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Allylpalladium(II) Histidylidene Complexes and Their Application in Z-Selective Transfer Semihydrogenation of Alkynes

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We have studied the use of amino acid histidine as a precursor for *N*-heterocyclic carbene (NHC) ligands. This natural amino acid possesses an imidazole substituent, which makes it an interesting NHC precursor that contains both an acid and an amino functionality. These functionalities may be used for further tuning of NHC complexes. We have developed routes for the synthesis of symmetric and dissymmetric alkyl, benzyl, and aryl-substituted histidinium salts.

Subsequently, the corresponding Ag and Pd histidylidenes were synthesized and the palladium complexes were tested in the Z-selective transfer semihydrogenation of alkynes. Histidylidene palladium complexes that contain additional donor functionalities were found to display good selectivities. The best catalytic results were obtained with a Pd-histidylidene complex that contains two picolyl functional groups.

Introduction

N-Heterocyclic carbenes (NHCs) have found application in functional materials, transition-metal catalysis, organo-catalysis, bioorganometallic chemistry, and organometallic chemistry.^[1–8] The development of imidazolium salts, NHC ligands, and methodologies that allow further modification of these compounds would have a great impact on their applications.

Imidazolium and imidazolinium salts are the most common NHC precursors and they also form the basis of many types of ionic liquids.^[1,9] Imidazoles and their derivatives possess four sites for functionalization: the wing tips and the backbone of the imidazole. These compounds can be synthesized through five archetypal routes: (I) multicomponent synthesis of imidazolium compounds, (II) multicomponent synthesis of a substituted imidazole and its subsequent functionalization, (III) two-step functionalization of imidazole (derivatives), (IV) synthesis of a diamine compound and subsequent ring-closure with tri-

ethylorthoformate, and (V) reacting formamidines with di-electrophiles, which provides an imidazolidine.^[1,10–13] Synthesis of backbone-functionalized NHCs through these routes is less trivial.^[14–16] Nevertheless, alternative strategies toward these compounds would lead to a wider versatility in NHC ligands and options for the fine-tuning of catalyst reactivity. This makes development of such strategies desirable.^[15]

Applying readily available backbone functionalized imidazoles as starting materials for NHC ligands may circumvent laborious or challenging synthetic procedures; therefore, the use of the naturally occurring amino acid histidine is an appealing strategy. Both the amine and acid functional groups of histidine can be functionalized by using well-established chemistry.^[17–21] Histidine can be converted into a histidinium salt through a methodology that is similar to Route III described above. This allows the synthesis of NHC precursors that possess four handles for further functionalization (Scheme 1), which makes histidylidenes very versatile ligands. An additional reason why histidine is an interesting precursor for NHC ligands is that it is present in many biological molecules. Hence, the development of histidine as a precursor for NHC ligands is also relevant for bioinorganic and bioorganometallic applications.^[22,23]

Histidylidenes, NHCs that are derived from histidine, have only recently been explored by Erker et al.^[24] and by Albrecht et al.^[25–28] The alkylation of histidine was also reported in studies toward chiral ionic liquids.^[29,30] The publications by Albrecht et al. and several other publications show that NHCs, histidylidenes, and other NHCs derived

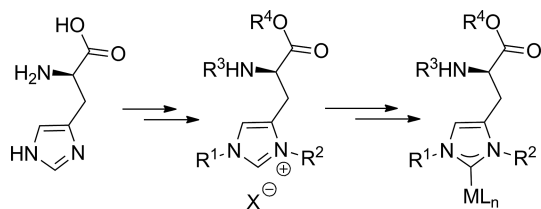
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Scheme 1. Histidine as a starting material for NHCs.

from natural compounds^[31–35] are highly interesting compounds for bioorganometallic applications.^[4,36] For instance, amino acid derived Au and Ag-NHC compounds have been demonstrated to possess antitumor activity.^[37–39]

Until now, only histidylidenes bearing simple alkyl wing-tip substituents have been reported. The wing tips of the NHC are important for the fine-tuning of the catalytic performance of the transition-metal complex. A wider variation in these precursors should increase the applicability of these compounds. Therefore, we set out to expand the synthetic methodologies for relevant precursors of histidylidene transition-metal catalysts. We investigated methodologies that allow the synthesis of symmetric and dissymmetric alkyl-, benzyl-, and aryl-substituted histidinium salts. Subsequently, the newly developed ligand precursors were applied in the synthesis of Ag^I and Pd^{II} histidylidene complexes. The catalytic properties of the palladium complexes in the *Z*-selective transfer semihydrogenation of alkynes were also investigated.^[40–46]

The semihydrogenation of alkynes is one of the most reliable methods with which to selectively synthesize *Z*-alkenes,^[41,47] which are part of many biologically and pharmaceutically active compounds. The alkenes are produced both as bulk and as specialty compounds.^[41,48–50] For laboratory-scale synthetic purposes, the transfer semihydrogenation is a more practical methodology because it circumvents the use of hydrogen gas by using a hydrogen donor molecule. Most often the donor is ammonium formate. In transfer semihydrogenation, the chemoselectivity of the catalyst is a key aspect because many side products may be formed such as the corresponding *E*-alkene and alkene migration products as well as the corresponding alkane, which is the product of further reduction of those alkenes. The substitution of NHC catalysts has a pronounced influence on the selectivity of the transfer semihydrogenation reaction.^[40] Therefore, the extended possibilities for functionalization and the ease of access to histidylidenes may lead to

the development of NHC-based catalysts with improved selectivity for transfer semihydrogenation. To this end, we studied the influence of the histidylidene substitution pattern on the selectivity.

Results and Discussion

Synthesis of Histidinium Salts

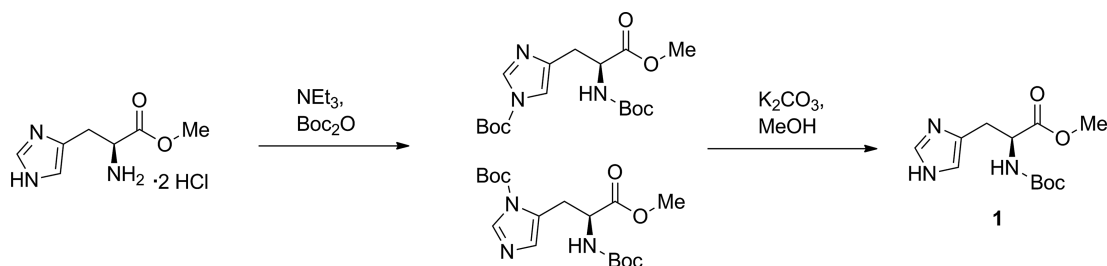
One of the reasons for our interest in histidine as a precursor for NHC complexes is that it provides four handles for functionalization: the two nitrogen atoms of the imidazolyl, the amino, and the acid group (Scheme 2). The amine and the acid group are protected to allow the selective synthesis of the histidinium salts. We chose protecting groups that can be removed selectively so that both the free acid and amine histidylidenes can be obtained. This design allows the incorporation of histidylidenes in, for instance, catalyst heterogenization or synthetic biomolecular scaffolds.^[51]

The carboxylic acid group was protected in the form of a methyl ester, which can be removed under basic conditions. We chose a *tert*-butyloxycarbonyl (Boc) group for the protection of the amine. This group affords a carbamate that is unreactive under basic conditions, but may be cleaved by trifluoroacetic acid (TFA) or a 4 M solution of HCl in an organic solvent. Boc-protection of the histidine methyl ester is performed in a two-step reaction, which affords precursor **1** (Scheme 2).^[19]

We then employed three routes to synthesize histidinium salts: 1) Direct benzylation of Boc-protected histidine; 2) the cyclic urea route; and 3) the arylation of Boc-protected histidine.

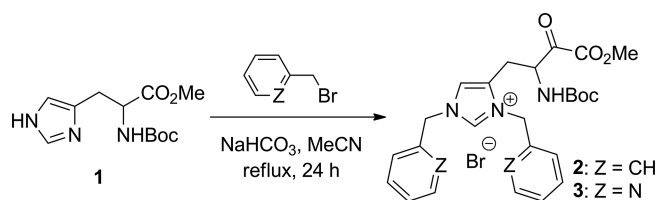
Direct Benzylation

The direct benzylation of protected histidine (Scheme 3) **1** provides symmetrically substituted benzyl functionalized imidazolium bromides. When benzyl (Bn) bromide was used (*Z* = CH), compound **2** was obtained in quantitative yield. When picolyl (Pic) bromide was used (*Z* = N), formation of several side products was observed by TLC analysis. Column chromatography allowed isolation of the pure product **3** in a decent yield of 80%. The ¹H NMR spectra show two separate A-B systems for the diastereotopic benz-



Scheme 2. Boc-histidine methyl ester, as precursor for the synthesis of the histidinium salts.

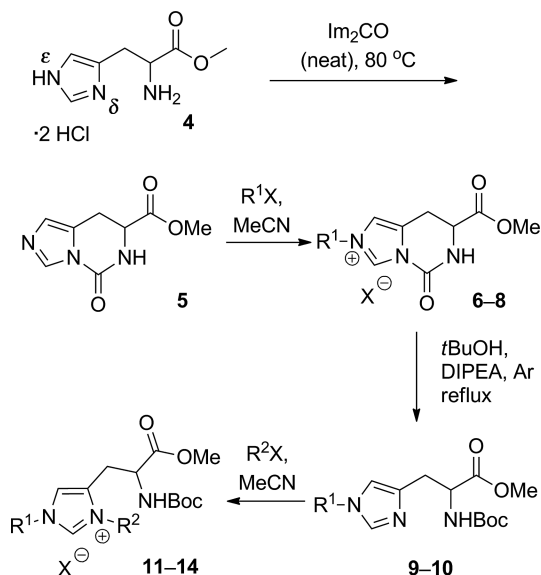
ylic CH₂ protons, indicating that these protons are not equivalent on the NMR timescale.



Scheme 3. Synthesis of symmetrically substituted benzylic histidinium bromides.

The Cyclic Urea Approach

Subsequently, we employed the cyclic urea approach, which allows the synthesis of dissymmetrically substituted histidinium salts and further tuning of the properties of the NHC metal complex. This is not straightforward because histidine has two tautomeric forms, which means that the δ - and the ϵ -nitrogen of the imidazole possess both imine and amine character (compound **4**, Scheme 5).^[20] Therefore, mixtures of regioisomers are obtained when the imidazole is reacted with one equivalent of an electrophile. To obtain the desired dissymmetrically substituted histidinium salts, we applied a route based on the report by Hodges and Chivikas,^[17] and was improved by Brégeon et al.^[30] (Scheme 4).



Scheme 4. The cyclic urea route toward dissymmetrically substituted histidinium salts.

This cyclic urea route induces regioselectivity because only the six-membered cyclic urea **5** can be formed. The second nitrogen atom can then be functionalized selectively through nucleophilic substitution. Subsequently, the R¹-functionalized urea compounds can be ring-opened by reaction with an alcohol, which liberates the δ -nitrogen atom of the imidazole, and provides a carbamate-protected amine. The use of *t*BuOH affords the Boc-protected histidine,

which is the protection group we chose in the design of the general synthetic route (Scheme 3). A disadvantage of applying *t*BuOH as a ring-opening reagent is its poor nucleophilicity, which is the cause of the low yields. The report by Brégeon shows that the yields could be improved by using less sterically hindered alcohols, such as methanol.^[30] Therefore, the overall yields may be improved by a minor synthetic variation, if the deprotection of the amine is not required. Compounds **9** and **10** (Table 1) can then be alkylated, once more, with another electrophile (R²-X) to afford histidinium salts.

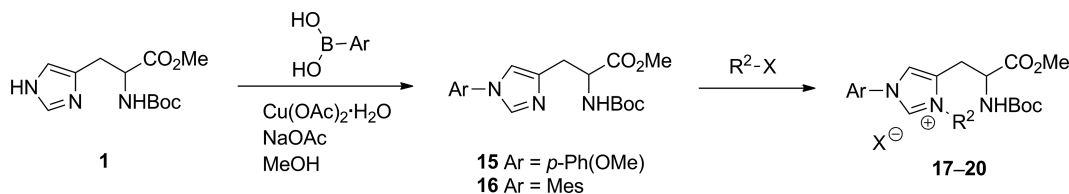
Table 1. Histidines and histidinium salts synthesized through the cyclic urea route.

	R ¹	R ²	X	Yield [%]
6	Bn			>99
7	Pic			72
8	<i>i</i> Pr			0
9	Bn			30
10	Pic			25
11	Bn	Me	I	>99
12	Bn	Pic	Br	68
13	Bn	<i>i</i> Pr	I	0
14	Pic	Me	I	58

By using this cyclic urea route, we synthesized **6** and **7**, R¹-functionalized imidazoles **9** and **10**, and histidinium salts **11–14**. However, we were unable to functionalize both the urea and the R¹-substituted imidazole compounds with isopropyl iodide (entries 3 and 8).

Chan–Lam–Evans Arylation and Subsequent Quaternization

A synthetic route to NHC ligands that have an aryl substitution on the wingtips is also highly desirable because many NHC compounds bearing aryl substituents display the best reactivities in catalytic applications.^[1,3] This is also true for our model reaction: the semihydrogenation of alkynes towards *Z*-alkenes.^[40,52] Several methods have been developed for the arylation of imidazoles; for instance, the Ullman^[53] and Buchwald^[54] coupling reactions. These methodologies have been applied in the arylation of imidazoles with aryl halides,^[55,56] aryllead(IV) reagents,^[57] arylboronic acids,^[58,59] and trifluoroaryl borates.^[60] Despite the tautomeric equilibrium of imidazoles, several *N*-arylation reactions were reported to have good chemoselectivities toward the ϵ -nitrogen atom of backbone-functionalized imidazoles.^[55,57] However, some of these methods are unpractical and may not be compatible with more functionalized histidine imidazoles.^[61,62] The Chan–Lam–Evans reaction with aryl boronic acids is an alternative reaction that operates under very mild conditions (Scheme 5).^[63,64] The regioselective *N*-arylation of a benzyl carbamate-protected histidine methyl ester with 4-methoxyphenylboronic acid gave yields of less than 10%.^[64] However, the improved Chan–Lam–Evans method developed by Campagne and co-workers gave yields of up to 31% of the desired compound. We adapted this protocol by performing the reac-



Scheme 5. Application of the Chan–Lam–Evans method to synthesize aryl-functionalized histidinium salts.

tion at room temperature and extending the reaction times. With these adjustments, we were able to obtain the *para*-methoxyphenyl **15** and mesityl **16** and *N*-arylated products in satisfactory yields of 84 and 61%, respectively.

Subsequently, these two aryl-functionalized histidines **15** and **16** were alkylated with a range of electrophiles (R^2 -X), which afforded another set of histidinium salts **17–20** (Table 2). This method proved to be reliable and gave access to a wide variety of histidylidene precursors. Histidinium salts **19** and **20** were obtained in reasonable to good yields, and were synthesized through the reaction of histidine **16** with a Pic or lutidyl (Lut) bromide, which appears to decompose during the reaction causing the decrease in yield.^[65] NMR spectroscopy and mass spectrometry suggest that the decomposition product also gives rise to transesterification of **16** and its product histidinium salts.

Table 2. *N*-Arylation of histidine precursor **1** and its subsequent alkylation to give aryl-substituted histidinium salts.

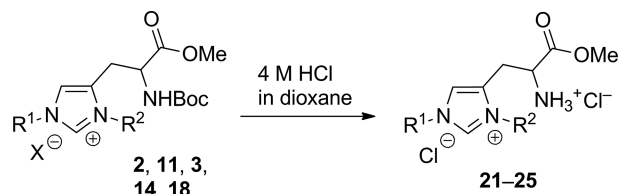
	Ar	R^2	X	Yield [%]
15	<i>p</i> -OMePh	–	–	84
16	Mes	–	–	61
17	<i>p</i> -OMePh	Me	I	>99
18	Mes	Me	I	>99
19	Mes	Pic	Br	51
20	Mes	Lut	Br	80

Histidinium Deprotection

After the development of the three routes for the synthesis of a variety of histidinium salts, we studied an approach for the deprotection of the amine and acid group. In the initial design, the protection groups were chosen in such a way that the amine and/or the acid functionality could be deprotected selectively. In this way, the free amine or acid compound could be prepared from a common precursor. Deprotection may be performed either after the synthesis of the histidinium salt, or after the synthesis of the histidylidene metal complex. NHCs generally lead to the formation of highly stable compounds. However, a wide range of transition-metal complexes and precursors may not be stable under the conditions that are used in the deprotection step. Therefore, deprotection of the desired functionality before complexation to the metal was considered desirable.

Boc-deprotection of an amino acid is a common synthetic procedure in organic chemistry. It is usually performed with TFA, or a 4 M solution of HCl in dioxane. In general, the synthesis of the desired NHC transition-metal complexes often involves a transmetalation step with a pre-

formed silver-NHC complex, which is driven by the precipitation of a silver halide. The application of TFA in the Boc-deprotection step may cause scrambling of the counterions of the imidazolium salt, which could give rise to issues later on in the synthesis during the transmetalation step. Therefore, the application of HCl in dioxane is preferred over TFA. An excess of HCl is used, therefore, anion metathesis takes place concurrently with deprotection, yielding products with only chloride anions. In the case of simple histidinium salts, which do not contain additional basic functionalities, the dicationic HCl salts are obtained. If additional basic functionalities are present in the compound (for instance picolyl moieties), tri- or tetracationic HCl salts are obtained (Scheme 6 and Table 3).

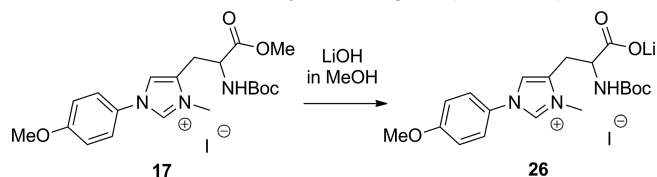


Scheme 6. Boc-Deprotection of histidinium salts.

Table 3. Yields for Boc-deprotection.

	R^1	R^2	Yield [%]
21	Bn	Bn	>99
22	Bn	Me	>99
23	Pic	Pic	>99
24	Pic	Me	>99
25	Mes	Me	92

Saponification of the methyl ester of **17** was performed by stirring the compound in a solution of MeOH with 10 equiv. LiOH, which provided **26**. TLC analysis showed full conversion of the starting material and, after workup, ¹H NMR spectroscopic analysis showed the presence of the imidazolium proton as well as the complete disappearance of the characteristic methyl ester signal (Scheme 7).



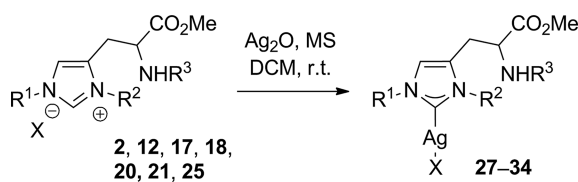
Scheme 7. Methyl ester deprotection of **17**.

Synthesis of Ag^I-Histidylidenes

After development of the methods for the synthesis of the histidinium salts, we investigated the generation of Ag^I

carbenes with silver oxide. The silver carbenes may subsequently be employed as carbene transfer agents to obtain the desired Pd histidylidene precatalysts. Our preference for this methodology was based on two factors: firstly, transmetalation from silver to the target precursor is a highly reliable and commonly applied method to obtain NHC complexes for a wide range of transition metals. This makes the synthesis of the silver carbenes also relevant for other possible transition-metal compounds.^[1,66] Secondly, this methodology is very mild and highly tolerant towards a variety of functionalities that are present in the histidinium salts.^[67]

Ag^I NHCs are generally synthesized by the reaction of an imidazolium salt with silver(I) oxide, which functions as a base as well as a complexing agent. We synthesized a wide range of Ag^I histidylidenes by stirring the ligand with 0.55 equiv. Ag₂O under inert conditions and with the exclusion of light (Scheme 8 and Table 4). The silver carbene is represented as an [Ag^I(NHC)(halido)] complex. However, a multitude of [Ag^INHC] coordination compounds may be formed.^[66,67] For simplicity, this representation was chosen. ¹H NMR spectroscopic analysis shows the absence of the imidazolium proton, and signals were observed in the ¹³C NMR spectrum around 180 ppm, which is a value that is typical for a silver carbene. For the Boc-protected histidinium salts, good to excellent yields were obtained for a range of R¹- and R²-substituents (compounds 27–32; Table 4).



Scheme 8. Synthesis of Ag^I histidylidenes.

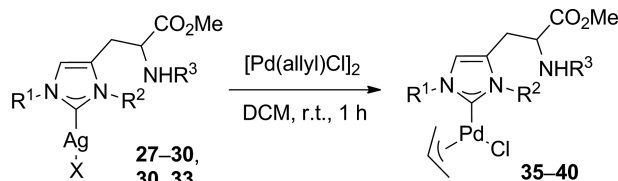
Table 4. Synthesized Ag^I histidylidenes.

	R ¹	R ²	R ³	X	Yield [%]
27	Bn	Bn	Boc	Br	95
28	Bn	Pic	Boc	Br	85
29	Pic	Pic	Boc	Br	80
30	<i>p</i> -OMePh	Me	Boc	I	78
31	Mes	Me	Boc	I	86
32	Mes	Lut	Boc	Br	89
33	Bn	Bn	H	Cl	96
34	Mes	Me	H	Cl	22

Complexes **27** and **29** display a high stability and can be stored as a solid for several weeks; they also tolerate manipulations in air. We also synthesized free-amine analogues **33** and **34**. Their precursors are ammonium chloride salts of the histidinium salts. An ammonium proton is more acidic than a histidinium proton. Therefore, we applied an extra half equivalent of Ag₂O as a base in the synthesis of **33** and **34** (Table 4). The presence of the free amine, which is a better ligand for silver than a carbamate, does not seem to interfere in the synthesis of **33**.

Synthesis of Pd^{II}-Histidylidenes

From these Ag^I carbenes, we performed transmetalation with [Pd^{II}(η³-allyl)Cl]₂ to obtain the histidylidene analogues of [Pd^{II}(NHC)(η³-allyl)Cl] complexes, which are highly stable, readily synthesized, and are good precatalysts for several reactions such as cross-coupling,^[68–72] and cyclopropanation,^[73] as well as the *Z*-selective semihydrogenation of alkynes^[74] (Scheme 9).



Scheme 9. Synthesis of Pd^{II} histidylidenes through transmetalation from their Ag^I histidylidene precursors.

With this method, we successfully synthesized a variety of compounds (Table 5), for which we observed several noteworthy properties. In previous studies, we found that the presence of hemilabile donors has a positive effect on the catalytic performance as well as on the stability of the complexes.^[52,74,75] For the described ligands, we find that the presence of a hemilabile picolyl or lutidyl group is also beneficial for the synthesis of the Pd complexes. Complexes **36**, **37** and **38** could be purified by column chromatography. This is in contrast to compounds **35** and **39**, which do not possess a hemilabile moiety, and decomposed during column chromatography forming [Pd(allyl)Cl]₂ and a cationic bis-NHC [Pd(histidylidene)₂(allyl)]⁺Cl[−] complex **41** (Figure 1). Similar complexes have been obtained with noncoordinating counterions.^[76,77]

Table 5. Synthesized Pd^{II}(allyl) histidylidenes.

	R ¹	R ²	R ³	Yield [%]
35	Bn	Bn	Boc	41
36	Bn	Pic	Boc	53
37	Pic	Pic	Boc	>99
38	Mes	Lut	Boc	93
39	<i>p</i> -OMePh	Me	Boc	0
40	Bn	Bn	H	31

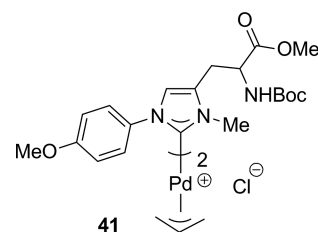


Figure 1. Cationic bis-NHC [Pd(histidylidene)₂(allyl)]Cl complex **41**.

The stability of complexes **37** and **38**, possessing hemilabile groups, is not surprising. We previously reported a wide variety of highly stable NHCs bearing a triazole group as a secondary donor.^[74] The instability of complexes not bearing a hemilabile donor and concomitant formation of

bis-histidylidene complexes is unexpected. In fact, similar NHC analogues that are not functionalized on the backbone could be isolated by column chromatography without decomposition.^[46,78] The difference between those species and those described here is that the NHC complexes without backbone functionalization bear an *N*-mesityl substituent. Possibly, the extra bulk of the mesityl group provides additional stabilization through steric protection. In this case, the incorporation of large (aryl) wingtips seems to be important for the stability of these compounds. Therefore, the Chan–Lam–Evans approach, which allows the introduction aryl functionalities on the wingtips of the NHC, may be particularly relevant.

We investigated the viability of using Boc-deprotection of Pd^{II} histidylidene complexes to obtain free amine species. Subjecting compound **35** to a solution with TFA resulted in decomposition of the complex. However, free amine Pd^{II} histidylidenes such as **40** can be synthesized through the previously developed route that uses free amine histidinium salts as ligand precursors (Scheme 9, Table 5).

We studied the structure of the histidylidenes further with X-ray crystallography. X-ray quality crystals were obtained through slow vapor diffusion of cyclohexane into a solution of **38** in tetrahydrofuran (THF) in the presence of nitric acid. This gave crystals of complex **42** that had a non-coordinating nitrate counterion (Figure 2).

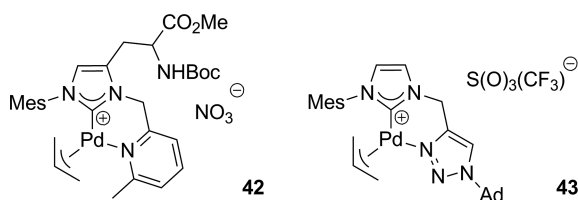


Figure 2. Complexes **42** and **43**.

The crystal structure contains cocrystallized cyclohexane and THF solvent molecules, some of which were heavily disordered and were treated as diffuse electron density by using the SQUEEZE algorithm.^[79] The absolute structure determination using Bijvoet pairs showed that the overall crystal structure is enantiopure, as indicated by the Flack parameter [$x = -0.02(2)$]^[93] (see Exp. Sect.). The asymmetric unit of the enantiopure crystal contains two independent Pd molecules. The chiral carbon of the amino acid moiety of both of these molecules is in the *S*-configuration (Figure 3). However, the metallacycles of these molecules are inverted with respect to each other (see the Supporting Information, SI2). The chirality of the starting material is thus retained in the crystal that was measured. This may indicate that, as for the similar method developed by Albrecht et al., the synthetic route reported herein leads to optically pure compounds.^[27] Further inspection of the crystal structure shows that the η^3 -coordinated allyl ligand was disordered and it was refined with a disorder model. This is in line with previous observations that there is no preference for either orientation of the allyl group. The observed bond lengths and geometry of **42** are normal for this type of compound (Figure 3, Table 6).^[69,80,81]

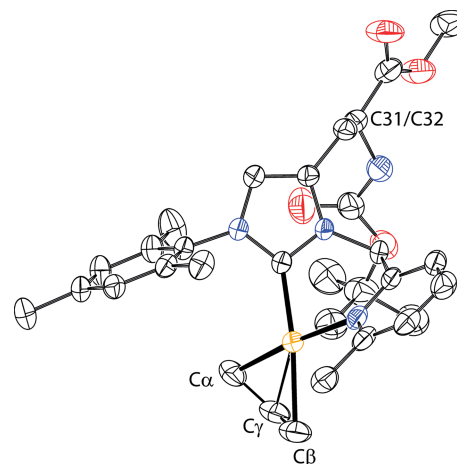


Figure 3. ORTEP representation of the cationic Pd^{II} histidylidene η^3 -allyl complex **42**. Ellipsoids are drawn at 50% probability. Hydrogen atoms, nitrate anion, and solvent molecules are omitted for clarity. Only one of two independent molecules is displayed. The disorder of the allyl ligand is not shown.

Table 6. Selected bond lengths and angles of **42** and **43**.^[74]

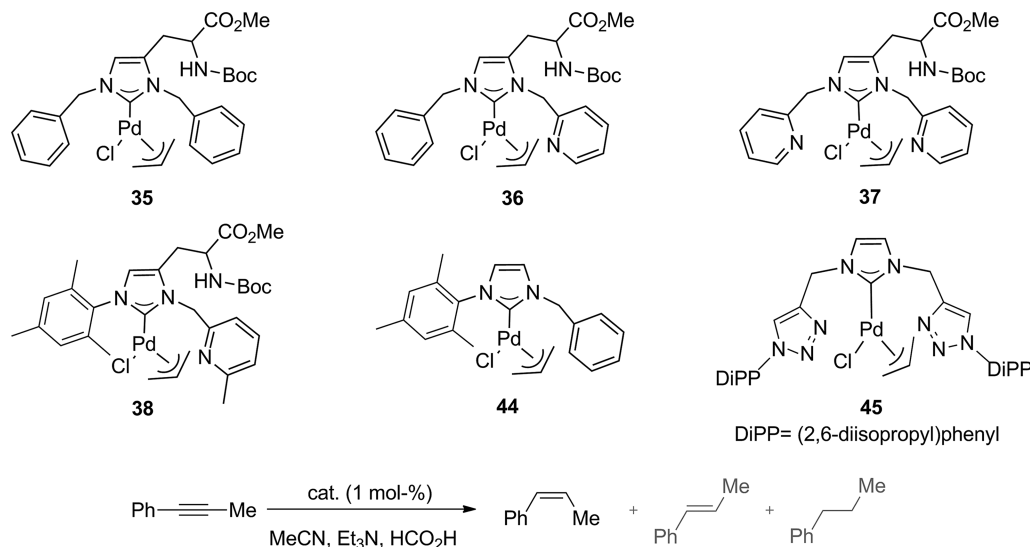
Entry	Bond lengths [Å]	42	43 ^[74]
1	Pd–NHC	2.015(5)/1.999(5)	2.044(3)
2	Pd–N	2.135(4)/2.148(5)	2.098(2)
3	Pd–C β	2.226(6)/2.111(7)	2.186(4)
4	Pd–C γ	2.139(10)/2.101(13)	2.163(7)
5	Pd–C α	2.102(5)/2.221(7)	2.111(5)
Entry	Angle [°]	42	43 ^[74]
6	NHC–Pd–N	85.31(16)/84.53(17)	86.42(11)
7	NHC–Pd–C α	100.0(2)/166.1(3)	103.05(15)
8	N–Pd–C β	106.4(2)/176.0(3)	101.94(11)

We compared the structure of **42** to the previously reported complex **43**^[74] (Figure 3, Table 6). These structures are similar, cationic, square planar [Pd^{II}(NHC)(η^3 -allyl)] bidentate complexes that possess a noncoordinating counterion. The Pd–NHC and the Pd–N distances are significantly longer for **42** (Table 6 entries 1 and 2). The CPK model of **42** suggests a steric interaction between the methyl of the lutidyl donor and the allyl ligand, and an interaction between the allyl ligand and the mesityl wingtip substituent (see the Supporting Information, SI3). We attribute the differences in bond lengths to this steric congestion around the Pd center. The large Boc-group may also contribute to the steric crowding around the Pd center.

Transfer Semihydrogenation

Subsequently, we tested complexes **35–38** as well as **44** and **45**^[46] in the transfer semihydrogenation of 1-phenyl-1-propyne toward *Z*-1-phenyl-1-propene (Scheme 10).

We evaluated the influence of the (protected) amino acid functionality, and the hemilabile donors on the reaction with this set of precatalysts (Table 7). The performance of **35–38** was put into context by comparison with the previously discussed complexes **44** and **45**.



Scheme 10. Investigated precatalysts in the Z-selective transfer semihydrogenation of 1-phenyl-1-propyne.

Table 7. The results of the Z-selective transfer semihydrogenation of 1-phenyl-1-propyne.^[a]

Cat.	TOF _{15%} ^[b]	Z-yield [%] ^[c]	Z-sel ^[d] (conv) [%]	Time to FC [h] ^[e]
35	9.6	38	94 (40)	[g]
36	12	80	95 (84) ^[f]	10.3 ^[h]
37	7.2	91	92 (>99)	28
38	18	68	68 (<99) ^[f]	18 ^[h]
44	38	88	92 (97) ^[f]	5.6
45	8.5	61	94 (64)	>>24 h ^[g]

[a] Reaction conditions: catalyst (1 mol-%), 1-phenyl-1-propyne (2.7 mmol), 70 °C. [b] In mol_{subs}/mol_{cat}·h. [c] GC-yield for the Z-alkene. [d] Selectivity toward the Z-alkene in% ([response factor corrected GC area of Z-alkene]/[response factor corrected GC area of the total products]·100%) at the corresponding conversion, given in parentheses. [e] Time to reach full conversion of the substrate. [f] Strong over-reduction and isomerization of the Z-alkene product was observed after full substrate conversion. [g] Reaction was stopped after 24 h. [h] Extrapolated time to full conversion.

Compounds **35**, **36**, and **38** give over-reduction and isomerization of the product Z-alkene after full consumption of the substrate. This was also observed for compounds **44** and **45**. However, other systems were reported that do not display further conversion of the product Z-alkene.^[40,46,82–86] The substitution on the histidylidene ligand seems to be crucial for the performance of the catalyst. Incorporation of an aryl wingtip substituent on the ligand seems not only beneficial for the synthesis of these histidylidene complexes, but also for their catalytic performance. The bisbenzylic compound **35** loses activity during the reaction, most likely due to catalyst decomposition.

Conclusions

We have developed versatile and robust methodologies for the synthesis of symmetrically and dissymmetrically functionalized histidylidene ligand precursors. Especially, the methodology for arylation of histidine imidazoles,

which are notoriously difficult, has been improved. By careful selection of the protection groups, both the protected and selectively deprotected amino acid functionalities can be obtained. This allows facile access to a range of compounds via a single synthetic intermediate and provides a histidylidene precursor with four handles for the adaptation of its catalyst systems as well as implementation of these ligands in complex systems. These ligands are, therefore, interesting intermediates for the heterogenization of this type of compound and for their implementation in bioconjugates.^[4] We have synthesized a variety of Ag^I and Pd^{II}(η³-allyl) histidylidenes and investigated the activities of the palladium complexes in the Z-selective transfer semihydrogenation of an alkyne. We found that the substitution pattern of the ligand, and especially the presence of hemilabile groups, has significant effects on the reactivity of these compounds. Moreover, the presence of a mesityl substituent on the wingtips seems important for successful catalysis.

Experimental Section

General: Complex synthesis was performed by using Schlenk techniques under an atmosphere of dry nitrogen. Synthesis of the histidinium salts was performed in air, unless stated otherwise. When anhydrous solvents were used, these were prepared according to standard procedures and distilled prior to use.^[87] [Pd(η³-C₃H₅-Cl)₂], triethylamine, formic acid, and potassium *tert*-butoxide were purchased from Sigma–Aldrich. Compound **6** was synthesized according to the procedure reported by Jain et al.^[20] NMR spectra were recorded with Bruker AV 400 MHz, Bruker DRX 300, Bruker DRX 500 MHz, or Varian Mercury 300 MHz spectrometers. High-resolution mass spectra were recorded with a JEOL JMS SX/SX102A four-sector mass spectrometer; mass samples were loaded in a matrix solution (3-nitrobenzyl alcohol) onto a stainless steel probe and bombarded with xenon atoms with an energy of 3 keV. During the high-resolution FAB-MS measurements a resolving power of 10 000 (10% valley definition) was used.

1,3-Dibenzyl-4-{2-[(*tert*-butoxycarbonyl)amino]-3-methoxy-3-oxopropyl}-1*H*-imidazol-3-ium Bromide (2): NaHCO₃ (188 mg,

2.23 mmol) was added to a stirred solution of **1** (547 mg, 2.03 mmol) and benzyl bromide (725 μ L, 6.09 mmol) in MeCN (20 mL). The suspension was stirred and heated to reflux for 22 h, after which, TLC analysis (KMnO₄ indicator; CH₂Cl₂/MeOH, 9:1) showed full consumption of **1**. The reaction mixture was filtered and volatiles were removed by rotary evaporation. The crude product was dissolved in a minimal amount of CH₂Cl₂ and added dropwise to vigorously stirred Et₂O (200 mL). The white precipitate was filtered off, washed with Et₂O, and dissolved in CH₂Cl₂. All volatiles were removed to afford the title compound (1.1 g, >99%) as a white foam. ¹H NMR (400 MHz CD₂Cl₂): δ = 10.62 (s, 1 H, NCHN), 7.52–7.38 (m, 10 H, Ar), 7.13 (br. s, 1 H, Im-bb), 5.75 (d, J = 6.1 Hz, 1 H, NH), 5.56 (dd, J = 50.1, 15.2 Hz, 2 H, NCH₂Ar), 5.52 (dd, J = 20.4, 14.6 Hz, 1 H, NCH₂Ar), 4.46 (br. s, 1 H, α -CH), 3.68 (s, 3 H, OCH₃), 3.13 (ddd, J = 15.9, 5.1, 0.7 Hz, 1 H, β -CHH), 3.04 (ddd, J = 16.0, 7.8, 0.7 Hz, 1 H, β -CHH), 1.41 [s, 9 H, C(CH₃)₃] ppm. ¹³C NMR (75 MHz CD₂Cl₂): δ = 171.2 [CO(OMe)], 155.7 [CO(O*t*Bu)], 137.4 (NCHN), 133.6 [Im-bb(C_q)], 133.3 (C_q), 132.3 (C_q), 129.6 (ArCH), 129.6 [Ar(CH)], 129.4 [Ar(CH)], 129.2 [Ar(CH)], 128.5 [Ar(CH)], 120.9 [Im-bb(CH)], 80.5 [C(CH₃)₃], 53.3 (NCH₂Ph), 53.0 (α -CH), 52.3 (OMe), 51.3 (NCH₂Ph), 28.3 [C(CH₃)₃], 26.8 (β -CH₂) ppm. MS (FAB-TOF): m/z calcd. for C₂₆H₂₃O₄N⁺ 450.2387; found 450.2397.

4-{2-[(*tert*-Butoxycarbonyl)amino]-3-methoxy-3-oxopropyl}-1,3-bis-(pyridin-2-ylmethyl)-1*H*-imidazol-3-ium Bromide (3): NaHCO₃ (439 mg, 4.98 mmol) was added to a stirred suspension of **1** (134 mg, 0.50 mmol) and 2-(bromomethyl)pyridine hydrobromide (264 mg, 1.05 mmol) in MeCN (10 mL) and the suspension was stirred and heated to reflux for 16 h, after which, TLC analysis (silica; KMnO₄ indicator; CH₂Cl₂/MeOH, 9:1) showed full consumption of **1**. The reaction mixture was filtered and volatiles were removed by rotary evaporation. The crude product was dissolved in a minimal amount of CH₂Cl₂ and was added dropwise to vigorously stirred Et₂O (100 mL). The light-brown precipitate was filtered off, washed with Et₂O, and dissolved in CH₂Cl₂. The mixture was concentrated and purified by column chromatography (CH₂Cl₂/MeOH, 95:5→9:1) to afford **3** (219 mg, 80%) as a light-brown foam. ¹H NMR (400 MHz, CD₂Cl₂): δ = 10.52 (d, J = 1.1 Hz, NCHN), 8.62–8.50 (m, 2 H, Py-*H*2, Py-*H*2'), 7.78 (ddd, J = 15.9, 7.7, 1.8 Hz, 2 H, Py-*H*4, Py-*H*4'), 7.68 (t, J = 8.8 Hz, 2 H, Py-*H*3, Py-*H*3'), 7.47 (s, 1 H, Im-bb), 7.34–7.30 (m, Py-*H*5, Py-*H*5'), 5.99 (d, J = 6.5 Hz, 1 H, NH), 5.68 (dd, J = 66.3, 15.5 Hz, 2 H, NCH₂Py), 5.60 (s, 2 H, NCH₂Py), 4.53 (d, J = 5.7 Hz, 1 H, α -CH), 3.70 (s, 2 H), 3.27 (dd, J = 14.6, 4.2 Hz, 1 H, β -CHH), 3.22 (dd, J = 15.3, 6.4 Hz, 1 H, β -CHH), 1.37 [s, 9 H, C(CH₃)₃] ppm. ¹³C NMR (126 MHz, CD₂Cl₂): δ = 171.6 [CO(OMe)], 155.9 [CO(O*t*Bu)], 153.4 (Py-C6, Py-C6'), 150.5 (Py-C2), 150.4 (Py-C2'), 138.9 (NCHN), 138.0 (Py-C4), 138.0 (Py-C4'), 132.7 [Im-bb(C_q)], 124.4 [Py(CH)], 124.3 [Py(CH)], 124.0 [Py(CH)], 123.8 [Py(CH)], 121.6 [Im-bb(CH)], 80.7 [C(CH₃)₃], 54.9 (NCH₂Py), 53.3 (NCH₂Py), 53.0 (α -CH), 52.4 (OMe), 28.6, 27.1 ppm. MS (FAB-TOF): m/z calcd. for C₂₄H₃₀O₄N₅⁺ 452.2298; found 452.2294.

Methyl 5-Oxo-5,6,7,8-tetrahydroimidazo[1,5-*c*]pyrimidine-7-carboxylate (5): A method adapted from Hodges et al. was applied.^[17] L-Histidine methyl ester dihydrochloride (5.0 g, 20.7 mmol) and 1,1-carbonyldiimidazole (3.68 g, 22.7 mmol) were heated at 85 °C under vigorous mechanical stirring for 45 min. The slurry was cooled to ambient temperature and the reaction was quenched with H₂O (5 mL). After 45 min stirring, the suspension was extracted with CH₂Cl₂ (10 \times 20 mL, each checked by TLC for content). Organic fractions were combined, dried with MgSO₄ and concentrated by rotary evaporation. The crude product was washed with

Et₂O (2 \times 100 mL) and dried in vacuo to afford **5** (2.8 g, 72%) as a white solid. ¹H NMR (400 MHz, CDCl₃): δ = 8.15 (d, J = 0.5 Hz, 1 H, NCHN), 6.88 (d, J = 0.9 Hz, 1 H, Im-bb), 6.47 (br. s, 1 H, NH), 4.37 (dd, J = 8.4, 5.4 Hz, 1 H, α -CH), 3.81 (s, 3 H, OMe), 3.38 (ddd, J = 15.7, 5.3, 1.0 Hz, 1 H, β -CHH), 3.15 (ddd, J = 15.7, 8.7, 1.3 Hz, 1 H, β -CHH) ppm.

7-(Methoxycarbonyl)-5-oxo-2-(pyridin-2-ylmethyl)-5,6,7,8-tetrahydroimidazo[1,5-*c*]pyrimidin-2-ium Bromide (7): 2-(Bromomethyl)pyridine hydrobromide (142 mg, 0.56 mmol) was neutralized with saturated aqueous NaHCO₃ solution. The liberated 2-bromomethylpyridine was extracted with Et₂O (4 \times 15 mL). Organic fractions were combined, dried with anhydrous MgSO₄ and filtered. The solution was concentrated to approximately 3 mL then added to a stirred solution of **5** (142 mg, 0.56 mmol) in MeCN (5 mL). The diethyl ether was removed in vacuo and the reaction mixture was stirred for 5 d at room temperature and subsequently overnight at 50 °C, after which TLC analysis showed the absence of **5**. Volatiles were removed under reduced pressure and the crude product was dissolved in a minimal amount of CH₂Cl₂ and added dropwise to vigorously stirred Et₂O (25 mL). The orange precipitate was filtered off, washed with Et₂O, and dissolved in CH₂Cl₂. All volatiles were removed in vacuo, affording the title compound (136 mg, 72%) as an orange solid. ¹H NMR (400 MHz, CD₃CN): δ = 9.43 (d, J = 1.6 Hz, 1 H, NCHN), 8.58 (dd, J = 4.8, 4.0 Hz, 1 H, Py-*H*2), 8.00 (br. s, 1 H, NH), 7.87 (dt, J = 7.6, 2.0 Hz, 1 H, Py-*H*4), 7.55 (d, J = 7.6 Hz, Py-*H*5), 7.44–7.42 (m, 3 H, Im-bb, Py-*H*3), 5.57 (dd, J = 18.1, 16.0 Hz, 2 H, NCH₂Py), 4.60–4.56 (m, 1 H, α -CH), 3.73 (s, 3 H, OCH₃), 3.38 (d, J = 5.2 Hz, 2 H, β -CH₂) ppm. ¹³C NMR (101 MHz, CD₃CN): δ = 171.0 [CO(OMe)], 153.2 [Py(C_q)], 150.8 [Py(CH)], 145.1 [N(CO)N], 138.6 (Ar), 136.0 (Ar), 129.6 (Ar), 125.0 (Ar), 124.3 (Ar), 120.8 (Ar), 118.3 (Ar), 55.1 (α -CH), 53.9 (NCH₂Py), 52.6 (OMe), 22.8 (β -CH₂) ppm. HRMS (FAB): m/z calcd. for C₁₄H₁₅O₃N₄⁺ 287.1139; found 287.1142.

Methyl 2-[(*tert*-Butoxycarbonyl)amino]-3-[1-(pyridin-2-ylmethyl)-1*H*-imidazol-4-yl]propanoate (10): The method was adapted from Hodges et al.^[17] DIPEA (65 μ L, 0.39 mmol) was added to a suspension of **7** (130 mg, 0.35 mmol) in anhydrous *t*BuOH (2.5 mL) under an argon atmosphere. The reaction mixture was stirred overnight at 85 °C. Volatiles were evaporated and the residue was dissolved in CH₂Cl₂ (20 mL). The solution was washed with H₂O (2 \times 10 mL), washed with brine (10 mL), dried with MgSO₄ and concentrated to give a brown oil. The oil was impregnated on silica and purified by column chromatography (CH₂Cl₂/MeOH/acetone, 95:5:10) to afford **10** (44 mg, 35%) as a brown oil. ¹H NMR (400 MHz, CDCl₃): δ = 8.56 (m, 1 H, Py-*H*2), 7.65 (dt, J = 8.0, 2.0 Hz, 1 H, Py-*H*4), 7.49 (d, J = 1.2 Hz, NCHN), 7.26–7.22 (m, 1 H, Py-*H*3), 6.89 (d, J = 7.6 Hz, 2 H, Py-*H*5), 6.73 (s, 1 H, Im-bb), 5.90 (d, J = 8.0 Hz, 1 H, NH), 5.15 (s, 2 H, NCH₂Py), 4.55–4.51 (m, 1 H, α -CH), 3.64 (s, 3 H, OMe), 3.02 (dd, J = 16.1, 5.2 Hz, 1 H, β -CHH), 2.99 (dd, J = 14.4, 4.8 Hz, 1 H, β -CHH), 1.41 [s, 9 H, C(CH₃)₃] ppm. ¹³C NMR (101 MHz, CDCl₃): δ = 172.7 [CO(OMe)], 156.2 [CO(O*t*Bu)], 155.7 (Py-C6), 149.8 (Py-C2), 138.3 [Im-bb(C_q)], 137.6 (NCHN), 137.4 (Py-C4), 123.1 (Py-C5), 121.2 (Py-C3), 117.2 [Im-bb(CH)], 79.7 [C(CH₃)₃], 53.7 (α -CH), 52.6 (NCH₂Py), 52.2 (OMe), 30.5 (β -CH₂), 28.5 [C(CH₃)₃] ppm. MS (FAB-TOF): m/z calcd. for C₁₈H₂₅O₄N₄⁺ 361.1870; found 361.1875.

Methyl 3-(1-Benzyl-1*H*-imidazol-4-yl)-2-[(*tert*-butoxycarbonyl)amino]propanoate (9): The title compound was obtained as described for **10** and was previously reported by Hodges et al.^[17] ¹H NMR (400 MHz CDCl₃): δ = 7.42 (d, J = 8.2 Hz, 1 H, NCHN), 7.35–7.25 (m, 3 H, Ar), 7.08 (d, J = 6.7 Hz, 2 H, *o*-Ar), 6.62 (s, 1

H, Im-bb), 5.94 (d, $J = 8.2$ Hz, 1 H, NH), 5.01 (s, 2 H, NCH₂Ar), 4.54–4.46 (m, 1 H, α -CH), 3.60 (s, 3 H, OMe), 3.04 (A-B, $J = 14.8$, 5.5 Hz, 1 H, β -CHH), 2.95 (dd, $J = 14.6$, 4.8 Hz, 1 H, β -CHH), 1.40 [s, 9 H, C(CH₃)₃] ppm.

1-Benzyl-4-{2-[(*tert*-butoxycarbonyl)amino]-3-methoxy-3-oxopropyl}-3-methyl-1*H*-imidazol-3-ium Iodide (11): This compound was previously reported by Nakamura et al.^[88] Methyl iodide (25 μ L, 0.39 mmol) was added to a stirred solution of **6** (48 mg, 0.13 mmol) in MeCN (3 mL). The mixture was stirred and heated to reflux overnight, then volatiles were evaporated and the crude product was dissolved in a minimal amount of CH₂Cl₂. The mixture was added dropwise to vigorously stirred Et₂O (50 mL). The white precipitate was collected by filtration, washed with Et₂O and dissolved in CH₂Cl₂. All volatiles were removed in vacuo, which afforded the title compound (84 mg >99%) as a white foam. ¹H NMR (400 MHz, CDCl₃): $\delta = 10.01$ [s, 1 H, (NCHN)], 7.54–7.42 (m, 2 H, *o*-Ar), 7.42–7.35 (m, 3 H, Ar), 7.11 (s, 1 H, Im-bb), 5.62 (d, $J = 6.6$ Hz, 1 H, NH), 5.45 (dd, $J = 18.4$, 14.5 Hz, 2 H, NCH₂Ar), 4.51 (d, $J = 5.5$ Hz, 1 H, α -CH), 3.94 (s, 3 H, NMe), 3.71 (s, 3 H, OMe), 3.22 (dd, $J = 15.8$, 5.2 Hz, 1 H, β -CHH), 3.14 (dd, $J = 15.8$, 7.7 Hz, 1 H, β -CHH), 1.35 [s, 9 H, C(CH₃)₃].

3-Benzyl-5-{2-[(*tert*-butoxycarbonyl)amino]-3-methoxy-3-oxopropyl}-1-(pyridin-2-ylmethyl)-1*H*-imidazol-3-ium Bromide (12): 2-(Bromomethyl)pyridine hydrobromide (76 mg) was neutralized with saturated aqueous NaHCO₃ solution. The liberated 2-bromomethylpyridine was extracted with Et₂O (4 \times 15 mL) and the organic fractions were combined, dried with anhydrous MgSO₄, and filtered. The solution was concentrated to approximately 3 mL and then added to a stirred solution of **9** (97 mg, 0.27 mmol) in MeCN (5 mL). The Et₂O was removed in vacuo and the mixture was heated at 50 °C for 5 d, after which, TLC analysis showed the absence of **9**. Volatiles were evaporated in vacuo and the crude product was purified by column chromatography on a silica column (CH₂Cl₂/MeOH, 95:5) to afford the title compound (101 mg, 71%) as a white foam. ¹H NMR (400 MHz, CD₂Cl₂): $\delta = 10.30$ (s, 1 H, NCHN), 8.51 (d, $J = 4.4$ Hz, 1 H, Py-H2), 7.76 (td, $J = 7.7$, 1.8 Hz, 1 H, Py-H4), 7.67 (d, $J = 7.8$ Hz, 1 H, Py-H5), 7.51–7.36 (m, 5 H, Ar), 7.33–7.19 (m, 2 H, Ar), 6.22 (d, $J = 7.0$ Hz, 1 H, NH), 5.83 (d, $J = 15.6$ Hz, 1 H, NCHHPy), 5.67 (d, $J = 15.6$ Hz, 1 H, NCHHPy), 5.46 (s, 2 H, NCH₂Ph), 4.48 (d, $J = 6.4$ Hz, 1 H, α -CH), 3.64 (s, 3 H, OCH₃), 3.26–3.14 (m, 2 H, β -CH₂), 1.34 [s, 9 H, C(CH₃)₃] ppm. ¹³C NMR (101 MHz, CDCl₃): $\delta = 170.9$ [CO(OMe)], 155.4 [CO(O*t*Bu)], 152.2 (Py-C6), 149.6 (Py-C2), 137.5 (Py-C4), 132.8 (C_q), 132.2 (C_q), 129.1 [Ar(CH)], 128.7 [Ar(CH)], 123.7 [Ar(CH)], 123.1 [Ar(CH)], 119.9 [Im-bb(CH)], 80.1 [C(CH₃)₃], 53.1 (Im-CH₂-Ar), 52.6 (α -CH), 52.1 (OMe), 51.4 (Im-CH₂-Ar), 28.0 [C(CH₃)₃], 26.2 (β -CH₂) ppm. MS (FAB-TOF): m/z calcd. for C₂₅H₃₁O₄N₄⁺ 451.2340; found 451.2351.

5-{2-[(*tert*-Butoxycarbonyl)amino]-3-methoxy-3-oxopropyl}-1-methyl-3-(pyridin-2-ylmethyl)-1*H*-imidazol-3-ium Iodide (14): Methyl iodide (21 μ L, 0.33 mmol) was added to a stirred solution of **10** (40 mg, 0.11 mmol) in MeCN (2 mL). The mixture was stirred and heated to reflux overnight. Volatiles were evaporated and the crude product was dissolved in a minimal amount of CH₂Cl₂ and added dropwise to vigorously stirred Et₂O (50 mL). The white precipitate was filtered off, washed with Et₂O and dissolved in CH₂Cl₂. All volatiles were removed in vacuo to give the title compound (32 mg, 58%) as a white foam. ¹H NMR (400 MHz, CDCl₃): $\delta = 10.10$ (s, 1 H, NCHN), 8.54–8.52 (m, 1 H, Py-H2), 7.82–7.70 (m, 2 H, Py-H4, Py-H5), 7.40 (s, 1 H, Im-bb), 7.33–7.26 (m, 1 H, Py-H3), 5.63 (dd, $J = 20.5$, 14.7 Hz, 2 H, NCH₂Py), 5.54 (d, $J = 7.0$ Hz, 1 H, NH), 4.55 (d, $J = 5.3$ Hz, 1 H, α -CH), 3.94 (s, 3 H, NCH₃), 3.76

(s, 3 H, OMe), 3.26 (dd, $J = 15.7$, 5.2 Hz, 1 H, β -CHH), 3.15 (dd, $J = 15.8$, 7.2 Hz, 1 H, β -CHH), 1.37 [s, 9 H, C(CH₃)₃] ppm. ¹³C NMR (101 MHz, CDCl₃): $\delta = 170.7$ [CO(OMe)], 152.3 (Py-C6), 150.0 (Py-C2), 137.9 (Py-C4), 131.2 [Im-bb(C_q)], 124.2 (Py-C5), 124.1 (Py-C3), 121.2 [Im-bb(CH)], 80.9 [C(CH₃)₃], 54.1 (NCH₂Py), 53.3 (α -CH), 52.3 (OMe), 34.6 (NMe), 28.3 [C(CH₃)₃], 26.7 (β -CH₂) ppm. MS (FAB-TOF): m/z calcd. for C₁₉H₂₇O₄N₄⁺ 375.2032; found 375.2037.

Methyl 2-[(*tert*-Butoxycarbonyl)amino]-3-[1-(4-methoxyphenyl)-1*H*-imidazol-4-yl]propanoate (15): To a stirred solution of **1** (0.103 g, 0.382 mmol), NaOAc (0.094 g, 1.15 mmol), and Cu(OAc)₂·H₂O (7.62 mg, 0.0382 mmol) in MeOH (2 mL), 4-methoxyphenylboronic acid (0.174 g, 1.15 mmol) was added. The mixture was stirred at 20 °C for 26 h and concentrated in vacuo. The residue was dissolved in CH₂Cl₂ (35 mL), washed with H₂O (10 mL) and brine (10 mL), dried with MgSO₄, and concentrated in vacuo. Flash column chromatography of the residue (silica; EtOAc/*n*-hexane, 1:4) afforded the title product (120 mg, 0.320 mmol, 84%) as a yellow oil. ¹H NMR (300 MHz, CDCl₃): $\delta = 7.66$ (s, 1 H, NCHN), 7.29–7.21 (m, 2 H, Ar), 7.05–6.89 (m, 3 H, Ar, Im-bb), 5.91 (d, $J = 8.2$ Hz, 1 H, NH), 4.66–4.50 (m, 1 H, α -CH), 3.83 (s, 3 H, OMe), 3.72 (s, 3 H, OMe), 3.11 (m, 2 H, β -CH₂), 1.43 (s, 9 H, CH₃) ppm. ¹³C NMR (101 MHz, CDCl₃): $\delta = 172.57$ [CO(OMe)], 158.84 (*p*-Ar), 155.61 [CO(O*t*Bu)], 138.31 (NCHN), 135.49 (Im-bb), 130.51 (*i*-Ar), 122.91 (Ar), 116.28 (Im-bb), 114.87 (Ar), 79.64 [C(CH₃)₃], 55.59 (Ar-OMe), 53.49 (α -CH), 52.25 [CO(OMe)], 30.27 (β -CH₂), 28.34 [C(CH₃)₃] ppm. MS (FAB-TOF): m/z calcd. for C₁₉H₂₆N₃O₅⁺ 376.1872; found 376.1869.

Methyl 2-[(*tert*-Butoxycarbonyl)amino]-3-(1-mesityl-1*H*-imidazol-4-yl)propanoate (16): To a stirred solution of **1** (0.092 g, 0.342 mmol), NaOAc (0.080 g, 1.02 mmol), and Cu(OAc)₂·H₂O (6.8 mg, 0.0342 mmol) in MeOH (2 mL), 2,4,6-trimethylphenylboronic acid (0.166 g, 1.01 mmol) was added. The mixture was stirred at 20 °C for 6 d in an open air vessel. The mixture was dried over 6 d and the green residue was then dissolved in CH₂Cl₂ (35 mL), washed with H₂O (10 mL) and brine (5 mL), dried with MgSO₄ and concentrated in vacuo. Flash column chromatography of the residue (silica; EtOAc/*n*-hexane, 1:4) gave the title compound (80 mg, 0.206 mmol, 61%) as a yellow oil. ¹H NMR (300 MHz, CDCl₃): $\delta = 7.33$ (s, 1 H, NCHN), 6.94 (s, 2 H, Mes), 6.64 (s, 1 H, Im-bb), 6.03 (d, $J = 8.5$ Hz, 1 H, NH), 4.78–4.54 (m, 1 H, α -CH), 3.67 (s, 3 H, OMe), 3.12 (m, 2 H, β -CH₂), 2.32 [s, 3 H, *p*-Mes(Me)], 1.96 [d, $J = 8.7$ Hz, 6 H, *o*-Mes(Me)], 1.43 [s, 9 H, [C(CH₃)₃]] ppm. ¹³C NMR (101 MHz, CDCl₃): $\delta = 172.53$ [CO(OMe)], 155.54 [CO(O*t*Bu)], 138.89, 137.39, 137.22 (NCHN), 135.30 (*o*-Ar), 135.18 (*o*-Ar), 132.89 (*i*-Ar), 128.82 (*m*-Ar), 117.55 [Im-bb(CH)], 79.62 [C(CH₃)₃], 53.48 (α -CH), 52.29 (OMe), 30.05 (β -CH₂), 28.22 [C(CH₃)₃], 21.06 [Mes(*p*-Me)], 17.27 [Mes(*o*-Me)], 14.14 [Mes(*o*-Me)] ppm. MS (FAB-TOF): m/z calcd. for C₂₁H₃₀N₃O₄⁺ 388.2236; found 388.2234.

4-{2-[(*tert*-Butoxycarbonyl)amino]-3-methoxy-3-oxopropyl}-1-*p*-methoxyphenyl-3-methyl-1*H*-imidazol-3-ium Iodide (17): To a stirred solution of **15** (0.530 g, 1.41 mmol) in MeCN (12 mL), methyl iodide (0.44 mL, 7.06 mmol) was added. The mixture was stirred and heated to reflux for 6 h, then concentrated in vacuo to give the title compound (0.729 g, 1.41 mmol, 99%) as a yellow solid. ¹H NMR (300 MHz, CDCl₃): $\delta = 10.22$ (s, 1 H, NCHN), 7.65 (d, $J = 8.9$ Hz, 2 H, Ar), 7.46 (s, 1 H, Im-bb), 7.04 (d, $J = 8.9$ Hz, 2 H, Ar), 5.71 (d, $J = 7.3$ Hz, 1 H, NH), 4.66 (s, 1 H, α -CH), 4.12 (s, 3 H, NMe), 3.86 (s, 3 H, OMe), 3.83 (s, 3 H, OMe), 3.46–3.07 (m, 2 H, β -CH₂), 1.41 [s, 9 H, C(CH₃)₃] ppm. ¹³C NMR (75 MHz, CDCl₃): $\delta = 170.68$ [CO(OMe)], 160.80 (Ar), 155.47 [CO(O*t*Bu)],

135.40 (NCHN), 132.30, 127.33, 123.51 [Ar(CH)], 119.15 [Im-bb(CH)], 115.52 [Ar(CH)], 80.92 [C(CH₃)₃], 55.79 [*p*-Ar(OMe)], 53.24 (α -CH), 51.95 [CO(OMe)], 34.77 (NMe), 28.21 [C(CH₃)₃], 26.90 (β -CH₂) ppm. MS (FAB-TOF): *m/z* calcd. for C₂₀H₂₅N₃O₅⁺ 390.2029; found 390.2029.

4-{2-[(*tert*-Butoxycarbonyl)amino]-3-methoxy-3-oxopropyl}-1-mesityl-3-methyl-1*H*-imidazol-3-ium Iodide (18): To a stirred solution of **16** (0.500 g, 1.29 mmol) in MeCN (12 mL), methyl iodide (0.40 mL, 6.45 mmol) was added. The mixture was heated to reflux overnight and then concentrated in vacuo to give the title compound (0.686 g, 1.29 mmol, >99%) as a yellow solid. ¹H NMR (300 MHz, CDCl₃): δ = 9.79 (s, 1 H, NCHN), 7.05 (s, 1 H, Im-bb), 6.98 (s, 2 H, Ar), 5.64 (d, *J* = 7.4 Hz, 1 H, NH), 4.65 (s, 1 H, α -CH), 4.23 (s, 3 H, NMe), 3.79 (s, 3 H, OMe), 3.6–3.4 (m, 2 H, β -CH₂), 2.33 (s, 3 H, MeAr), 2.09 (s, 6 H, MeAr), 1.39 [s, 9 H, (CH₃)₃] ppm. ¹³C NMR (101 MHz, CD₃OD): δ = 170.93 [CO(OMe)], 156.15 [CO(O*t*Bu)], 140.90, 137.27 (NCN), 134.28, 132.90, 130.90, 129.16 (ArH), 122.0 [Im-bb(CH)], 79.56 [C(CH₃)₃], 51.99, 51.80 (OMe/ α -CH), 33.61 (NMe), 27.17 [C(CH₃)₃], 25.85 (β -CH₂), 19.67 [Mes(Me)], 16.25 [Mes(Me)], 16.22 [Mes(Me)] ppm. MS (FAB-TOF): *m/z* calcd. for C₂₂H₃₂N₃O₄⁺ 402.2393; found 402.2389.

4-{2-[(*tert*-Butoxycarbonyl)amino]-3-methoxy-3-oxopropyl}-1-mesityl-3-(pyridin-2-ylmethyl)-1*H*-imidazol-3-ium Bromide (19): To a solution of 2-(bromomethyl)pyridine hydrobromide (0.234 g, 0.927 mmol) in cold H₂O (10 mL), a saturated aqueous solution of Na₂CO₃ (10 mL) was added dropwise. The liberated 2-(bromomethyl)pyridine was extracted into Et₂O (3 \times 10 mL) at 0 °C, dried with MgSO₄ and filtered. The filtrate was concentrated to ca. 2 mL and added to a solution of **16** (0.116 g, 0.299 mmol) in MeCN (8.5 mL) at 0 °C. The ether was removed under reduced pressure and the resulting solution was warmed to room temperature. Molecular sieves (4 Å) were added after 2 h, and the mixture was stirred for 7 d. The molecular sieves were removed by filtration, then Et₂O was added to the filtrate, which caused the precipitation of a red solid. The organic layer was collected and concentrated in vacuo to give the title compound (86 mg, 0.154 mmol, 51%) as a yellow oil. ¹H NMR (400 MHz, CDCl₃): δ = 9.88 (s, 1 H, NCHN), 8.53 (d, *J* = 4.1 Hz, 1 H, Pyr), 7.92 (d, *J* = 7.7 Hz, 1 H, Pyr), 7.85 (t, *J* = 7.5 Hz, 1 H, Pyr), 7.36 (m, 1 H, Pyr), 7.12 (s, 1 H, Im-bb), 6.98 (s, 2 H, Mes), 6.18 (A-B system, 2 H, Im-CH₂-Pyr), 4.64–4.63 (m, 1 H, NH), 3.75 (s, 3 H, OMe), 3.39 (d, *J* = 6.6 Hz, 2 H, β -CH₂), 2.33 [s, 3 H, Mes(Me)], 2.09 [s, 3 H, Mes(Me)], 2.06 [s, 3 H, Mes(Me)], 1.39 [s, 9 H, [C(CH₃)₃]] ppm. ¹³C NMR (101 MHz, CDCl₃): δ = 170.87 [CO(OMe)], 160.08 (Pyr), 159.69 (Py), 155.47 [CO(O*t*Bu)], 151.86, 148.74, 141.10 (Ar), 138.59 (Ar), 138.25 (Ar), 134.21 (Ar), 134.12 (Ar), 132.80 (Ar), 130.55 (Ar), 129.65 (Ar), 124.08 (Ar), 124.03 (Ar), 120.87 (Ar), 80.44 [C(CH₃)₃], 52.85, 52.16, 50.84, 28.11 [C(CH₃)₃], 26.63 (β -CH₂), 20.97 [Mes(Me)], 17.39 [Mes(Me)] ppm. MS (FAB-TOF): *m/z* calcd. for C₂₇H₃₆N₄O₄⁺ 480.2731; found 480.2737.

5-{2-[(*tert*-Butoxycarbonyl)amino]-3-methoxy-3-oxopropyl}-3-mesityl-1-[(6-methylpyridin-2-yl)methyl]-1*H*-imidazol-3-ium Bromide (20): Compound **16** (410 mg, 1.06 mmol) and 2-(bromomethyl)-6-methylpyridine (236 mg, 1.27 mmol) were dissolved in MeCN (20 mL). The mixture was heated to reflux for 72 h, after which, TLC analysis showed the full conversion of **16**. All volatiles were removed in vacuo and the crude product was purified by column chromatography (silica;CH₂Cl₂/MeOH, 95:5 to 9:1) to give the title compound (527 mg, 87%) as an off-white foam. ¹H NMR (400 MHz, CD₂Cl₂): δ = 9.87 (s, 1 H, NCHN), 7.67 (t, *J* = 7.7 Hz, 1 H, Py-*H*4), 7.54 (d, *J* = 7.7 Hz, 1 H, Py-*H*3), 7.18–7.12 (m, 2 H, Im-bb, Py-*H*5), 7.05 (s, 2 H, Mes), 6.10 (d, *J* = 7.7 Hz, 1 H, NH),

6.06–5.95 (A-B system, 2 H, NCH₂Py), 4.63 (br. s, 1 H, α -CH), 3.73 (s, 3 H, OMe), 3.39–3.30 (m, 2 H, β -CH₂), 2.44 [s, 3 H, Lut(Me)], 2.35 [s, 3 H, Mes(*p*-CH₃)], 2.12 [s, 3 H, Mes(*o*-Me)] 2.1 [s, 3 H, Mes(*o*-Me)], 1.37 [s, 9 H, C(CH₃)₃] ppm. ¹³C NMR (126 MHz, CD₂Cl₂): δ = 171.6 [CO(OMe)], 159.4 (Py-C6), 155.9 [CO(O*t*Bu)], 152.7 (Py-C2), 141.4 (Ar), 139.4 (Ar), 137.9 (Ar), 135.0 (Ar), 133.5 (Ar), 131.7 (Ar), 130.1 (Ar), 123.4 (Ar), 122.4 (Ar), 120.3 (Ar), 80.1 [C(CH₃)₃], 53.0 (NCH₂Py), 52.7 (α -CH), 52.1 (OMe), 28.5 [C(CH₃)₃], 26.6 (β -CH₂), 24.3 [Lut(CH₃)], 21.1 [Mes(*p*-Me)], 17.7 [Mes(*o*-Me)] ppm. MS (FAB-TOF): *m/z* calcd. for C₂₈H₃₇O₄N₄⁺ 493.2808; found 493.2818.

4-(2-Ammonio-3-methoxy-3-oxopropyl)-1,3-dibenzyl-1*H*-imidazol-3-ium Chloride Hydrochloride (21): Compound **2** (265 mg, 0.5 mmol) was dissolved in 5 mL of a 4.0 M HCl solution in dioxane. The reaction mixture was stirred overnight at room temperature. Volatiles were removed in vacuo and the residue was stripped with MeOH (3 \times 10 mL). The crude product was dissolved in a small amount of MeOH and was added dropwise to vigorously stirred Et₂O (100 mL). The resulting white suspension was stirred for 30 min and then filtered. The residue was washed with Et₂O and dissolved in MeOH. The mixture was concentrated and stripped with CH₂Cl₂ to give the title compound (239 mg, >99%) as a yellow foam. ¹H NMR (400 MHz CD₃OD): δ = 9.16 (s, 1 H, NCHN), 7.66 (s, 1 H, Im-bb), 7.50–7.35 (m, 10 H, Ar), 5.51 (s, 2 H, NCH₂Ph), 5.44 (s, 2 H, NCH₂Ph), 4.23 (s, 1 H, α -CH), 3.72 (s, 3 H, OMe), 3.40–3.18 (m, 2 H, β -CH₂) ppm. ¹³C NMR (100 MHz CD₃OD): δ = 169.1 [CO(OMe)], 135.0 [Ar(C_q)], 134.4 [Ar(C_q)], 130.9 [Im-bb(C_q)], 130.8 [Ar(CH)], 130.6 [Ar(CH)], 130.5 [Ar(CH)], 130.5 [Ar(CH)], 130.2 [Ar(CH)], 129.6 [Ar(CH)], 124.2 [Im-bb(CH)], 55.0 (Im-CH₂-Ph), 54.6 (α -CH), 52.6 (Im-CH₂-Ph), 52.3 (OMe), 26.0 (β -CH₂) ppm. MS (FAB-TOF): *m/z* calcd. for C₂₁H₂₅O₂N₃²⁺ 351.1936; found 351.1946.

5-(2-Ammonio-3-methoxy-3-oxopropyl)-3-benzyl-1-methyl-1*H*-imidazol-3-ium Chloride Hydrochloride (22): Prepared as described for **21**, yield 81%; red solid. ¹H NMR (400 MHz, CD₃OD): δ = 9.08 (s, 1 H, NCHN), 7.61 (s, 1 H, Im-bb), 7.50–7.38 (m, 5 H, Ar), 5.42 (s, 2 H, NCH₂Ph), 4.48 (t, *J* = 7.1 Hz, 1 H, α -CH), 3.91 (s, 3 H, NMe), 3.79 (s, 3 H, OMe), 3.46 (dd, *J* = 16.1, 7.2 Hz, 1 H, β -CHH), 3.37 (dd, *J* = 16.6, 7.1 Hz, 1 H, β -CHH) ppm. ¹³C NMR (101 MHz, CD₃OD): δ = 169.2 [CO(OMe)], 138.6 (NCHN), 134.9 [Ar(C_q)], 131.0 [Im-bb(C_q)], 130.4 [Ar(CH)], 130.4 [Ar(CH)], 130.0 [Ar(CH)], 123.2 [Im-bb(CH)], 54.4 (NCH₂Ph), 54.3 (α -CH), 52.2 (α -OMe), 34.9 (NCH₃), 25.4 (β -CH₂) ppm. HRMS (FAB): *m/z* calcd. for C₁₅H₂₁O₂N₃Cl₂²⁺ 345.1011; found 345.0983.

2-[(5-(2-Ammonio-3-methoxy-3-oxopropyl)-1*H*-imidazol-3-ium-3-yl)methyl]-1,3-bispyridin-1-ium Chloride Dihydrochloride (23): Prepared as described for **21**. Quantitative yield (99%); off-white foam. ¹H NMR (400 MHz CD₃OD): δ = 9.62 (s, 1 H, NCHN), 8.93 (d, *J* = 5.3 Hz, 1 H, Py-*H*2), 8.87 (d, *J* = 5.1 Hz, 1 H, Py-*H*2'), 8.65 (t, *J* = 7.6 Hz, 1 H, Py-*H*4), 8.51 (t, *J* = 7.5 Hz, 1 H, Py-*H*4'), 8.23 (d, *J* = 7.8 Hz, 1 H, Py-*H*5), 8.13–8.02 (m, 3 H, Py-*H*5', Im-bb, Py-*H*3), 8.00–7.92 (m, 1 H, Py-*H*3'), 6.09 (s, 2 H, NCH₂Py), 6.07 (s, 2 H, NCH₂Py'), 4.62 (t, *J* = 6.4 Hz, 1 H, α -CH), 3.85 (s, 3 H, OMe), 3.57 (dd, *J* = 16.8, 6.5 Hz, 1 H, β -CHH), 3.45 (dd, *J* = 16.3, 7.0 Hz, 1 H, β -CHH) ppm. ¹³C NMR (75 MHz CD₃OD): δ = 169.0 [CO(OMe)], 149.9 (Py-C6), 149.5 (Py-C6'), 148.0 [Py(CH)], 146.6 [Py(CH)], 146.1 [Py(CH)], 144.7 (PyCH), 141.3 [Py(CH)], 132.1 [Im-bb(C_q)], 128.3 [Py(CH)], 127.8 [Py(CH)], 127.4 [Py(CH)], 124.6 [Im-bb(CH)], 54.4 (NCH₂Py), 52.2 (NCH₂Py'), 51.3 (α -CH), 25.5 (β -CH₂) ppm. MS (FAB-TOF): *m/z* calcd. for C₁₉H₂₄O₂N₅³⁺ 354.1914; found 354.1928.

2-[(5-(2-Ammonio-3-methoxy-3-oxopropyl)-1-methyl-1*H*-imidazol-3-ium-3-yl)methyl]pyridin-1-ium Chloride Hydrochloride (24): Pre-

pared as described for **23**. Quantitative yield; red solid. ^1H NMR (400 MHz, CD_3OD): $\delta = 9.23$ (s, 1 H, NCHN), 8.80 (d, $J = 5.1$ Hz, 1 H, Py-H2), 8.41 (t, $J = 7.8$ Hz, 1 H, Py-H4), 7.95 (d, $J = 7.8$ Hz, 1 H, Py-H5), 7.90–7.84 (m, 1 H, Py-H3), 7.79 (s, 1 H, Im-bb), 5.85 (s, 2 H, Im-CH₂-Py), 4.53 (t, $J = 7.0$ Hz, 1 H, α -CH), 3.97 (s, 3 H, NMe), 3.87 (s, 3 H, OMe), 3.54 (dd, $J = 16.2$, 6.4 Hz, 1 H, β -CHH), 3.38 (dd, $J = 16.3$, 7.6 Hz, 1 H, β -CHH) ppm. ^{13}C NMR (101 MHz, CD_3OD): $\delta = 169.1$ [CO(OMe)], 150.4 (Py-C6), 147.1 (Py-C2), 145.3 (Py-C4), 131.6 [Im-bb(C_q)], 127.9 (Py-C5), 127.6 (Py-C3), 124.0 [Im-bb(CH)], 54.4 (α -CH), 52.2 (OMe), 51.5 (NCH₂Py), 35.1 (NMe), 25.4 (β -CH₂) ppm.

4-(2-Ammonio-3-methoxy-3-oxopropyl)-1-mesityl-3-methyl-1H-imidazol-3-ium Chloride Hydrochloride (25): Prepared as described for **21**, yield 92%; off-white foam. ^1H NMR (400 MHz, CD_3OD): $\delta = 9.17$ (s, 1 H, NCHN), 7.70 (s, 1 H, Im-bb), 7.13 (s, 2 H, Mes), 4.61 (t, $J = 6.6$ Hz, 1 H, α -CH), 4.04 (s, 3 H, NCH₃), 3.86 (s, 3 H, OMe), 3.60–3.40 (m, 2 H, β -CH₂), 2.36 [s, 3 H, Mes(*p*-Me)], 2.11 [s, 6 H, Mes(*o*-Me)] ppm. ^{13}C NMR (75 MHz, CD_3OD): $\delta = 167.85$ [CO(-OMe)], 141.20 (Mes), 138.16 (NCN), 134.43, 130.94, 130.37, 129.30 [Mes(CH)], 123.23 [Im-bb(CH)], 52.86 (OMe), 50.75 (α -CH), 33.67 (NMe), 24.10 (β -CH₂), 19.70 [Mes(Me)], 16.14 [Mes(Me)] ppm. MS (FAB-TOF): m/z calcd. for $\text{C}_{17}\text{H}_{24}\text{DN}_3\text{O}_2^+$ 304.2010; found 304.2025.

4-{2-[(*tert*-Butoxycarbonyl)amino]-3-carboxylate}-1-*p*-methoxyphenyl-3-methyl-1H-imidazol-3-ium Iodide (26): Compound **17** (0.125 g, 0.24 mmol) was dissolved in methanol (20 mL), then H₂O (2 mL) and LiOH (60 mg, 2.4 mmol) were added. The solution was stirred overnight, after which TLC analysis showed the disappearance of the starting material. The solvent was removed in vacuo and the obtained yellow oil was stripped twice with methanol. The crude product was further purified by column chromatography (silica; CH₂Cl₂/MeOH, 9:1) to give the product (0.08 g, 65%). ^1H NMR (400 MHz, CD_3OD): $\delta = 9.36$ (s, 1 H, NCHN), 7.72 (s, 1 H, Im-bb), 7.62 (d, $J = 8.9$ Hz, 2 H, Ar), 7.16 (d, $J = 9.0$ Hz, 2 H, Ar), 4.36–4.11 (m, 1 H, α -CH), 4.00 (s, 3 H, NMe), 3.89 (s, 3 H, OMe), 3.11 (m, 2 H, β -CH₂), 1.39 [s, 9 H, C(CH₃)₃] ppm. ^{13}C NMR (101 MHz, MeOD): $\delta = 174.72$ (COO⁻), 160.71 (Ar), 157.87 (Ar), 155.99 [CO(O*t*Bu)], 133.53 (NCHN), 127.77 [Im-bb(C_q)], 123.03 (Ar), 119.43 [Im-bb(CH)], 114.91 (Ar), 79.01 [C(CH₃)₃], 54.90 (Ar-OMe), 48.38 (α -CH), 33.10 (NMe), 27.36 (β -CH₂), 27.17 [C(CH₃)₃] ppm. MS (FAB-TOF): m/z calcd. for $\text{C}_{19}\text{H}_{24}\text{DLiN}_3\text{O}_5^+$ 383.2012; found 383.2287.

(1,3-Dibenzyl-4-{2-[(*tert*-butoxycarbonyl)amino]-3-methoxy-3-oxopropyl}-1H-imidazol-2-(3H)-ylidene)silver(I) Bromide (27): Compound **2** (223 mg, 0.42 mmol) was dried azeotropically by co-evaporation with toluene (3 × 3 mL). Ag₂O (54 mg, 0.23 mmol), and 4 Å molecular sieves were added and the Schlenk flask was purged with argon twice. CH₂Cl₂ (10 mL) was added and the mixture was stirred overnight at room temperature with exclusion of light. The mixture was filtered through a pad of Celite in air and the residue was washed with CH₂Cl₂ (10 mL). All volatiles were removed in vacuo to afford the title compound (203 mg, 96%) as an off-white foam. ^1H NMR (400 MHz CD_2Cl_2): $\delta = 7.48$ –7.08 (m, 10 H, Ar), 6.82 (s, 1 H, Im-bb), 5.47 (s, 2 H, NCH₂Ph), 5.33 (s, 2 H, NCH₂Ph'), 5.07 (s, 1 H, NH), 4.42 (m, 1 H, α -CH), 2.90–2.84 (m, 1 H, β -CHH), 2.67–2.61 (m, 1 H, β -CHH), 1.32 [d, $J = 48.6$ Hz, 9 H, C(CH₃)₃] ppm. ^{13}C NMR (75 MHz CD_2Cl_2): $\delta = 183.2$ (Ag-C), 171.5 [CO(OMe)], 155.4 [CO(O*t*Bu)], 136.2 [Ar(C_q)], 136.2 [Ar(C_q)], 130.9 [Im-bb(C_q)], 129.4 (ArCH), 128.9 [Ar(CH)], 128.6 [Ar(CH)], 128.1 [Ar(CH)], 127.1 [Ar(CH)], 120.4 [Im-bb(CH)], 80.7 [C(CH₃)₃], 56.2 (NCH₂Ph), 53.4 (NCH₂Ph'), 52.9 (α -CH), 52.8 (OMe), 28.3 (β -CH₂), 28.0 [C(CH₃)₃] ppm. MS (FAB-TOF): m/z calcd. for $\text{C}_{52}\text{H}_{62}\text{O}_8\text{N}_6^{109}\text{Ag}^+$ 1007.3677; found 1007.3674.

(1-Benzyl-4-{2-[(*tert*-butoxycarbonyl)amino]-3-methoxy-3-oxopropyl}-3-(pyridin-2-ylmethyl)-1H-imidazol-2-(3H)-ylidene)silver(I) Bromide (28): The title compound was prepared as described for **27**. The compound was obtained as a mixture of species, which are presumably coordination oligomers. The compounds were applied in the transmetalation reactions and gave the desired Pd complex in good yields. ^1H NMR (400 MHz, CD_2Cl_2): $\delta = 8.55$ (d, $J = 2.9$ Hz, 1 H, Py-H2), 8.42 (d, $J = 3.8$ Hz, 0.5 H, Py-H2'), 7.68 (t, $J = 7.0$ Hz, 1 H, Py-H4), 7.55 (t, $J = 7.6$ Hz, 0.5 H, Py-H4'), 7.38–7.08 (m, 12 H, Ar), 6.89 (s, 0.5 H, Im-bb'), 6.86 (s, 1 H, Im-bb), 6.02 (s, 1 H, NH), 5.41 (m, 3 H, NCH₂Ar), 5.21 (s, 2 H, NCH₂Ar), 5.13 (s, 1 H, NCH₂Ar'), 4.64 (s, 0.5 H, α -CH), 4.46 (s, 1 H, α -CH'), 3.63 (s, 3 H, OMe), 3.47 (s, 1.5 H, OMe'), 3.14 (dd, $J = 15.8$, 4.8 Hz, 1 H, β -CHH), 3.04 (dd, $J = 15.9$, 8.3 Hz, 1 H, β -CHH), 2.87–2.61 (m, 1 H, β -CH₂'), 1.37 [s, 9 H, C(CH₃)₃], 1.26 [s, 4.5 H, C(CH₃)₃] ppm. ^{13}C NMR (101 MHz, CDCl_3): $\delta = 170.88$ [CO(O*t*Bu)], 155.37, 152.20, 149.58, 137.50, 132.82, 132.15, 129.14, 128.73, 123.65, 123.08, 119.84 [Im-bb(CH)], 80.07 [C(CH₃)₃], 53.09 (α -CH₂), 52.60 (Im-CH₂-Ar), 52.07 (Im-CH₂-Ar), 51.35 (OMe), 27.99 [C(CH₃)₃], 26.21 (β -CH₂) ppm (^{13}C NCN signal was not observed). HRMS (FAB): m/z calcd. for $\text{C}_{50}\text{H}_{60}\text{O}_8\text{N}_8^{109}\text{Ag}^+$ 1009.3582; found 1009.3591.

(4-{2-[(*tert*-Butoxycarbonyl)amino]-3-methoxy-3-oxopropyl}-1,3-bis(pyridin-2-ylmethyl)-1H-imidazol-2-(3H)-ylidene)silver(I) Bromide (29): Prepared as described for compound **27**, yield 80%; white foam. ^1H NMR (400 MHz, CD_2Cl_2): $\delta = 8.56$ (d, $J = 3.6$ Hz, 2 H, Py-H2, Py-H2'), 7.83–7.63 (m, 2 H, Py-H4, Py-H4'), 7.36 (d, $J = 7.6$ Hz, 1 H, Py-H5), 7.32–7.19 (m, 4 H, Py), 7.02 (s, 1 H, Im-bb), 5.93 (d, $J = 7.4$ Hz, 1 H, NH), 5.42 (AB system, $J = 28.7$, 15.9 Hz, 2 H, NCH₂Py), 5.35 (s, 2 H, NCH₂Py'), 4.51 (s, 1 H, α -CH), 3.68 (s, 3 H, OMe), 3.17 (dd, $J = 15.8$, 4.9 Hz, 1 H, β -CHH), 3.06 (dd, $J = 15.9$, 8.0 Hz, 1 H, β -CHH), 1.37 [s, 9 H, C(CH₃)₃] ppm. ^{13}C NMR (126 MHz, CD_2Cl_2): $\delta = 184.4$ (NCN), 171.9 [CO(OMe)], 156.0 (Py-C6), 155.9 (Py-C6'), 155.7 [CO(O*t*Bu)], 150.2 (Py-C2, Py-C2'), 137.8 (Py-C4), 137.6 (Py-C4'), 131.4 [Im-bb(C_q)], 123.7 [Py(CH)], 123.6 [Py(CH)], 122.9 [Py(CH)], 122.9 [Py(CH)], 120.5 [Im-bb(CH)], 80.5 [C(CH₃)₃], 57.8 (NCH₂Py), 54.4 (α -CH), 52.8 (OMe), 28.5 [C(CH₃)₃], 27.7 (β -CH₂) ppm. MS (FAB-TOF): m/z calcd. for $\text{C}_{24}\text{H}_{29}\text{O}_4\text{N}_5^{107}\text{Ag}^+$ 558.1270; found 558.1269.

(4-{2-[(*tert*-Butoxycarbonyl)amino]-3-methoxy-3-oxopropyl}-1-(4-methoxyphenyl)-3-methyl-1H-imidazol-3-ium-2-yl)silver(I) Iodide (30): The title compound was prepared as described for **27**. The ^1H spectrum was very broad and the ^{13}C spectrum showed double peaks, probably due to coordination oligomers, or multiple coordination modes of the histidylidene to the silver. The compound was used as obtained, and yielded the corresponding Pd-compound. ^1H NMR (400 MHz, CD_2Cl_2): $\delta = 7.47$ (d, $J = 8.8$ Hz, 2 H, Ar), 7.12 (s, 1 H, Im-bb), 6.96 (d, $J = 8.8$ Hz, 2 H, Ar), 5.50 (s, 1 H, NH), 4.63 (s, 1 H, α -CH), 3.89 (s, 3 H, NMe), 3.86 (s, 3 H, OMe), 3.80 (s, 3 H, OMe), 3.29 (AB-M system dd, $J = 10.8$, 4.8 Hz, 1 H, β -CH₂), 3.12 (AB-M system dd, $J = 8.0$, 7.6 Hz, 1 H, β -CH₂), 1.41 [s, 9 H, C(CH₃)₃] ppm. ^{13}C NMR (101 MHz, CD_2Cl_2): $\delta = 180.87$ (NCN), 171.31 [CO(OMe)], 159.60, 155.30 [CO(O*t*Bu)], 137.82, 133.17, 132.92, 130.80, 128.82, 128.01, 125.09 [Ar(CH)], 125.00 [Ar(CH)], 120.38 [Im-bb(CH)], 120.19 [Im-bb(CH)], 114.44 [Ar(CH)], 114.21 [Ar(CH)], 79.80 [C(CH₃)₃], 77.94 [C(CH₃)₃], 55.50 (Ar-OMe), 52.53 (CH₃), 52.22 (CH₃), 36.35 (NMe), 36.29 (NMe), 28.05 [C(CH₃)₃], 27.86 [C(CH₃)₃], 27.35 (β -CH₂), 27.15 (β -CH₂) ppm. MS (FAB-TOF) calculated for $\text{C}_{40}\text{H}_{54}\text{N}_6\text{O}_{10}^{107}\text{Ag}^+$ 887.2949, found 887.2964.

Bis(4-{2-[(*tert*-butoxycarbonyl)amino]-3-methoxy-3-oxopropyl}-1-mesityl-3-methyl-1H-imidazol-2-ylidene)silver(I) Silver(I) Diiodide

(31): Prepared as described for **27**, yield 86%; yellow foam. ^1H NMR (400 MHz, CD_2Cl_2): $\delta = 7.01$ (s, 2 H, Ar), 6.79 (s, 1 H, Im-bb), 5.33 (d, $J = 7.4$ Hz, 1 H, NH), 4.64 (m, 1 H, α -CH), 3.87 (s, 3 H, Me), 3.78 (s, 3 H, Me), 3.12 (AB-M system, dd, $J = 15.7$, 5.1 Hz, 1 H, α -CH), 2.38 (s, 3 H, Mes), 1.96 (d, $J = 4.2$ Hz, 6 H, Mes), 1.44 [s, 9 H, $\text{C}(\text{CH}_3)_3$] ppm. ^{13}C NMR (400 MHz, CD_2Cl_2): $\delta = 183.80$ (NCN), 171.19 [CO(OMe)], 154.97 [CO(OtBu)], 138.89, 135.43, 134.84, 130.19, 128.93, 120.57 [Im-bb(CH)], 80.03 [C(CH₃)₃], 52.71 (OMe), 52.50 (α -CH), 36.73 (NMe), 27.90 [C(CH₃)₃], 27.52 (β -CH₂), 20.80 (Mes), 17.52 (Mes), 17.49 (Mes) ppm. MS (FAB-TOF): m/z calcd. for $\text{C}_{44}\text{H}_{62}\text{N}_6\text{O}_8^{107}\text{Ag}^+$ 911.3677; found 911.3693.

(4-{2-[(*tert*-Butoxycarbonyl)amino]-3-methoxy-3-oxopropyl}-1-mesityl-3-[(6-methylpyridin-2-yl)methyl]-1*H*-imidazol-2-(3*H*)-ylidene)silver(I) Bromide (32): Prepared as described for **27**, yield 89%; yellow foam. ^1H NMR (400 MHz, CD_2Cl_2): $\delta = 7.61$ (t, $J = 7.7$ Hz, 1 H, Py-*H4*), 7.27–7.02 (m, 2 H, Py-*H3*, Py-*H5*), 6.99 (s, 2 H, Mes), 6.82 (s, 1 H, Im-bb), 5.81 (d, $J = 6.1$ Hz, 1 H, NH), 5.4 (br. s, 2 H, NCH_2Py), 4.59 (d, $J = 5.1$ Hz, 1 H, α -CH), 3.69 (s, 3 H, OMe), 3.21 (dd, $J = 15.9$, 5.1 Hz, 1 H, β -CHH), 3.14 (dd, $J = 15.9$, 7.3 Hz, 1 H, β -CHH), 2.50 [s, 3 H, Lut(CH₃)], 2.34 [s, 3 H, Mes(*p*-Me)], 1.98 [s, 3 H, Mes(*o*-Me)], 1.97 [s, 3 H, Mes(*p*-Me)], 1.36 [s, 9 H, C(CH₃)₃] ppm. ^{13}C NMR (126 MHz, CD_2Cl_2): $\delta = 185.2$ (NCN), 171.9 [CO(OMe)], 159.7 (Py-C6), 155.7 [CO(OtBu)], 155.4 (Py-C2), 140.1 (Ar), 138.0 (Ar), 136.4 (Ar), 135.5 (Ar), 135.5 (Ar), 131.6 (ArC), 129.9 (Ar), 128.7 (Ar), 123.3 (Ar), 121.7 (Ar), 119.3 (Ar), 80.8 [C(CH₃)₃], 54.7 (NCH_2Py), 53.6 (α -CH), 53.0 (OMe), 28.6 [C(CH₃)₃], 28.2 (β -CH₂), 24.6 [Lut(Me)], 21.4 [Mes(*p*-Me)], 17.9 [Mes(*o*-Me)] ppm. MS (FAB-TOF): m/z calcd. for $\text{C}_{28}\text{H}_{36}\text{O}_4\text{N}_4^{107}\text{Ag} [\text{M}^+ - \text{Br}]$ 599.1787; found 599.1766.

[4-(2-Amino-3-methoxy-3-oxopropyl)-1,3-dibenzyl-1*H*-imidazol-2-(3*H*)-ylidene]silver(I) Chloride (33): Compound **21** (183 mg, 0.43 mmol) was dried azeotropically by coevaporation with toluene (3 × 3 mL). Ag_2O (125 mg, 0.54 mmol) and molecular sieves were added, then the Schlenk flask was purged twice and placed under an argon atmosphere. CH_2Cl_2 (10 mL) was added and the mixture was stirred overnight at room temperature with exclusion of light. The mixture was filtered through a pad of Celite in air and the residue was washed with CH_2Cl_2 (10 mL). All volatiles were removed in vacuo to give the title compound (203 mg, 96%) as an off-white foam. ^1H NMR (400 MHz CD_2Cl_2): $\delta = 7.45$ –7.24 (m, 8 H, Ar), 7.18–7.12 (m, 2 H, Ar), 6.91 (s, 1 H, Im-bb), 5.43 (s, 2 H, NCH_2Ph), 5.30 (s, 2 H, $\text{NCH}_2\text{Ph}'$), 3.59 (s, 3 H, OMe), 3.52–3.40 (m, 1 H, α -CH), 2.84 (dd, $J = 15.6$, 5.2 Hz, 1 H, β -CHH), 2.61 (dd, $J = 15.6$, 7.8 Hz, 1 H, β -CHH), 1.43 (d, $J = 7.2$ Hz, 2 H, NH₂) ppm. ^{13}C NMR (126 MHz CD_2Cl_2): $\delta = 181.9$ (NCN), 174.9 [CO(OMe)], 136.6 [Ar(C_q)], 136.5 (Ar-C_q), 132.3 [Im-bb(C_q)], 129.6 [Ar(CH)], 129.5 [Ar(CH)], 129.0 [Ar(CH)], 128.7 [Ar(CH)], 128.3 [Ar(CH)], 127.2 [Ar(CH)], 120.6 [Im-bb(CH)], 56.4 (NCH_2Ph), 54.2 ($\text{NCH}_2\text{Ph}'$), 53.7 (α -CH), 52.5 (OMe), 30.2 (β -CH₂) ppm. MS (FAB-TOF): m/z calcd. for $\text{C}_{21}\text{H}_{25}\text{N}_3\text{O}_2^+$ 351.1947; found 351.1946.

Bis[4-(2-amino-3-methoxy-3-oxopropyl)-1-mesityl-3-methyl-imidazol-2-ylidene]silver(I) Silver(I) Dichloride (34): Prepared as described for **33**, yield 27 mg (22%); off-white hygroscopic solid. ^1H NMR (400 MHz, CD_2Cl_2): $\delta = 7.03$ (s, 2 H, Ar), 6.87 (s, 1 H, Im-bb), 3.91 (s, 3 H, OMe), 3.81 (s, 1 H, α -CH), 3.73 (s, 3 H, NMe), 3.05 (ddd, $J = 52.6$, 15.5, 6.4 Hz, 2 H, β -CH₂), 2.38 [s, 3 H, Mes(*p*-Me)], 2.01 [s, 6 H, Mes(*o*-Me)], 1.63 (s, 2 H, NH₂) ppm. ^{13}C NMR (75 MHz, CDCl_3): $\delta = 181.20$ (NCN), 174.48 [CO(OMe)], 139.36, 135.65, 134.88, 131.00, 129.17 [Ar(CH)], 120.70 [Im-bb(CH)], 53.80 (OMe/ α -CH), 52.14 (OMe/ α -CH), 36.55 (NCH₃), 29.64 (β -CH₂),

20.79 (Mes), 17.41 (Mes) ppm. MS (FAB-TOF): m/z calcd. for $\text{C}_{34}\text{H}_{46}^{109}\text{AgN}_6\text{O}_4^+$ 711.2628; found 711.2634.

(1,3-Dibenzyl-4-{2-[(*tert*-butoxycarbonyl)amino]-3-methoxy-3-oxopropyl}-1*H*-imidazol-2-(3*H*)-ylidene)allylpalladium(II) Chloride (35): A solution of **28** (223 mg, 0.35 mmol) in CH_2Cl_2 (11 mL) was added dropwise to a stirred solution of [Pd(allyl)Cl]₂ (64 mg, 0.175 mmol) in CH_2Cl_2 (5.5 mL). The mixture was stirred for 1 h at room temperature, then filtered through a pad of Celite in air and the residue was rinsed with CH_2Cl_2 (10 mL). Volatiles were evaporated and the crude product was purified by selective precipitation of the impurity by gradual cooling of a CH_2Cl_2 /pentane solution to give the title compound (90 mg, 41%) as an off-white solid. ^1H NMR (400 MHz, CD_2Cl_2): $\delta = 7.39$ –7.26 (m, 8 H, Ar), 7.23–7.18 (m, 2 H, Ar), 6.82 (s, 1 H, Im-bb), 5.63–5.34 (m, 4 H, NCH_2Ph), 5.12–5.00 (m, 2 H, NH, allyl), 4.39 (br. s, 1 H, α -CH), 4.08 (dd, $J = 7.5$, 2.1 Hz, 1 H, allyl), 3.62 (s, 3 H, OMe), 3.12 (br. s, 1 H, allyl), 3.02 (d, $J = 13.1$ Hz, 1 H, allyl), 2.98–2.87 (m, 1 H, β -CHH), 2.84–2.71 (m, 1 H, β -CHH), 1.93 (d, $J = 12.0$ Hz, 1 H, allyl), 1.38 [br. s, 9 H, C(CH₃)₃] ppm. ^{13}C NMR (101 MHz, CD_2Cl_2): $\delta = 182.7$ (NCN), 171.8 [CO(OMe)], 155.3 [CO(OtBu)], 137.2 [Ar(C_q)], 137.1 [Ar(C_q)], 130.6 [Ar(CH)], 129.1 [Ar(CH)], 128.4 [Ar(CH)], 128.3 [Ar(CH)], 128.3 [Ar(CH)], 128.1 [Ar(CH)], 127.3 [Ar(CH)], 120.3 [Im-bb(CH)], 115.1 (allyl), 80.5 [C(CH₃)₃], 71.7 (allyl), 55.1 (NCH_2Ph), 52.9 (α -CH), 52.6 (OMe), 52.4 (allyl), 28.3 [C(CH₃)₃], 28.1 (β -CH₂) ppm. MS (FAB-TOF): m/z calcd. for $\text{C}_{29}\text{H}_{36}\text{O}_4\text{N}_3\text{Pd}^+$ 596.1741; found 596.1743.

(1-Benzyl-4-{2-[(*tert*-butoxycarbonyl)amino]-3-methoxy-3-oxopropyl}-3-(pyridin-2-ylmethyl)-1*H*-imidazol-2-(3*H*)-ylidene)allylpalladium(II) Chloride (36): A solution of **29** (95 mg, 0.15 mmol) in CH_2Cl_2 (3 mL) was added dropwise to a stirred solution of [Pd(allyl)Cl]₂ (23 mg, 0.075 mmol) in CH_2Cl_2 (2 mL). The mixture was stirred for 24 h at room temperature, then filtered through a pad of Celite in air and the residue was washed with CH_2Cl_2 (5 mL). Volatiles were evaporated, and the crude product was purified by column chromatography (silica; CH_2Cl_2 to CH_2Cl_2 /MeOH, 9:1) to give the title compound (70 mg, 74%) as an off-white foam. ^1H NMR (400 MHz, CD_2Cl_2): $\delta = 8.63$ (d, $J = 4.4$ Hz, 1 H, Py-*H2*), 7.84–7.67 (m, 2 H, Ar), 7.40–7.19 (m, 6 H, Ar), 6.81 (s, 1 H, Im-bb), 6.56 (br. s, 1 H, NH), 5.73–5.47 (m, 2 H, NCH_2Py), 5.30 (s, 2 H, NCH_2Ph), 5.5.21–5.14 (m, 1 H, allyl), 4.45 (dd, $J = 13.1$, 7.3 Hz, 1 H, α -CH), 4.13 (d, $J = 7.6$ Hz, 1 H, allyl), 3.65 (s, 3 H, OMe), 3.16 (dd, $J = 14.7$, 10.0 Hz, 2 H, β -CH₂), 3.01 (br. s, 2 H, 2 × allyl), 2.0 (br. s, 1 H, allyl), 1.36 [s, 9 H, C(CH₃)₃] ppm. ^{13}C NMR (101 MHz, CD_2Cl_2): $\delta = 180.9$ (NCN), 172.0 [CO(OMe)], 156.1 (Py-C6), 155.9 [CO(OtBu)], 151.4 (Py-C2), 138.2 (Py-C4), 136.8 [Ar(C_q)], 131.9 [Im-bb(C_q)], 129.1 [Ar(CH)], 128.5 [Ar(CH)], 128.0 [Ar(CH)], 124.6 (Py-C5), 123.8 (Py-C3), 119.7 [Im-bb(CH)], 116.8 (allyl), 80.0 [C(CH₃)₃], 72.7 (allyl), 55.2 (NCH_2Py), 53.7 (α -CH), 52.8 (NCH_2Ph), 52.7 (OCH₃), 48.6 (allyl), 28.4 [C(CH₃)₃], 27.2 (β -CH₂) ppm. MS (FAB-TOF): m/z calcd. for $\text{C}_{28}\text{H}_{35}\text{O}_4\text{N}_4\text{Pd}^+$ 597.1693; found 597.1697.

(4-{2-[(*tert*-Butoxycarbonyl)amino]-3-methoxy-3-oxopropyl}-1,3-bis-(pyridin-2-ylmethyl)-1*H*-imidazol-2-(3*H*)-ylidene)allylpalladium(II) Chloride (37): Prepared as described for **36**, yield quantitative; off-white foam. ^1H NMR (400 MHz, CD_2Cl_2): $\delta = 8.62$ (d, $J = 4.4$ Hz, 1 H, Py-*H2*), 8.59 (d, $J = 4.9$ Hz, 1 H, Py-*H2'*), 7.89–7.68 (m, 2 H, Py-*H4*, Py-*H4'*), 7.64 (d, $J = 7.5$ Hz, 1 H, Py-*H5*), 7.41 (d, $J = 7.6$ Hz, 1 H, Py-*H5'*), 7.34–7.24 (m, 2 H, Py-*H3*, Py-*H3'*), 7.17 (s, 1 H, Im-bb), 6.56 (d, $J = 6.7$ Hz, 1 H, NH), 5.66–5.54 (m, 4 H, NCH_2Py), 5.31–5.19 (m, 1 H, allyl), 4.44 (d, $J = 4.9$ Hz, 1 H, α -CH), 4.19 (d, $J = 7.6$ Hz, 1 H, allyl), 3.27 (d, $J = 13.6$ Hz, 1 H, allyl), 3.23–3.04 (m, 3 H, β -CH₂, allyl), 2.1 (br. s, 1 H, allyl), 1.34

[s, 9 H, C(CH₃)₃] ppm. ¹³C NMR (126 MHz, CD₂Cl₂): δ = 182.6 (Pd-C), 172.2 [CO(OMe)], 156.8 (Py-C6), 156.7 (Py-C6'), 155.8 [CO(OtBu)], 150.7 (Py-C2), 150.4 (Py-C2'), 137.7 (Py-C4), 137.6 (Py-C4'), 131.8 [Im-bb(C_q)], 123.8 (Py-CH), 123.8 (Py-CH), 123.5 (Py-CH), 123.4 (Py-CH), 120.7 [Im-bb(CH)], 116.4 (allyl), 80.5 [C(CH₃)₃], 72.8 (allyl), 57.1 (NCH₂Py), 53.5 (α-CH), 52.8 (OMe), 48.7 (allyl), 28.6 [C(CH₃)₃], 27.8 (β-CH₂) ppm. MS (FAB-TOF): *m/z* calcd. for C₂₇H₃₄O₄N₅Pd⁺ 598.1646; found 598.1646.

(4-{2-[(*tert*-Butoxycarbonyl)amino]-3-methoxy-3-oxopropyl}-1-mesityl-3-[(6-methylpyridin-2-yl)methyl]-1*H*-imidazol-2-(3*H*)-ylidene}allylpalladium(II) Chloride (38): Prepared as described for **36**, yield 93%; off-white foam. ¹H NMR (400 MHz, CD₂Cl₂): δ = 7.61 (t, *J* = 7.5 Hz, 1 H, Py-*H*4), 7.40 (br. s, 1 H, Py-*H*5), 7.12 (d, *J* = 7.6 Hz, 1 H, Py-*H*3), 6.94 (br. s, 2 H, Mes), 6.84 (br. s, 1 H, Im-bb), 6.79 (s, 1 H, NH), 5.83–5.40 (m, 2 H, Mes), NCH₂Py, 4.66 (br. s, 1 H, allyl), 4.62–4.45 (m, 1 H, α-CH), 3.90 (d, *J* = 7.2 Hz, 1 H, allyl), 3.73 (s, 3 H, OMe), 3.43 (d, *J* = 4.1 Hz, 1 H, allyl), 3.37 (dd, *J* = 16.1, 6.1 Hz, 1 H, β-*CHH*), 3.22 (dd, *J* = 14.9, 2.7 Hz, 1 H, β-*CHH*), 2.80–2.59 (m, 2 H, 2 × allyl), 2.54 (s, 3 H, Py-CH₃), 2.31 [s, 3 H, Mes(*p*-Me)], 2.23–1.93 [m, 6 H, Mes(*o*-Me)], 1.31 [s, 9 H, C(CH₃)₃] ppm. ¹³C NMR (126 MHz, CD₂Cl₂): δ = 184.1 (NCN), 172.1 [CO(OMe)], 159.3 (Py-C6), 156.9 (Py-C2), 155.9 [CO(OtBu)], 139.4 (Ar), 137.5 (Ar), 137.1 (Ar), 136.2 (Ar), 135.8 (Ar), 131.8 (Ar), 129.4 (Ar), 129.3 (Ar), 122.7 (Ar), 121.2 (Ar), 120.8 (Ar), 115.1 (allyl), 80.2 [C(CH₃)₃], 71.3 (allyl), 54.1 (NCH₂Py), 52.9 (α-CH), 52.8 (OMe), 48.9 (allyl), 28.5 [C(CH₃)₃], 27.9 (β-CH₂), 24.7 [Lut(CH₃)], 21.3 [Mes(*p*-Me)], 18.5 [Mes(*o*-Me)], 18.2 [Mes(*o*-CH₃)] ppm. MS (FAB-TOF): *m/z* calcd. for C₃₁H₄₁O₄N₄Pd⁺ 693.2163; found 693.2174.

[4-(2-Amino-3-methoxy-3-oxopropyl)-1,3-dibenzyl-1*H*-imidazol-2-(3*H*)-ylidene]allylpalladium(II) Chloride (40): Prepared as described for **36**, yield 31%. ¹H NMR (400 MHz, CD₂Cl₂): δ = 7.42–7.26 (m, 8 H, Ar), 7.19 (d, *J* = 7.1 Hz, 2 H, Ar), 6.88 (s, 1 H, Im-bb), 5.64–5.33 (m, 4 H, NCH₂Ph), 5.13–5.02 (m, 1 H, allyl), 4.07 (dd, *J* = 7.5, 1.6 Hz, 1 H, allyl), 3.60 (s, 3 H, OMe), 3.45 (d, *J* = 5.7 Hz, 1 H, α-*CH*), 3.08–3.02 (m, 2 H, 2 × allyl), 2.89–2.80 (m, 1 H, β-*CHH*), 2.63–2.56 (m, 1 H, β-*CHH*), 1.92 (d, *J* = 11.9 Hz, 1 H, allyl), 1.4 (br. s, 2 H, NH₂) ppm. ¹³C NMR (101 MHz, CD₂Cl₂): δ = 182.4 (NCN), 175.0 [CO(OMe)], 137.4 [Ar(C_q)], 137.3 [Ar(C_q)], 131.7 [Im-bb(C_q)], 129.1 [Ar(CH)], 129.1 [Ar(CH)], 128.3 [Ar(CH)], 128.3 [Ar(CH)], 128.0 [Ar(CH)], 127.3 [Ar(CH)], 120.4 [Im-bb(CH)], 115.2 (allyl), 71.9 (allyl), 55.1 (NCH₂Ph), 52.5 (α-CH), 52.4 (OMe), 49.3 (allyl), 30.2 (β-CH₂) ppm. MS (FAB-TOF): *m/z* calcd. for C₂₄H₂₈O₂N₃Pd⁺ 496.1216; found 496.1221.

Bis(4-{2-[(*tert*-butoxycarbonyl)amino]-3-methoxy-3-oxopropyl}-1-mesityl-3-methyl-1*H*-imidazol(3*H*)-2-ylidene}allylpalladium(II) Chloride (41): A solution of **30** (0.288 g, 0.46 mmol) in CH₂Cl₂ (5 mL) was added dropwise to a stirred solution of [Pd(allyl)Cl]₂ (0.168 g, 0.46 mmol) in CH₂Cl₂ (5 mL). The solution was stirred for 1 h, then the mixture was filtered through a pad of Celite in air, which was rinsed with additional CH₂Cl₂ (5 mL). The volatiles were removed in vacuo to give a yellow foamy solid. The compound contained an excess of the Pd precursor. The crude product was purified by column chromatography [CH₂Cl₂ to CH₂Cl₂/MeOH (95:5), to CH₂Cl₂/MeOH (9:1)]. The fractions containing the product were combined. The solution was concentrated on a rotavap apparatus, and the remaining solvent was removed in vacuo to give the product (0.162 g, 0.17 mmol, 36%) as a light-yellow foamy solid. ¹H NMR (400 MHz, CD₂Cl₂): δ = 7.16 (s, 2 H, Im-bb), 7.05–6.90 (m, 8 H, Ar), 6.35 (s, 2 H, NH), 5.34–5.20 (m, 1 H, allyl), 4.55–4.36 (m, 2 H, α-CH), 3.96–3.86 (m, 10 H, allyl, OMe), 3.78 (s, 6 H, OMe), 3.24–2.94 (m, 10 H, β-CH₂, NMe), 2.71–2.50 (m, 2

H, allyl), 1.42 [s, 18 H, CO(OtBu)] ppm. ¹³C NMR (101 MHz, CD₂Cl₂): δ = 175.90 (NCN), 171.52 [CO(OMe)], 159.44 (*p*-Ar), 155.43 [CO(OtBu)], 133.13 [Im-bb(C_q)], 130.79 (*i*-Ar), 125.83 (*m*-Ar), 121.40 [Im-bb(CH)], 118.00 (allyl), 114.13 (*o*-Ar), 79.34 [C(CH₃)₃], 58.45 (allyl), 55.57 (Ar-OMe), 52.25 {α-CH/[CO(OMe)]}, 51.90 [α-CH/CO(OMe)], 34.78 (NMe), 27.84 [C(CH₃)₃], 26.57 (β-CH₂) ppm. MS (ESI-Coldspray): *m/z* calcd. for C₄₃H₅₉N₆O₁₀ClPd⁺ 960.3016; found 960.3029.

Catalytic Transfer Semihydrogenation of Alkynes: A Radleys' twelve-place reaction station with integrated heating and cooling setup was used for all catalytic experiments. Samples were taken at regular time intervals by filtering aliquots of the reaction mixture over short silica pads and eluting with CH₂Cl₂. Samples were analyzed with a Thermo Scientific Trace GC Ultra equipped with an R-Rxi 5ms column (30 m, ID 0.25 mm) and quantified by using the response factor corrected GC-area in respect to the internal standard. Samples were further analyzed by NMR spectroscopy with a Bruker 400 MHz spectrometer.

General Procedure: A stock solution was prepared by adding in their respective order: acetonitrile (320 mL, 250.3 g), 1-phenyl-1-propyne (6.4 g, 55 mmol), *p*-xylene (internal standard, 5.68 g, 54 mmol), triethylamine (27.00 g, 267 mmol), and formic acid (11.48 g, 267 mmol), and the solution was saturated with nitrogen gas by gently bubbling N₂ for 20 min. An aliquot (20 mL) was taken from the stock solution by using a syringe and added to one of the twelve reaction vessels. The exact amount of added stock solution was determined by weighing; for this reason, molar and weight percentages were applied to determine quantities and further calculations. The Radleys' station was heated to 70 °C, after which the appropriate amount of catalyst was added in aluminum weighing trays. Reaction rates were determined by taking the first order derivative of the conversion at 15%.

X-ray Crystal Structure Determination of 42: C₃₁H₄₁N₄O₄Pd 0.5 C₆H₁₂ 0.5 C₄H₈O, disordered solvent; Fw = 780.21*; pale-brown block; 0.40 × 0.18 × 0.11 mm³; monoclinic; *P*2₁ (no. 4); *a* = 14.5823(3), *b* = 14.2173(4), *c* = 20.5565(4) Å, β = 103.670(1)°; *V* = 4141.06(16) Å³; *Z* = 4; D_x = 1.251 g/cm³*; μ = 0.50 mm⁻¹*; * derived values do not contain the contribution of the disordered solvent molecules. 74792 Reflections were measured with a Bruker Kappa ApexII diffractometer with sealed tube and Triumph monochromator (λ = 0.71073 Å) at a temperature of 150(2) K up to a resolution of (sin θ/λ)_{max} = 0.65 Å⁻¹. Intensity integration was performed with the software Eval15.^[89] Multiscan absorption correction and scaling was performed with SADABS^[90] (correction range 0.65–0.75). 19045 Reflections were unique (*R*_{int} = 0.026), of which 16710 were observed [*I* > 2σ(*I*)]. The structure was solved by using the program SHELXT.^[91] Least-squares refinement was performed with SHELXL-2013^[92] against *F*² of all reflections. Because of the large shifts of the structure along the polar *b*-axis, the *y*-coordinate of PdI was fixed in the refinement. All other non-hydrogen atoms were refined freely with anisotropic displacement parameters. The coordinated allyl groups, one of the noncoordinated nitrate ions, and the cyclohexane molecule were refined with disordered models. The crystal structure additionally contains voids (526 Å³/unit cell), filled with disordered cyclohexane and THF solvent molecules. Their contribution to the structure factors was secured by back-Fourier transformation using the SQUEEZE algorithm of PLATON,^[79] resulting in 161 electrons/unit cell. All hydrogen atoms were introduced in calculated positions and refined with a riding model. 1011 Parameters were refined with 292 restraints concerning the disordered moieties. *R*₁/*wR*₂ [*I* > 2σ(*I*)]: 0.0401/0.1029; *R*₁/*wR*₂ [all refl.]: 0.0492/0.1085; *S* = 1.037. The absolute structure

was confirmed by a refinement as an inversion twin, resulting in a Flack parameter^[93] $x = -0.02(2)$. Residual electron density between -1.58 and $1.33 \text{ e} \text{ \AA}^{-3}$. Geometry calculations and checking for higher symmetry were performed with the PLATON program.^[79]

CCDC-1033618 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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