A New Synthetic Route to *p*-Methoxy-2,6-disubstituted Anilines and their Conversion into N-Heterocyclic Carbene Precursors

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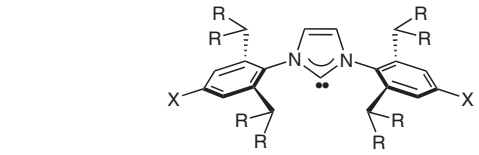
Abstract: The development of new N-heterocyclic carbenes (NHC) is a key feature in this now mainstream research area to access novel chemical properties and reactivity that are essential for the discovery of original applications. Up to now, only a few reliable methods have proven suitable for the preparation of methoxylated anilines to ultimately access methoxylated NHC. We are pleased to report here a straightforward and scalable approach to address this matter.

Key words: ligands, nucleophilic aromatic, copper, catalysis, carbenes

The discovery of the first bottleable-free N-heterocyclic carbenes (NHCs) by Arduengo in 1991[1] opened new horizons in organic and organometallic chemistry and in catalysis.[2] Since the late 1990s, NHCs have become essential tools in chemistry and their use has resulted in a plethora of applications.[2] The further development of these existing applications and the discovery of others lie into the success of designing tailor-made NHC.

Among the many possible uses of NHCs, their role as ligands in transition-metal catalysis is of major interest. In this context, the use of very bulky but flexible NHCs has been shown to be beneficial to the catalytic activity of metal–NHC complexes.[3] More recently an increase of their σ-donation ability by appropriate modification of their anilyl N-substituents was successfully employed for tuning these properties.[4] More precisely, comparison between sterically hindered IPr* and IPr*^{OMe} (Figure 1) revealed that the additional methoxy substituent had a positive impact in palladium-catalyzed Buchwald–Hartwig arylamination.[4]

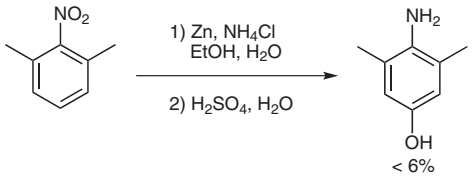
In order to further investigate this concept and to ultimately examine its ramifications in catalysis, the preparation of other methoxylated NHC (NHC^{OMe}) was necessary. The recently reported 'ITent' series appeared to be ideally suited for this task (Figure 1). The ITent NHC family, with 'Tent' standing for 'Tentacular', was very recently described by us as a new class of NHC bearing highly flexible bulk.[5] This class of NHC includes the well-known IPr, Organ's IPent,[6] and the IHept and INon more recently reported by us.[5] Their flexible bulk increases significantly as the size of the R alkyl groups become larger: IPr > IPent > IHept > INon. This feature is considered as a key parameter for the stabilization of metal–NHC complexes and the ultimate optimization of their catalytic properties.[4,5] However, unlike the IPr*^{OMe} which was easily accessed from the inexpensive and commercially available *p*-anisidine,[4] the synthesis of ITents^{OMe} required the preparation of non-readily available *p*-methoxyanilyl NHC precursors in a rapid and cost-effective manner.



IPr*	R = Ph	X = Me	IPr*^{OMe}	R = Ph	X = OMe
IPr	R = Me	X = H	IPr^{OMe}	R = Me	X = OMe
IPent	R = Et	X = H	IPent^{OMe}	R = Et	X = OMe
IHept	R = *n*-Pr	X = H	IHept^{OMe}	R = *n*-Pr	X = OMe
INon	R = *n*-Bu	X = H	INon^{OMe}	R = *n*-Bu	X = OMe

Figure 1 Known NHC vs. methoxylated NHC

To our surprise, a literature search revealed a lack of reliable procedure to achieve the *p*-methoxylation of anilines. The historical Bamberger rearrangement[7] reported for the conversion of 2,6-dimethylnitrobenzene into 2,6-dimethyl-4-aminophenol first appeared as an attractive method (Equation 1).[8] However, this two-step process starting from nitroarenes is limited by its temperamental behavior and its substrate specificity. Moreover, the final 4-aminophenol generated in low yield remains to be selectively methylated. These serious drawbacks forced us to envisage another strategy.



Equation 1 Bamberger rearrangement of 2,6-dimethylnitrobenzene

The well-known copper-catalyzed Ullmann C–O coupling was next explored for the methoxylation of the known ITent anilines **1**–**4**[5] in *para* position. This more direct approach, based on the coupling of alcohols and aryl halides, has received significant attention.[9] However, free aniline moieties were incompatible with this reaction and required to be first protected as pyrrole to secure good conversions.[10] Interestingly, a single-step alternative de-

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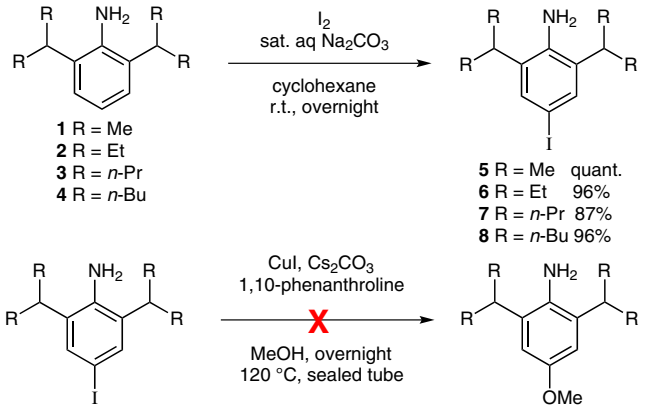
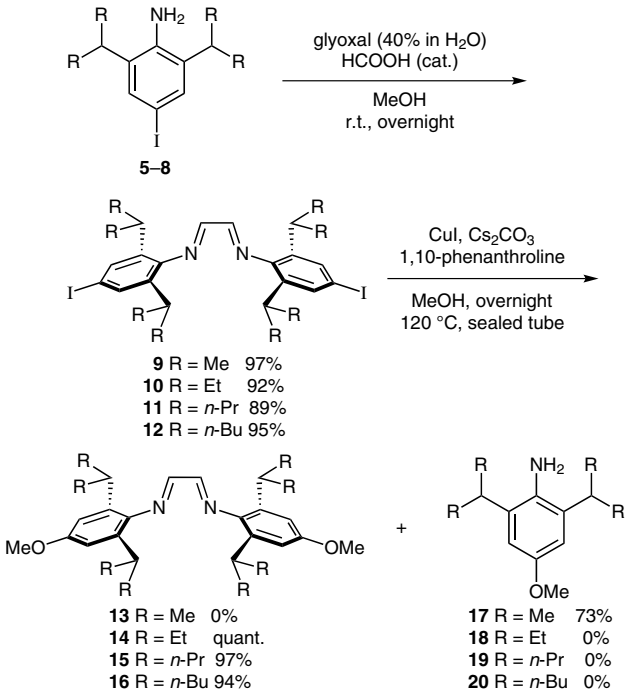
scribed by Buchwald reported the copper-mediated Ullman C–O coupling of unprotected iodoanilines.[11] This methodology appeared more suitable to achieve our goal.

A straightforward procedure[12] was successfully employed for the iodination of the ITent anilines **1**–**4**[5] (Scheme 1). The resulting *p*-iodoanilines **5**–**8** were obtained in excellent yield and purity with no purification needed and were then subjected to the Buchwald–Ullman conditions.[11] However, in our hands, no coupling was observed, and further attempts all failed to give the desired *p*-methoxyanilines (Scheme 1). Interestingly, a modified procedure using 3,4,7,8-tetramethyl-1,10-phenanthroline (Me_4Phen) in place of the inexpensive 1,10-phenanthroline was later reported by Buchwald[13] and successfully utilized by Louie.[14] Although Me_4Phen was described as a more efficient ligand for copper-catalyzed C–O couplings, its cost appeared to be a major issue. Most importantly, this new protocol required strictly anhydrous conditions.[13,14]



Scheme 1 Initial methoxylation strategy

As our search for a cost-effective process continued, the protection of the aniline moiety was instead reconsidered. The classical diimine precursors of imidazolium chloride salts were envisaged as ideally suited candidates for this reaction. Indeed, the diimine bridge may possibly act as a perfect protecting group, in the same way as pyrrole,[10] and allow for our methoxylation to take place. Consequently, the newly prepared *p*-iodoanilines **5**–**8** were reacted with glyoxal to easily afford the desired diimines **9**–**12** in good yields and excellent purity (Scheme 2). Straightforward purification by flash column chromatography was preferably employed on small scale for yield accuracy, as reported in the supplementary information. However, larger quantities were usually isolated by simple filtration at the end of the reaction after appropriate cooling, providing the pure products **9**–**12** in similar yields. The *p*-iododiimines **9**–**12** were then subjected to the initial Buchwald methoxylation conditions.[11] After optimization, very encouraging results were obtained. The initial premix of copper and 1,10-phenanthroline, together with the use of pressure (4 bar) was demonstrated to be critical for the substitution to take place. However, the internal pressure needed (4 bar) was simply generated by heating the solvent (MeOH) beyond its boiling point in a thick-glass Schlenk reactor/flask. Most importantly, the inexpensive 1,10-phenanthroline proved to be a suitable ligand and no anhydrous conditions were required.[13,14] The use of aryl iodides as starting substrates was also crucial for the success of the coupling. Although no optimization of the base or the catalyst loading was attempted, our preliminary data strongly suggest that much lower quantities of copper(I) iodide and 1,10-phenanthroline could be used without detrimental effects on the reaction overall yield. Other alkoxylations using others alcohols as solvents could very possibly be used and this hypothesis is currently being explored.

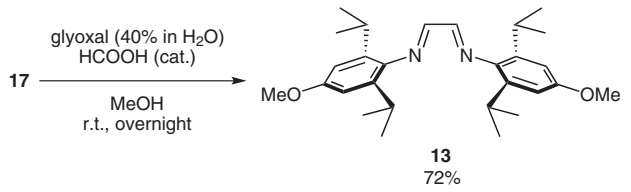


Scheme 2 New methoxylation strategy

This methoxylation procedure appeared to be very straightforward and convenient, high yielding and scalable, requiring only minimal purification. Surprisingly, the methoxylation of IPr diimine **9** underwent the simultaneous cleavage of the diimine bridge over the course of the reaction, providing the unexpected free *p*-methoxyaniline **17** rather than the expected *p*-methoxydiimine **13** (Scheme 2). Conversely, methoxylation of IPent, IHept, and INon *p*-iododiimines **10**–**12**, showed only traces of free *p*-methoxyanilines (<3%). This observation is particularly interesting as it experimentally supports that, regardless of the apparent structural similarity between the ITent family members, a dramatic steric difference really does exist between these congeners. This experimental observation is critical and supports our working hypothesis in designing ITent NHC as sterically hindered but flexible NHC ligands for enhanced catalysis.[5]

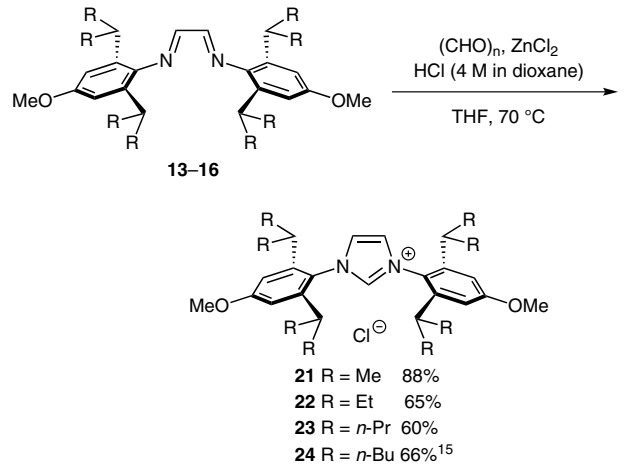
The free *p*-methoxyaniline **17**, which is by far the most readily accessible and scalable, was easily purified by distillation under reduced pressure. The resulting aniline **17**

was obtained in large quantity and excellent purity and was converted into the corresponding diimine through the standard procedure (Equation 2).



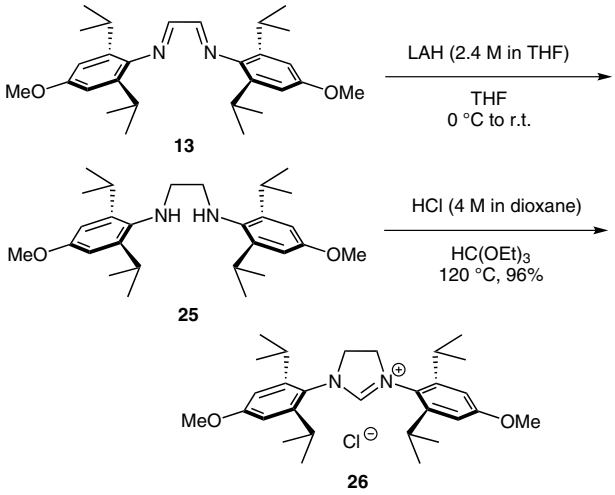
Equation 2 Preparation of diimine **13**

The *p*-methoxydiimines **13**–**16** were all obtained in excellent purity and did not require any further purification (Scheme 2 and Equation 2). However, flash column chromatography was used to guarantee the complete removal of any copper traces for ultimate catalytic applications as well as to confirm the near quantitative yields. On larger scales, the solid *p*-methoxydiimines **13**–**16** were also successfully further purified by recrystallization when needed. Finally, diimines **13**–**16** were all converted into their corresponding imidazolium chlorides via the usual $(CHO)_n/ZnCl_2/HCl$ procedure[4] in good yield and CHN purity (Equation 3).[15] It must be noted that the Hintermann cylization procedure[16] with TMSCl was also successfully used to obtain **21** as a whiter solid in similar yield and purity. However, it proved inefficient for the cyclization of bulkier diimines.[5]



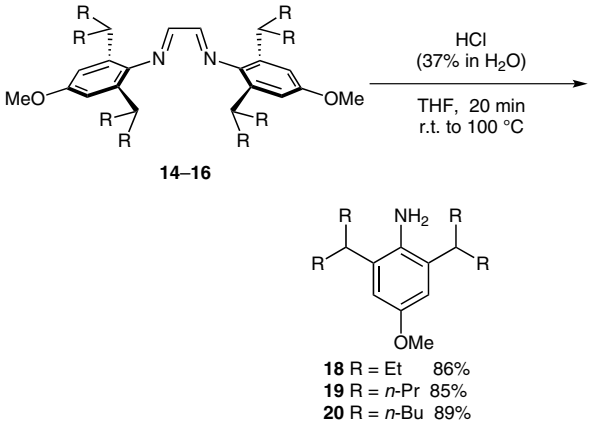
Equation 3 Preparation of *p*-methoxylatedimidazolium chlorides

As recently described by Organ,[17] bulky saturated imidazolinium chlorides such as SIPent·HCl could not be made via the standard $HC(OEt)_3$ cyclization procedure. The same observation was made here for the preparation of SIPr*·HCl, SIPr*^{OMe}·HCl, or SITent·HCl as their anilyl groups were too bulky to allow the cyclization to take place. However, in the case of SIPr^{OMe}·HCl **26**, cyclization proceeded smoothly (Scheme 3). Compound **26** was obtained as a bright white powder in 94% yield (2 steps from **13**) in using the slightly modified $LiAlH_4$ reduction–$HC(OEt)_3$ cyclization two-step sequence. The newly prepared (S)ITent^{OMe}·HCl **21**–**26** salts are currently being investigated as promising ligands for homogenous catalysis.



Scheme 3 Preparation of *p*-methoxylatedimidazolinium chloride **26**

Finally, in order to demonstrate the versatility of our approach, and compare it to the literature,[9] the diimine bridge was easily cleaved to release the free anilines. The *p*-methoxydiimines **14**–**16** were efficiently deprotected to the free anilines **18**–**20** with great ease, good yields, and excellent purity, proving that the diimine functionality can also be considered as an inexpensive conventional protecting group (Equation 4). These reaction/deprotection conditions were not optimized.



Equation 4 Cleavage of diimine-protecting bridge

A new inexpensive, rapid, and easy-to-handle methodology has been developed for the high-yield synthesis of methoxylated anilines. The key step is an air- and moisture-robust copper-catalyzed methoxylation which could be extended to other alkoxylations. This methodology not only provided a reliable and reproducible way to prepare *p*-methoxyanilines efficiently, but also provided access to a new range of electronically enriched NHC. It should also be noted that preliminary results confirmed the possibility of applying our method to multiple substitutions. In-

deed, polyiodoanilyl diimines were proved to be suitable candidates to access polyalkoxylated anilines or diimines.

Acknowledgment

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Supporting Information for this article is available online at http://www.thieme-connect.com/ejournals/toc/synlett. The procedures for the syntheses of compounds **6**, **10**, **14**, **18**, **22** and **13**, **17**, **25**, **26** are provided as typical procedures in References and Notes.[18]

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(15) All imidazolium chlorides **21**–**23** and **26** were obtained as pure white powders as confirmed by elemental analysis. However $INon^{OMe}$·HCl **24** was contaminated by an undetermined impurity forming during the cyclization step. All efforts to suppress the formation of this impurity or to further purify $INon^{OMe}$·HCl **24** were unsuccessful. However, $INon^{OMe}$·HCl **24** was successfully taken on crude to other transformations that allowed for the ultimate elimination of the impurity.

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(18) **4-Iodo-2,6-di(3-pentyl)aniline (6, R = Et)**
A solution of aniline **2** (2.40 g, 10.3 mmol, 1.0 equiv) in cyclohexane (7.0 mL) was treated with a sat. aq solution of Na_2CO_3 (2.90 mL, ca. 5.7 mmol, 0.6 equiv) followed by solid iodine (2.90 g, 11.4 mmol, 1.1 equiv) at r.t. The reaction was stirred overnight at r.t. (11 h). The crude solution was diluted with Et_2O (15 mL) and washed with a sat. aq solution of $Na_2S_2O_3$ (3 × 10 mL). The organic layer was then dried over anhydrous Na_2SO_4 and concentrated under vacuum. The resulting dark greenish to black oil (4.10 g) was obtained in excellent purity but was preferably filtered through silica and eluted with a 1% solution of Et_2O in pentane to remove some of the colored impurities. Solvents were evaporated to afford the pure desired iodoaniline **6** as an orange crystalline solid (3.53 g, 96%). ^1H NMR (400 MHz, $CDCl_3$): δ = 0.83 (12 H, t, $J = 2 \times 7.4$ Hz,

4 × CH_3), 1.57 (4 H, m, 2 × CH_2), 1.70 (4 H, m, 2 × CH_2), 2.40 (2 H, m, 2 × CH), 3.64 (2 H, v br s, NH_2), 7.15 (2 H, s, $H^{m\text{-Ar}}$). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 11.9 (4 × CH_3), 27.9 (4 × CH_2), 42.2 (2 × CH), 81.3 (I-C_{IV}^{Ar}), 132.6 (2 × $C_{IV}^{o\text{-Ar}}$), 132.7 (2 x× $CH^{m\text{-Ar}}$), 142.5 (NC_{IV}^{Ar}). HRMS (NSI^+): *m/z* calcd for $C_{16}H_{27}NI$: 360.1183; found: 360.1186 $[M + H]^+$.

N,N′-Bis[4-iodo-2,6-di(3-pentyl)phenyl]1,4-diazabutadiene (10, R = Et)

A solution of 4-iodoaniline **6** (3.53 g, 9.82 mmol, 2.0 equiv) in MeOH (20 mL) was treated with formic acid (1 drop) followed by the dropwise addition of glyoxal (40% in H_2O, 640 µL, 5.82 mmol, 1.2 equiv) at 70 °C. The solution was stirred at this temperature for 3 h, and the MeOH was evaporated under vaccum and replaced by Et_2O. The solution was dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by flash column chromatography (silica gel, 1–5% Et_2O in pentane) to yield the pure desired diimine **10** as a bright yellow solid (3.33 g, 92%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.79 (24 H, t, *J* = 7.4 Hz, 8 × CH_3), 1.53 (8 H, m, 4 × CH_2), 1.64 (8 H, m, 4 × CH_2), 2.40 (4 H, m, 4 × CH), 7.37 (4 H, m, $H^{m\text{-Ar}}$), 7.96 (2 H, s, 2 × CH=N). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 12.1 (8 × CH_3), 28.8 (8 × CH_2), 42.5 (4 × CH), 90.0 (2 × $IC_{IV}^{p\text{-Ar}}$), 133.0 (2 × $CH^{m\text{-Ar}}$), 136.5 (2 × $C_{IV}^{o\text{-Ar}}$), 150.5 (2 × NC_{IV}^{Ar}), 163.9 (2 × CH=N). HRMS (NSI^+): *m/z* calcd for $C_{34}H_{51}N_2I_2$: 741.2136; found: 741.2139 $[M + H]^+$.

4-Methoxy-2,6-diisopropylaniline (17, R = Me)

A sealed tube was charged with MeOH (50 mL), CuI (2.46 g, 12.9 mmol, 0.5 equiv), phenanthroline (3.73 g, 20.7 mmol, 0.8 equiv), and Cs_2CO_3 (34.2 g, 105 mmol, 4.3 equiv) at r.t. To this brown mixture was added the starting diiododiimine **9** (15.4 g, 24.5 mmol, 1.0 equiv), and the reaction was stirred overnight (10 h) at 110 °C. The reaction was allowed to cool down to r.t. and was filtered through cotton wool. The remaining solid was washed with Et_2O (3 × 50 mL), and the filtrate was transferred into a separating funnel. The organic layer was washed with 10% NH_4OH (3 × 50 mL), then brine (50 mL), and was then dried over anhydrous Na_2SO_4. Concentration in vacuo afforded the crude methoxyaniline as viscous brown oil (10.4 g) that was purified by flash column chromatography (silica gel, 5–50% Et_2O in pentane). The pure desired methoxyaniline **17** was obtained as dark reddish viscous oil (7.40 g, 73%). On larger scale, the crude oil was successfully purified by distillation under reduced pressure (110–120 °C at 0.8 mbar). Our data were in full agreement with those reported in the literature.[13b,14] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.34 (12 H, d, *J* = 6.7 Hz, 4 × CH_3), 3.04 (2 H, m, 2 × CH), 3.52 (2 H, v br s, NH_2), 3.85 (3 H, s, OCH_3), 6.73 (2 H, s, $H^{m\text{-Ar}}$). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 22.3 (4 × CH_3), 28.0 (2 × CH), 55.4 (OCH_3), 108.5 (2 × $CH^{m\text{-Ar}}$), 133.8 (NC_{IV}^{Ar}), 134.1 (2 × $C_{IV}^{o\text{-Ar}}$), 152.6 (OC_{IV}^{Ar}).

N,N′-Bis(4-methoxy-2,6-diisopropylphenyl)1,4-diazabutadiene (13, R = Me)

A solution of 4-methoxy-2,6-diisopropylaniline (**17**, 15.2 g, 73.4 mmol, 2.0 equiv) in MeOH (300 mL) was treated with formic acid (2 drops) followed by the dropwise addition of glyoxal (40% in H_2O, 6.43 mL, 74.4 mmol, 1.0 equiv) at r.t. The solution was stirred at this temperature for 2 h, and the MeOH was evaporated under vacuum and replaced by pentane (300 mL). The solution was dried over anhydrous Na_2SO_4, filtered, and partially concentrated in vacuo. Although good purity was obtained, the residual oil was preferably purified by flash column chromatography (silica gel, 10% Et_2O in pentane) to yield the pure desired diimine **13** as an orange solid (11.5 g, 72%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.81 (24 H, d, *J* = 6.9 Hz, 8 × CH_3), 3.04 (4 H, m, 4 × CH), 3.87 (OCH_3), 6.79 (4 H, s, 4 × $H^{m\text{-Ar}}$), 8.14 (2 H, s, 2 × HC=N). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 23.3 (8 × CH_3), 28.1 (4 × CH), 55.1 (2 × OCH_3), 108.6 (4 × $CH^{m\text{-Ar}}$), 138.6 (4 × $C_{IV}^{o\text{-Ar}}$), 141.6 (2 × NC_{IV}^{Ar}), 157.2 (2 × OC_{IV}^{Ar}), 163.5 (2 × HC=N). HRMS (NSI^+): *m/z* calcd for $C_{28}H_{41}O_2N_2$: 437.3163; found: 437.3158 $[M + H]^+$.

N,N′-Bis[4-methoxy-2,6-di(3-pentyl)phenyl]1,4-diazabutadiene (14, R = Et)A sealed tube was charged with MeOH (20 mL), CuI (450 mg, 2.36 mmol, 0.5 equiv), phenanthroline (681 mg, 3.78 mmol, 0.8 equiv), and Cs_2CO_3 (6.26 g, 19.2 mmol, 4.3 equiv) at r.t. To this brown mixture was added the starting diiododiimine **10** (3.33 g, 4.50 mmol, 1.0 equiv), and the reaction was stirred overnight (10 h) at 110 °C. The reaction was allowed to cool to r.t. and was filtered through cotton wool. The remaining solid was washed with Et_2O (3 × 20 mL), and the filtrate was transferred into a separating funnel. The organic layer was washed with 10% NH_4OH (3 × 20 mL), then brine (20 mL), and was then dried over anhydrous Na_2SO_4. Concentration in vacuo afforded the crude dimethoxydiimine as viscous brown oil (2.60 g) that was filtered through silica and eluted with pentane. The filtrate was evaporated to yield the pure desired diimine **14** as brown viscous oil (2.47 g, quant.). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.81 (24 H, t, *J* = 7.3 Hz, 8 × CH_3), 1.47–1.73 (16 H, m, 8 × CH_2), 2.54 (4 H, m, 4 × CH), 3.82 (OCH_3), 6.65 (4 H, s, 4 × $H^{m\text{-Ar}}$), 8.02 (2 H, s, 2 × HC=N). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 12.1 (8 × CH_3), 28.9 (8 × CH_2), 42.6 (4 × CH), 55.1 (OCH_3), 109.2 (4 × $CH^{m\text{-Ar}}$), 135.6 (4 × $C_{IV}^{o\text{-Ar}}$), 144.8 (2 × NC_{IV}^{Ar}), 157.0 (2 × OC_{IV}^{Ar}), 164.4 (2 × HC=N). HRMS (NSI^+): *m/z* calcd for $C_{36}H_{57}O_2N_2$: 549.4415; found: 549.4403 $[M + H]^+$.

1,3-Bis[4-methoxy-2,6-di(3-pentyl)phenyl]imidazolium Chloride (22, R = Et, IPent^{OMe}·HCl)

A solution of diimine **14** (2.30 g, 4.19 mmol, 1.0 equiv) in THF (164 mL) was treated with anhydrous $ZnCl_2$ (571 mg, 4.19 mmol, 1.0 equiv) at 70 °C and stirred for 5 min. *p*-Formaldehyde (132 mg, 4.40 mmol, 1.1 equiv) was subsequently added followed by the dropwise addition of anhydrous HCl (4.0 M in dioxane, 1.6 mL, 6.4 mmol, 1.5 equiv). The reaction was stirred for 3 h at 70 °C and concentrated under vacuum. The residue was dissolved in EtOAc (150 mL) and was washed with H_2O (3 × 100 mL) and brine (100 mL). The combined aqueous phases were extracted with EtOAc (50 mL), and the organic phases were combined and dried over anhydrous $MgSO_4$. The solvent was evaporated under vacuum, and the resulting brown solid (2.62 g) was triturated with pentane (3 × 65 mL) affording the pure desired imidazolium chloride **22** (1.62 g, 65%) as a beige solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.58 (12 H, t, *J* = 7.4 Hz, 4 × CH_3), 0.63 (12 H, t, *J* = 7.4 Hz, 4 × CH_3), 1.32–1.58 (16 H, m, 8 × CH_2), 1.68 (4 H, m, 4 × CH), 3.70 (6 H, s, 2 × OCH_3), 6.56 (4 H, s, 4 × $H^{m\text{-Ar}}$), 7.90 (2 H, s, 2 × HC=N), 8.38 (1 H, s, NCHN). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 11.9 (4 × CH_3), 12.0 (4 × CH_3), 28.0 (4 × CH_2), 28.7 (4 × CH_2), 43.2 (4 × CH), 55.2 (2 × OCH_3), 110.0 (4 × $CH^{m\text{-Ar}}$), 125.0 (4 × $C_{IV}^{o\text{-Ar}}$), 127.7 (2 × HC=N), 136.4 (NCHN), 143.6 (2 × NC_{IV}^{Ar}), 161.4 (2 × OC_{IV}^{Ar}). Anal. Calcd for $C_{35}H_{53}ClN_2$: C, 74.40; H, 9.62; N, 4.69. Found: C, 74.30; H, 9.79; N, 4.74.

N,N′-Bis-(4-methoxy-2,6-diisopropylphenylamino)ethane (25)

A solution of diimine **13** (11.5 g, 26.3 mmol, 1.0 equiv) in anhydrous THF (200 mL) was cooled to –20 °C and treated with $LiAlH_4$ (2.4 M in THF, 44.0 mL, 106 mmol, 4.0 equiv). Upon addition of $LiAlH_4$, the yellow solution rapidly turned very dark purple and important bubbling was observed.

After 15 min at –20 °C, the color of the reaction changed back to clear orange, and the reaction was allowed to stirr for 45 min at r.t. The reaction was then cooled to 0 °C, diluted with Et_2O (200 mL), and carefully quenched with H_2O (5.0 mL). After stirring for 10 min, a 15% aqueous solution of NaOH (5.0 mL) was added, followed by H_2O (12 mL). The suspension was allowed to warm to r.t. and was stirred for 15 min before anhydrous $MgSO_4$ was added until a fine solid was obtained. The solids were discarded by filtration, and the filtrate was concentrated in vacuo affording a clear orange and very viscous oil (11.80 g) in excellent purity. However, the oil was preferably purified by flash column chromatography (silica, 10–20% Et_2O in pentane) to provide the pure desired diamine **25** as an orange viscous oil (11.35 g, 98%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.26 (24 H, d, *J* = 6.9 Hz, 4 × CH_3), 3.08 (6 H, v br s, 2 × CH_2 + 2 × NH), 3.40 (4 H, m, 4 × CH), 3.82 (6 H, m, 2 × OCH_3), 6.68 (4 H, s, 4 × $H^{m\text{-Ar}}$). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 24.2 (8 × CH_3), 27.9 (4 × CH), 52.6 (2 × CH_2), 55.2 (2 × OCH_3), 108.9 (4 × $CH^{m\text{-Ar}}$), 136.4 (2 × $OC_{IV}{}^{p\text{-Ar}}$), 144.6 (4 × $C_{IV}{}^{o\text{-Ar}}$), 156.2 (2 × $NC_{IV}{}^{Ar}$). HRMS (NSI$^+$): *m/z* calcd for $C_{28}H_{45}O_2N_2$: 441.3476; found: 441.3470 $[M + H]^+$.

1,3-Bis-(4-methoxy-2,4-diisopropylphenyl)-imidazolinium Chloride (26, SIPr^{OMe}·HCl)

A solution of diamine **25** (7.35 g, 16.7 mmol, 1.0 equiv) in triethyl orthoformate (60 mL) was heated to 120 °C and treated with the rapid addition of HCl (4.0 M in dioxane, 5.0 mL, 1.2 equiv). Upon addition of HCl, the clear solution immediately turned into a white suspension, and the stirring was continued for 10 min at 120 °C. The reaction was cooled to r.t. and was diluted with pentane (60 mL). The white solid was isolated by filtration and washed with pentane (3 × 60 mL). After drying under high vacuum, the desired imidazolinium chloride **25** was obtained as a bright white powder (7.80 g, 96%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.14 (12 H, d, *J* = 6.9 Hz, 4 × CH_3), 1.25 (12 H, d, *J* = 6.9 Hz, 4 × CH_3), 2.84 (4 H, m, 4 × CH), 3.74 (6 H, m, 2 × OCH_3), 4.58 (4 H, s, 2 × NCH_2), 6.62 (4 H, s, 4 × $H^{m\text{-Ar}}$), 8.64 (1 H, s, N=CHN). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 23.3 (4 × CH_3), 25.1 (4 × CH_3), 29.1 (4 × CH), 55.2 (2 × OCH_3), 109.8 (4 × $CH^{m\text{-Ar}}$), 121.9 (2 × $CH^{p\text{-Ar}}$), 147.4 (4 × $C_{IV}{}^{o\text{-Ar}}$), 159.4 (NCHN), 161.1 (2 × $NC_{IV}{}^{Ar}$). Anal. Calcd for $C_{29}H_{43}ClN_2O_2$: C, 71.51; H, 8.90; N, 5.75. Found: C, 71.40; H, 9.01; N, 5.85.

4-Methoxy-2,6-di(3-pentyl)aniline (18, R = Et)

A solution of IPent diimine **14** (2.75 g, 5.01 mmol, 1.0 equiv) in EtOH (23 mL) was treated with a HCl solution (37% in H_2O, 11.6 mL, 120 mmol, 28 equiv) at r.t. The reaction turned brown upon the addition of HCl and after 10 min at r.t. it was allowed to stir at 100 °C for a further 10 min. The reaction was cooled to r.t. and carefully neutralized with a sat. aq solution of NaOH (6 mL). The mixture was then extracted with pentane (3 × 25 mL), dried over anhydrous Na_2SO_4, and concentrated under vacuum. The crude aniline (5.05 g) was obtained in excellent purity but was preferably purified by flash column chromatography (silica, 1–5% Et_2O in pentane) to afford the pure desired aniline **18** as an orange clear viscous oil (2.28 g, 86%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.84 (12 H, t, *J* = 7.4 Hz, 4 × CH_3), 1.51–1.78 (8 H, m, 4 × CH_2), 2.53 (2 H, m, 2 × CH), 3.34 (2 H, v br s, NH_2), 3.76 (3 H, s, OCH_3), 6.51 (2 H, s, $H^{m\text{-Ar}}$). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 12.0 (4 × CH_3), 28.2 (4 × CH_2), 42.5 (2 × CH), 55.4 (OCH_3), 109.5 (2 × $CH^{m\text{-Ar}}$), 132.0 (2 × $C_{IV}{}^{o\text{-Ar}}$), 136.3 ($OC_{IV}{}^{Ar}$), 152.7 ($NC_{IV}{}^{Ar}$). HRMS (NSI$^+$): *m/z* calcd for $C_{17}H_{30}ON$: 264.2322; found: 264.2321 $[M + H]^+$.

