′),

7.26 (d; 2H, $^3J_{HH}$ = 7.8 Hz, H-8′, H-10′), 7.22 (d; $^3J_{HH}$ = 7.7 Hz, 2H, H-8, H-10), 6.30 (d; 1H, $^3J_{HH}$ = 2.4 Hz, H-4), 6.24 (d, 1H, $^3J_{HH}$ = 2.4, H-5), 4.77 (d; 1H, $^3J_{HH}$ = 12.0 Hz, H-19), 3.43 (d; 1H, $^3J_{HH}$ = 12.0 Hz, H-18), 3.25 (sep; 2H, $^3J_{HH}$ = 6.9 Hz, H-12, H-15), 3.15 (sep; 2H, $^3J_{HH}$ = 6.9 Hz, H-12′, H-15′), 1.24–1.16 (m; 30H, CH_3); ^{13}C-APT-NMR (151 MHz, THF-d_8): δ = 149.4 (d; 2C, C7′, C11′), 148.8 (d; 2C, C7, C11), 145.4 (d; 1C, C2), 137.3 (d; 1C, C6), 134.9 (d; 1C, C6′), 129.8 (u; 1C, C9), 129.7 (u; 1C, C9′), 125.0 (u; 2C, C8 and C10 or C8′ and C10′), 124.5 (u; 2C, C8 and C10 or C8′ and C10′), 120.9 (u; 1C, C19), 117.3 (u; 1C, C5), 116.0 (u; 1C, C4), 111.6 (d; 1C, C20), 67.9 (u; 1C, C18), 29.4 (u; 2C, C12, C15), 29.3 (u; 2C, C12′, C15′), 26.1 (u; 1C, C21), 24.3 (u; 2C, C13 and C16 or C13′ and C16′), 24.3 (u; 2C C13 and C16 or C13′and C16′), 24.1 (u; 2C, C14′, C17′), 23.3 (u; 2C, C14, C17), 17.1 (u; 1C, C22); ESI-MS: m/z 457 [M+H$^+$].

1,3-Bis-(2,6-diisopropylphenyl)-2-(3-trimethylsilylprop-2-ynylidene)-2,3-dihydro-1*H*-imidazole (6). **1** (10.9 mg, 0.026 mmol) and KO*t*Bu (6 mg, 0.05 mmol) were dissolved in THF-d_8 (0.6 mL). 1-Bromo-3-(trimethylsilyl)-prop-2-yne (3.7 µL, 0.026 mmol) was added whereupon the solution turned dark purple and cloudy. ^{1}H-NMR (600 MHz, THF-d_8): δ = 7.38 (t; 1H, $^3J_{HH}$ = 7.9 Hz, H-9′), 7.35 (t; 1H, $^3J_{HH}$ = 7.7 Hz, H-9), 7.28 (d; 2H, $^3J_{HH}$ = 7.9 Hz, H-8′, H-10′), 7.16 (d; 2H, $^3J_{HH}$ = 7.7 Hz, H-8, H-10), 6.49 (d; 1H, $^3J_{HH}$ = 2.4 Hz, H-4), 6.45 (d; 1H, $^3J_{HH}$ = 2.4 Hz, H-5), 3.13 (sep; 2H, $^3J_{HH}$ = 6.9 Hz, H-12, H-15), 2.99 (sep; 2H, $^3J_{HH}$ = 7.0 Hz, H-12′, H-15′), 2.76 (s; 1H, H-18), 1.35 (d; 6H, $^3J_{HH}$ = 6.9 Hz, H-13, H-16), 1.27 (d; 6H, $^3J_{HH}$ = 7.0 Hz, H-13′, H-16′), 1.21 (d; 6H, $^3J_{HH}$ = 6.9 Hz, H-14, H-17), 1.19 (d; 6H, $^3J_{HH}$ = 7.0 Hz, H-14′, H-17′), –0.26 (s; 9H, H-21); ^{13}C-APT-NMR (151 MHz, THF-d_8): δ = 152.0 (d; 1C, C2), 148.8 (d; 4C, C7, C11, C7′, C11′), 135.2 (d; 1C, C6), 133.9 (d; 1C, C6′), 130.4 (u; 1C, C9 or C9′), 130.1 (u; 1C, C9 or C9′), 125.1 (u; 2C, C8′, C10′), 123.9 (u; 2C, C8, C10), 118.1 (u; 1C, C5), 116.7 (u; 1C, C4), 108.0 (d; 1C, C19), 90.9 (d; 1C, C20), 46.2 (u; 1C, C18), 29.6 (u; 2C, C12, C15), 29.4 (u; 2C, C12′, C15′), 24.4 (u; 2C, CH(CH_3)$_2$), 24.3 (u; 2C, CH(CH_3)$_2$), 23.9 (u; 2C, CH(CH_3)$_2$), 23.8 (u; 2C, CH(CH_3)$_2$), 1.01 (u; 3C, C21); ESI-MS: m/z 499 [M+H$^+$], 427 [M+H$^+$–TMS].

(*E*)-1,3-Bis-(2,6-diisopropylphenyl)-2-(3-phenylprop-2-enylidene)-2,3-dihydro-1*H*-imidazole (7). **1** (11.2 mg, 0.026 mmol) and KO*t*Bu (0.054 mmol in THF-d_8) were mixed in THF-d_8 (0.5 mL). Distilled (*trans*)-cinnamyl chloride (3.6 µL, 0.026 mmol) was added. The colour of the solution turned yellow. ^{1}H-NMR (600 MHz, THF-d_8): δ = 7.53 (t; 1H, $^3J_{HH}$ = 7.8 Hz, H-9), 7.41 (t; 1H, $^3J_{HH}$ = 7.8 Hz, H-9′), 7.38 (d; 2H, $^3J_{HH}$ = 7.8 Hz, H-8, H-10), 7.31 (d; 2H, $^3J_{HH}$ = 7.8 Hz, H-8′, H-10′), 6.79 (t; 2H, $^3J_{HH}$ = 7.8 Hz, H-23, H-25), 6.57 (t; 1H, $^3J_{HH}$ = 7.8 Hz, H-24), 6.52 (d; 1H, $^3J_{HH}$ = 2.4 Hz, H-4), 6.51 (d; 1H, $^3J_{HH}$ = 2.4 Hz, H-5), 6.41 (d; 2H, $^3J_{HH}$ = 7.8 Hz, H-22, H-26), 5.95 (dd; 1H, $^3J_{HH}$ = 14.4 Hz and 12.6 Hz, H-19), 5.16 (d; 1H, $^3J_{HH}$ = 14.4 Hz, H-20), 3.86 (d; 1H, $^3J_{HH}$ = 12.6 Hz, H-18), 3.19 (sep; 2H, $^3J_{HH}$ = 6.6 Hz, H-12, H-15), 3.07 (sep; 2H, $^3J_{HH}$ = 6.6 Hz, H-12′, H-15′), 1.26 (d; 6H, $^3J_{HH}$ = 6.6 Hz, CH(CH_3)$_2$), 1.24 (d; 6H, $^3J_{HH}$ = 6.6 Hz, CH(CH_3)$_2$), 1.22 (d; 6H, $^3J_{HH}$ = 6.6 Hz, CH(CH_3)$_2$), 1.21 (d; 6H, $^3J_{HH}$ = 6.6 Hz, CH(CH_3)$_2$); ^{13}C-DEPTQ-NMR (151 MHz, THF-d_8): 149.1 (d; 2C, C7′, C11′), 148.3 (d; 2C, C7, C11), 147.1 (d; 1C, C2), 142.7 (d; 1C, C21), 136.6 (d; 1C, C6), 134.2 (d; 1C, C6′), 130.4 (u; 1C, C9), 130.3 (u; 1C, C9′), 128.4 (u; 2C, C23, C25), 126.5 (u; 1C, C19), 125.3 (u; 2C, C8, C10), 125.2 (u; 2C, C8′, C10′), 123.7 (u; 2C, C22, C26), 122.1 (u; 1C, C24), 118.1 (u; 1C, C5), 116.9 (u; 1C, C4), 111.4 (u; 1C, C20), 73.0 (u; 1C, C18), 29.6 (u; 2C, C12, C15), 29.4 (u; 2C, C12′, C15′), 24.3 (u; 4C, CH(CH_3)$_2$), 23.9 (u; 2C, CH(CH_3)$_2$), 23.5 (u; 2C, CH(CH_3)$_2$); ESI-MS: m/z 505 [M+H$^+$].

1,3-Bis-(2,6-diisopropylphenyl)-2-(prop-2-enylidene)-2,3-dihydro-1*H*-imidazole (8). **1** (10.4 mg, 0.024 mmol) and KO*t*Bu (6 mg, 0.05 mmol) were dissolved in THF-d_8 (0.6 mL). Distilled allyl chloride (6.0 µL, 0.072 mmol) was added whereupon the solution turned slightly green. ^{1}H-NMR (600 MHz, THF-d_8): δ = 7.39–7.35 (m; 2H, H-9, H-9′), 7.27–7.24 (m; 4H, H-8, H-10, H-8′, H-10′), 6.35 (s; 1H, H-4), 6.30 (s; 1H, H-5), 5.29 (m; 1H, H-19), 3.78 (d; 1H, $^3J_{HH}$ = 16.0 Hz, *cis*-H-20), 3.67 (d; 1H, $^3J_{HH}$ = 11.8 Hz, H-18), 3.38 (d; 1H, $^3J_{HH}$ = 9.9 Hz, *trans*-H-20), 3.21 (sep; 2H, $^3J_{HH}$ = 6.9 Hz, H-12, H-15), 3.09 (sep; 2H, $^3J_{HH}$ = 6.9 Hz, H-12′, H-15′), 1.29–1.16 (m; 24H, CH(CH_3)$_2$); ^{13}C-APT-NMR (151 MHz, THF-d_8): δ = 149.2 (d; 2C, C7′, C11′), 148.7 (d; 2C, C7, C11), 146.5 (d; 1C, C2), 136.9 (d; 1C, C6), 134.7 (d; 1C, C6′), 132.7 (u; 1C, C19), 130.0 (u; 2C, C9, C9′), 125.0 (u; 2C, C8 and C10 or C8′ and C10′), 124.8 (u; 2C, C8 and C10 or C8′ and C10′), 117.6 (u; 1C, C5), 116.2 (u; 1C, C4), 95.1 (d; 1C, C20), 72.2 (u; 1C, C18), 29.5 (u; 2C, C12, C15), 29.4 (u; 2C, C12′, C15′), 24.3 (u; 2C, CH(CH_3)$_2$), 23.9 (u; 2C, CH(CH_3)$_2$), 23.7 (u; 2C, CH(CH_3)$_2$), 23.4 (u; 2C, CH(CH_3)$_2$); ESI-MS: m/z 429 [M+H$^+$].

1-(1,3-Bis-(2,6-diisopropylphenyl)imidazole-2-ylidene)-propanone (9). **1** (11.9 mg, 0.028 mmol) and KO*t*Bu (7 mg, 0.06 mmol) were dissolved in THF-d_8 (0.6 mL with TMS). Epibromohydrin (2.4 µL, 0.028 mmol) was added whereupon the solution turned pink then green. A precipitate formed. Conversion (after 4 h): 75%. ^{1}H-NMR (600 MHz, THF-d_8): δ = 7.33 (t; 2H, $^3J_{HH}$ = 7.8 Hz, H-9, H-9′), 7.21 (d; 4H, $^3J_{HH}$ = 7.8 Hz, H-8, H-10, H-8′, H-10′), 6.71 (s; 2H, H-4,H-5), 3.97 (s; 1H, H-18), 2.89 (sep; 4H, $^3J_{HH}$ = 6.9 Hz, H-12, H-15, H-12′, H-15′), 1.39 (s; 3H, H-20), 1.23 (d; 12H, $^3J_{HH}$ = 6.9 Hz, H-13, H-16, H-13′, H-16′), 1.19 (d; 12H, $^3J_{HH}$ = 6.9 Hz, H-14, H-17, H-14′, H-17′); ^{13}C-APT-NMR (151 MHz, THF-d_8): δ = 182.9 (d; 1C, C19), 151.8 (d; 1C, C2), 147.0 (d; 4C, C7, C11, C7′, C11′), 136.0 (d; 2C, C6, C6′), 129.8 (u; 2C, C9, C9′), 124.3 (u; 4C, C8, C10, C8′, C10′), 119.0 (u; 2C, C4, C5), 74.1 (u; 1C, C18), 29.6 (u; 4C, C12, C15, C12′, C15′), 29.3 (u; 1C, C20), 24.4 (u; 4C, C14, C17, C14′, C17′), 23.6 (u; 4C, C13, C16, C13′, C16′); HRMS(ESI): calcd. for $C_{30}H_{41}N_2O$: 445.3219 ([M+H]$^+$); found: 445.322 (±0.0015).

2-Cyclopropylmethylidene-1,3-bis-(2,6-diisopropylphenyl)-2,3-dihydro-1*H*-imidazole (10). **1** (10.9 mg, 0.026 mmol) and KO*t*Bu (0.055 mmol) were dissolved in THF-d_8 (0.6 mL with TMS). Bromomethylcyclopropane (2.8 µL, 0.029 mmol) was added. After 3 d, the solution was bright yellow and a white precipitate had formed. Conversion: >90%. ^{1}H-NMR (600 MHz, THF-d_8): δ = 7.29–7.26 (m; 2H, H-9, H-9′), 7.19 (d; 2H, $^3J_{HH}$ = 7.7 Hz, H-8′, H-10′), 7.17 (d; 2H, $^3J_{HH}$ = 7.7 Hz, H-8, H-10), 6.13 (d; 1H, $^3J_{HH}$ = 2.4 Hz, H-4), 6.12 (d; 1H, $^3J_{HH}$ = 2.4 Hz, H-5), 3.44 (sep; 2H, $^3J_{HH}$ = 6.9 Hz, H-12, H-15), 3.20 (sep; 2H, $^3J_{HH}$ = 6.9 Hz, H-12′, H-15′), 1.99 (d; 1H, $^3J_{HH}$ = 8.2 Hz, H-18), 1.33 (d; 6H, $^3J_{HH}$ = 6.9 Hz, H-13, H-16), 1.24 (d; 6H, $^3J_{HH}$ = 6.9 Hz, H-14, H-17), 1.23 (d; 6H, $^3J_{HH}$ = 6.9 Hz, H-13′, H-16′), 1.19 (d; 6H, $^3J_{HH}$ = 6.9 Hz, H-14′, H-17′), 0.32 (m; 1H, H-19), 0.06 (m; 2H, H-20a, H-21a), –0.44 (m; 2H, H-20b, H-21b); ^{13}C-APT-NMR (151 MHz, THF-d_8): δ = 149.7 (d; 2C, C7′, C11′), 149.2 (d; 2C, C7, C11),

147.1 (d; 1C, C2), 137.7 (d; 1C, C6), 135.5 (d; 1C, C6′), 129.4 (u; 1C, C9 or C9′), 129.2 (u; 1C, C9 or C9′), 124.9 (u; 2C, C8′, C10′), 124.1 (u; 2C, C8, C10), 116.6 (u; 1C, C5), 115.3 (u; 1C, C4), 68.0 (u; 1C, C18), 29.3 (u; 2C, C12, C15), 29.1 (u; 2C, C12′, C15′), 24.7 (u; 2C, C13, C16), 24.4 (u; 2C, C13′, C16′), 24.0 (u; 2C, C14′, C17′), 23.3 (u; 2C, C14, C17), 9.1 (d; 2C, C20, C21), 7.4 (u; 1C, C19); ESI-MS: *m/z*: 443.2 [M+H$^+$].

1,3-Bis-(2,6-diisopropylphenyl)-2-(2-oxiranylethylidene)-2,3-dihydro-1*H*-imidazole (11). **1** (13.8 mg, 0.032 mmol) and KO*t*Bu (7.6 mg, 0.068 mmol) were dissolved in THF-d_8 (0.6 mL with TMS). 1-Bromo-3,4-epoxybutane[28] (5.6 μL, 0.059 mmol) was added whereupon a white precipitate formed. After 2 d, the solution turned dark green and enediamine **11** started to slowly decompose. Observed conversion to **11**: 25% (instability of **11**!). ^{1}H-NMR (600 MHz, THF-d_8): δ = 7.34–7.30 (m; 2H, H-9, H-9′), 7.21 (d; 4H, H-8, H-10, H-8′, H-10′), 6.17 (d; 1H, $^3J_{HH}$ = 2.4 Hz, H-4), 6.12 (d; 1H, $^3J_{HH}$ = 2.4 Hz, H-5), 3.35 (sep; 2H, $^3J_{HH}$ = 6.9 Hz, H-12, H-15), 3.22–3.16 (m; 2H, H-12′, H-15′), 2.33-2.27 (m; 2H, H-18, H-20), 2.23 ("t"; J_{HH} = 4.4 Hz, 1H, H-21a), 1.91 (dd; 1H, $^3J_{HH}$ = 5.6 Hz, $^2J_{HH}$ = 2.5 Hz, H-21b), 1.68–1.60 (m; 2H, H-19a), 1.38–1.32 (m; 1H, H-19b), 1.34–1.05 (m; 24H, CH(CH_3)$_2$); ^{13}C-APT-NMR (151 MHz, THF-d_8): δ = 149.7 (d; 2C, C7′, C11′), 149.1 (d; 2C, C7, C11), 147.0 (d; 1C, C2), 137.5 (d; 1C, C6), 135.4 (d; 1C, C6′), 129.6 (u; 2C, C9, C9′), 125.0 (u; 2C, C8′, C10′), 124.5 (u; 2C, C8, C10), 116.7 (u; 1C, C4), 115.7 (u; 1C, C5), 56.9 (u; 1C, C18 or C20), 53.6 (u; 1C, C18 or C20), 46.2 (d; 1C, C21), 29.3 (u; 2C, C12 and C15 or C12′ and C15′), 29.2 (u; 2C, C12 and C15 or C12′ and C15′), 28.6 (d; 1C, C19) 24.8–23.0 (multiple u; 8C, CH(CH_3)$_2$); ESI-MS: *m/z* 459 [M+H$^+$].

Ethyl 2-[1,3-Bis-(2,6-diisopropylphenyl)-1,3-dihydro-imidazol-2-ylidenemethyl]acrylate (12). **1** (12.5 mg, 0.029 mmol) and KO*t*Bu (6.8 mg, 0.061 mmol) were dissolved in THF-d_8 (0.6 mL with TMS). α-Bromomethyl-ethylacrylate (4.0 μL, 0.029 mmol) was added whereupon the solution turned brown. Conversion: 56%. ^{1}H-NMR (600 MHz, THF-d_8): δ = 7.36 (t; 1H, $^3J_{HH}$ = 7.7 Hz, H-9′), 7.30 (t; 1H, $^3J_{HH}$ = 7.8 Hz, H-9), 7.27 (d; 2H, $^3J_{HH}$ = 7.7 Hz, H-8′, H-10′), 7.17 (d; 2H, $^3J_{HH}$ = 7.8 Hz, H-8, H-10), 6.46 (d; 1H, $^3J_{HH}$ = 1.9 Hz, H-5), 6.38 (d; 1H, $^3J_{HH}$ = 1.9 Hz, H-4), 4.69 (s; 1H, H-21a), 3.83 (q; 2H, $^3J_{HH}$ = 7.1 Hz, H-22), 3.76 (s; 1H, H-18), 3.37 (s; 1H, H-21b), 3.28 (sep; 2H, $^3J_{HH}$ = 7.1 Hz, H-12, H-15), 3.06 (sep; 2H, $^3J_{HH}$ = 6.9 Hz, H-12′, H-15′), 1.27–1.19 (m; 24H, CH(CH_3)$_2$), 1.01 (t; 3H, $^3J_{HH}$ = 7.1 Hz, H-23); ^{13}C-APT-NMR (151 MHz, THF-d_8): δ = 169.0 (d; 1C, C20), 149.2 (d; 2C, C7′, C11′), 148.2 (d; 2C, C7, C11), 148.0 (d; 1C, C2), 137.2 (d; 1C, C6), 134.8 (d; 1C, C6′), 134.2 (d; 1C, C19), 130.1 (u; 1C, C9′), 129.7 (u; 1C, C9), 125.1 (u; 2C, C8′, C10′), 124.0 (u; 2C, C8, C10), 118.2 (u; 1C, C4), 116.9 (u; 1C, C5), 107.5 (d; 1C, C21), 66.4 (u; 1C, C18), 60.0 (d; 1C, C22), 29.4 (u; 2C, C12′, C15′), 29.2 (u; 2C, C12, C15), 24.7 (u; 2C, C13, C16), 24.4 (u; 2C, C13′, C16′), 23.9 (u; 2C, C14′, C17′), 22.9 (u; 2C, C14, C17), 14.5 (u; 1C, C23).

[1,3-Bis-(2,6-diisopropylphenyl)-1,3-dihydroimidazol-2-ylidene]-acetonitrile (13). **1** (9.4 mg, 0.022 mmol) and KO*t*Bu (6 mg, 0.05 mmol) were dissolved in THF-d_8 (0.6 mL with TMS). Chloroacetonitrile (2.8 μL, 0.044 mmol) was added whereupon the solution turned dark brown. Conversion: 50%. ^{1}H-NMR (600 MHz, THF-d_8): δ = 7.43 (t; 1H, $^3J_{HH}$ = 7.8 Hz, H-9′), 7.37 (t; 1H, $^3J_{HH}$ = 7.8 Hz, H-9), 7.32 (d; 2H, $^3J_{HH}$ = 7.8 Hz, H-8′, H-10′), 7.21 (d; 2H, $^3J_{HH}$ = 7.8 Hz, H-8, H-10), 6.70 (d; 1H, $^3J_{HH}$ = 2.2 Hz, H-4), 6.68 (d; 1H, $^3J_{HH}$ = 2.2 Hz, H-5), 2.98 (sep; 2H, $^3J_{HH}$ = 6.8 Hz, H-12, H-15), 2.88 (sep; 2H, $^3J_{HH}$ = 6.9 Hz, H-12′, H-15′), 2.38 (s; 1H, H-18), 1.34 (d; 6H, $^3J_{HH}$ = 6.8 Hz, H-13, H-16), 1.27–1.20 (m; 18H, H13′, H-16′, H-14, H-16, H-14′, H-16′); ^{13}C-APT-NMR (151 MHz, THF-d_8): δ = 153.5 (d; 1C, C2), 148.4 (d; 2C, C7, C11), 148.4 (d; 2C, C7′, C11′), 133.4 (d; 1C, C6), 133.0 (d; 1C, C6′), 130.9 (u; 1C, C9 or C9′), 130.0 (u; 1C, C9 or C9′), 125.4 (u; 2C, C8′, C10′), 124.4 (u; 2C, C8, C10), 120.0 (d; 1C, C19), 118.7 (u; 1C, C5), 117.5 (u; 1C, C4), 33.2 (u; 1C, C18), 29.7 (u; 2C, C12, C15), 29.5 (u; 2C, C12′, C15′), 24.5 (u; 2C, C13, C16), 24.3 (u; 2C, C13′, C16′), 23.8 (u; 2C, C14′, C17′), 23.5 (u; 2C, C14, C17); HRMS(ESI): calcd. for $C_{29}H_{38}N_3$: 428.3066 ([M+H]$^+$); found: 428.306 (±5 ppm).

Secondary substitution products

1,3-Bis-(2,6-diisopropylphenyl)-2-(4-methylbenzyl)-imidazolium iodide (3). **1** (88.2 mg, 0.208 mmol) was stirred for 5 min with KO*t*Bu (57 mg, 0.51 mmol in 2.7 mL THF) at room temperature. *p*-Methylbenzyl bromide (53 mg, 0.29 mmol in 2.1 mL THF) was added. The resulting yellow solution was stirred for 1 h and kept over night without stirring. The resulting white precipitate was filtered off under inert conditions. Trimethylsilyl iodide (71 μL, 0.50 mmol) was added whereupon the solution turned dark. After standing at rt overnight, square yellow crystals of imidazolium iodide **3** (9 mg, 7%) had formed. ^{1}H-NMR (600 MHz, CD_3OD): δ = 8.32 (s; 2H, H-4, H-5), 7.76 (t; 2H, $^3J_{HH}$ = 7.8 Hz, H-9, H-9′), 7.57 (d; 4H, $^3J_{HH}$ = 7.8 Hz, H-8, H-10, H-8′, H-10′), 6.97 (d; 2H, $^3J_{HH}$ = 7.9 Hz, H-21, H-23), 6.39 (d; 2H, $^3J_{HH}$ = 7.9 Hz, H-20, H-24), 3.95 (s; 2H, H-18), 2.35 (sep; 4H, $^3J_{HH}$ = 6.8 Hz, H-12, H-15, H-12′, H-15′), 2.25 (s; 3H, H-25), 1.28 (d; 12H, $^3J_{HH}$ = 6.8 Hz, CH(CH_3)$_2$), 1.28 (d; 12H, $^3J_{HH}$ = 6.8 Hz, CH(CH_3)$_2$); ^{13}C-DEPTQ (151 MHz, CD_3OD): δ = 149.0 (d; 1C, C2), 146.9 (d; 4C, C7, C7′), 140.0 (d; 1C, C22), 134.1 (u; 2C, C9, C9′), 131.2 (u; 2C, C21, C23), 131.1¶ (d; 2C, C6, C6′), 130.5 (u; 2C, C20, C24), 128.9 (d; 1C, C19), 127.4 (u; 2C, C4, C5), 126.8 (u; 4C, C8, C8′, C10, C10′), 31.7 (d; 1C, C18), 31.1 (u; 4C, C12, C15, C12′, C15′), 26.3 (u; 4C, C13, C16, C13′, C16′), 22.7 (u; 4C, C14, C17, C14′, C17′), 21.2 (u; 1C, C25), HRMS: calcd. for $C_{35}H_{45}N_2$ (M–I$^-$): 493.3582; found: 493.358; ATR-IR: 2963, 2921, 2866, 1734, 1599, 1551, 1493, 1457, 1364, 1238, 1102, 1059, 933, 806, 752; UV/Vis λ_{max}(THF)/nm = 234; for crystal structure data see Table 2.

1,3-Bis-(2,6-diisopropylphenyl)-2-(1-*p*-tolylethyl)-imidazolium iodide (14). **1** (113.8 mg, 0.268 mmol) was reacted with a solution of KO*t*Bu (75 mg, 0.67 mmol) in THF (3.5 mL) and *p*-methylbenzyl bromide (70 mg, 0.38 mmol in 1.7 mL THF). After filtration, the solvent was removed under reduced pressure, the residue dissolved in THF (6 mL) and methyl iodide (15 μL, 0.24 mmol) added. The resultant precipitate was collected and dissolved in MeOH. After removal of the solvent, a white solid (23.7 mg, 14%) was obtained. ^{1}H-NMR (600 MHz, CD_3OD): δ = 8.19 (s; 2H, H-4, H-5), 7.74 ("t"; 2H, $^3J_{HH}$ = 7.9 Hz, H-9, H-9′), 7.60 (dd; 2H, $^3J_{HH}$ = 7.9 Hz, $^4J_{HH}$ = 1.1 Hz, H-10, H-10′), 7.45 (dd; 2H, $^3J_{HH}$ = 7.9 Hz, $^4J_{HH}$ = 1.1 Hz, H-8, H-8′), 6.95 (d; 2H, $^3J_{HH}$ = 8.0 Hz, H-21, H-23), 6.43 (d; 2H, $^3J_{HH}$ = 8.0 Hz, H-20, H-24), 4.30 (q; 1H, $^3J_{HH}$ = 7.6 Hz, H-18), 2.50 (sep; 2H, $^3J_{HH}$ = 6.8 Hz,

¶ determined from H,C-HMBC

Table 2 Crystal structure data for compounds **3**, **16**, and **19**

Compound reference	**3**	**16**	**19**
Chemical formula	$C_{35}H_{45}N_2{\cdot}I$	$C_{43}H_{53}N_2{\cdot}Br$	$C_{34}H_{49}N_2{\cdot}I$
Formula Mass	620.63	677.78	612.65
Crystal system	Triclinic	Monoclinic	Orthorhombic
a/Å	9.9198(3)	14.5466(18)	17.0042(8)
b/Å	10.5205(4)	16.0087(16)	18.6505(13)
c/Å	16.6770(6)	20.286(3)	20.0765(14)
α (°)	83.068(2)	90.00	90.00
β (°)	85.616(2)	128.613(8)	90.00
γ (°)	69.015(2)	90.00	90.00
Unit cell volume/Å^3	1612.08(10)	3691.3(8)	6367.0(7)
T/K	90(2)	100(2)	100(2)
Space group	$P\bar{1}$	$P21/c$	$Pbca$
No. of formula units per unit cell, Z	2	4	8
No. of reflections measured	11853	9022	29869
No. of independent reflections	7035	6004	6958
R_{int}	0.0262	0.0501	0.1138
Final R_1 values ($I > 2\sigma(I)$)	0.0294	0.0581	0.0799
Final w$R(F^2)$ values ($I > 2\sigma(I)$)	0.0629	0.1186	0.2172
Final R_1 values (all data)	0.0399	0.1496	0.2076
Final w$R(F^2)$ values (all data)	0.0655	0.1393	0.2583

C*H*(CH$_3$)$_2$), 2.23 (s; 3H, H-25), 2.17 (sep; 2H, $^3J_{HH}$ = 6.8 Hz, C*H*(CH$_3$)$_2$), 1.46 (d; 3H, $^3J_{HH}$ = 7.6 Hz, H-26), 1.45 (d; 6H, $^3J_{HH}$ = 6.8 Hz, CH(C*H*$_3$)$_2$), 1.25 (d; 6H, $^3J_{HH}$ = 6.8 Hz, CH(C*H*$_3$)$_2$), 1.17 (d; 6H, $^3J_{HH}$ = 6.8 Hz, CH(C*H*$_3$)$_2$), 1.05 (d; 6H, $^3J_{HH}$ = 6.8 Hz, CH(C*H*$_3$)$_2$); ^{13}C-APT-NMR (151 MHz, CD$_3$OD): δ = 151.0 (d; 1C, C2), 147.3 (d; 2C, C7, C7′), 146.9 (d; 2C, C11, C11′), 140.3 (d; 1C, C22), 134.2 (u; 2C, C9, C9′), 133.9 (d; 1C, C19), 131.8 (d; 2C, C6, C6′), 131.0 (u; 2C, C21, C23), 129.6 (u; 2C, C20, C24), 127.8 (u; 2C, C4, C5), 126.7 (u; 4C, C8, C8′, C10, C10′), 38.2 (u; 1C, C18), 31.2 (u; 2C, *C*H(CH$_3$)$_2$), 31.0 (u; 2C, *C*H(CH$_3$)$_2$), 27.0 (u; 2C, CH(*C*H$_3$)$_2$), 26.6 (u; 2C, CH(*C*H$_3$)$_2$), 22.4 (u; 2C, CH(*C*H$_3$)$_2$), 22.2 (u; 2C, CH(*C*H$_3$)$_2$), 21.2 (u; 1C, C25), 19.4 (u; 1C, C26); HRMS(ESI): m/z calcd. for $C_{36}H_{47}N_2$ (M–I$^-$): 507.3739; found: 507.374 (±0.0015).

1,3-Bis-(2,6-diisopropylphenyl)-2-(4-methyl-1-*p*-tolylpent-3-enyl)-imidazolium bromide (15). **1** (61.2 mg, 0.144 mmol) was reacted with KO*t*Bu (40 mg, 0.36 mmol in 1.7 mL THF) and *p*-methylbenzyl bromide (37 mg, 0.20 mmol in 1.7 mL THF). After filtration, distilled prenyl bromide (16 µL, 0.14 mmol) was added. After 4 d, the solvent was removed to give an oily yellow residue (yield n. d.). ^{1}H-NMR (600 MHz, THF-d_8): δ = 9.24 (s; 2H, H-4, H-5), 7.65 (“t”; 2H, $^3J_{HH}$ = 7.8 Hz, H-9, H-9′), 7.54 (d; 2H, $^3J_{HH}$ = 7.8 Hz, H-10, H-10′), 7.37 (d; 2H, $^3J_{HH}$ = 7.8 Hz, H-8, H-8′), 6.86 (d; 2H, $^3J_{HH}$ = 8.1 Hz, H-21), 6.24 (d; 2H, $^3J_{HH}$ = 8.1 Hz, H-20), 4.34 (t; 1H, $^3J_{HH}$ = 5.4 Hz, H-27), 3.98 (dd; 1H, $^3J_{HH}$ = 13.2 Hz and 4.2 Hz, H-18), 2.69 (m; 2H, H-26), 2.64 (sep; 2H, $^3J_{HH}$ = 6.8 Hz, H-12, H-12′), 2.26 (sep; 2H, $^3J_{HH}$ = 6.8 Hz, H-15, H-15′), 2.19 (s; 3H, H-25), 1.43 (br; 3H, H-30), 1.42 (d; 6H, $^3J_{HH}$ = 6.8 Hz, H-14, H-14′), 1.36 (br; 3H, H-29), 1.30 (d; 6H, $^3J_{HH}$ = 6.8 Hz, H-13, H-13′), 1.21 (d; 6H, $^3J_{HH}$ = 6.8 Hz, H-16, H-16′), 0.93 (d; 6H, $^3J_{HH}$ = 6.8 Hz, H-17, H-17′); ^{13}C-APT-NMR (151 MHz, THF-d_8): δ = 148.1 (d; 1C, C2), 147.3 (d; 2C, C11, C11′), 146.8 (d; 2C, C7, C7′), 139.1 (d; 1C, C22), 135.9 (d; 1C, C28), 132.9 (u; 2C, C9, C9′), 131.7 (d; 2C, C6, C6′), 131.0 (d; 1C, C19), 130.3 (u; 2C, C20, C24), 130.1 (u; 2C, C21, C23), 129.3 (u; 2C, C4, C5), 125.7 (u; 2C, C8, C8′), 125.6 (u; 2C, C10, C10′), 120.1 (u; 1C, C27), 43.5 (u; 1C, C18), 31.6 (d; 1C, C26), 30.6 (u; 2C, C12, C12′), 30.4 (u; 2C, C15, C15′), 27.2 (u; 2C, C13, C13′), 26.7 (u; 2C, C16, C16′), 25.4 (u; 1C, C29), 22.2 (u; 2C, C14, C14′), 21.9 (u; 2C, C17, C17′), 20.9 (u; 1C, C25), 18.7 (u; 1C, C30); HRMS(ESI): m/z: calcd. for $C_{40}H_{53}N_2$ (M–Br$^-$): 561.4209; found: 561.420 (±0.0015).

Corresponding base: 1,3-Bis(2,6-diisopropylphenyl)-2-(4-methyl-1-*p*-tolylpent-3-enyliden)-2,3-dihydro-1*H*-imidazole (21). According to the general procedure for NMR studies, **1** (9.8 mg, 0.023 mmol) was reacted with KO*t*Bu (7.7 g, 0.069 mmol in 0.6 mL THF-d_8 (with TMS). *p*-Methylbenzyl bromide (6.8 mg, 0.037 mmol in THF-d_8) was added. After reaction control by NMR, distilled prenyl bromide (4.8 mg, 0.032 mmol) was added. The yellow solution exhibited 53% conversion to **21**. ^{1}H-NMR (600 MHz, THF-d_8): δ = 7.30 (t; 1H, $^3J_{HH}$ = 7.6 Hz, H-9′), 7.23 (d; 2H, $^3J_{HH}$ = 7.6 Hz, H-8′, H-10′), 6.93 (t; 1H, $^3J_{HH}$ = 7.6 Hz, H-9), 6.82 (d; 2H, $^3J_{HH}$ = 7.6 Hz, H-8, H-10), 6.55 (d; 2H, $^3J_{HH}$ = 8.0 Hz, H-20, H-24), 6.44 (d; 2H, $^3J_{HH}$ = 8.0 Hz, H-21, H-23), 6.13 (d; 1H, $^3J_{HH}$ = 2.4 Hz, H-4), 6.12 (d; 1H, $^3J_{HH}$ = 2.4 Hz, H-5), 4.49 (t; 1H, $^3J_{HH}$ = 6.1 Hz, H-27), 3.53 (sep; 2H, $^3J_{HH}$ = 7.0 Hz, H-12′, H-15′), 3.30 (sep; 2H, $^3J_{HH}$ = 6.8 Hz, H-12, H-15), 2.59 (d; 2H, $^3J_{HH}$ = 6.1 Hz, H-26), 1.98 (s; 3H, H-25), 1.35 (d; 6H, $^3J_{HH}$ = 7.0 Hz, H-14′, H-17′), 1.32 (s; 3H, H-29), 1.25 (d; 6H, $^3J_{HH}$ = 6.8 Hz, H-13, H-16), 1.23 (d; 6H, $^3J_{HH}$ = 7.0 Hz, H-13′, H-16′), 1.10 (d; 6H, $^3J_{HH}$ = 6.8 Hz, H-14, H-17), 0.94 (s; 3H, H-30); ^{13}C-APT-NMR (151 MHz, THF-d_8): δ = 148.4 (d; 2C, C7′, C11′), 147.2 (d; 2C, C7, C11), 145.1 (d; 1C, C2), 140.4 (d; 1C, C19), 139.0 (d; 1C, C6′), 138.5 (d; 1C, C6), 131.7 (d; 1C, C22), 130.4 (u; 2C, C20, C24), 129.1 (u, 1C, C9′), 128.4 (d; 1C, C28), 128.1 (u; 1C, C9), 127.9 (u; 2C, C21, C23), 127.0 (u; 1C, C20), 125.0 (u; 2C, C8′, C10′), 124.1 (u; 2C, C8, C10), 119.3 (u; 1C, C5), 118.2 (u; 1C, C4), 79.8 (d; 1C, C18), 32.1 (d; 1C, C26), 29.3 (u; 2C, C12′, C15′), 28.9 (u; 2C, C12, C15), 26.0 (u; 2C, C14, C17), 25.7 (u; 1C, C29), 25.5 (u; 2C, C13′, C16′), 23.1 (u; 2C, C14′, C17′), 22.5 (u; 2C, C13, C16), 21.0 (u; 1C, C25), 17.6 (u; 1C, C30); ESI-MS m/z 561 [M+H]$^+$.

1,3-Bis-(2,6-diisopropylphenyl)-2-(1,2-di-*p*-tolylethyl)-imidazolium bromide (16). Under anaerobic conditions, KO*t*Bu (0.48 g, 4.3 mmol in 20 mL THF) was added to **1** (0.97 g, 2.0 mmol), followed by the addition of *p*-methylbenzyl bromide (0.43 g, 2.4 mmol in 10 mL THF). The reaction mixture was kept overnight at 2 °C. The yellow solution was then separated from the white precipitate. *p*-Methylbenzyl bromide (0.31 g, 1.7 mmol in 10 mL THF) was added. After 3 d at rt, the solvent was removed under reduced pressure to afford a slightly orange solid (1.06 g, 80%). ^{1}H-NMR (600 MHz, THF-d_8): δ = 9.22 (s; 2H, H-4, H-5), 7.69 ("t"; 2H, $^3J_{HH}$ = 7.9 Hz, H-9, H-9′), 7.57 (dd; 2H, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.0 Hz, H-8, H-8′), 7.40 (dd; 2H, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.0 Hz, H-10, H-10′), 6.76 (d; 2H, $^3J_{HH}$ = 8.0 Hz, H-21, H-23), 6.72 (d; 2H, $^3J_{HH}$ = 8.0 Hz, H-29, H-31), 6.38 (d; 2H, $^3J_{HH}$ = 8.0 Hz, H-28, H-32), 6.26 (d; 2H, $^3J_{HH}$ = 8.0 Hz, H-20, H-24), 4.30 (dd; 1H, $^3J_{HH}$ = 13.4 Hz, $^3J_{HH}$ = 2.4 Hz, H-18), 3.21 (dd; 1H, $^2J_{HH}$ = 13.4 Hz, $^3J_{HH}$ = 2.4 Hz, H-26a), 3.07 ("t"; 1H, J_{HH} = 13.4 Hz, H-26b), 2.66 (sep; 2H, $^3J_{HH}$ = 6.7 Hz, H-15, H-15′), 2.35 (sep; 2H, $^3J_{HH}$ = 6.7 Hz, H-12, H-12′), 2.12 (s; 3H, H-25), 2.06 (s; 3H, H-33), 1.42 (d; 6H, $^3J_{HH}$ = 6.7 Hz, H-17, H-17′), 1.30 (d; 6H, $^3J_{HH}$ = 6.7 Hz, H-16, H-16′), 1.24 (d; 6H, $^3J_{HH}$ = 6.7 Hz, H-13, H-13′), 0.99 (d; 6H, $^3J_{HH}$ = 6.7 Hz, H-14, H-14′); ^{1}H-NMR (300 MHz, CD_3OD): δ = 8.38 (s; 2H, H-4, H-5), 7.83 ("t"; 2H, $^3J_{HH}$ = 7.8 Hz, H-9, H-9′), 7.71 (dd; 2H, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.0 Hz, H-8, H-8′), 7.53 (dd; 2H, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.0 Hz, H-10, H-10′), 6.81 ("t"; 4H, J_{HH} = 7.9 Hz, H-21, H-23, H-29, H-31), 6.33 (d; 2H, $^3J_{HH}$ = 7.9 Hz, H-28, H-32), 6.32 (d; 2H, $^3J_{HH}$ = 7.9 Hz, H-20, H-24), 4.37 (dd; 1H, $^3J_{HH}$ = 9.0 Hz, $^3J_{HH}$ = 6.8 Hz, H-18), 3.12 (m; 2H, H-26), 2.64 (sep; 2H, $^3J_{HH}$ = 6.8 Hz, H-15, H-15′), 2.28 (sep; 2H, $^3J_{HH}$ = 6.8 Hz, H-12, H-12′), 2.18 (s; 3H, H-25), 2.13 (s; 3H, H-33), 1.55 (d; 6H, $^3J_{HH}$ = 6.8 Hz, H-17, H-17′), 1.31 (d; 6H, $^3J_{HH}$ = 6.8 Hz, H-16, H-16′), 1.25 (d; 6H, $^3J_{HH}$ = 6.8 Hz, H-13, H-13′), 1.07 (d; 6H, $^3J_{HH}$ = 6.8 Hz, H-14, H-14′); ^{13}C-DEPTQ (151 MHz, THF-d_8): δ = 148.0 (d; 1C, C2), 147.0 (d; 2C, C11, C11′), 146.5 (d; 2C, C7, C7′), 139.0 (d; 1C, C22), 136.9 (d; 1C, C30), 134.1 (d; 1C, C27), 133.1 (u; 2C, C9, C9′), 131.7 (d; 2C, C6, C6′), 130.4 (u; 2C, C20, C24), 130.2 (d; 1C, C19), 130.0 (u; 2C, C21, C23), 129.6 (u; 2C, C29, C31), 129.2 (u; 2C, C4, C5), 129.0 (u; 2C, C28, C32), 125.9 (u; 2C, C10, C10′), 125.8 (u; 2C, C8, C8′), 45.2 (u; 1C, C18), 38.1 (d; 1C, C26), 30.6 (u; 2C, C15, C15′), 30.5 (u; 2C, C12, 12′), 27.0 (u; 2C, C16, C16′), 26.9 (u; 2C, C13, C13′), 22.2 (u: 2C, C17, C17′), 22.0 (u; 2C, C14, C14′), 20.8 (u; 2C, C25, C33); HRMS(ESI): calcd for $C_{43}H_{53}N_2$ ($M–Br^-$): 597.4209; found: 597.420 (±0.0015); for crystal structure data see Table 2.

Corresponding base 1,3-Bis-(2,6-diisopropylphenyl)-2-(1,2-diphenylethylidene)-2,3-dihydro-1*H*-imidazole (20). ^{1}H-NMR (600 MHz, THF-d_8): δ = 7.26 (t; 1H, $^3J_{HH}$ = 7.8 Hz, H-9′), 7.19 (d; 2H, $^3J_{HH}$ = 7.8 Hz, H-8′, H-10′), 6.94 (t; 1H, $^3J_{HH}$ = 7.7 Hz, H-9), 6.81 (d; 2H, $^3J_{HH}$ = 7.7 Hz, H-8, H-10), 6.71 (d; 2H, $^3J_{HH}$ = 7.8 Hz, H-21, H-23), 6.53 (d; 2H, $^3J_{HH}$ = 7.8 Hz, H-20, H-24), 6.44 (d; 2H, $^3J_{HH}$ = 8.0 Hz, H-28, H-32), 6.33 (d; 2H, $^3J_{HH}$ = 8.0 Hz, H-29, H-31), 6.17 (d; 1H, $^3J_{HH}$ = 2.5 Hz, H-4), 6.15 (d; 1H, $^3J_{HH}$ = 2.5 Hz, H-5), 3.56 (sep; 2H, $^3J_{HH}$ = 6.9 Hz, H-12′, H-15′), 3.36 (sep; 2H, $^3J_{HH}$ = 6.8 Hz, H-12, H-15), 3.21 (s; 2H, H-26), 2.12 (s; 3H, H-25), 1.94 (s; 3H, H-33), 1.28–1.13 (m; 24H, $CH(CH_3)_2$); ^{13}C-APT-NMR (151 MHz, THF-d_8): δ = 148.4 (d; 2C, C7, C11), 147.1 (d; 2C, C7′, C11′), 145.6 (d; 1C, C2), 141.1 (d; 1C, C19), 140.0 (d; 1C, C27), 139.3 (d; 1C, C6), 138.7 (d; 1C, C6′), 134.3 (d; 1C, C22), 132.0 (d; 1C, C30), 130.6 (u; 2C, C28, C32), 129.4 (u; 1C, C9′) 129.2 (u; 2C, C20, C24), 129.1 (u; 2C, C8′, C10′) 128.6 (u; 2C, C21, C23), 128.3 (u; 1C, C9), 127.7 (u; 2C, C29, C31), 124.0 (u; 2C, C8, C10), 119.8 (u; 1C, C4), 117.8 (u; 1C, C5), 80.1 (d; 1C, C26), 39.1 (d; 1C, C18), 29.3 (u; 2C, C12′, C15′), 29.0 (u; 2C, C12, C15), 25.9 (u; 2C, $CH(CH_3)_2$), 25.8 (u; 2C, $CH(CH_3)_2$), 23.2 (u; 2C, $CH(CH_3)_2$), 22.4 (u; 2C, $CH(CH_3)_2$), 21.0 (u; 1C, C25), 20.9 (u; 1C, C33); ESI-MS: *m*/*z* 597 [M+H$^+$].

1,3-Bis-(2,6-diisopropylphenyl)-2-[2-(4-nitrophenyl)-1-*p*-tolylethyl]-imidazolium bromide (17). Under anaerobic conditions, **1** (578.2 mg, 1.315 mmol) was stirred with KO*t*Bu (310 mg, 2.76 mmol) in 14.5 mL THF. *p*-Methylbenzyl bromide (259 mg, 2.76 mmol in 8.8 mL THF) was added whereupon the solution turned yellow. After 2.5 h at rt, *p*-nitrobenzyl bromide (0.287 g, 1.33 mmol in 6 mL THF) was added. The resulting purple solution was stirred for 1.25 h. The reaction mixture was then filtered and the solvent removed under reduced pressure to give a dark blue solid (0.992 mg, > 99% yield). ^{1}H-NMR (600 MHz, THF-d_8): δ = 8.86 (s; 2H, H-4, H-5), 7.79 (d; 2H, $^3J_{HH}$ = 8.2 Hz, H-29, H-31), 7.67 (t; 2H, $^3J_{HH}$ = 7.7 Hz, H-9, H-9′), 7.55 (d; 2H, $^3J_{HH}$ = 7.7 Hz, H-8, H-8′), 7.41 (d; 2H, $^3J_{HH}$ = 7.7 Hz, H-10, H-10′), 7.02 (d; 2H, $^3J_{HH}$ = 8.2 Hz, H-28, H-32), 6.81 (d; 2H, $^3J_{HH}$ = 7.7 Hz, H-21, H-23), 6.26 (d; 2H, $^3J_{HH}$ = 7.7 Hz, H-20, H-24), 4.35 (d; 1H, $^3J_{HH}$ = 13.9 Hz, H-18), 4.03 (d; 1H, $^3J_{HH}$ = 13.9 Hz, H-26), 3.28 (t; 1H, $^3J_{HH}$ = 13.9 Hz, H-26), 2.88 (sep; 2H, $^3J_{HH}$ = 6.6 Hz, H-15, H-15′), 2.59 (sep; 2H, $^3J_{HH}$ = 6.7 Hz, H-12, H-12′), 2.14 (s; 3H, H-25), 1.38 (d; 6H, $^3J_{HH}$ = 6.6 Hz, H-16, H-16′), 1.27 (d; 6H, $^3J_{HH}$ = 6.6 Hz, H-17, H-17′), 1.21 (d; 6H, $^3J_{HH}$ = 6.7 Hz, H-13, H-13′), 1.00 (d; 6H, $^3J_{HH}$ = 6.7 Hz, H-14, H-14′); ^{13}C-APT-NMR (151 MHz, THF-d_8): δ = 148.1 (d; 1C, C2), 147.7 (d, 1C, C30), 147.5 (d; 2C, C11, C11′), 147.2 (d; 2C, C7, C7′), 145.7 (d; 1C, C27), 139.5 (d; 1C, C22), 133.1 (u; 2C, C9, C9′), 131.9 (d; 2C, C6, C6′), 130.7 (u; 2C, C28, C32), 130.5 (u; 2C, C20, C24), 130.3 (u; 2C, C21, C23), 130.2 (d; 1C, C19), 128.4 (u; 2C, C4, C5), 126.1 (u; 2C, C8, C8′), 125.9 (u; 2C, C10, C10′), 123.8 (u; 2C, C29, C31), 44.9 (u; 1C, C18), 37.9 (d; 1C, C26), 30.5 (u; 4C, C12, C12′, C15, C15′), 27.0 (u; 2C, C17, C17′), 26.9 (u; 2C, C13, C13′), 22.4 (u; 2C, C16, C16′), 22.2 (u; 2C, C14, C14′), 20.9 (u; 1C, C25); ESI-MS: *m*/*z* 628 ($M–Br^-$).

1,3-Bis-(2,6-diisopropylphenyl)-2-(1,3-dimethylbut-2-enyl)imidazolium iodide (18). Under anaerobic conditions, **1** (350 mg, 0.823 mmol) and KO*t*Bu (196 mg, 1.75 mmol) were stirred at rt in THF (11 mL) for 2 h. Prenyl bromide (105 µL, 0.905 mmol) was added to the cloudy solution whereupon it turned yellow. Stirring was continued for 18 h, then methyl iodide (155 µL, 2.47 mmol) was added and the reaction stirred for 3 h. All volatiles were removed under reduced pressure, the residue triturated with toluene producing a white solid (366 mg, 56%).‖ ^{1}H-NMR (600 MHz, CD_3OD): δ = 8.25 (s; 2H, H-4, H-5), 7.78 (t; 2H, $^3J_{HH}$ = 7.8 Hz, H-9, H-9′), 7.63 (d; 2H, $^3J_{HH}$ = 7.8 Hz, H-8, H-8′), 7.60 (d; 2H, $^3J_{HH}$ = 7.8 Hz, H-10, H-10′), 4.87 (d; 1H, $^3J_{HH}$ = 9.1 Hz, H-19), 3.94 (m; 1H, H-18), 2.49 (sep; 2H, $^3J_{HH}$ = 6.9 Hz, H-15, H-15′), 2.42 (sep; 2H, $^3J_{HH}$ = 6.9 Hz, H-12, H-12′), 1.61 (s; 3H, H-21), 1.48 (d; 6H, $^3J_{HH}$ = 6.9 Hz, H-16, H-16′), 1.37 (d; 6H, $^3J_{HH}$ = 6.9 Hz, H-13, H-13′), 1.31 (d; 6H, $^3J_{HH}$ = 6.9 Hz, H-14, H-14′), 1.29 (d; 6H, $^3J_{HH}$ = 6.9 Hz, H-17,

‖ Product contains 1 equiv. KCl and 1 equiv. KBr.

H-17′), 1.07 (s; 3H, H-22), 1.06 (d; 3H, $^3J_{HH}$ = 7.3 Hz, H-23); ^{13}C-DEPTQ-NMR (151 MHz, CD_3OD): δ = 151.3 (d; 1C, C2), 147.2 (d; 2C, C11, C11′), 146.9 (d; 2C, C7, C7′), 139.2 (d; 1C, C20), 134.2 (u; 2C, C9, C9′), 131.7 (d; 2C, C6, C6′), 127.5 (u; 2C, C4, C5), 126.8 (u; 2C, C10, C10′), 126.7 (u; 2C, C8, C8′), 120.7 (u; 1C, C19), 33.3 (u; 1C, C18), 31.2 (u; 2C, C12, C12′), 31.1 (u; 2C, C15, C15′), 26.5 (u; 2C, C14, C14′), 26.3 (u; 2C, C17, C17′), 26.2 (u; 1C, C21), 22.8 (u; 2C, C16, C16′), 22.5 (u; 2C, C13, C13′), 19.3 (u; 1C, C23), 17.5 (u; 1C, C22); HRMS(ESI): calcd. for $C_{33}H_{47}N_2$ ($M–I^-$): 471.3739; found: 471.374 (±3 ppm).

1,3-Bis-(2,6-diisopropylphenyl)-2-(1,3,3-trimethylbut-1-enyl)-imidazolium iodide (19). Under anaerobic conditions, **1** (82.4 mg, 0.194 mmol) and NaH (10.5 mg, 0.438 mmol) were stirred in THF (5.0 mL) for 1.5 h. Freshly distilled prenyl bromide (24.6 µL, 0.213 mmol) was added to the cloudy reaction mixture whereupon it turned yellow. After stirring overnight at rt, methyl iodide (36 µL, 0.58 mmol) was added and stirring was continued for 4 h which resulted in partial decolorization. All volatiles were removed under reduced pressure, the residue dissolved in benzene, and the yellow solution filtered through a pad of silica. Crystals were collected from the filtrate (yield n. d.). ^{1}H-NMR (600 MHz, CD_3OD): δ = 8.26 (s; 2H, H-4, H-5), 7.73 (t; 2H, $^3J_{HH}$ = 7.8 Hz, H-9, H-9′), 7.57 (d; 4H, $^3J_{HH}$ = 7.8 Hz, H-8, H-8′, H-10, H-10′), 5.64 (s; 1H, H-19), 2.47 (sep; 4H, $^3J_{HH}$ = 6.9 Hz, H-12, H-12′, H-15, H-15′), 1.80 (s; 3H, H-24), 1.40 (d; 12H, $^3J_{HH}$ = 6.9 Hz, H-14, H-14′, H-17, H-17′), 1.32 (d; 12H, $^3J_{HH}$ = 6.9 Hz, H-13, H-16, H-13′, H-16′), 0.96 (s; 9H, H-21, H-22, H-23); ^{13}C-APT-NMR (151 MHz, CD_3OD): δ = 154.5 (u; 1C, C19), 150.4 (d; 1C, C2), 146.6 (d; 4C, C7, C11, C7′, C11′), 133.7 (u; 2C, C9, C9′), 132.1 (d; 2C, C6, C6′), 126.9 (u; 2C, C4, C5), 126.8 (u; 4C, C8, C10, C8′, C10′), 118.3 (d; 1C, C18), 72.4 (d; 1C, C20), 31.0 (u; 4C, C12, C15, C12′, C15′), 30.0 (u; 3C, C21, C22, C23), 26.1 (u; 4C, C13, C16, C13′, C16′), 23.0 (u; 4C, C14, C17, C14′, C17′), 15.7 (u; 1C, C24); for crystal structure data, see Table 2.

2-(1,2-Di-*p*-tolylethyl)-1-ethyl-3-methylimidazolium bromide (23). Under anaerobic conditions, **22** (1.10 g, 5.76 mmol) and KO*t*Bu (1.36 g, 12.1 mmol) were stirred in THF (36 mL) for 1.5 h at rt. Upon addition of *p*-methylbenzyl bromide (1.16 g, 6.29 mmol in 20 mL THF), the reaction turned from cloudy white to yellow. Stirring was continued for 23 h. The solution was separated from the precipitate and *p*-methylbenzyl bromide (1.05 g, 5.67 mmol in 15 mL THF) added. After stirring for 1.5 h, a yellow oil precipitated. The resultant oil was separated, dried *in vacuo* to afford **23** (1.26 g, 55%). ^{1}H-NMR: (600 MHz, CD_3OD): δ = 7.58 (d; 1H, $^3J_{HH}$ = 2.0 Hz, H-5), 7.49 (d; 1H, $^3J_{HH}$ = 2.0 Hz, H-4), 7.33 (d; 2H, $^3J_{HH}$ = 8.1 Hz, H-12, H-14), 7.29 (d; 2H, $^3J_{HH}$ = 8.1 Hz, H-11, H-15), 7.14 (d; 2H, $^3J_{HH}$ = 7.9 Hz, H-20, H-22), 7.03 (d; 2H, $^3J_{HH}$ = 7.9 Hz, H-19, H-23), 5.24 (dd; 1H, $^3J_{HH}$ = 11.9 Hz, $^3J_{HH}$ = 5.1 Hz, H-9), 4.08–4.01 (m; 1H, H-6), 3.93–3.86 (m; 1H, H-6), 3.80 (dd; 1H, $^2J_{HH}$ = 13.3 Hz, $^3J_{HH}$ = 5.1 Hz, H-17a), 3.53 (“t”; 1H, J_{HH} = 12.3 Hz, H-17b), 3.51 (s; 3H, H-8), 2.41 (s; 3H, H-16), 2.33 (s; 3H, H-24), 1.06 (t; 3H, $^3J_{HH}$ = 7.2 Hz, H-7); ^{13}C-DEPTQ-NMR (151 MHz, CD_3OD): δ = 148.3 (d; 1C, C2), 139.8 (d; 1C, C13), 138.8 (d; 1C, C21), 135.8 (d; 1C, C18), 134.7 (d; 1C, C10), 131.4 (u; 2C, C12, C14), 131.0 (u; 2C, C20, C22), 130.1 (u; 2C, C19, C23), 128.6 (u; 2C, C11, C15), 125.3 (u; 1C, C4), 122.6 (u; 1C, C5), 45.1 (d; 1C, C6), 43.5 (u; 1C, C9), 36.9 (d; 1C, C17), 36.6 (u; 1C, C8), 21.4 (u; 2C, C16, C24), 15.2 (u; 1C, C7); HRMS(ESI): calcd. for $C_{22}H_{27}N_2$ ($M–Br^-$): 319.2174, found: 319.218 (±0.0015); ATR-IR ν_{max}/cm^{-1} 3044, 3023, 2976, 2914, 1609, 1578, 1515, 1446, 1381, 1232, 1194, 1109, 1034, 1017, 810, 783, 749.

Corresponding base 2-(1,2-Di-*p*-tolylethylidene)-1-ethyl-3-methyl-2,3-dihydro-1*H*-imidazole (24). Under *in situ* NMR conditions, **23** (9.6 mg, 0.024 mmol) and KO*t*Bu (2.7 mg, 0.024 mmol) were reacted in THF-d_8 (0.6 mL). ^{1}H-NMR (500 MHz, THF-d_8): δ = 7.13 (d; 2H, $^3J_{HH}$ = 7.7 Hz, H-19, H-23), 6.92 (d; 2H, $^3J_{HH}$ = 7.7 Hz, H-20, H-22), 6.76 (d; 2H, $^3J_{HH}$ = 8.7 Hz, H-12, H-14), 6.74 (d; 2H, $^3J_{HH}$ = 8.7 Hz, H-11, H-15), 6.30 (d; 1H, $^3J_{HH}$ = 2.3 Hz, H-4), 6.28 (d; 1H, $^3J_{HH}$ = 2.3 Hz, H-5), 3.89 (s; 2H, H-17), 3.35 (q; 2H, $^3J_{HH}$ = 7.2 Hz, H-6), 2.93 (s; 3H, H-8), 2.21 (s; 3H, H-24), 2.13 (s; 3H, H-16), 1.05 (t; 3H, $^3J_{HH}$ = 7.2 Hz, H-7); ^{13}C-APT (126 MHz, THF-d_8): δ = 152.0 (d; 1C, C2), 143.0 (d; 1C, C10), 142.1 (d; 1C, C18), 134.7 (d; 1C, C21), 129.2 (u; 2C, C20, C22), 129.1 (u; 2C, C12, C14), 128.9 (u; 2C, C19, C23), 127.4 (d; 1C, C13), 124.3 (u; 2C, C11, C15), 119.3 (u; 1C, C4), 116.3 (u; 1C, C5), 70.6 (d; 1C, C9), 44.4 (d; 1C, C6), 37.9 (d; 1C, C17), 37.7 (u; 1C, C8), 21.0 (u; 2C; C16, C24), 14.4 (u; 1C, C7).

1-Ethyl-3-methyl-2-(1-methyl-1,2-di-*p*-tolylethyl)-imidazolium bromide (25). Under anaerobic conditions, **23** (386 mg, 0.967 mmol) was reacted with KO*t*Bu (130 mg, 1.16 mmol) in 11 mL THF. After stirring for 1 h at ambient temperature, methyl iodide (180 µL, 2.90 mmol) was added. The reaction mixture was stirred for 42 h, then all volatiles were removed under reduced pressure. The white residue (0.61 g, quant.)** contained the desired product in a mixture with 1 equiv. of KBr. ^{1}H-NMR (600 MHz, CD_3OD): δ = 7.66 (d; 1H, $^3J_{HH}$ = 2.1 Hz, H-5), 7.51 (d; 1H, $^3J_{HH}$ = 2.1 Hz, H-4), 7.34 (d; 2H, $^3J_{HH}$ = 8.1 Hz, H-12, H-14), 7.30 (d; 2H, $^3J_{HH}$ = 8.1 Hz, H-11, H-15), 7.14 (d; 2H, $^3J_{HH}$ = 7.8 Hz, H-20, H-22), 6.74 (d; 2H, $^3J_{HH}$ = 7.8 Hz, H-19, H-23), 4.03–3.96 (m; 1H, H-6), 3.86–3.79 (m; 1H, H-6), 3.75 (d; 1H, $^2J_{HH}$ = 13.1 Hz, H-17a), 3.56 (d; 1H, $^2J_{HH}$ = 13.1 Hz, H-17b), 3.40 (s; 3H, H-8), 2.41 (s; 3H, H-16), 2.35 (s; 3H, H-24), 1.94 (s; 3H, H-25), 1.03 (t; 3H, $^3J_{HH}$ = 7.3 Hz, H-7); ^{13}C-APT-NMR (151 MHz, CD_3OD): δ = 150.3 (d; 1C, C2), 144.2 (d; 1C, C10), 139.3 (d; 1C, C13), 139.0 (d; 1C, C21), 134.1 (d; 1C, C18), 131.6 (u; 2C, C12, C14), 131.4 (u; 2C, C19, C23), 130.7 (u; 2C, C20, C22), 127.2 (u; 2C, C11, C15), 126.8 (u; 1C, C4), 123.4 (u; 1C, C5), 50.0 (d; 1C, C9), 47.1 (d; 1C, C6), 44.7 (d; 1C, C17), 39.9 (u; 1C, C8), 30.3 (u; 1C, C25), 21.4 (u; 1C, C16 or C24), 21.3 (u; 1C, C16 or C24), 15.1 (u; 1C, C7); HRMS(ESI): calcd. for $C_{23}H_{29}N_2$: 333.2331 ($M–I^-$), found: 333.233 (±0.001).

1-Ethyl-3-methyl-2-[1-(4-methylbenzyl)-1,2-di-*p*-tolyl-ethyl]-imidazolium bromide (26). Under anaerobic conditions, **23** (49.6 mg, 0.146 mmol) was reacted with KO*t*Bu (20 mg, 0.18 mmol) in 2 mL THF. After stirring for 1.5 h at ambient temperature, *p*-methylbenzyl bromide (44.1 mg, 0.238 mmol in 2.5 mL THF) was added, the mixture stirred for 6 h, and filtered. The solvent was removed under reduced pressure to afford a pasty, slightly yellow residue (yield n. d.). ^{1}H-NMR (600 MHz, CD_3OD): δ = 7.20 (d; 2H, $^3J_{HH}$ = 7.5 Hz, H-12, H-14), 7.08 (d; 4H, $^3J_{HH}$ = 7.8 Hz, H-20, H-22, H-28, H-30), 6.97 (d; 2H, $^3J_{HH}$ = 7.5 Hz, H-11,

** Under consideration of KBr contamination.

H-15), 6.84 (d; 4H, $^3J_{HH}$ = 7.8 Hz, H-19, H-23, H-27, H-31), 3.72 (d; 2H, $^2J_{HH}$ = 13.0 Hz, H-17a, H-25a), 3.61 (d; $^2J_{HH}$ = 13.0 Hz, H-17b, H-25b), 2.39 (s; 3H, H-16), 2.32 (s; 6H, H-24, H-32)††; ^{1}H-NMR (600 MHz, DMSO-d_6, 348 K): δ = 7.71 (d; 1H, $^3J_{HH}$ = 1.7 Hz, H5), 7.61 (d; 1H, $^3J_{HH}$ = 1.7 Hz), 7.15 (d; 2H, $^3J_{HH}$ = 8.0 Hz, H-12, H-14), 7.03 (d; 4H, $^3J_{HH}$ = 7.9 Hz, H-20, H-22, H-28, H-30), 6.99 (d; 2H, $^3J_{HH}$ = 8.0 Hz, H-11, H-15), 6.74 (d; 4H, $^3J_{HH}$ = 7.9 Hz, H-19, H-23, H-27, H-31), 3.76 (br; 2H, H-6), 3.63 (d; 2H, $^2J_{HH}$ = 13.1 Hz, H-17a, H-25a), 3.53 (d; $^2J_{HH}$ = 13.1 Hz, H-17b, H-25b), 3.44 (br; 3H, H-8), 2.32 (s; 3H, H-16), 2.26 (s; 6H, H-24, H-32), 0.97 (t; 3H, $^3J_{HH}$ = 7.0 Hz, H-7); ^{13}C-APT-NMR (151 MHz, CD_3OD): δ = 151.3 (d; 1C, C2), 139.6 (d; 1C, C13), 138.7 (d; 2C, C21, C29), 133.5 (d; 2C, C18, C26), 132.0 (u; 4C, C19, C23, C27, C31), 131.1 (u; 2C, C12, C14), 130.4 (u; 4C, C20, C22, C28, C30), 128.9 (u; 2C; C11, C15), 41.6 (d; 2C, C17, C25), 21.3 (u; 3C, C16, C24, C32)**; HRMS(ESI): calcd. for $C_{30}H_{35}N_2$: 423.2800 ($M–Br^-$), found: 423.281 (± <4 ppm)

(*E*)-α,4,4′-Trimethylstilbene (27). Under anaerobic conditions, **25** (55 mg, 0.096 mmol) and KO*t*Bu (16 mg, 0.14 mmol) were suspended in 2 mL toluene and heated to 100 °C for 19 h. Then, the solvent was removed under reduced pressure and the residue purified by silica gel flash column chromatography (cyclohexane/ethylacetate 20/1) to afford **27** in 80% yield. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.40 (d; 2H, $^3J_{HH}$ = 8.1 Hz, Ar), 7.25 (d; 2H, $^3J_{HH}$ = 7.8 Hz, Ar), 7.16 (d; 4H, $^3J_{HH}$ = 8.1 Hz, Ar), 6.77 (s; 1H, C*H*), 2.36 (s; 6H, *p*-CH_3), 2.25 (d; 3H, $^4J_{HH}$ = 1.1 Hz, CH_3); ^{13}C-APT-NMR (75 MHz, $CDCl_3$): δ = 141.2 (d; 1C, CH*C*CH_3), 136.8 (d; 1C, C_q-arom.), 136.5 (d; 1C, C_q-arom.), 136.0 (d; 1C, C_q-arom.), 135.6 (d; 1C, C_q-arom.), 129.0 (u; 1C, *C*H-arom.), 129.0 (u; 1C, *C*H-arom.), 128.8 (u; 1C, *C*H-arom.), 126.9 (u; 1C, *C*HCCH_3), 125.8 (u; 1C, *C*H-arom.), 21.2 (u; 1C, *p*-*C*H_3), 21.2 (u; 1C, *p*-*C*H_3), 17.4 (u; 1C, CHC*C*H_3); GC-MS: 9.38 min; *m*/*z*: 223, 222[$M^{+\cdot}$], 208, 207, 206, 193, 192, 191, 189, 165, 129, 119, 117, 115, 91.

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