One-pot synthesis of β-diketimine ligands

Ibrahim El-Zoghbi, Aysha Ased, Paul O. Oguadinma, Ekou Tchirioua, and Frank Schaper

Abstract: Symmetric *N*,*N*′-dialkyl-2-amino-4-imino-pent-2-enes (nacnac^{R}H) can be prepared in high yields in a simple one-pot reaction from acetylacetone and 2 equiv. of amine. Optimized conditions require the azeotropic removal of water, use of a minimum amount of solvent, and of 1 equiv. of acid. Either *para*-toluenesulfonic acid, hydrochloric acid, or a mixture of both can be employed, with the latter being most advantageous. Symmetric nacnac^{R}H are thus obtained in higher than 95% purity and with 65% yield for R = Me and 80%–95% yields for R = *n*-Pr, *i*-Pr, *i*-Bu, Bn, Cy, and (+)-CH(Me)Ph.

Key words: diketimines, one-pot synthesis.

Résumé : On peut préparer les *N*,*N*′-dialkyl-2-amino-4-iminopent-2-ènes (nacnac^{R}H) avec des rendements élevés en réalisant la réaction monotope de l'acétylacétone avec deux équivalents d'amine. Les conditions optimisées nécessitent l'élimination azéotropique de l'eau, l'utilisation d'une quantité minimale de solvant et un équivalent d'acide qui peut être l'acide *para*-toluènesulfonique, l'acide chlorhydrique ou un mélange des deux; ce dernier est le plus avantageux. Des nacnac^{R}H symétriques peuvent ainsi être obtenus avec une pureté de plus de 95 % et un rendement de 65 % lorsque R = Me et des rendements allant de 80 à 95 % lorsque le groupe R = *n*-Pr, *i*-Pr, *i*-Bu, Bu, Cy et (+)-CH(Me)Ph.

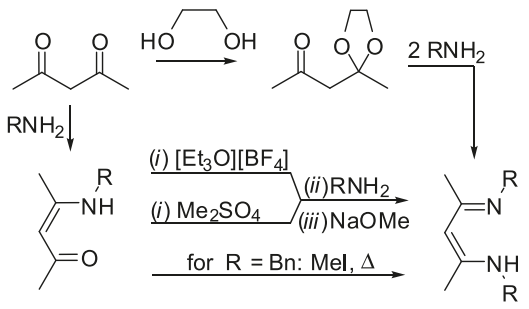
Mots-clés : dicétimines, synthèse monotope.

Introduction

Preparation of β-diketimines (''nacnac'' ligands), based on diimine analogues of acetylacetone, was described already in 1950,[1] and their first metal complexes in 1968.[2,3] They played only a marginal role in coordination chemistry until the introduction of nacnac^{dipp} (dipp = 2,6-diisopropylphenyl) as a spectator ligand in the late 1990s.[4] Since then, β-diketiminate ligands have become some of the most widely used bidentate N-donor ligands in coordination chemistry.[5] Interest in diketiminate ligands concentrated mostly on their N-aryl derivatives, and N-alkyl substituted diketimines were used only sparingly, mostly as low-molecular-weight ligands for chemical vapour deposition and atomic layer deposition applications.[6] We recently started to investigate the coordination chemistry of diketiminate ligands with aliphatic N-substituents.[7–11] For these investigations, we required a simple, efficient, and economic access to these compounds.

The most efficient and versatile preparation of 2-amino-4-imino-pent-2-enes is condensation of acetylacetone with amines. While condensation of the first amine proceeds readily, the resulting enaminoketone has to be activated for the second condensation.[2,5] This might be achieved by transformation into the ketal, and the ethylene glycol monoketal has been used successfully as starting material for the synthesis of nacnac^{Bn}H and some macrocyclic diketimines (Scheme 1).[12,13] Alternatively, in the case of aryl N-substituents, reaction in ethanolic HCl yielded the desired dicondensation product, probably by intermediate formation of the diethyoxyketal.[3] For the diketimines with N-alkyl substituents of interest here, alkylation of the enaminoketone obtained after the first condensation with Meerwein salt and subsequent reaction with a second equivalent of amine is the most commonly employed method.[2] In an isolated report, nacnac^{Bn}H, **1**, has been obtained by refluxing the monocondensation product acnac^{Bn}H, **1b**, in methyl iodide.[14] The mechanism of this reaction (no second equivalent of amine was added) remains unclear. Recently, Bradley et al. showed that Meerwein salt can be replaced by the less toxic and more economic methyl sulfate as alkylating agent (Scheme 1).[15] The latter, to our knowledge, is the most efficient synthesis described, and diketimines were obtained in yields of 46%–87% starting from the enaminoketone intermediate after distillation. Diketimines with aliphatic substituents are thus accessible, but their synthesis still requires a two-step reaction, often distillation of the obtained product for purification, ex-

Scheme 1.



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clusion of moisture, and the use of toxic alkylating reagents. In the following, we describe a one-step preparation of these compounds, which avoids these drawbacks.

Results and discussion

Initial explorations

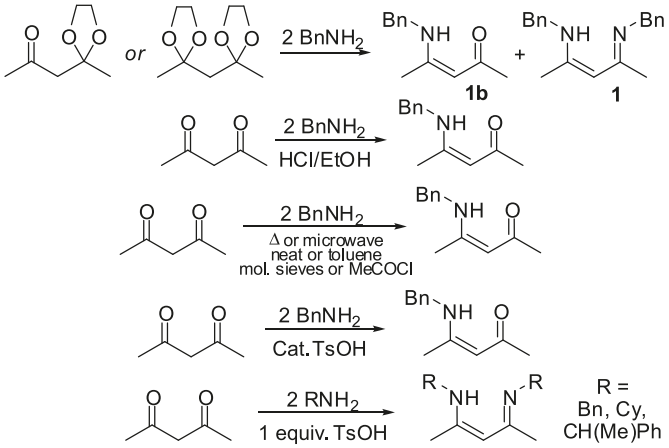
We repeated the preparation of nacnac^{Bn}H, **1**, described by Dorman[12] using either acetylacetone ethylene glycol mono- or di-ketal as starting material. We found, however, the reaction to give varying yields of diketimine product and to be highly dependent on reaction conditions (Scheme 2). If the reaction is carried out in diluted toluene solution, only the monocondensation product **1b** was obtained. Reaction of acetylacetone with 2 equiv. benzylamine in ethanolic HCl, following the procedure described by Parks and Holm[3] and Feldman et al.[16] for N-aryl substituted diketimines, also yielded only **1b**. Direct condensation of acetylacetone and benzylamine (no solvent, $T > 100$ °C, in the presence of molecular sieves or thionyl chloride), under microwave heating (neat or in toluene solution, without or with addition of molecular sieves or acetyl chloride), or under azeotropic removal of water (toluene solution, catalytic quantities of *para*-toluenesulfonic acid, several days) yielded either **1b** or decomposition products and at best traces (<10%) of the desired **1**.

While aryl-substituted diketimines have been sometimes obtained under typical "Dean–Stark conditions", i.e., catalytic amounts of acid and azeotropic removal of water, yields have been generally low-to-moderate. Budzelaar et al. reported the synthesis of nacnac^{Xyl}H, **2**, (Xyl = 2,6-dimethylphenyl) in 75% yield in the presence of stoichiometric amounts of acid. Applying this protocol, we had previously obtained nacnac^{Bn}H,[8] nacnac^{Cy}H,[10] and nacnac$^{CH(Me)Ph}$H[7] in 67%–82% yield. The initially obtained tosylate salt can be neutralized using a variety of bases of which aqueous potassium hydroxide proved to be the most convenient (aqueous $NaHCO_3$ failed in some cases to deprotonate the tosylate salt). Azeotropic water removal is required and reaction of $BnNH_2$ (or *i*-$BuNH_2$), acetylacetone, and 1 equiv. TsOH either in toluene or without solvent only yielded the monocondensation product **1b**.

Optimization of the reaction conditions

Attempts to widen the synthesis described above to diketimines with simple alkyl substituents such as Me, *i*-Pr, *n*-Pr, and *i*-Bu yielded even after prolonged heating only mixtures of bis- and mono-condensation products with less than 60% of the desired diketimine according to NMR analysis. Use of more than 1 equiv. of TsOH showed no or only detrimental influence on product yields. While it has never been clarified why reactions proceed differently when catalytic or stoichiometric amounts of acid are used, we find it reasonable to assume that alkylation of the intermediate enaminoketone is replaced by its (reversible) protonation and that the latter requires amounts of acid, which are equal or slightly higher than those of the amine. In agreement with this putative mechanism, presence of excess amine reduced the yield of diketimine when not compensated with excess TsOH (Table 1). Since the presence of excess amine and TsOH in equimolar amounts did not increase the yield when compared to the stoichiometric reaction (Table 1), loss of the low-boiling amine seems not to be responsible for the low yields obtained.

Scheme 2.



Inspired by the decrease in yields in the reaction of acetylacetone ketal with amines on dilution, we found that concentration of the reaction mixture reduced drastically the amounts of monocondensation product and impurities formed (Table 2). Best results were obtained when the minimum amount of toluene necessary to operate the Dean–Stark apparatus was employed.

Reactions with other primary and secondary amines showed that concentration of the solution in general improved product yields and in most cases shortened reaction times to less than one day (Table 3). The low isolated yields for nacnac^{Me}H are related to its high volatility and its high sensitivity towards hydrolysis.[15] Reactions with isopropyl amine and isobutyl amine, however, did not show conversions above 30% even under these conditions. Substituting *p*-toluenesulfonic acid with sulfuric acid led to strongly decreased yields. The use of concentrated hydrochloric acid, on the other hand, increased the yields to 85%–95% for R = *i*-Pr and *i*-Bu, respectively. In addition, use of concentrated HCl prevented the formation of impurities observed in reactions with TsOH, and diketimines were obtained analytically pure for R = *i*-Bu, *i*-Pr, and *n*-Pr without the need for further purification. Diketimines with R = Bn or CH(Me)Ph were obtained with >90% purity according to NMR (the main contamination being the monocondensation product), which is in most cases sufficient for their use in subsequent reactions. Analytically pure compounds were obtained by recrystallization from ethanol. For methylamine and cyclohexylamine, yields were drastically reduced by replacing *para*-toluenesulfonic acid with HCl. In both cases, the formation of an insoluble precipitate even at reflux temperature indicated that this might be related to the insolubility of the respective ammonium chloride salt. Consequently, use of an equimolar mixture of HCl/TsOH restored the yields observed for TsOH in these two cases, but did not otherwise affect reactions for other amines (Table 3).

Non-symmetric diketimines

Synthesis of non-symmetrically substituted diketimines with different substituents on N and N′ is a challenge and

Scheme 3.

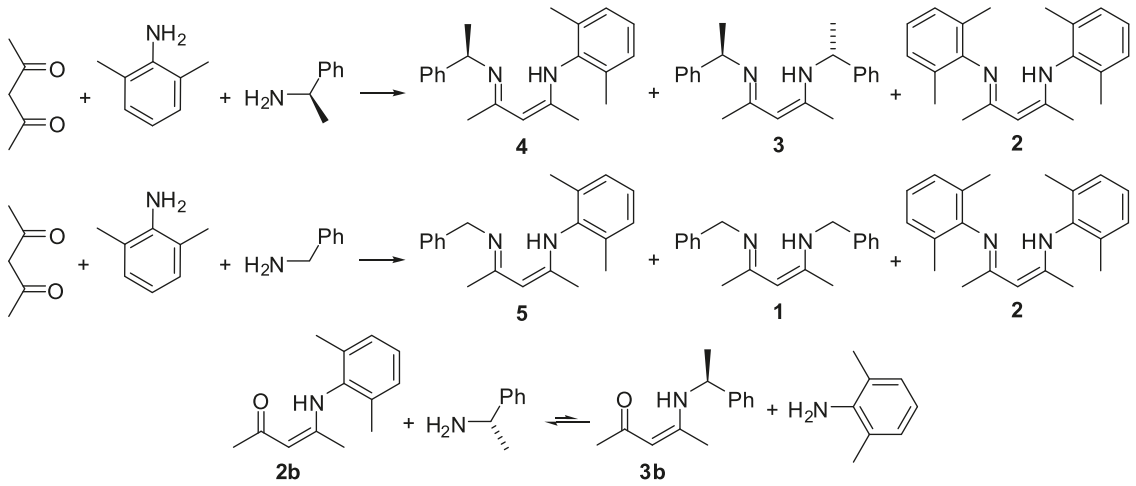


Table 1. Influence of excess base in the preparation of nacnac$^{i\text{-Bu}}$H.

i-BuNH$_2$/acacH	TsOH/acacH	Reaction time (h)	nacnac$^{i\text{-Bu}}$H (%)[a]	acnac$^{i\text{-Bu}}$H (%)[a]
2	1.1	24	60	30
3	1.1	24	5	70
3	1.5	20	15	30
3	2.2	18–54	60	30

[a]Determined by ^{1}H NMR from the crude product after basic workup.

Table 2. Influence of concentration in the preparation of nacnac$^{n\text{Pr}}$H.

[acacH] (mol/L)	Reaction time (h)	nacnac$^{i\text{-Bu}}$H (%)[a]	acnac$^{i\text{-Bu}}$H (%)[a]
0.048	68	62	18
1.2	68	80	Traces
4.0	16	90	Traces

Note: acacH/*n*-PrNH$_2$/TsOH = 1:2:1; toluene solution; azeotropic removal of water.

[a]Determined via ^{1}H NMR from the crude product after washing with aqueous KOH.

stepwise reaction using alkylating reagents such as Meerwein salt led to product mixtures.[17,18] We thus explored if non-symmetric diketimines can be obtained using the one-pot procedure established above. Reactions of acetylacetone with 1 equiv. 2,6-dimethylaniline and 1 equiv. of either (+)-methylbenzylamine or benzylamine yielded product mixtures containing the non-symmetric diketimines **4** or **5** in higher than statistical amounts, but always accompanied by the two symmetric diketimines (Scheme 3).

The preferred formation of the non-symmetric diketimine can be rationalized by the trapping of the more reactive 2,6-dimethylaniline in the monocondensation product, which diminishes its concentration in solution. Following reactions between acnac^{Xyl}H, **2b**, with methylbenzylamine, and vice versa of acnac$^{CH(Me)Ph}$H, **3b**, with 2,6-dimethylaniline by NMR showed that scrambling between the monocondensation products and free amines was observed already before significant amounts of diketimine were obtained (Scheme 3). In all cases, acnac^{Xyl}H was obtained preferentially. In particular at the beginning of the reaction, diketimines were thus formed from the two species present in the highest concentrations, i.e., acnac^{Xyl}H and either methylbenzylamine or benzylamine. As was previously observed by others, separation of non-symmetrical substituted diketimines from their symmetric counterparts is nearly impossible.[18] Despite their disproportionally high amount in the obtained product mixtures, **4** and **5** were not separated from the symmetric diketimines **1**–**3** by recrystallization, sublimation, or column chromatography (extensive hydrolysis in the latter case). For **5**, diketimine **1** could be separated by recrystallization and **5** was obtained in 30% yield and 90% purity, still contaminated by 10% of **2**.

Summary and conclusions

β-Diketimines with aliphatic substituents on nitrogen can be obtained in simple one-pot condensation reactions between acetylacetone and primary or secondary amine, provided that water is removed azeotropically and that one equivalent of acid is present. Under optimized reaction conditions, we employed an equimolar mixture of hydrochloric and *para*-toluenesulfonic acids, and the amount of solvent was kept to the minimum required for water removal. Symmetric diketimines can thus be obtained very economically, without the need of toxic alkylating reagents or moisture-free conditions.

For non-symmetric diketimines, the fast scrambling between free amine and monocondensation products makes the proposed protocol less efficient. Although they are obtained in higher than statistic ratio, their separation from the symmetric diketimines, invariably formed as side products, was not possible and the synthetically more demanding routes proposed by Park et al.[18,19] are still more advantageous.

Table 3. Yields in diketimine synthesis for different combinations of amines and acids (purity is given in parentheses).

R	TsOH (c_{acacH} < 1 mol/L)	TsOH	HCl	HCl/TsOH	Reaction time
n-Pr	50% (EA)	80% (90%)	90% (EA)		72 h
Bn	82% (EA)[a]	80% (>95%)	75% (>95%)		24 h
CH(Me)Ph	70% (EA)[b]	80% (90%)	80% (90%)	80% (90%)	5 d
i-Bu	35% (EA)	30%	95% (EA)		18 h
i-Pr	23% (90%)[c]	30% (>95%)	85% (EA)	95% (EA)	24 h
Cy	69% (EA)[d]	90% (>95%)	0%	90% (90%)	72 h
Me	60% (50%)	50% (95%)	5%	65% (>95%)	18 h

Note: Purity was estimated by ^{1}H NMR, EA indicates correct elemental analysis. Reaction conditions: acacH/RNH_2/acid = 1:2:1; minimum amount of toluene used with exception of the first column.

[a] c_{acacH} = 0.5 mol/L.[8]
[b] c_{acacH} = 0.1 mol/L, 5 d.[7]
[c] c_{acacH} = 0.2 mol/L, 3 d.[9]
[d] c_{acacH} = 0.1 mol/L, 3 d.[10]

Experimental section

All chemicals were obtained from commercial suppliers and used as received. Elemental analyses were performed at the Laboratoire d'Analyse Élémentaire (Université de Montréal). NMR spectra were recorded on a Bruker ARX 400 MHz spectrometer and referenced to residual solvent ($CHCl_3$: δ 7.26).

General procedure for the synthesis of symmetric diketimines

Acetylacetone and 1 equiv. of the desired acid or acid mixture (see Table 3) were combined in a minimum volume of toluene, usually equal to the combined volumes of all reactants. The mixture was stirred for 10 min and 2 equiv. of the desired amine were added to give a white suspension, which was allowed to stir for approximately 20 min. The reaction mixture was then refluxed for the required time (Table 3) with azeotropic removal of water (Dean–Stark apparatus). The brown precipitate formed after cooling to room temperature and standing for 3–4 h was isolated by decantation. Ether (50 mL) and aqueous KOH (11.2 g, 0.2 mol, 50 mL) were added and the mixture stirred for 15 min. The ether phase was separated, dried over Na_2SO_4, and the solvent evaporated. Yields and purities of the obtained products, estimated from ^{1}H NMR, are given in Table 3. Characterization data and quantities are given below for selected experiments.

nacnac^{Bn}H, 1

Acetylacetone (2.00 g, 20 mmol), HCl (12.1 mol/L, 1.65 mL, 20 mmol), and benzylamine (4.28 g, 40 mmol) in toluene (7 mL) gave a red brown solid (2.90 g, 75%, >95% purity). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 11.49 (bs, 1H, NH), 7.22–7.30 (m, 10H, Ph), 4.64 (s, 1H, $CH(C{=}N)_2$), 4.46 (s, 4H, CH_2), 1.95 (s, 6H, Me). Recrystallization from a saturated ethanol solution at –20 °C gave the following: Anal. calcd. for $C_{21}H_{26}N_2$: C, 81.97; H, 7.97; N, 10.06. Found: C, 81.75; H, 8.19; N, 10.05.[2,14,15]

nacnac$^{CH(Me)Ph}$H, 3

Acetylacetone (1.00 g, 10 mmol), HCl (12.1 mol/L, 0.82 mL, 10 mmol), and (+)-phenylethylamine (2.42 g, 20 mmol) in toluene (6 mL) gave a red brown oil (2.45 g, 80%, 92% purity). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 11.89 (bs, 1H, NH), 7.20–7.35 (m, 10H, Ph), 4.68 (q, 2H, *J* = 7 Hz, C*H*(Me)Ph), 4.48 (s, 1H, $CH(C{=}N)_2$), 1.82 (s, 6H, Me(C=N)), 1.49 (d, 6H, *J* = 7 Hz CH(*Me*)Ph). Recrystallization from a saturated ethanol solution at –20 °C gave the following: Anal. calcd. for $C_{21}H_{26}N_2$: C, 82.31; H, 8.55; N, 9.15. Found: C, 81.75; H, 8.52; N, 9.06.[7,20]

nacnac$^{n\text{-}Pr}$H

Acetylacetone (2.00 g, 20 mmol), HCl (12.1 mol/L, 1.65 mL, 20 mmol), and *n*-propylamine (2.36 g, 40 mmol) in toluene (5 mL) gave a dark brown oil (3.3 g, 90%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 10.04 (bs, 1H, NH), 4.47 (s, 1H, $CH(C{=}N)_2$), 3.17 (t, *J* = 9 Hz, 4H, NCH_2), 1.87 (s, 6H, Me(C=N)), 1.61 (m, 4H, $CH_2CH_2CH_3$), 0.97 (t, *J* = 9 Hz, 6H, CH_2CH_3). Anal. calcd. for $C_{11}H_{22}N_2$: C, 72.47; H, 12.16; N, 15.37. Found C, 72.41; H, 11.81; N, 15.39.[15]

nacnac$^{i\text{-}Pr}$H

Obtained from acetylacetone (2.00 g, 20 mmol), HCl (12.1 mol/L, 1.65 mL, 20 mmol), and isopropylamine (2.36 g, 40 mmol) in toluene (5 mL). To eliminate monocondensation product, the oil obtained after decantation of toluene was treated with excess saturated aqueous $NaHCO_3$ and ether (20 mL). Ether and water phases were decanted from the remaining oil. Ether (50 mL) and aqueous KOH (11.2 g, 0.2 mol, 50 mL) were added and the mixture stirred. The ether phase was separated, dried over Na_2SO_4, and evaporated to dryness to give a dark-red oil (3.4 g, 85%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 11.43 (bs, 1H, NH), 4.38 (s, 1H, $CH(C{=}N)_2$), 3.06 (hept., *J* = 6 Hz, 2H, $CH(CH_3)_2$), 1.89 (s, 6H, $CH_3(C{=}N)$), 1.16 (d, *J* = 6 Hz, 12H, $CH(CH_3)_2$). Anal. calcd. for $C_{11}H_{22}N_2$: C, 72.47; H, 12.16; N, 15.37. Found C, 72.06; H, 12.08; N, 15.15.[2]

nacnac$^{i\text{-}Bu}$H

Acetylacetone (2.00 g, 20 mmol), HCl (12.1 mol/L, 1.65 mL, 20 mmol), and isobutylamine (2.92 g, 40 mmol) in toluene (5 mL) gave a brown oil (4.3 g, 95%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 11.07 (bs, 1H, NH), 4.48 (s, 1H, $CH(C{=}N)_2$), 3.05 (d, *J* = 9 Hz, 4H, CH_2), 1.88 (m, 2H, $CH(CH_3)_2$), 1.86 (s, 6H, $CH_3(C{=}N)$), 0.96 (d, *J* = 9 Hz, 12H, $CH(CH_3)_2$). Anal. calcd. for $C_{13}H_{26}N_2$: C, 74.23; H, 12.46; N, 13.32. Found C, 74.06; H, 13.03; N, 12.99.[15,21]

nacnac^{Cy}H

Acetylacetone (2.00 g, 20 mmol), HCl (12.1 mol/L, 0.82 mL, 10 mmol), *p*-toluenesulfonic acid monohydrate (2.00 g, 11 mmol), and cyclohexylamine (3.98 g, 40 mmol) in toluene (15 mL) gave a colorless oil that crystallizes into colorless crystals upon standing for 2–3 h (4.75 g, 90%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 11.72 (bs, 1H, NH), 4.44 (s, 1H, $CH(C=N)_2$), 3.32–3.35 (m, 2H, Cy CH), 1.90 (s, 6H, Me(C=N)), 1.80–1.35 (m, 20H, Cy). Anal. calcd. for $C_{13}H_{26}N_2$: C, 77.80; H, 11.52; N, 10.64. Found C, 77.44; H, 11.57; N, 10.67.[22]

nacnac^{Me}H

Acetylacetone (3.00 g, 30 mmol), HCl (12.1 mol/L, 1.24 mL, 15 mmol), *p*-toluenesulfonic acid monohydrate (2.99 g, 16 mmol), and methylamine (40%, 4.65 g, 0.06 mol) in toluene (6 mL). The aqueous phase was re-extracted with ether (3 × 300 mL), and the combined organic phases were dried over Na_2SO_4 and evaporated to dryness. The dark-yellow oil obtained solidifies to an orange precipitate that darkens upon standing to room temperature (2.5 g, 65%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 10.04 (bs, 1H, NH), 5.2 (s, 1H, $CH(C=N)_2$), 2.99 (s, 6H, NMe), 1.86 (s, 6H, $CH_3(C=N)$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 400 MHz): δ 162.1 (C=N), 93.9 ($CH(C=N)_2$), 33.3 (Me), 19.0 ($CH_3(C=N)$). Elemental analysis data were unsatisfactory due to easy decomposition.[2,15]

nacnac^{Xyl,Bn}H

Acetylacetone (3.00 g, 30 mmol), HCl (12.1 mol/L, 2.5 mL, 30 mmol), and 2,6-dimethylaniline (3.63 g, 30 mmol) in toluene (12 mL) were refluxed for approximately 2 h. To the obtained yellow suspension, benzylamine (3.27 g, 30 mmol) was added and allowed to reflux for 3 days under azeotropic removal of water in a Dean–Stark apparatus. After cooling to room temperature and decantation of toluene, the brown oil obtained was treated with ether (50 mL) and aqueous KOH (16.8 g, 0.3 mol, 50 mL). The ether phase was separated and evaporated to dryness. The obtained red-brown oil was dissolved in a minimum amount of ethanol and kept at –20 °C for several days. Crystals of nacnac^{Bn}H formed were removed by filtration, and the remaining ethanol solution was evaporated to dryness to yield a brown oil (2.62 g, 30%, in 90% purity containing 10% of **2**). Further recrystallizations in MeOH or in EtOH as well as sublimation still yielded product mixtures. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 11.18 (bs, 1H, NH), 7.22–7.30 (m, 8H, Ph), 4.45 (s, 1H, $CH(C=N)_2$), 4.43 (s, 2H, CH_2), 2.07 (s, 6H, Ar Me), 1.90 (s, 3H, Me(C=N)), 1.63 (s, 3H, Me(C=N)). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 400 MHz): δ 160.1 (C=N), 140.1 (C=N), 128.4, 128.3, 127.6, 127.5, 127.2, 127.0, 126.7, 126.3 (all Ph), 93.9 ($CH(C=N)_2$), 46.5 (CH_2), 21.2 (*Me*(C=N)), 19.1 (*Me*(C=N)), 18.3 (Me_2Ph). EI-HR-MS (*m*/*z*): calcd. for $C_{20}H_{25}N_2$ $[M + H]^+$: 293.2012; found: 293.2013.[5]

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