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2,6-Dimethoxyphenyl-Substituted N-Heterocyclic Carbenes (NHCs): A Family of Highly Electron-Rich Organocatalysts

Michael Schedler,[a] Roland Fröhlich,[a,b] Constantin-G. Daniliuc,[a,b] and Frank Glorius*[a]

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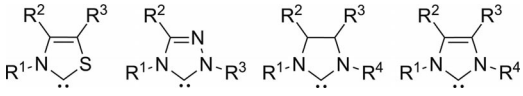
Based on our recent finding that 2,6-dimethoxyphenyl-substituted NHCs show superior reactivity in the hydroacylation reactions of electron-neutral olefins compared with known NHCs, we now report the syntheses and crystal structures of four highly electron-rich 2,6-dimethoxyphenyl-substituted NHCs and show the increase in efficiency caused by the electron-rich aryl substituent in hydroacylation reactions.

Introduction

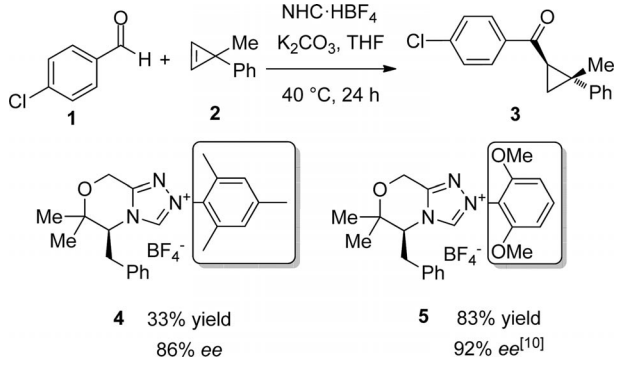
The observation that N-heterocyclic carbenes[1] (NHCs, cf. Scheme 1) are able to catalyze the condensation of two aldehydes to benzoin[2] has led to widespread interest in the use of NHCs as organocatalysts.[3] The unique catalytic behavior of NHCs can be explained by the formation of the Breslow intermediate, which leads to the umpolung of an aldehyde. The ease of handling of azolium salts, which are convenient NHC precursors, has facilitated the development of various NHC-catalyzed reactions.[4] In addition to the benzoin condensation reaction, the addition of the Breslow intermediate to α,β-unsaturated carbonyls (the Stetter reaction) has been studied extensively.[5]



Scheme 1. NHCs commonly used in organocatalysis.

These classical NHC-catalyzed reactions have been enriched by the reaction between the Breslow intermediate and rather electron-neutral multiple bonds,[6–8] initially in intramolecular hydroacylations,[6] but more recently in intermolecular hydroacylations.[7,8] When investigating the asymmetric hydroacylation of cyclopropene **2**, we recognized that none of the chiral NHCs commonly used in organocatalysis was reactive and selective enough to achieve this transformation in a satisfactory manner.[8]

Thus, we focused on the design of new NHC precursors following the observation that NHCs with electron-rich aromatic substituents at one of the nitrogens showed higher reactivity.[7b] In addition, we hoped that a more electron-rich substituent would improve the enantioselectivity, as predicted by the calculations of Hawkes and Yates.[9] Our synthetic efforts led to the new highly electron-rich NHC precursor **5** carrying a 2,6-dimethoxyphenyl moiety, which led to an optimized enantioselectivity and also a quantitative conversion in the catalyzed hydroacylation reaction (cf. Scheme 2).



Scheme 2. Effect of the 2,6-dimethoxyphenyl group on the hydroacylation reaction of **2**.[8]

Results and Discussion

It would be highly desirable to have more of these electron-rich NHCs at hand, but no other 2,6-dimethoxyphenyl-substituted triazolium salt has been reported before. Furthermore, no thiazolium or imidazolium salt with the 2,6-dimethoxyphenyl moiety is known. Only a few ex-

[a] Westfälische Wilhelms-Universität Münster, Organisch-Chemisches Institut,
Corrensstrasse 40, 48149 Münster, Germany
Fax: +49-251-8333202
E-mail: glorius@uni-muenster.de
[b] Laboratory of Single-Crystal X-ray Structure Determination, Westfälische Wilhelms-Universität Münster, Organisch-Chemisches Institut,
Corrensstrasse 40, 48149 Münster, Germany
Fax: +49-251-83-33293
E-mail: frohlic@uni-muenster.de

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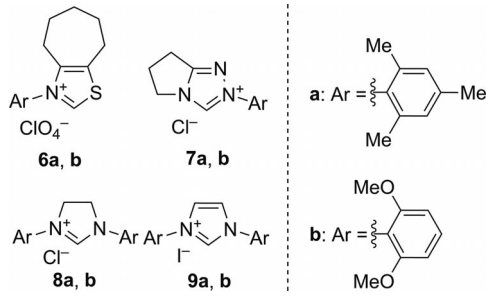
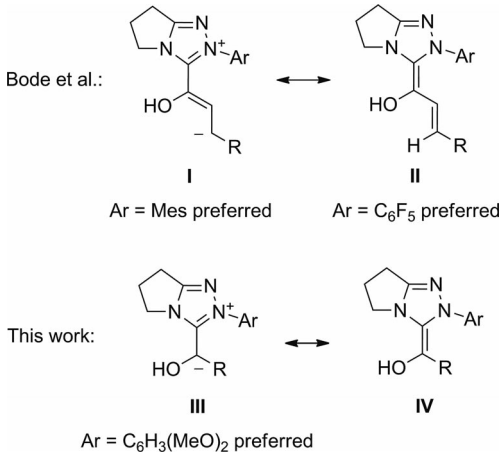
amples of imidazolinium-derived NHCs with 2,6-dimethoxyphenyl groups are known, and these have only been used as ligands in transition-metal catalysis.[11] Lüning and co-workers used a bimacrocyclic concave imidazolinium-derived NHC with 2,6-alkoxy substituents as an organocatalyst.[12]

Thus, herein we report the synthesis of 2,6-dimethoxyphenyl-substituted versions of four commonly used NHC organocatalysts (cf. Scheme 3), which are representative examples of the four NHC scaffolds (cf. Scheme 1). We wanted to investigate whether our aforementioned findings were simply a stroke of luck or whether the effect of the 2,6-dimethoxyphenyl substituent is a general phenomenon that leads to a new class of NHCs beyond the known mesityl-, phenyl-, and C_6F_5-substituted NHCs.[13] By using the newly synthesized NHCs as catalysts we hoped to prove that the highly electron-rich aryl substituent increases the nucleophilicity of the carbene and hence amplifies the reactivity of the Breslow intermediate. As shown by Bode et al.,[13] the electron-rich *ortho* substituents have two crucial functions in the formation of the Breslow intermediate. First, electron-rich NHCs are poorer leaving groups than electron-deficient NHCs, hence the initial addition of the NHC to the aldehyde is reversible for C_6F_5-substituted NHCs but irreversible for mesityl-substituted NHCs. Therefore the addition of our 2,6-dimethoxy-substituted NHCs to aldehydes should be faster as the NHC is even more electron-rich and it should also be irreversible. Secondly, the steric effects of the *ortho* substituents destabilize the initial tetrahedral adduct and accelerate the formal 1,2-H-shift to the planar Breslow intermediate. In addition, Bode states that the electron-rich aryl substituents stabilize the homoenolate **I** over the acyl anion **II** (cf. Scheme 4). Thus, the positive charge in the azolium core is stabilized by the electron-rich 2,6-dimethoxyphenyl substituent **III**, making the aldehyde carbon more nucleophilic and more reactive especially in the reaction with poor electrophiles like olefins.



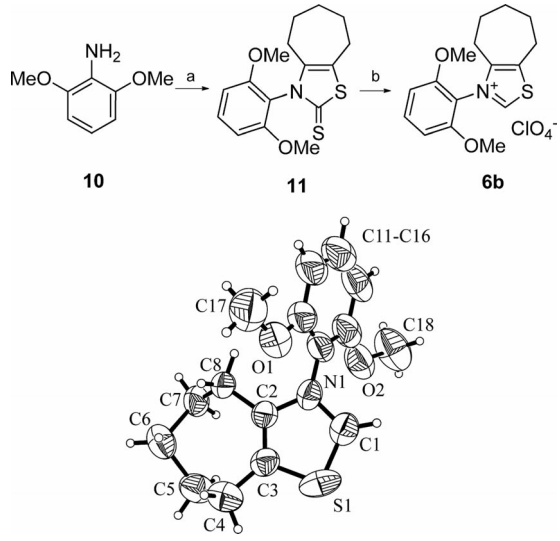
Scheme 3. Scaffolds of commonly used NHCs in organocatalysis.



Scheme 4. Influence of the electron-rich aryl substituents on the reactivity of NHCs.

Synthesis of the 2,6-Dimethoxyphenyl-Substituted NHCs

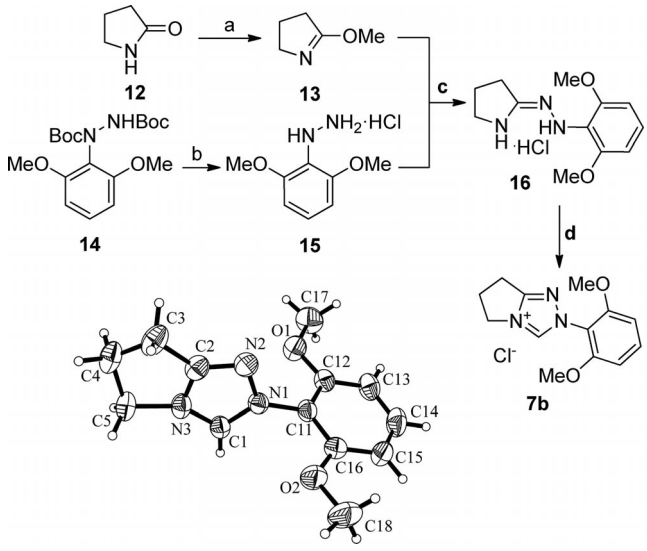
To synthesize the four new NHCs we had to design three synthetic routes (the IMes and SIMes derivatives **8b** and **9b** could be synthesized from the same precursor). We began with the synthesis of the new thiazolium-derived NHC **6b** based on the scaffold of the mesityl-substituted Isa-NHC·$HClO_4$ (**6a**), which has shown superb reactivity in intramolecular hydroacylation reactions.[6a,6b,6d] Following the synthesis[14] described for **6a**, we synthesized the sought after thiazolium salt **6b** in a two-step process starting from 2,6-dimethoxyaniline (**10**) . The structure of **6b** was unambiguously proved by single-crystal X-ray diffraction (cf. Scheme 5).



Scheme 5. Synthesis and X-ray crystal structure of the thiazolium salt **6b**. Reagents and conditions: a) aq. NaOH, CS_2, DMSO, then α-bromocycloheptanone, 45%; b) H_2O_2, aq. HOAc, then $NaClO_4$, MeOH, H_2O, 56%. The counterion has been omitted from the crystal structure for clarity.[16]

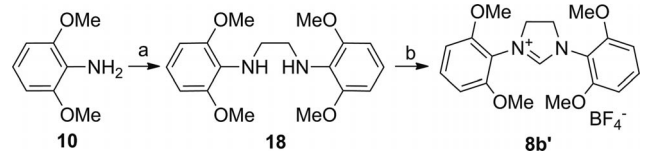
As the triazolium salt **7a** is not only one of the most often used NHC precursors but also very efficient in the racemic hydroacylation of cyclopropenes,[7b] the synthesis of the 2,6-dimethoxyphenyl-substituted triazolium salt **7b** was targeted following the procedure described by Struble and Bode,[15] that was previously adapted by our group to synthesize **5**.[8] Following this protocol yielded only traces of **7b**, which could be attributed to the low stability of the

amidrazone **16** at 120 °C, the temperature that is normally needed for the cyclization step. Lowering the reaction temperature to 40 °C was beneficial but did not yield the triazolium salt **7b**, instead the water adduct of the NHC was formed, which was attributed to traces of water present during the reaction and the fact that **7b** is more sensitive to traces of water than known triazolium salts. The addition of molecular sieves and an increase in the temperature to 80 °C were finally found to be the best conditions for the synthesis of **7b**.[16] The structure of **7b** was verified by X-ray structural analysis (cf. Scheme 6).



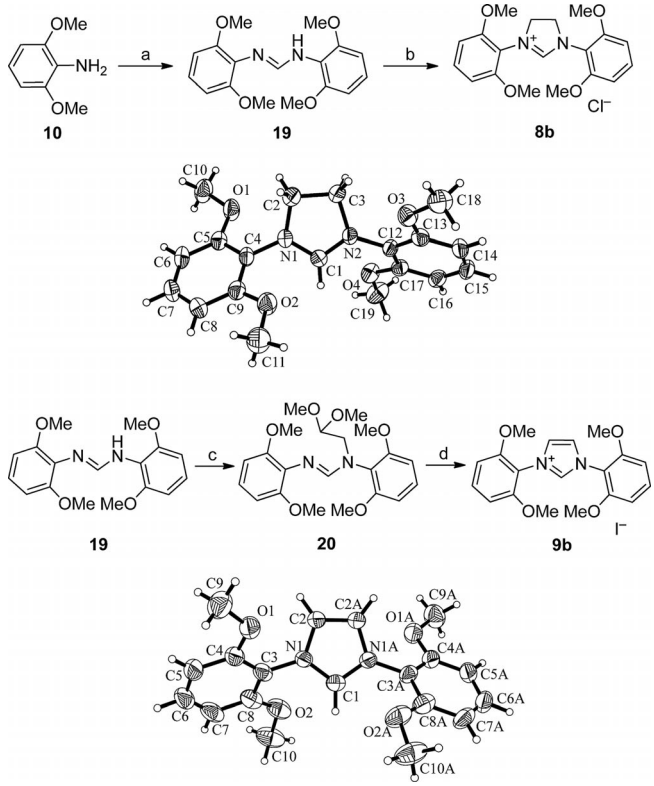
Scheme 6. Synthesis and X-ray crystal structure of the triazolium salt **7b**. Reagents and conditions: a) Me_3OBF_4, CH_2Cl_2; b) HCl in dioxane, MeOH; c) HCl in dioxane, MeOH; d) $HC(OEt)_3$, PhCl, 4 Å MS, 80 °C, 16 h, 10% over three steps. The counterion has been omitted from the crystal structure for clarity.[16]

The imidazolinium salt **8b′** could be obtained from the diamine **18**, which can be accessed easily by the reaction of 2,6-dimethoxyaniline (**10**) with 1,2-dibromoethane. The cyclization of **18** with triethyl orthoformate and ammonium tetrafluoroborate yielded the imidazolinium tetrafluoroborate salt **8b′**.[17] This two-step reaction sequence proceeded to give a low yield of 16% (cf. Scheme 7), hence alternative pathways were investigated.



Scheme 7. Synthesis of imidazolium salt **8b′** via the diamine **18**. Reagents: a) 1,2-dibromoethane; b) $HC(OEt)_3$, NH_4BF_4, 16% over two steps.

An alternative synthetic route uses the formamidine **19**, which can be easily obtained from the aniline **10** in one step. The reaction of **19** with 1,2-dichloroethane under basic conditions gave the imidazolinium chloride **8b** in an improved yield of 47% (cf. Scheme 8).[18] The formamidine **19** can also be used to synthesize **9b**, the 2,6-dimethoxyphenyl variant of the well known IMes-carbene **9a**, which is generally synthesized by a one-pot reaction starting from the corresponding aniline, glyoxal, and triethyl orthoformate.[19] However, this one-pot reaction did not yield any product when the electron-rich 2,6-dimethoxyaniline was used. Another way of synthesizing imidazolium salts is the condensation of glyoxal with an aniline to obtain a diimine and cyclization of this diimine in a second step.[20] Again, this protocol did not work sufficiently well for 2,6-dimethoxyaniline. Hence, the synthetic route starting from formamidine **19** that was previously used by our group to synthesize a library of substituted imidazolium salts[21] seems to be the most efficient protocol for obtaining the imidazolium salt **9b** (cf. Scheme 8).[22]



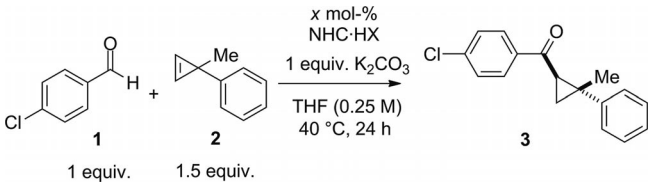
Scheme 8. Divergent synthesis and X-ray crystal structures of the imidazolinium salt **8b** and the imidazolium salt **9b**. Reagents and conditions: a) $HC(OEt)_3$, HOAc, 140→160 °C, 90%; b) $ClCH_2$-CH_2Cl, Hünig's base, 47%; c) NaH, bromoacetaldehyde dimethyl acetal, DMF, 86%; d) BF_3·Et_2O, MeCN, 77%. The counterions have been omitted from the crystal structures for clarity.[16]

Performance of the 2,6-Dimethoxy-Substituted NHCs in Hydroacylation Reactions

The four new NHCs were tested along with the established NHC precursors **6a** and **7a** as references in hydroacylation reactions that have been previously reported by our group.[6a,7b] The performance of the NHCs in the hydroacylation of 3-methyl-3-phenylcyclopropene (**2**) with *p*-chlorobenzaldehyde (**1**) is summarized in Table 1. The reaction proceeded quantitatively with 5 mol-% of **7a** (En-

try 1), as reported previously;[7b] lowering the catalyst loading of **7a** to 2.5 mol-% led to a lower yield (Entry 3). The electron-rich triazolium salt **7b** is evidently a more active catalyst than **7a** as it gave complete conversion with a catalyst loading of 2.5 mol-% (Entry 5). The thiazolium-based NHCs **6a** and **6b** yielded only small amounts of product (Entries 2 and 4) and the 2,6-dimethoxy-substituted NHCs **8b′** and **9b** showed no catalytic activity for this transformation (Entries 6 and 7). Further lowering the catalyst loading to 1 mol-% of **7b** was not tolerated and resulted in a yield of only 10% (Entry 8).

Table 1. Hydroacylation of cyclopropene **2** with the new NHCs.[a]



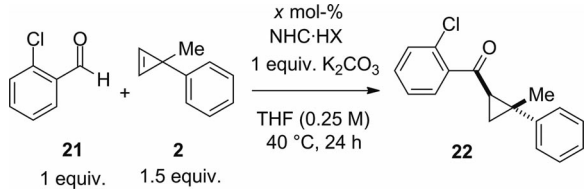
Entry	Catalyst	Cat. loading [mol-%]	Yield [%][b]
1	**7a**	5	96/4
2	**6a**	2.5	4/0
3	**7a**	2.5	85/4
4	**6b**	2.5	2/0
5	**7b**	2.5	97/3 (96[c])
6	**8b′**	2.5	0/0
7	**9b**	2.5	0/0
8	**7b**[d]	1	10/0

[a] General reaction conditions: **1** (0.2 mmol, 1 equiv.), **2** (0.3 mmol, 1.5 equiv.), NHC·HX (*x* mol-%), K_2CO_3 (1 equiv.), THF (0.25 M), 40 °C, 24 h. [b] The yields were determined by ^{1}H NMR spectroscopy with CH_2Br_2 as internal standard. For some catalysts the second diastereomer could also be detected (second yield). [c] The reaction was performed on a 0.5 mmol scale. Yield after purification. [d] Reaction performed on a 0.5 mmol scale.

The superiority of **7b** was validated by using the less reactive *o*-chlorobenzaldehyde (**21**) in the hydroacylation of 3-methyl-3-phenylcyclopropene (**2**; cf. Table 2). This reaction yielded, as previously reported,[7b] 67% of the acylcyclopropane **22** with 20 mol-% of **7a** (Entry 1). The reaction proceeded with only 10 mol-% of **7b** to give a similar yield of 62% (Entry 5), whereas the known catalyst **7a** gave a yield of only 34% with the lower catalyst loading (Entry 3).[7b] Again, **8b′** and **9b** showed only low catalytic activity (Entries 6 and 7), but the thiazolium salt **6b** yielded 20% of the product **22** (Entry 4), whereas the mesityl-substituted NHC **6a** only yielded 5% of the product (Entry 2).

The efficiency of the new catalysts was also investigated in the intramolecular hydroacylation of **23** (Table 3). With 20 mol-% of **6a** (Entry 1), a yield similar to the 57% reported previously was obtained.[6a] Performing this reaction with only 10 mol-% NHC revealed the superiority of **6b** as the hydroacylation proceeded with full conversion (Entry 4). Surprisingly, **6a** gave a higher yield of 98% with a lower catalyst loading (cf. Entries 2 and 4). This unexpected relationship between yield and catalyst loading is the subject of ongoing research.[16] The triazolium-based NHCs **7a** and **7b** gave yields of 44 and 62% (Entries 3 and 5, respectively). The two other dimethoxy-substituted NHCs **8b′** and **9b** gave lower yields (Entries 6 and 7).

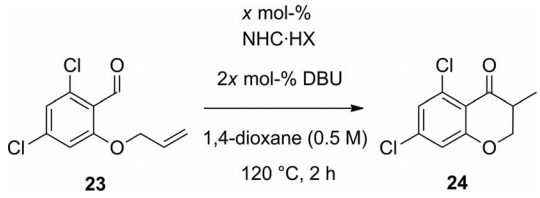
Table 2. Hydroacylation with a less reactive aldehyde.[a]



Entry	Catalyst	Cat. loading [mol-%]	Yield [%][b]
1	**7a**	20	67/5
2	**6a**	10	5/0
3	**7a**	10	34/2
4	**6b**	10	20/0
5	**7b**	10	62/3 (64[c])
6	**8b′**	10	7/0
7	**9b**	10	0/0

[a] General reaction conditions: **21** (0.1 mmol, 1 equiv.), **2** (0.15 mmol, 1.5 equiv.), NHC·HX (*x* mol-%), K_2CO_3 (1 equiv.), THF (0.25 M), 40 °C, 24 h. [b] The yields were determined by ^{1}H NMR spectroscopy with CH_2Br_2 as internal standard. For some catalysts the second diastereomer could also be detected (second yield). [c] The reaction was performed on a 0.5 mmol scale. Yield after purification.

Table 3. Intramolecular hydroacylation of **23**.[a]



Entry	Catalyst	Cat. loading [mol-%]	Yield [%][b]
1	**6a**	20	51
2	**6a**	10	98
3	**7a**	10	44
4	**6b**	10	quant.
5	**7b**	10	62
6	**8b′**	10	23
7	**9b**	10	9
8	**6a**	1	15
9	**6b**	1	quant. (91[c])
10	**6b**	0.5	20

[a] General reaction conditions: **23** (0.1 mmol, 1 equiv.), NHC·HX (*x* mol-%), DBU (2*x* mol-%), 1,4-dioxane (0.5 M), 120 °C, 2 h. [b] The yields were determined by ^{1}H NMR spectroscopy with CH_2Br_2 as internal standard. [c] The reaction was performed on a 0.5 mmol scale. Yield after purification.

When lowering the catalyst loading to 1 mol-%, the dimethoxy-substituted NHC **6b** still gave a quantitative yield (Entry 9), whereas the mesityl-substituted NHC **6a** only gave a yield of 15% (Entry 8).[16] Further lowering the catalyst loading led to a reduced yield (20% of **24** with 0.5 mol-% **6b**, Entry 10). The efficiency of **6b** in this reaction is quite remarkable and we wished to investigate whether the high reactivity even at the unusually low catalyst loading of

1 mol-% is only a result of the increased nucleophilicity of the dimethoxy-substituted NHC or whether the electron-rich aryl substituent also increased the stability of the NHC. We hence carried out the hydroacylation of **23** without the inert gas. Under these conditions no conversion was observed with 10 mol-% of **6a** and <5% of **24** was obtained with the new NHC **6b** (with 10 mol-% catalyst loading). Thus, it seems that the 2,6-dimethoxy substituent has no or little influence on the air/water-stability of the NHC and inert gas techniques are mandatory for NHC-catalyzed hydroacylation reactions.

Conclusions

Four new NHCs with an electron-rich 2,6-dimethoxyphenyl substituent have been synthesized and represent the four classes of commonly used NHC organocatalysts. Their structures were determined by X-ray diffraction analysis. The first applications of these new NHCs in catalysis showed the potential superiority of this new family of NHCs over known catalysts and the higher efficiency of the dimethoxy-substituted NHCs was proven by the full conversions observed for hydroacylation reactions with catalyst loadings as low as 1 mol-%. This higher reactivity can be explained by the higher nucleophilicity of both the NHC and the Breslow intermediate. Further research to improve the efficiency of known NHC-catalyzed reactions by using the new catalysts is ongoing. In addition, these catalysts should enable transformations that were out of reach with the previously known NHCs.

Experimental Section

General: All reactions were performed in oven- or flame-dried reaction vessels, modified Schlenk flasks, or round-bottomed flasks. The flasks were fitted with Teflon screw caps and reactions were conducted under argon. Gas-tight syringes with stainless-steel needles or cannulae were used to transfer air- and moisture-sensitive liquids. All moisture- and/or air-sensitive solid compounds were manipulated inside an argon-filled glovebox. Flash column chromatography was performed on silica gel (40–63 μm, 230–400 mesh, Merck). Analytical TLC was performed on silica gel 60 F_{254} aluminum plates (Merck) containing a 254 nm fluorescent indicator. TLC plates were visualized by exposure to short-wave ultraviolet light (254 nm) and to a solution of $KMnO_4$ (1 g of $KMnO_4$, 6 g of K_2CO_3, and 0.1 g of KOH in 100 mL of H_2O) or vanillin (2 g of vanillin and 4 mL of concentrated H_2SO_4 in 100 mL of EtOH) followed by heating.

Organic solutions were concentrated at 40 °C on Heidolph 4000 rotary evaporators at about 10 mbar followed by drying by means of a vacuum pump (p < 1 mbar). Commercial reagents and solvents were used as received with the following exceptions: THF was purified by heating at reflux over Na/benzophenone under a positive argon pressure followed by distillation; CH_2Cl_2 was purified by heating at reflux over CaH_2 under a positive argon pressure followed by distillation; K_2CO_3 was dried by heating at 110 °C for 12 h, cooling under argon, and storing inside an argon-filled glovebox; triethyl orthoformate was purified by distillation under argon and stored under argon. ^{1}H NMR spectra were recorded with a Bruker AV 300 or AV 400 spectrometer. ^{1}H chemical shifts are reported in parts per million (δ scale) and are referenced to residual protium in the NMR solvent [$CDCl_3$: δ = 7.26 ppm ($CHCl_3$)]. Data are reported as follows: chemical shift [multiplicity (s = singlet, d = doublet, t = triplet, sp = septet, m = multiplet, br. = broad signal), coupling constant(s) (Hz), integration]. ^{13}C NMR spectra were recorded with a Bruker AV 300 or AV 400 spectrometer. ^{13}C chemical shifts are reported in parts per million (δ scale) and are referenced to the carbon resonances of the solvent [δ = 77.16 ppm ($CDCl_3$)]. IR spectra were obtained with a Varian Associated FT-IR 3100 Excalibur spectrometer with an ATR unit and are reported in frequency of absorption (cm^{-1}). GC–MS spectra were recorded with an Agilent Technologies 7890A GC system with an Agilent 5975C VL MSD or 5975 inert Mass Selective Detector (EI) on a HP-5MS column (0.25 mm × 30 m; film: 0.25 μm). Method A began with an injection at temperature T0 (50 °C), which is held for 3 min. The column was then heated to temperature T1 (290 °C, ramp: 40 °C), which is held for 3 min. HRMS were recorded with a Bruker Daltonics MicroTof spectrometer using an electrospray (ESI) ionization source.

3-(2,6-Dimethoxyphenyl)-5,6,7,8-tetrahydro-4*H*-cyclohepta[*d*]thiazol-3-ium Perchlorate (6b):[14] 2,6-Dimethoxyaniline (**10**; 453 mg, 2.96 mmol, 1 equiv.) was dissolved in DMSO (1.5 mL, 2 M) and 20 M aq. NaOH (150 μL, 3 mmol, 1 equiv.) was added. CS_2 (179 μL, 2.96 mmol, 1 equiv.) was added and the resulting black solution was stirred for 1 h at room temperature. 2-Bromocycloheptanone (566 mg, 2.96 mmol, 1 equiv.) was added to the reaction and the mixture was stirred overnight. H_2O (3 mL) was added leading to a precipitate. The water was decanted and the precipitate washed twice with water. The precipitate was suspended in EtOH (3.5 mL) and concentrated HCl (0.15 mL) was added. The mixture was heated at reflux for 1 h and after cooling to room temperature was stored in the fridge overnight to complete the precipitation. The precipitate was filtered off and washed with pentane, resulting in **11** as a beige solid (429 mg, 1.34 mmol, 45%), which was used in the next step without further purification. R_f (pentane/EtOAc, 7:3) = 0.22 (UV, $KMnO_4$). FTIR (ATR): $\tilde{\nu}$ = 3005, 2925, 2842, 1593, 1481, 1460, 1434, 1330, 1297, 1260, 1233, 1209, 1106, 1053, 1027, 983, 925, 841, 822, 780, 747, 696, 659, 609 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.40 (t, J = 8.5 Hz, 1 H), 6.68 (d, J = 8.5 Hz, 2 H), 3.80 (s, 6 H), 2.62–2.59 (m, 2 H), 2.26–2.24 (m, 2 H), 1.79–1.74 (m, 4 H), 1.60–1.52 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 186.9, 156.4, 142.1, 131.2, 123.0, 115.8, 104.9, 56.4, 31.1, 29.0, 27.5, 27.3, 26.0 ppm. GC–MS (Method A): R_T = 11.83 min (321, 290, 288, 273, 260, 166, 154. 133, 197, 97. 91, 77, 65, 39). HRMS (ESI): calcd. for $C_{16}H_{19}NO_2S_2H^+$ 322.0930; found 322.0932; calcd. for $C_{16}H_{19}NO_2S_2Na^+$ 344.0749; found 344.0751.

Compound **11** (408 mg, 1.34 mmol, 1 equiv.) was suspended in acetic acid (5.5 mL, 0.25 M) and H_2O_2 (35% in H_2O, 378 μL, 4.42 mmol, 3.3 equiv.) was added slowly while keeping the reaction mixture at room temperature. The resulting red solution was stirred for 45 min at room temperature. All volatiles were removed in vacuo and the resulting red oil was dissolved in methanol (1 mL). $NaClO_4 \cdot H_2O$ (753 mg, 5.36 mmol, 4 equiv.) dissolved in a mixture of methanol (3.1 mL) and water (1.6 mL) was added to the reaction at 0 °C. After stirring for 30 min the mixture was warmed to room temperature and water (2.5 mL) was added. The mixture was extracted with CH_2Cl_2 (3× 5 mL). The combined organic phases were dried with $MgSO_4$, filtered, and the volatiles removed in vacuo. The resulting red oil was purified by flash column chromatography (CH_2Cl_2/MeOH, 95:5) on silica gel resulting in **6b** as a beige solid (292 mg, 0.75 mmol, 56%). R_f (CH_2Cl_2/MeOH, 95:5) = 0.31 (UV). FTIR (ATR): $\tilde{\nu}$ = 3074, 2930, 2851, 1604, 1592,

1485, 1303, 1264, 1075, 958, 780, 732, 621, 566 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.41 (s, 1 H), 7.49 (t, J = 8.6 Hz, 1 H), 6.71 (d, J = 8.6 Hz, 2 H), 3.77 (s, 6 H), 3.02–3.00 (m, 2 H), 2.53–2.50 (m, 2 H), 1.92–1.77 (m, 4 H), 1.61–1.56 (m, 2 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 156.6, 154.6, 149.1, 138.2, 133.6, 113.5, 104.6, 56.5, 30.8, 27.9, 27.1, 26.5, 25.0 ppm. HRMS (ESI): calcd. for $C_{16}H_{20}NO_2S^+$ 290.1209; found 290.1217.

2-(2,6-Dimethoxyphenyl)-2,5,6,7-tetrahydropyrrolo[2,1-*c*][1,2,4]triazol-4-ium Chloride (7b):[8,16] 2-Pyrrolidone (**12**; 779 μL, 10.1 mmol, 1 equiv.) was dissolved in CH_2Cl_2 (50 mL, 0.2 M) and Me_3OBF_4 (1793 mg, 12.1 mmol, 1.2 equiv.) was added. The mixture was stirred at room temperature overnight. Saturated $NaHCO_3$ solution (50 mL) was added slowly (15 min) to the reaction mixture. The organic phase was separated and the aqueous phase was extracted with CH_2Cl_2 (3 × 50 mL). The combined organic phases were dried with Na_2SO_4 and filtered. Most of the CH_2Cl_2 was removed on a rotary evaporator at 40 °C and a pressure of ≥200 mbar (the imidate is volatile!) to give **13** as a colorless oil, which was used directly without further purification.

Di-*tert*-butyl 1-phenylhydrazine-1,2-dicarboxylate (**14**; 3.72 g, 10.1 mmol, 1 equiv.) was dissolved in methanol (25 mL) and HCl (4 M in 1,4-dioxane, 25 mL, 101 mmol, 10 equiv.) was added slowly to the solution. The mixture was stirred for 4 h at room temperature. Thereafter, all the volatiles were removed in vacuo to give the hydrazine hydrochloride **15** as an orange solid.[23]

The imidate **13** was dissolved in methanol (40 mL, 0.4 M) and added to the hydrazine hydrochloride **15**. HCl (4 M in 1,4-dioxane, 250 μL, 1.01 mmol, 0.1 equiv.) was added to the reaction and the mixture was stirred at room temperature overnight. All the volatiles were removed in vacuo and the resulting amidrazone **16** was used without purification in the next step. R_f (CH_2Cl_2/MeOH, 90:10) = 0.19 (UV, $KMnO_4$).

The amidrazone **16** was dissolved in chlorobenzene (10 mL, 1 M) and activated molecular sieves (4 Å) were added to the solution. Triethyl orthoformate (13.3 mL, 80 mmol, 8 equiv.) and HCl (4 M in 1,4-dioxane, 2.50 mL, 10 mmol, 1 equiv.) were added to the reaction mixture. The mixture was heated to 80 °C overnight resulting in a homogeneous solution. The molecular sieves were filtered off, washed with CH_2Cl_2, and the filtrate was concentrated in vacuo. The resulting oil was purified by flash column chromatography (CH_2Cl_2/MeOH, 95:5 to 90:10) on silica gel resulting in **7b** as a colorless solid (273 mg, 0.97 mmol, 10% over three steps). R_f (CH_2Cl_2/MeOH, 90:10) = 0.08 (UV, $KMnO_4$). FTIR (ATR): $\tilde{\nu}$ = 3437, 3014, 2947, 2843, 1674, 1588, 1526, 1585, 1549, 1434, 1384, 1303, 1265, 1176, 1106, 1017, 969, 907, 781, 727, 640, 597 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 11.23 (s, 1 H), 7.48 (t, J = 8.6 Hz, 1 H), 6.66 (d, J = 8.6 Hz, 2 H), 4.92–4.90 (m, 2 H), 3.81 (s, 6 H), 3.22 (t, J = 7.7 Hz, 2 H), 2.92–2.82 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 161.5, 155.7, 144.4, 133.6, 113.3, 104.3, 56.5, 48.7, 27.0, 22.2 ppm. HRMS (ESI): calcd. for $C_{13}H_{16}N_3O_2^+$ 246.1237; found 246.1246.

***N*,*N*′-Bis(2,6-dimethoxyphenyl)formamidine (19):**[21] Triethyl orthoformate (689 μL, 4.14 mmol, 1 equiv.) and acetic acid (12 μL, 0.21 mmol, 0.05 equiv.) were added to a round-bottomed flask containing 2,6-dimethoxyaniline (**10**; 1.26 g, 8.27 mmol, 2 equiv.). The flask was equipped with a distillation apparatus and flushed with argon. The mixture was heated at 140 °C for 3 h and afterwards at 160 °C for 0.5 h. Upon cooling the reaction mixture to room temperature it solidified. Pentane (20 mL) was added, the mixture was stirred, and the resulting precipitate was filtered off and washed with pentane resulting in 1.18 g (3.72 mmol, 90%) of **19** as a colorless solid. R_f (CH_2Cl_2/MeOH, 95:5) = 0.24 (UV). FTIR (ATR): $\tilde{\nu}$ = 2999, 2934, 2831, 1664, 1581, 1461, 1430, 1311, 1256, 1204, 1108, 1033, 984, 801, 768, 715, 616 cm^{-1}. ^{1}H NMR (300 MHz, C_6D_6): δ = 9.04 (s, 1 H), 6.79 (t, J = 8.3 Hz, 2 H), 6.36 (d, J = 8.3 Hz, 4 H), 3.26 (s, 12 H) ppm. ^{13}C NMR (101 MHz, C_6D_6): δ = 154.7, 152.3, 125.5, 122.2, 100.5, 55.6 ppm. HRMS (ESI): calcd. for $C_{17}H_{20}N_2O_4H^+$ 317.1496; found 317.1500.

1,3-Bis(2,6-dimethoxyphenyl)-4,5-dihydro-1*H*-imidazol-3-ium Chloride (8b):[18] Formamidine **19** (268 mg, 0.85 mmol, 1 equiv.) was dissolved in dry 1,2-dichloroethane (670 μL, 8.46 mmol, 10 equiv.) in a flame-dried Schlenk tube. Hünig's base (158 μL, 0.93 mmol, 1.1 equiv.) was added to the mixture and the Schlenk tube was evacuated until the solvent started bubbling. The tube was sealed under static vacuum and the mixture stirred at 120 °C for 24 h. All the volatiles were removed in vacuo and the resulting yellow solid was purified by flash column chromatography (CH_2Cl_2/MeOH, 95:5 to 90:10) on silica gel and **8b** was obtained as an off-white solid (152 mg, 0.40 mmol, 47%). R_f (CH_2Cl_2/MeOH, 90:10) = 0.18 (UV, $KMnO_4$). FTIR (ATR): $\tilde{\nu}$ = 3006, 2941, 2838, 1614, 1597, 1479, 1449, 1251, 1169, 1106, 981, 854, 774, 728, 558, 533 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.26 (s, 1 H), 7.33 (t, J = 8.5 Hz, 2 H), 6.65 (d, J = 8.6 Hz, 4 H), 4.62 (s, 4 H), 3.93 (s, 12 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 160.4, 155.2, 131.2, 112.8, 104.7, 56.7, 51.6 ppm. HRMS (ESI): calcd. for $C_{19}H_{23}N_2O_4^+$ 343.1652; found 343.1666.

1,3-Bis(2,6-dimethoxyphenyl)-4,5-dihydro-1*H*-imidazol-3-ium Tetrafluoroborate (8b′):[17] 2,6-Dimethoxyaniline (**10**; 872 mg, 5.69 mmol, 2 equiv.) was dissolved in 1,2-dibromoethane (245 μL, 2.85 mmol, 1 equiv.) in a flame-dried Schlenk tube and the flask was sealed under argon. The mixture was stirred at 100 °C for 14.5 h resulting in a solid reaction mixture, which was dissolved in CH_2Cl_2 (20 mL) and 1 M aq. NaOH (20 mL). The aqueous phase was extracted with CH_2Cl_2 (3 × 20 mL) and the mixed organic phases were washed with brine, dried with Na_2SO_4, and filtered. Removal of all the volatiles in vacuo resulted in diamine **18** as a red-colored oil, which was used directly in the next step without further purification.

The diamine **18** was dissolved in triethyl orthoformate (5 mL, 30 mmol, 10 equiv.) in a flame-dried Schlenk tube and ammonium tetrafluoroborate (312 mg, 2.97 mmol, 1.05 equiv.) was added. The sealed tube was stirred at 120 °C for 16.5 h. All the volatiles were removed in vacuo and the resulting brown oil was purified by flash column chromatography (toluene/MeOH, 90:10) on silica gel resulting in **8b′** as an off-white solid (195 mg, 0.45 mmol, 16% over two steps). R_f (toluene/MeOH, 90:10) = 0.05 (UV, $KMnO_4$). FTIR (ATR): $\tilde{\nu}$ = 3098, 3017, 2951, 2847, 1614, 1599, 1484, 1435, 1316, 1300, 1258, 188, 1113, 1051, 1024, 775, 723 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.02 (s, 1 H), 7.36 (t, J = 8.5 Hz, 2 H), 6.67 (d, J = 8.5 Hz, 4 H), 4.55 (s, 4 H), 3.94 (s, 12 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 160.4, 155.2, 131.3, 112.7, 104.7, 56.7, 51.3 ppm. HRMS (ESI): calcd. for $C_{19}H_{23}N_2O_4^+$ 343.1652; found 343.1669.

1,3-Bis(2,6-dimethoxyphenyl)-1*H*-imidazol-3-ium Iodide (9b):[22] Formamidine **19** (511 mg, 1.62 mmol, 1 equiv.) was dissolved in DMF (16 mL, 0.1 M) and the solution was cooled to 0 °C. After adding NaH (60% dispersion in mineral oil, 116 mg, 2.91 mmol, 1.8 equiv.), the mixture was stirred for 5 min at 0 °C, warmed to room temperature, and stirred for 100 min. Bromoacetaldehyde dimethyl acetal (380 μL, 3.23 mmol, 2 equiv.) was added and the mixture was heated at 76 °C for 90 min. All the volatiles were removed in vacuo and acetonitrile (20 mL) was added to the resulting yellow solid. The mixture was filtered and the colorless precipitate was washed with acetonitrile. The solvent of the filtrate was removed

in vacuo and the resulting yellow oil was purified by flash column chromatography (CH_2Cl_2 to CH_2Cl_2/MeOH, 95:5) on silica gel to yield **20** (563 mg, 1.39 mmol, 86%). R_f (CH_2Cl_2/MeOH, 90:10) = 0.41 (UV).

Compound **20** (563 mg, 1.39 mmol, 1 equiv.) was dissolved in acetonitrile (14 mL, 0.1 M) and $BF_3{\cdot}Et_2O$ (1.05 mL, 8.35 mmol, 6 equiv.) was added to the solution. After stirring the mixture at 70 °C for 3 h, additional $BF_3{\cdot}Et_2O$ (3 equiv.) was added. The mixture was stirred at 70 °C for 16 h. After cooling to room temperature all the volatiles were removed in vacuo and methanol (14 mL, 0.1 M) and sodium iodide (1.04 g, 6.95 mmol, 5 equiv.) were added to the residue. The mixture was heated at reflux for 30 min and subsequently all the volatiles were removed in vacuo. The residue was purified by flash column chromatography (CH_2Cl_2/MeOH, 97.5:2.5 to 90:10) on silica gel to obtain **9b** (503 mg, 1.07 mmol, 77%) as a slightly yellow solid. R_f (CH_2Cl_2/MeOH, 95:5) = 0.20 (UV). FTIR (ATR): $\tilde{\nu}$ = 3188, 3168, 3016, 2982, 2943, 2841, 1676, 1596, 1551, 1484, 1434, 1330, 1301, 1262, 1110, 1085, 1051, 1023, 959, 783, 753, 728, 651, 605 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.92 (t, J = 1.5 Hz, 1 H), 7.63 (d, J = 1.5 Hz, 2 H), 7.45 (t, J = 8.6 Hz, 2 H), 6.74 (d, J = 8.6 Hz, 4 H), 3.90 (s, 12 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 154.1, 138.9, 132.5, 124.1, 111.8, 104.9, 56.9 ppm. HRMS (ESI): calcd. for $C_{19}H_{21}N_2O_4^+$ 341.1496; found 341.1499.

General Procedure for the Catalysis

Hydroacylation of Cyclopropene 2: A flame-dried Schlenk tube was charged with aldehyde (1 equiv.), K_2CO_3 (1 equiv.), and the NHC precursor (x mol-%). Dry THF (0.25 M) and 3-methyl-3-phenylcyclopropene (**2**; 1.5 equiv.) were added through a syringe. The tube was sealed under argon and stirred at 40 °C for 24 h. The reaction mixture was filtered through a short pad of silica and all the volatiles of the filtrate were removed in vacuo. The yield was either measured by ^1H NMR spectroscopy using CH_2Br_2 as internal standard or by isolation of the acylcyclopropane by flash column chromatography on silica gel (pentane/ethyl acetate, 98:2).

Intramolecular Hydroacylation of 23: A flame-dried Schlenk tube was charged with the aldehyde **23** (1 equiv.) and the NHC precursor (x mol-%) in a glovebox. Dry dioxane (0.5 M) and DBU (2x mol-%) were added through a syringe. The tube was sealed and stirred at 120 °C for 2 h. The reaction mixture was filtered through a short pad of silica and all the volatiles were removed in vacuo. The yield was either measured by ^1H NMR spectroscopy using CH_2Br_2 as internal standard or by isolation of the chromanone **24** by flash column chromatography on silica gel (pentane/ethyl acetate, 95:5).

Supporting Information (see footnote on the first page of this article): Details of the synthesis of the starting materials, description of the catalysis, NMR spectra, and crystallographic data.

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[23] As reported previously (see ref.[8]), deprotection also yields about 15% of 4-chloro-2,6-dimethoxyaniline. As this byproduct was unreactive in the following steps and easily removed in the subsequent reactions, the crude mixture of **15** and the chlorinated aniline was used without further purification.

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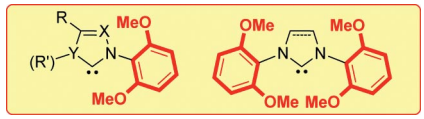
Organocatalysts

The synthesis and crystal structures of four highly electron-rich 2,6-dimethoxyphenyl-substituted NHCs are reported. These NHCs should have interesting applications as ligands or in NHC organocatalysis.



Keywords: Carbenes / Organocatalysis / Umpolung / Hydroacylation

