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Highly tunable anionic tethered N-heterocyclic carbene of Pd(II) complexes for asymmetric allylic alkylation reaction

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ABSTRACT

The versatility of the anionic tethered NHC ligand system for the Pd-catalyzed allylic asymmetric alkylation (AAA) reaction was investigated. A well defined anionic amidate/NHC–Pd(II) complex catalyzed the AAA reaction of 1,3-diphenylprop-3-en-1-yl acetate (**5**) with $NaCH(CO_2Me)_2$. Similarly, the AAA reaction occurred by employing an NHC–Pd(II) complex that was generated *in situ*. Screening of a wide variety of NHC ligand precursors revealed that the combination of $[Pd(allyl)Cl]_2$ and the azolium salt **9**, containing a 3-pentyl group at N(3) position in the NHC ring, efficiently promoted the AAA reaction to afford the corresponding alkylated product **7** with 67% ee. Furthermore, it was found that the Pd/NHC ratio was an important factor; the AAA reaction with a Pd/NHC ratio of 1:1 took place smoothly, whereas utilization of a Pd/NHC ratio of 1:2 resulted in low conversion of the substrates probably by the formation of the catalytically inert bis(NHC)–Pd(II) complex. In fact, an independent experiment showed that the bis(NHC)–Pd(II) complex was formed by treating $[Pd(allyl)Cl]_2$ with two equivalents of NHC–Ag complex. Further investigations on the catalytic AAA reaction revealed significant improvements in both the product yield (99%) and the enantioselectivity (81% ee) when cyclopentyl methyl ether was used as a solvent. A plausible reaction intermediate was discussed.

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1. Introduction

Since the first formative studies by Wanzlick, Öfele, and Lappert in the 1960s and 1970s focused on the synthesis of N-heterocyclic carbene (NHC) complexes, investigations on their applications in catalysis have been initiated [1]. The decisive breakthrough was achieved in 1995 by Herrmann and coworkers, who reported that NHC-containing well defined palladium(0) and palladium(II) complexes efficiently catalyzed the Heck reaction [2]. Because of the strong bonds between NHCs and transition metals, the interest in these ligands for applications in catalysis has grown rapidly [3]. Another feature that makes NHCs a very interesting class of ligands is the easy access to their respective precursors (mostly azolium salts). This allows the design of a wide variety of NHC ligands and the rapid elaboration of NHC ligand libraries.

An important step in the development of functionalized NHC ligands is their chiral modification for asymmetric reactions [3,4]. For design of an efficient chiral NHC ligand, the introduction of donor functionalities at the NHC ligand provides relatively inflexible chelating NHC-based ligand, which is expected to offer a key structure for the construction of efficient stereodirecting group. The donor-functionalized NHC contains an *anionic* or *neutral* 2e donor atom (e.g., C, N, O, S or P), which acts as a polydentate ligand upon coordination to a metal center [3c]. Therefore, one obvious way for achieving asymmetric reactions would be the use of the *anionic* or *neutral* donor-functionalized chiral NHC ligand.

The Pd-catalyzed asymmetric allylic alkylation (AAA) reaction has become an extremely useful synthetic methodology for stereoselective C–C bond formation [5]. In comparison to reports on oxazoline- or phosphine-based ligands, fewer studies on the use of the NHC-based chiral ligand have appeared dealing with this transformation (Scheme 1) [4]. Douthwaite et al. introduced the imine-functionalized NHC containing a *neutral* donor N atom [6]. By employing the neutral, bidentate CN ligand system, 92% ee was achieved in the Pd-catalyzed AAA reaction of 1,3-diphenylprop-3-en-1-yl acetate with dimethyl malonate. Fernández et al. developed a Pd complex with a chelating *neutral* thioether/NHC ligand, and tested the complex in the AAA reaction affording good yields of product and moderate to good ee values [7]. Buono et al. reported a study on synergistic effects between NHC and P-ligand [8]. The combination of NHC and chiral P-donor ligands led to an enhancement in the enantioselectivity. However, the reported attempts to apply NHC in AAA found limited success, despite the variety of monodentate or bidentate (CN, CP, or CS) NHC families explored [9]. In addition, little attention has been paid to *anionic*

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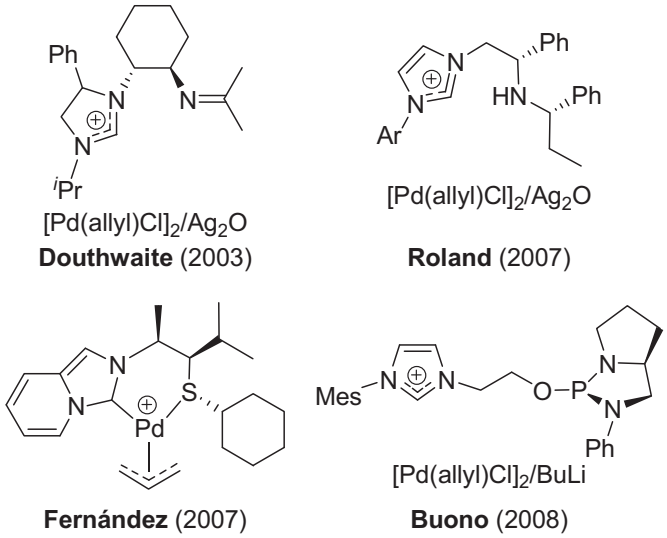
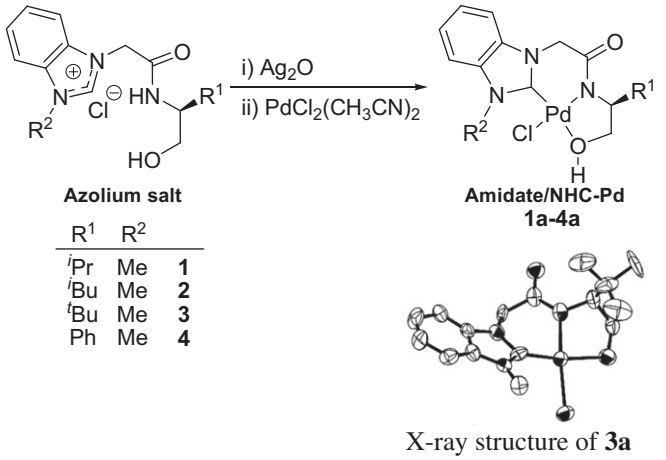


Scheme 1. Representative donor-functionalized NHC containing *neutral* 2e donor atom (N, S, P) chelating ligand for Pd-catalyzed AAA reaction.



R^1	R^2	
^{i}Pr	Me	**1**
^{i}Bu	Me	**2**
^{t}Bu	Me	**3**
Ph	Me	**4**

Scheme 2. One-pot synthesis of well defined *anionic* amidate/NHC–Pd(II) complexes **1a**–**4a** from chiral hydroxy-amide functionalized azolium salts **1**–**4**.

tethered NHC–Pd complexes, although the *anionic* tightly coordinating polydentate NHC ligand system is expected to enhance the catalyst stability and to offer a key structure for the construction of efficient stereodirecting elements.

Recently, we synthesized and fully characterized new anionic amidate/NHC–Pd(II) and dianionic amidate/alkoxy/NHC–Pd(II) complexes [10]. Importantly, the well defined and highly purified NHC–Pd complex catalyzed Heck-type reactions of arylboronic acids with alkenes with high enantioselectivities. In addition, NHC ligand precursors such as hydroxy-amide functionalized azolium salts were tested for the Cu-catalyzed asymmetric conjugate addition of enones with dialkylzincs [11]. In contrast to the Pd-catalyzed Heck-type reaction, the Cu-catalyzed asymmetric 1,4-addition reaction performed *in situ* generated the catalytic system; enones were allowed to react with R_2Zn in the presence of catalytic amounts of a Cu salt combined with a chiral azolium salt to afford the corresponding conjugate adducts with excellent enantioselectivities.

In this study, we investigated the versatility of the anionic tethered NHC ligand system for the Pd-catalyzed AAA reaction. The most attractive feature of the ligand is that the NHC with an anionic amidate group induces the generation of a strongly coordinating polydentate ligand able to lock stereodirecting functionalized groups in a fixed conformation. Moreover, the hydroxy-amide functionalized azolium ligand precursors are easily accessible in two steps from enantiopure β-amino alcohols. Therefore, we reasoned that a suitable ligand could be produced from the screening of a large library through variation of the substituents at the NHC ligand. Here, we report the AAA reaction of 1,3-diphenylprop-3-en-1-yl acetate with dimethyl malonate catalyzed by the well defined Pd(II) complex showing a highly tunable anionic amidate/NHC ligand. We also explore the AAA reaction under the influence of a NHC–Pd catalyst generated *in situ* from the combination of an appropriate palladium catalyst precursor and a chiral azolium ligand precursor.

2. Results and discussion

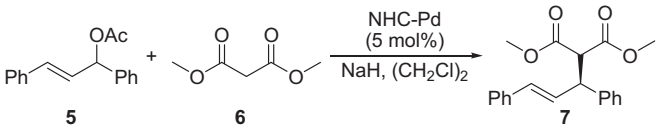
2.1. Synthesis of anionic amidate/NHC–Pd(II) complexes

The hydroxy-amide functionalized azolium compounds were reacted with Ag_2O to cleanly afford the corresponding silver carbene complexes, and these materials were used as a carbene transfer agent. Reaction of the resulting NHC–Ag complexes with $PdCl_2(CH_3CN)_2$ yielded the tridentate NHC–Pd(II) complexes **1a**–**4a** (Scheme 2). Notably, these complexes were air- and moisture-stable products easily handled under air atmosphere and stored as solids without any special precaution. In preceding papers, we reported X-ray diffraction studies of the NHC–Pd complexes **1a**, **2a**, and **4a** [10a,c]. Herein, a new complex **3a** was synthesized and characterized by ^{1}H and ^{13}C NMR spectroscopies and elemental analysis. In addition, **3a** was successfully obtained as single crystals, and X-ray diffraction studies were performed.

2.2. Catalytic studies

The potential application of the amidate/NHC–Pd(II) complexes was explored in the Pd-catalyzed AAA reaction (Table 1). First, (*E*)-1,3-diphenylprop-2-en-1-yl acetate (**5**) was allowed to react with dimethyl malonate (**6**) under the influence of a well defined amidate/NHC–Pd(II) complex **1a** ($R^1 = {}^i$Pr, R^2 = Me) in the presence of NaH in 1,2-dichloroethane at 80 °C for 15 h. Unfortunately, the corresponding desired product **7** was obtained with a poor yield

Table 1
Initial studies on AAA reaction.[a]



Entry	Catalyst	Temp. (°C)	Yield (%)	ee (%)
1	**1a**	80	3	5
2	**2a**	80	4	9
3	**3a**	80	5	20
4	**4a**	80	3	7
5[b]	**3**; $PdCl_2(CH_3CN)_2$	80	5	19
6[b,c]	**3**; $[Pd(allyl)Cl]_2$	80	12	21
7[b,c]	**3**; $[Pd(cinnamyl)Cl]_2$	80	9	20
8[b,c]	**3**; $[Pd(allyl)Cl]_2$	70	3	24
9[b,c]	**3**; $[Pd(allyl)Cl]_2$	95	48	16

[a] Reaction conditions: see Experimental section for detail. **5** (0.2 mmol), **6** (0.6 mmol), NaH (0.57 mmol), NHC–Pd(II) complex (0.01 mmol), $(CH_2Cl)_2$ (3 mL), 15 h.
[b] Reaction conditions: see Experimental section for detail. Pd precursor (0.01 mmol), azolium salt **3** (0.01 mmol), Ag_2O (0.005 mmol).
[c] Pd precursor (0.005 mmol).

(3%) and enantioselectivity (5% ee) (Table 1, entry 1). This result is in contrast to the previously reported Pd(II)-catalyzed asymmetric Heck-type reaction, where highly enantioselective cross-coupling reaction was successfully achieved by employing the NHC–Pd(II) complex derived from azolium salt **1** (R^1 = ^{i}Pr, R^2 = Me) [10a,b]. Several well defined NHC–Pd(II) complexes **1a**–**4a** were screened (entries 1–4). Replacement of the alkyl substituent at the chiral carbon center of the ligand (R^1 group) from isopropyl group (complex **1a**) to more sterically hindered *tert*-butyl group (complex **3a**) led to slight improvements in the AAA stereoselectivity (20% ee) (entry 3).

Previously, we have reported on asymmetric transfer hydrogenation of acetophenone with isopropyl alcohol (IPA) catalyzed by well defined NHC–Ir complex prepared from an azolium NHC ligand precursor **3** through an Ag_2O method [12]. In addition, we have shown that the enantioselective reduction of acetophenone with IPA by employing the NHC–Ir catalyst that was generated *in situ* took place without the loss of enantioselectivity. Therefore, we decided to study the ability of the NHC–Pd complex that was generated *in situ* to promote the present AAA reaction (Table 1, entries 5–9). After the treatment of the relevant azolium salt **3** (R^1 = ^{t}Bu, R^2 = Me) with Ag_2O in CH_2Cl_2 at room temperature, $PdCl_2(CH_3CN)_2$ was added to the reaction vessel. The resulting mixture was stirred at room temperature, filtered with a membrane filter, and evaporated to dryness under vacuum. Subsequently, **5** was treated with $NaCH(CO_2Me)_2$ in the presence of the unpurified NHC–Pd catalyst in $(CH_2Cl)_2$ at 80 °C for 15 h. By means of this procedure, the reaction produced **7** in 5% yield and 19% ee (Table 1, entry 5). The advantage of this procedure lies in the operational simplicity, which allows easy ligand screening tests (*vide infra*, Table 2).

As shown in Scheme 1, most of the previously reported AAA reactions were performed by using a palladium catalyst generated *in situ* from $[Pd(allyl)Cl]_2$ and chiral NHC [6–9]. Thus, we assumed that a metal complex formed from $[Pd(allyl)Cl]_2$ would differ from complex **3a** formed from $PdCl_2(CH_3CN)_2$. In fact, **5** was alkylated under the combined catalytic system of $[Pd(allyl)Cl]_2$ and azolium salt **3** to give the desired product **7** in the product yield (12%) (Table 1, entry 6). In addition, the AAA reaction catalyzed by $[Pd(cinnamyl)Cl]_2$ combined with **3** proceeded in a similar manner as compared to the reaction using $PdCl_2(CH_3CN)_2$ (entry 5 vs. entry 7). Decreasing the reaction temperature to 70 °C led to slower reaction rates, while raising it to 90 °C resulted in the formation of **7** in moderate yield (48%) (entries 8 and 9).

As mentioned in the Introduction, the easy tuning of both N-anionic functional groups and N-alkyl groups of the hydroxy-amide functionalized azolium NHC precursor would allow the development of a huge variety of polydentate chiral ligands [10c,13]. Scheme 3 and Table 2 summarize results for the AAA reaction of **5** and **6** under the influence of catalytic amounts of $[Pd(allyl)Cl]_2$ combined with various chiral azolium precursors, **3** and **8**–**29**, containing a *tert*-butyl substituent at the stereogenic center (R^1 = ^{t}Bu). The use of an azolium salt **3**, prepared from 1-methylbenzimidazole, resulted in the formation of **7** with low yield and ee (entry 1). Conversely, it was found that the AAA reaction under the combination of $[Pd(allyl)Cl]_2$ and **8** or **9**, containing isopropyl or 3-pentyl group at N(3) position at the NHC ring, afforded **7** in 42% or 67% ee, respectively (entries 2 and 3). We performed the AAA reaction without filtration of the resulting of AgCl in the preparation of NHC–Pd catalyst (entry 4). However, the reaction resulted in the formation of **7** with lower yield.

Since significant improvements in the stereoselectivity of the AAA reaction were achieved by changing the R^2 group at NHC ring (Table 2, entries 1–3), further systematic studies were performed. Treatment of **5** with $NaCH(CO_2Me)_2$ in the presence of a palladium catalyst generated *in situ* from $[Pd(allyl)Cl]_2$ and **10** (R^2 = ^{n}Bu) furnished **7** with low enantioselectivity (38% ee) (entry 5). These results might indicate that azolium salt possessing a secondary alkyl group at R^2 substituent would be suitable for the present catalytic system (entries 1–5). Hence, the azolium salt **11** ($R^2 = CH(C_3H_7)_2$) was synthesized from 1-(4-heptyl)benzimidazole and subsequently evaluated. As expected, **5** was alkylated upon the palladium catalyst derived from $[Pd(allyl)Cl]_2$ and **11** to yield **7** in 64% ee (entry 6).

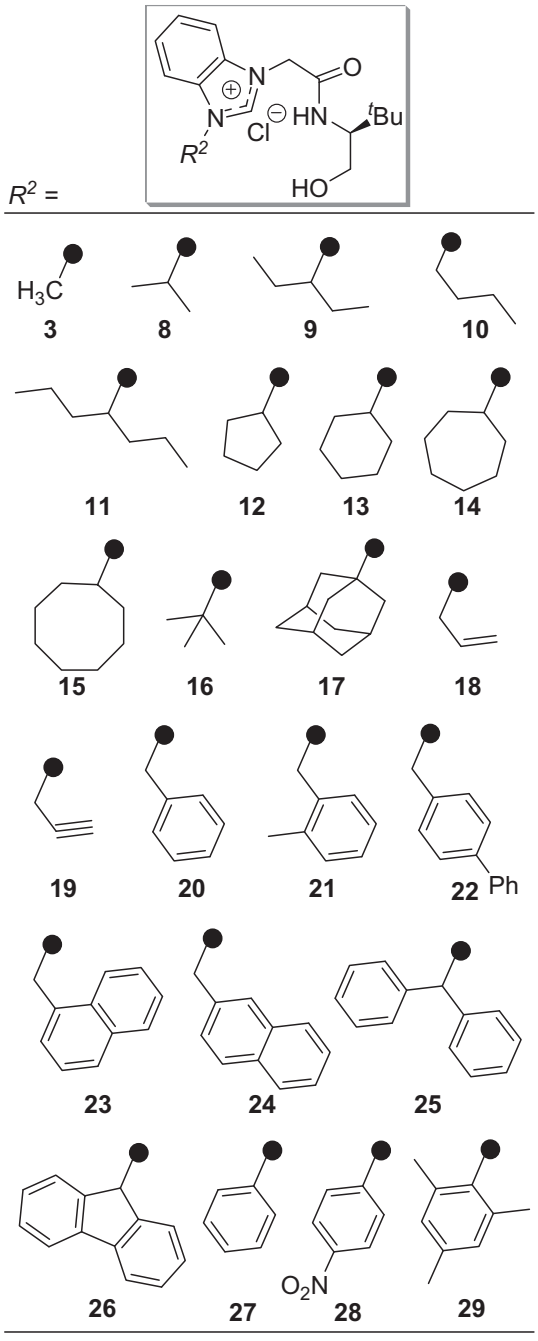
Moreover, we were interested in studying the influence of the conformational rigidity of cycloalkyl substituent (secondary alkyl group) at the R^2 position of the ligand, on the stereoselectivity of the AAA reaction. With this aim, a series of azolium ligand precursors **12**–**15** bearing cyclopentyl, cyclohexyl, cycloheptyl, or cyclooctyl substituent were evaluated (Table 2, entries 7–10). Although the enantioselectivity with **12** (R^2 = $^{cyclo}C_5H_9$) was comparable to that afforded with **11** ($R^2 = CH(C_3H_7)_2$), the product yield was very low (entry 7). In contrast to **12**, AAA reaction under **13** (R^2 = $^{cyclo}C_6H_{11}$) took place with lower stereoselectivity (28% ee) probably as a result of the conformational rigidness of the cyclohexyl group (entry 8). The utilization of **15** (R^2 = $^{cyclo}C_8H_{15}$) resulted in a racemic mixture of **7** (entry 10). In addition to these ligand precursors such as **8**, **9**, and **11**–**15**, bearing secondary alkyl group at the R^2 position, we prepared and evaluated tertiary alkyl groups such as *tert*-butyl and 1-adamantyl groups (azolium salts **16** and **17**). However, reaction was hardly produced under **16** or **17** (entries 11 and 12). This might be explained by the steric bulkiness of the tertiary alkyl group that hinders the approach of the substances to the palladium center.

While azolium ligand precursors possessing allyl and propargyl substituents such as **18** and **19** were inert (Table 2, entries 13 and 14), replacement of these substituents with a benzyl group (azolium salt **20**) led to a marked increase in the enantioselectivity of the AAA reaction of **5** with **6** (entry 15). Based on these results, several azolium salts **21**–**26** were screened (entries 16–21). Moderate ee (59%) was observed when **5** was treated with

Table 2
Influence of azolium ligand precursor on AAA reaction by *in situ* generated palladium catalyst.[a]

Entry	Azolium salt	Yield (%)	ee (%)
1	**3**	12	21
2	**8**	38	42
3	**9**	**65**	**67**
4[b]	**9**	16	69
5	**10**	21	38
6	**11**	44	64
7	**12**	9	64
8	**13**	32	28
9	**14**	22	28
10	**15**	12	2
11	**16**	6	5
12	**17**	4	−4
13	**18**	8	5
14	**19**	7	24
15	**20**	20	43
16	**21**	12	45
17	**22**	41	15
18	**23**	25	24
19	**24**	26	24
20	**25**	27	49
21	**26**	48	59
22	**27**	22	−41
23	**28**	6	−10
24	**29**	7	32

[a] Reaction conditions: see Experimental section for detail. **5** (0.2 mmol), **6** (0.6 mmol), NaH (0.57 mmol), $[Pd(allyl)Cl]_2$ (0.005 mmol), azolium salt (0.01 mmol), Ag_2O (0.005 mmol), $(CH_2Cl)_2$ (3 mL), 80 °C, 15 h.
[b] In the preparation of NHC–Pd complex, no filtration of the resulting AgCl was performed.



Scheme 3. List of chiral NHC precursors.

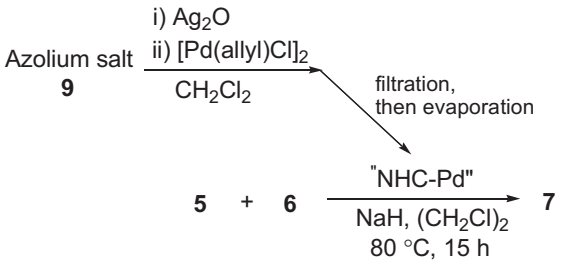
$NaCH(CO_2Me)_2$ under the influence of the NHC–Pd complex that was generated *in situ* from $[Pd(allyl)Cl]_2$ and **26** (R^2 = 9-fluorenyl) (entry 21). Surprisingly, the enantioselectivity in the AAA reaction was reversed by employing **27** (R^2 = Ph) (entry 22). While the reaction under **28** (R^2 = 4-$NO_2C_6H_4$) also led to the formation of *ent*-**7** (entry 23), the use of the azolium salt **29** (R^2 = mesityl) did not produce the alkylated product with the opposite configuration (e.g., *ent*-**7**) (entry 24). AAA reaction under these chiral ligand precursors containing aryl substituent at the R^2 position is currently under investigation.

During the course of this study, the ratio of the palladium precursor and the NHC ligand precursor was found to be an important factor (Scheme 4). As described above, the alkylation of **5** with $NaCH(CO_2Me)_2$ proceeded smoothly with a Pd/NHC ratio of 1:1 affording **7** with a 65% yield and 67% ee (Table 2, entry 3; Scheme 4, entry 1). On the other hand, most of the substrate was recovered unchanged when the AAA reaction was conducted with a Pd/NHC ratio of 1:2 (Scheme 4, entry 2). These results might be explained by the formation of a bis(NHC)–Pd complex **A** in the later case (*vide infra*, Scheme 5). We assumed that the difficulty of the reactant to approach the sterically hindered π-allyl palladium site on bis(NHC)–Pd complex **A** might cause the lower yield of the product in the AAA reaction.

Indeed, an independent experiment revealed that the reaction of $[Pd(allyl)Cl]_2$ with two equivalents of NHC–Ag complex yielded bis(NHC)–Pd complex **A** (Scheme 5). Treatment of 0.05 mmol of $[Pd(allyl)Cl]_2$ with 0.2 mmol of NHC–Ag in CH_2Cl_2 at room temperature afforded $[Pd(allyl)(NHC)_2]Cl$ **30** in 67% yield [14]. This new complex **30** was isolated as a white and air stable solid. In the literature, several types of well defined NHC–Pd(II) complexes such as π-allyl palladium complexes [Pd(allyl)X(NHC)] and solvent-coordinated π-allyl palladium complexes [Pd(allyl)(NHC)(solvent)]X have been reported [15]. However, the appearance of bis(NHC)–π-allyl palladium complexes $[Pd(allyl)(NHC)_2]X$ is rare. Recently, Chen and coworkers reported the synthesis and characterization of neutral π-allyl palladium(II) complexes containing bis(1,2,4-tirazol-5-ylidene-1-yl)borate ligands [15a].

The complex **30** was characterized by ^1H and ^{13}C NMR spectroscopies and elemental analysis (Fig. 1). The formation of the carbene–metal complex was evident from the distinctive Pd–$^{13}C_{carbene}$ peak, appearing at 191 ppm of **30**. Three ^1H NMR signals with a ratio of 2:2:1 and two ^{13}C NMR signals were observed for the allylic groups in **30**. The assignment of the H_{syn} and H_{anti} atoms in **30** was made based on the comparison with those reported for NHC–π-allyl palladium complexes [15a]. The peak of the *syn* H atoms is downfield from that the anti atoms. The J_{H-H} couplings between the CH and H_{syn} and H_{anti} atoms were 7.3 and 13.3 Hz, respectively. In ^{13}C NMR, the signals at δ 125 and 62 ppm corresponding to the allylic groups in **30** were observed.

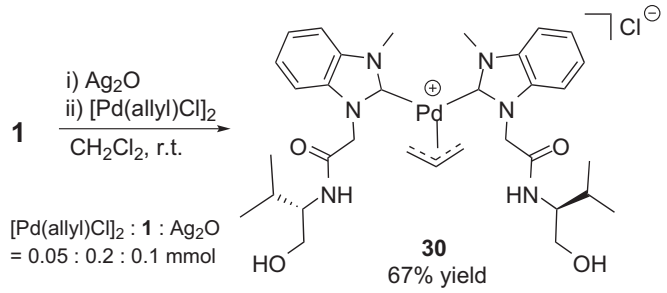
The thus-obtained well defined $[Pd(allyl)(NHC)_2]Cl$ complex **30** did not show any catalytic activity in the AAA reaction of **5** and **6**. These results strongly suggest the formation of a bis(NHC)–Pd species **A** when the reaction takes place under the influence of the Pd-catalyst generated *in situ* from $[Pd(allyl)Cl]_2$ and chiral azolium **9** with a Pd/NHC ratio of 1:2. Consequently, the occurrence of the alkylation reaction would be difficult as shown in Scheme 4, entry 2.



Entry		Yield (%)	Ee (%)
1[a]	*Pd:NHC = 1:1*	65	67
2[b]	*Pd:NHC = 1:2*	10	75

[a] Reaction conditions: **5** (0.2 mmol), **6** (0.6 mmol), NaH (0.57 mmol), $[Pd(allyl)Cl]_2$ (0.005 mmol), **9** (0.01 mmol), Ag_2O (0.005 mmol), $(CH_2Cl)_2$ (3 mL), 80 °C, 15 h. [b] **9** (0.02 mmol), Ag_2O (0.01 mmol).

Scheme 4. Influence of the Pd/NHC ratio.



Scheme 5. Reaction of $[Pd(allyl)Cl]_2$ with NHC–Ag complex derived from azolium salt **1** with a Pd/NHC ratio of 1:2.

It could be seen that a part of palladium precursor $[Pd(allyl)Cl]_2$ would be converted into $[Pd(allyl)(NHC)_2]Cl$ **A** even under a Pd/NHC ratio of 1:1 (Scheme 4, entry 1). Consequently, the formation of the catalytically inert bis(NHC)–Pd species **A** would lead to a moderate yield (65%) of the desired product **7**. According to this assumption, we hypothesized that the use of an ethereal solvent in place of a halogenated solvent such as $(CH_2Cl)_2$ could prevent the formation of bis(NHC)–Pd species **A** via coordination of palladium metal with the ether oxygen of the solvent. We assumed that in an ethereal solvent, [Pd(allyl)Cl(NHC)] and/or [Pd(allyl)(NHC)(solvent)]Cl might be formed instead of $[Pd(allyl)(NHC)_2]Cl$. The donor numbers of ethereal solvents were reported to be much higher than those of halogenated solvents [10d,16]. Hence, we investigated the AAA reaction by the NHC–Pd(II) catalyst generated *in situ* with a Pd/NHC ratio of 1:1 under the influence of an ethereal solvent (Table 3).

In contrast to the reaction in $(CH_2Cl)_2$, the use of an ethereal solvent such as THF led to an increase of the product yield even at a lower reaction temperature (70 °C), although a moderate enantioselectivity was obtained (Table 3, entry 1 vs. entry 2). Encouraged by this success, we examined various ethereal solvents for further optimizations (entries 3–7). The first promising result was obtained by employing diisopropyl ether (DIPE) at 70 °C, furnishing **7** in almost quantitative yield (99%) without loss of stereoselectivity (66% ee) (entry 1 vs. entry 5). Although the reaction in DIPE was performed at lower temperature (60 °C), almost the same ee value (68% ee) was obtained (entry 6). Fortunately, a significant improvement (79% ee) was achieved when the reaction was conducted in cyclopentyl methyl ether (CPME) (entry 7). Further optimization of the reaction conditions revealed that **5** was efficiently alkylated with $NaCH(CO_2Me)_2$ (5 equiv. with respect to **5**) in CPME at 80 °C for 15 h to produce **7** in 99% yield with 81% ee (entry 10). The reaction took place completely within 5 h under these reaction conditions (entry 11). Similar result was obtained in the reaction using $[Pd(cinnamyl)Cl]_2$ in place of $[Pd(allyl)Cl]_2$ (entry 12). In addition, the AAA reaction under the influence of **27** (R^2 = Ph) in place of **9** (R^2 = $CH(C_2H_5)_2$) in CPME solvent led to formation of the alkylated product with the opposite configuration (e.g., *ent*-**7**) with a slight increase in the product yield (Table 2, entry 22 vs. Table 3, entry 13).

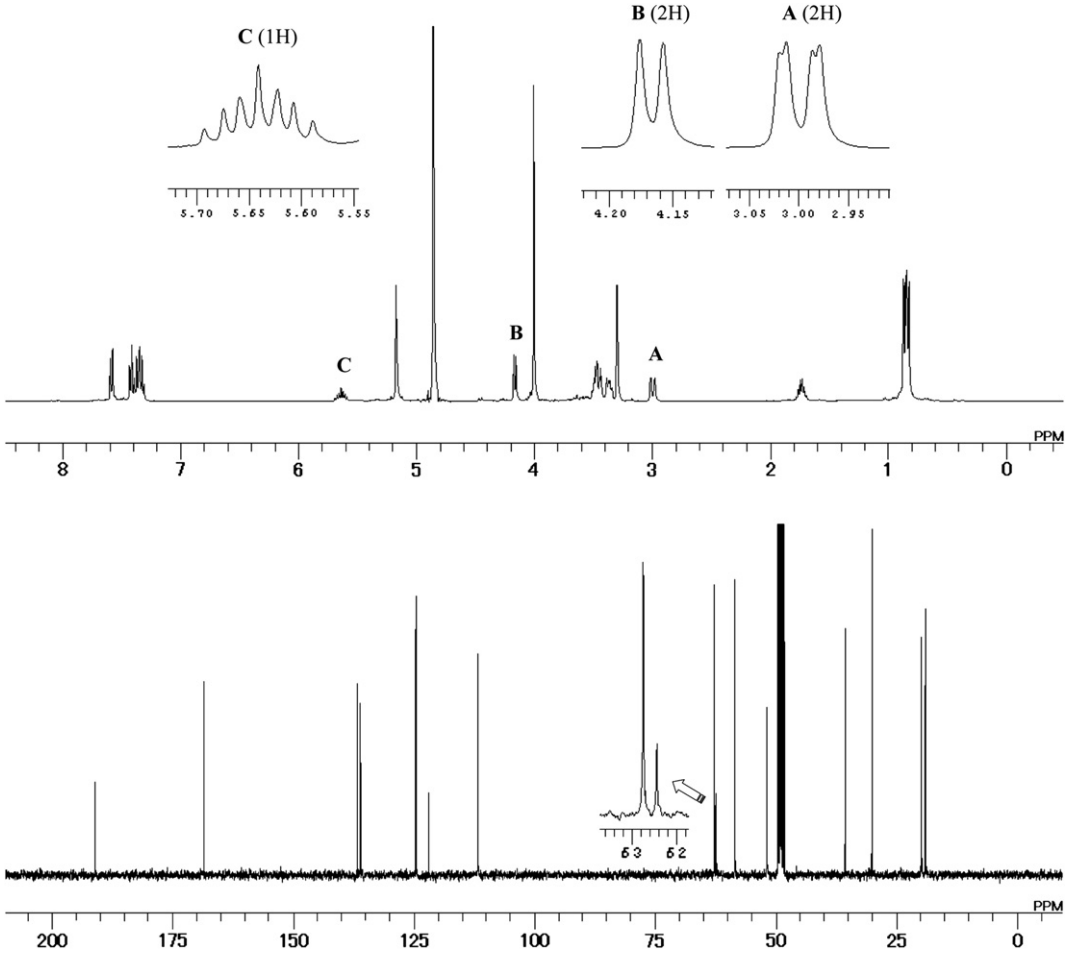


Fig. 1. ^1H NMR (upper) and ^{13}C NMR (lower) spectra of $[Pd(allyl)(NHC)_2]Cl$ **30**.

Table 3
Solvent effect in AAA reaction by *in situ* generated palladium catalyst with a Pd/NHC ratio of 1:1.[a]

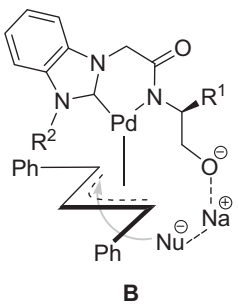
Entry	Solvent	Temp. (°C)	Yield (%)	ee (%)
1	$(CH_2Cl)_2$	80	65	67
2	THF	70	96	37
3	2-MeTHF[b]	80	58	47
4	TBME[c]	50	90	57
5	DIPE[d]	70	99	66
6	DIPE	60	70	68
7	CPME[e]	80	83	79
8	CPME	90	90	75
9	CPME	70	52	75
10[f]	**CPME**	**80**	**99**	**81**
11[f,g]	**CPME**	**80**	**97**	**81**
12[f,h]	**CPME**	**80**	**99**	**80**
13[i]	CPME	80	33	−41

[a] Reaction conditions: see Experimental section for detail. **5** (0.2 mmol), **6** (0.6 mmol), NaH (0.57 mmol), $[Pd(allyl)Cl]_2$ (0.005 mmol), **9** (0.01 mmol), Ag_2O (0.005 mmol), solvent (3 mL), 15 h.
[b] 2-MeTHF: 2-methyltetrahydrofuran.
[c] TBME: *tert*-butyl methyl ether.
[d] DIPE: diisopropyl ether.
[e] CPME: cyclopentyl methyl ether.
[f] **6** (1.0 mmol), NaH (0.95 mmol).
[g] Reaction was run for 5 h.
[h] $[Pd(cinnamyl)Cl]_2$ (0.005 mmol) in place of $[Pd(allyl)Cl]_2$ was used.
[i] **27** (0.01 mmol) in place of **9** was used.

2.3. Mechanistic aspects

At this stage, we had no experimental evidence to explain the reaction mechanism. A plausible reaction model involves the formation of an anionic amidate/palladium species **B** to lock a stereodirecting group (R^1) in a fixed conformation, as shown in Scheme 6. It is known that in the absence of overriding steric factors, the addition of soft nucleophiles to allyl complexes would occur with regioselective *trans* to the ligand, which is the strongest σ-donor [6,17]. In the reaction model **B**, the nucleophilic attack would therefore take place *trans* to the anionic amidate group. For stereoselective reaction, the orientation of the allyl moiety in the intermediate **B** is required, which is in agreement with the increasing bulkiness of both R^1 (^{t}Bu) and R^2 ($CH(C_2H_5)_2$) groups at the NHC ligand. Additionally, it seems likely that the hydroxy group in the NHC ligand is also an important factor. Thus, the hydroxy group would be converted into sodium alcoholate upon AAA conditions involving $NaCH(CO_2Me)_2$. The interaction between the sodium alcoholate and nucleophile would assist the approach of the nucleophile to the π-allyl palladium center [18].

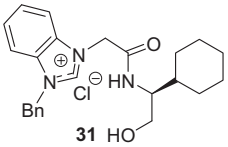
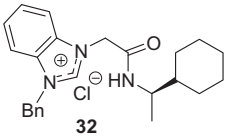
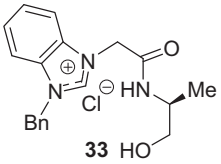
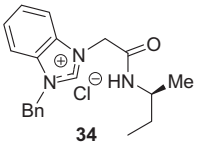
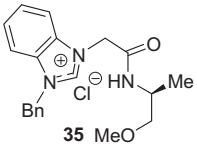
In order to obtain further information of the reaction pathway, two amide-functionalized azolium salts such as **31** and **32** were prepared (Table 4). While AAA of **5** with $NaCH(CO_2Me)_2$ by using the palladium catalyst generated *in situ* from $[Pd(allyl)Cl]_2$ and **31** ($R^1 = {}^{cyclo}C_6H_{11}$, R^2 = Bn) afforded **7** in 19% yield and 31% ee (entry 1), most of the substrate **5** was recovered unchanged when the reaction was carried out under the influence of **32** (entry 2). These results strongly suggested that the hydroxy-amide functionality on the NHC ligand not only induces the stereoselectivity of the AAA reaction but also enhances the reaction rate.



B

Scheme 6. Proposed allyl complex intermediate.

Table 4
AAA reaction by *in situ* generated palladium catalyst from $[Pd(allyl)Cl]_2$ and **31**–**35**.[a]

Entry	Azolium salt	**7**	
		Yield (%)	ee (%)
1	 **31**	19	31
2	 **32**	5	14
3[b]	 **33**	29 (65)	3 (8)
4[b]	 **34**	3 (26)	2 (8)
5[b]	 **35**	4 (23)	5 (5)

[a] Reaction conditions: see Experimental section for detail. **5** (0.2 mmol), **6** (0.6 mmol), NaH (0.57 mmol), $[Pd(allyl)Cl]_2$ (0.005 mmol), azolium salt (0.01 mmol), Ag_2O (0.005 mmol), $(CH_2Cl)_2$ (3 mL), 80 °C, 15 h.
[b] The numbers in parentheses showed the yield and ee in the AAA reaction using **6** (1.0 mmol), NaH (0.95 mmol), and CPME (3 mL).

In addition, azolium compounds **33**–**35** were synthesized from commercially available L-alaninol, (*S*)-*sec*-butylamine and (*S*)-1-methoxy-2-propanamine, respectively. The AAA reaction of **5** with $NaCH(CO_2Me)_2$ under the influence of the hydroxy-amide functionalized azolium salt **33** (R^1 = Me, R^2 = Bn) in $(CH_2Cl)_2$ or CPME yielded the alkylated product **7** in 29% or 65% yield, respectively, with low enantioselectivity (Table 4, entry 3). This is in contrast to the reaction using **20** ($R^1 = {}^t$Bu, R^2 = Bn), in which **7** was obtained with 43% ee (Table 2, entry 15). These results indicated that the choice of sterically hindered substituent at the R^1 position on the chiral ligand is an important factor. On the other hand, replacement of OH group (azolium **33**) by a CH_3 group or OCH_3 group (azolium **34** or **35**) in the chiral ligand led to a marked decrease in the product yield (Table 4, entries 4 and 5). This suggested again that the hydroxy functionality of the chiral ligand is of critical importance for AAA reaction.

3. Conclusion

We described the versatility of an *anionic* amidate/NHC–Pd complex for the AAA reaction. This AAA reaction catalyzed by the

NHC–Pd(II) complex that was generated *in situ* has been fully investigated. Changing the R^2 substituent at the NHC ring was found to have a drastic effect on the outcome. The ligand screening tests revealed the combination of $[Pd(allyl)Cl]_2$ and chiral ligand **9** ($R^1 = {}^tBu$, $R^2 = CH(C_2H_5)_2$) as the best catalytic system. In addition, the Pd precursor/ligand precursor ratio was found to be an important factor determining the efficiency of AAA. A new π-allyl palladium(II) complex containing a bis(NHC) ligand was obtained and characterized. According to the coordination chemistry, the AAA reaction was found to be favored in CPME, producing the desired product **7** with 81% ee. We believe that the present catalytic system involving an *anionic* amidate tethered NHC–Pd(II) complex would provide an alternative method for the Pd-catalyzed AAA reaction. Further applications of the chiral chelating polydentate ligand based on an NHC scaffold for efficient catalytic enantioselective transformations are the subject of ongoing research in our laboratory.

4. Experimental

4.1. General procedures

All chemicals were obtained from commercial sources and were used as received. ^1H and ^{13}C NMR spectra were recorded on spectrometers at 400 and 100 MHz, respectively. Chemical shifts were reported in ppm relative to TMS for ^1H and ^{13}C NMR spectra. $(CD_3)_2SO$, CD_3OD or $CDCl_3$ was used as the NMR solvent. Thin-layer chromatography (TLC) analysis was performed with glass-backed plates pre-coated with silica gel and examined under UV (254 nm) irradiation. Flash column chromatography was executed on silica gel 60 (230–400; particle size: 0.040–0.063 nm).

4.2. General procedure for preparation of amidate/NHC–Pd(II) complexes *1a*–*4a*

A suspension of azolium salt (0.12 mmol) and silver(I) oxide (0.07 mmol) in CH_2Cl_2 (5 mL) was stirred for 2 h in the dark at refluxing temperature. The reaction mixture was concentrated under reduced pressure to give a white solid. $PdCl_2(CH_3CN)_2$ (0.1 mmol) was added to a suspension of the resulting silver complex in CH_3CN (5 mL) in the dark. Then, the resulting suspension was stirred for 2 h in the dark at room temperature and filtered through a plug of glass fiber filter paper. The filtrate was evaporated to dryness in vacuo, and the Pd complexes were purified by reprecipitation from ethyl acetate and hexane. These complexes are very stable under air and could be stored for at least one month at room temperature. **1a**, **2a** and **4a** were reported in the preceding paper [10c]. **3a**: ^1H NMR (CD_3OD): δ 7.62 (br, 1H), 7.56–7.55 (m, 2H), 7.38–7.34 (m, 2H), 5.98 (d, J = 16.6 Hz, 1H), 5.42 (d, J = 16.6 Hz, 1H), 4.35 (s, 3H), 3.82–3.47 (m, 2H), 3.50–3.45 (m, 1H), 0.79 (s, 9H); ^{13}C NMR (CD_3CD): δ 169.0, 158.5, 136.2, 135.8, 125.0, 124.8, 112.3, 111.4, 62.2, 61.6, 52.6, 35.2, 34.6, 27.2. Anal. Calc. for $C_{16}H_{22}ClN_3O_2Pd \cdot 0.6CH_2Cl_2$: C, 41.43; H, 4.86; N, 8.73. Found: C, 41.36; H, 4.62; N, 8.98%. Crystallization of **3a** by slow evaporation from methanol solution gave colorless crystals suitable for study by X-ray diffraction. Crystal data: $C_{16}H_{22}O_2N_3ClPd$, M = 430.23, orthorhombic, a = 10.0266(3), b = 12.7397(5), c = 14.1604(5) Å, U = 1808.79(12) Å^3, T = 123(2) K, space group $P2_12_12_1$ (no. 19), Z = 4, μ(Mo-Kα) = 11.859 cm^{-1}. The final Rw was 0.1249 ($I > 2\sigma(I)$).

4.3. General procedure of preparation of azolium ligand precursors

To a flask were added N-alkylbenzimidazole (3 mmol), 1,4-dioxane (12 mL) and α-chloroacetoaminde derivative (3 mmol) derived from chloroacetyl chloride and (*S*)-*tert*-leucinol. After stirring the reaction mixture at 110 °C for 24 h, the solvent was removed under reduced pressure. The residue was dissolved in methanol, and then activated carbon (ca. 1 g) was added. After 16 h, the activated carbon was removed by filtration. After removing methanol in vacuo from the filtrate, the crude residue was purified by column chromatography (SiO_2, CH_2Cl_2/MeOH: 9/1) to yield the corresponding azolium salt. Azolium salts **1**–**4**, **8**–**10**, **16**, **20**, **23**, **25** and **26** were reported in our preceding papers [10–12]. Because of the hydroscopic character, elemental analysis of **11**–**15**, **27** and **29** were not performed.

4.3.1. 3-[2-{[(1S)-1-(Hydroxymethyl)-2,2-dimethylpropyl]amino}-2-oxoethyl]-1-(1-propylbutyl)-1H-benzimidazolium chloride (*11*)

White solid (yield: 80%); ^1H NMR ($(CD_3)_2SO$): δ 10.18 (s, 1H), 8.59 (d, J = 9.2 Hz, 1H), 8.22–8.19 (m, 1H), 8.04–8.01 (m, 1H), 7.69–7.64 (m, 2H), 5.47 (d, J = 16.5 Hz, 1H), 5.38 (d, J = 16.5 Hz, 1H), 4.94–4.87 (m, 1H), 4.67 (t, J = 6.0 Hz, 1H), 3.62–3.55 (m, 2H), 3.43–3.37 (m, 1H), 2.07–1.89 (m, 4H), 1.27–1.13 (m, 2H), 1.12–1.02 (m, 2H), 0.86 (s, 9H), 0.83 (t, J = 7.3 Hz, 6H); ^{13}C NMR ($(CD_3)_2SO$): δ 164.7, 142.6, 131.5, 130.8, 126.7, 126.6, 113.9, 113.7, 60.2, 59.8, 58.8, 48.9, 36.0, 33.6, 26.8, 18.4, 13.4. HRMS (ESI^+) calcd for $C_{22}H_{36}N_3O_2^+$: 374.2802, found 374.2794.

4.3.2. 3-[2-{[(1S)-1-(Hydroxymethyl)-2,2-dimethylpropyl]amino}-2-oxoethyl]-1-cyclopentyl-1H-benzimidazolium chloride (*12*)

White solid (yield: 84%); ^1H NMR ($(CD_3)_2SO$): δ 10.14 (s, 1H), 8.60 (d, J = 8.7 Hz, 1H), 8.12–8.09 (m, 1H), 8.00–7.98 (m, 1H), 7.69–7.64 (m, 2H), 5.48 (d, J = 16.5 Hz, 1H), 5.39 (d, J = 16.5 Hz, 1H), 5.25–5.18 (m, 1H), 4.70 (br, 1H), 3.62–3.56 (m, 2H), 3.43–3.37 (m, 1H), 2.38–2.30 (m, 2H), 2.06–1.98 (m, 2H), 1.93–1.83 (m, 2H), 1.80–1.71 (m, 2H), 0.87 (s, 9H); ^{13}C NMR ($(CD_3)_2SO$): δ 164.8, 141.8, 131.8, 130.7, 126.7, 126.4, 114.0, 113.8, 60.3, 59.8, 58.9, 48.8, 33.6, 31.6, 26.9, 23.2. HRMS (ESI^+) calcd for $C_{20}H_{30}N_3O_2^+$: 344.2332, found 344.2325.

4.3.3. 3-[2-{[(1S)-1-(Hydroxymethyl)-2,2-dimethylpropyl]amino}-2-oxoethyl]-1-cyclohexyl-1H-benzimidazolium chloride (*13*)

White solid (yield: 85%); ^1H NMR ($(CD_3)_2SO$): δ 10.02 (s, 1H), 8.48 (d, J = 8.7 Hz, 1H), 8.17–8.13 (m, 1H), 7.93–7.91 (m, 1H), 7.64–7.61 (m, 2H), 5.40 (d, J = 16.5 Hz, 1H), 5.31 (d, J = 16.5 Hz, 1H), 4.77–4.71 (m, 1H), 4.63 (br, 1H), 3.58–3.52 (m, 2H), 3.39–3.35 (m, 1H), 2.17–2.14 (m, 2H), 1.87–1.78 (m, 4H), 1.75–1.67 (m, 1H), 1.52–1.46 (m, 2H), 1.29–1.18 (m, 1H), 0.83 (s, 9H); ^{13}C NMR ($(CD_3)_2SO$): δ 164.8, 141.8, 131.6, 130.3, 126.7, 126.4, 114.1, 113.8, 60.3, 59.9, 56.8, 48.9, 33.6, 32.0, 26.9, 24.7, 24.6. HRMS (ESI^+) calcd for $C_{21}H_{32}N_3O_2^+$: 358.2489, found 358.2482.

4.3.4. 3-[2-{[(1S)-1-(Hydroxymethyl)-2,2-dimethylpropyl]amino}-2-oxoethyl]-1-cycloheptyl-1H-benzimidazolium chloride (*14*)

White solid (yield: 42%); ^1H NMR ($CDCl_3$): δ 10.41 (s, 1H), 8.92 (d, J = 9.2 Hz, 1H), 8.10–8.07 (m, 1H), 7.74–7.70 (m, 1H), 7.59–7.57 (m, 2H), 5.91 (d, J = 16.0 Hz, 1H), 5.84 (d, J = 16.0 Hz, 1H), 4.92 (t, J = 6.0 Hz, 1H), 4.77–4.70 (m, 1H), 3.85–3.79 (m, 1H), 3.75–3.70 (m, 2H), 2.29–2.14 (m, 4H), 1.89–1.86 (m, 2H), 1.70–1.63 (m, 6H), 0.93 (s, 9H); ^{13}C NMR ($CDCl_3$): δ 165.6, 141.5, 131.8, 129.7, 126.8, 126.3, 114.0, 112.6, 60.8, 60.7, 60.4, 49.5, 49.1, 34.1, 34.1, 33.3, 26.7, 26.7, 24.0. HRMS (ESI^+) calcd for $C_{22}H_{34}N_3O_2^+$: 372.2645, found 372.2638.

4.3.5. 3-[2-{[(1S)-1-(Hydroxymethyl)-2,2-dimethylpropyl]amino}-2-oxoethyl]-1-cyclooctyl-1H-benzimidazolium chloride (*15*)

White solid (yield: 74%); ^1H NMR ($(CD_3)_2SO$): δ 10.17 (s, 1H), 8.61 (d, J = 9.2 Hz, 1H), 8.14–8.10 (m, 1H), 8.02–7.98 (m, 1H), 7.68–7.64 (m, 2H), 5.48 (d, J = 16.0 Hz, 1H), 5.39 (d, J = 16.5 Hz, 1H), 5.06–5.01 (m, 1H), 4.71 (br, 1H), 3.61–3.55 (m, 2H), 3.43–3.39 (m, 1H), 2.23–2.16 (m, 2H), 2.10–2.04 (m, 2H), 1.77–1.60 (m, 10H), 0.87 (s, 9H); ^{13}C

NMR ($(CD_3)_2SO$): δ 164.8, 142.1, 131.6, 129.9, 126.7, 126.4, 114.1, 113.8, 60.3, 59.8, 58.5, 48.8, 33.6, 31.2, 26.9, 26.2, 24.8, 23.2. HRMS (ESI^+) calcd for $C_{23}H_{36}N_3O_2^+$: 386.2802, found 386.2794.

*4.3.6. 3-[2-{[(1S)-1-(Hydroxymethyl)-2,2-dimethylpropyl]amino}-2-oxoethyl]-1-(1-adamantyl)-1H-benzimidazolium chloride (**17**)*

White solid (yield: 73%); ^1H NMR ($(CD_3)_2SO$): δ 10.01 (s, 1H), 8.54 (d, J = 9.2 Hz, 1H), 8.41 (d, J = 8.2 Hz, 1H), 7.97–7.94 (m, 1H), 7.67–7.60 (m, 2H), 5.47 (d, J = 16.0 Hz, 1H), 5.38 (d, J = 16.0 Hz, 1H), 4.71 (t, J = 5.5 Hz, 1H), 3.62–3.55 (m, 2H), 3.43–3.99 (m, 1H), 2.37-2.28 (br, 7H), 1.87 (d, J = 12.4 Hz, 3H), 1.76 (d, J = 12.4 Hz, 3H), 0.87 (s, 9H); ^{13}C NMR ($(CD_3)_2SO$): δ 164.8, 141.8, 132.6, 129.1, 126.3, 126.0, 116.8, 114.2, 61.4, 60.3, 59.9, 48.7, 40.4, 34.9, 33.6, 29.1, 26.9. Anal. Calc. for $C_{25}H_{36}ClN_3O_2 \cdot 1.8H_2O$: C, 62.76; H, 8.34; N, 8.78. Found: C, 62.93; H, 8.26; N, 8.73%. M.p. 215.2–215.5 °C.

*4.3.7. 3-[2-{[(1S)-1-(Hydroxymethyl)-2,2-dimethylpropyl]amino}-2-oxoethyl]-1-(2-propenyl)-1H-benzimidazolium chloride (**18**)*

White solid (yield: 33%); ^1H NMR ($(CD_3)_2SO$): δ 9.88 (s, 1H), 8.52 (br, 1H), 8.02–7.98 (m, 2H), 7.69–7.67 (m, 2H), 6.17–6.07 (m, 1H), 5.56–5.33 (m, 4H), 5.25 (d, J = 5.4 Hz, 2H), 4.56 (t, J = 5.7 Hz, 1H), 3.63–3.56 (m, 2H), 3.42–3.37 (m, 1H), 0.87 (s, 9H); ^{13}C NMR ($(CD_3)_2SO$): δ 164.7, 143.4, 131.6, 131.0, 130.6, 126.7, 126.6, 120.2, 113.8, 113.6, 60.2, 59.8, 48.7, 35.0, 33.6, 26.8. Anal. Calc. for $C_{18}H_{26}ClN_3O_2 \cdot 0.2CHCl_3$: C, 58.18; H, 7.03; N, 11.18. Found: C, 58.17; H, 6.86; N, 11.35%. M.p. 220.8–221.0 °C.

*4.3.8. 3-[2-{[(1S)-1-(Hydroxymethyl)-2,2-dimethylpropyl]amino}-2-oxoethyl]-1-(2-propynyl)-1H-benzimidazolium chloride (**19**)*

White solid (yield: 38%); ^1H NMR ($(CD_3)_2SO$): δ 9.93 (s, 1H), 8.46 (d, J = 9.2 Hz, 1H), 8.06–8.04 (m, 1H), 8.02–7.97 (m, 1H), 7.75–7.69 (m, 2H), 5.61 (d, J = 2.3 Hz, 2H), 5.50 (d, J = 16.0 Hz, 1H), 5.39 (d, J = 16.0 Hz, 1H), 4.63 (t, J = 5.3 Hz, 1H), 3.88 (t, J = 2.3 Hz, 1H), 3.63–3.57 (m, 2H), 3.42–3.37 (m, 1H), 0.87 (s, 9H); ^{13}C NMR ($(CD_3)_2SO$): δ 164.6, 143.1, 131.6, 130.1, 126.9, 126.8, 113.8, 79.3, 75.5, 60.2, 59.8, 48.8, 36.7, 33.6, 26.8. Anal. Calc. for $C_{18}H_{24}ClN_3O_2 \cdot 0.2H_2O$: C, 61.16; H, 6.96; N, 11.89. Found: C, 61.03; H, 6.77; N, 11.86%. M.p. 225.4–225.9 °C.

*4.3.9. 3-[2-{[(1S)-1-(Hydroxymethyl)-2,2-dimethylpropyl]amino}-2-oxoethyl]-1-[(2-methylphenyl)methyl]-1H-benzimidazolium chloride (**21**)*

White solid (yield: 88%); ^1H NMR ($(CD_3)_2SO$): δ 9.75 (s, 1H), 8.42 (d, J = 9.2 Hz, 1H), 7.98–7.93 (m, 2H), 7.71–7.63 (m, 2H), 7.31–7.30 (m, 2H), 7.24–7.20 (m, 1H), 7.14 (d, J = 7.8 Hz, 1H), 5.85 (s, 2H), 5.46 (d, J = 16.5 Hz, 1H), 5.36 (d, J = 16.5 Hz, 1H), 4.66 (t, J = 5.5 Hz, 1H), 3.63–3.56 (m, 2H), 3.41–3.37 (m, 1H), 2.33 (s, 3H), 0.86 (s, 9H); ^{13}C NMR ($(CD_3)_2SO$): δ 164.8, 143.6, 138.3, 134.0, 131.7, 130.5, 129.3, 128.9, 128.7, 126.8, 126.7, 125.2, 113.9, 113.8, 60.3, 60.0, 49.8, 48.9, 33.6, 26.9, 21.0. Anal. Calc. for $C_{23}H_{30}ClN_3O_2 \cdot 0.3CH_3CO_2C_2H_5$: C, 65.70; H, 7.38; N, 9.50. Found: C, 65.68; H, 7.18; N, 9.38%. M.p. 150.3–150.8 °C.

*4.3.10. 3-[2-{[(1S)-1-(Hydroxymethyl)-2,2-dimethylpropyl]amino}-2-oxoethyl]-1-(4-biphenylmethyl)-1H-benzimidazolium chloride (**22**)*

White solid (yield: 33%); ^1H NMR ($(CD_3)_2SO$): δ 10.09 (s, 1H), 8.53 (d, J = 9.2 Hz, 1H), 8.07–7.93 (m, 2H), 7.71–7.58 (m, 8H), 7.46–7.42 (m, 2H), 7.37–7.33 (m, 1H), 5.90 (s, 2H), 5.51 (d, J = 16.5 Hz, 1H), 5.41 (d, J = 16.5 Hz, 1H), 4.66 (t, J = 5.5 Hz, 1H), 3.62–3.57 (m, 2H), 3.41–3.39 (m, 1H), 0.87 (s, 9H); ^{13}C NMR ($(CD_3)_2SO$): δ 164.8, 143.6, 140.6, 140.5, 139.3, 133.2, 131.7, 131.2, 130.5, 129.0, 128.9, 128.9, 127.8, 127.3, 126.8, 126.7, 60.3, 59.9, 49.5, 48.8, 33.6, 26.9. Anal. Calc. for $C_{28}H_{32}ClN_3O_2 \cdot 2.5H_2O$: C, 64.29; H, 7.13; N, 8.03. Found: C, 64.56; H, 7.20; N, 7.59%. M.p. 227.6–227.9 °C.

*4.3.11. 3-[2-{[(1S)-1-(Hydroxymethyl)-2,2-dimethylpropyl]amino}-2-oxoethyl]-1-(2-naphthalenylmethyl)-1H-benzimidazolium chloride (**24**)*

White solid (yield: 85%); ^1H NMR ($(CD_3)_2SO$): δ 10.04 (s, 1H), 8.48 (d, J = 9.1 Hz, 1H), 8.09–7.88 (m, 6H), 7.68–7.53 (m, 5H), 6.02 (s, 2H), 5.49 (d, J = 16.3 Hz, 1H), 5.38 (d, J = 16.3 Hz, 1H), 4.65 (t, J = 5.7 Hz, 1H), 3.63–3.57 (m, 2H), 3.42–3.37 (m, 1H), 0.86 (s, 9H); ^{13}C NMR ($(CD_3)_2SO$): δ 164.8, 143.7, 132.7, 132.7, 131.8, 131.4, 130.6, 128.9, 127.9, 127.7, 127.6, 126.8, 126.7, 125.6, 114.0, 113.8, 60.3, 59.8, 50.1, 48.8, 33.6, 26.8. Anal. Calc. for $C_{26}H_{30}ClN_3O_2 \cdot CH_3CO_2C_2H_5 \cdot 2H_2O$: C, 62.54; H, 7.35; N, 7.29. Found: C, 62.55; H, 6.87; N, 7.45%. M.p. 134.2–134.8 °C.

*4.3.12. 3-[2-{[(1S)-1-(Hydroxymethyl)-2,2-dimethylpropyl]amino}-2-oxoethyl]-1-phenyl-1H-benzimidazolium chloride (**27**)*

White solid (yield: 65%); ^1H NMR ($(CD_3)_2SO$): δ 10.43 (s, 1H), 8.62 (br, 1H), 8.14–8.09 (m, 1H), 7.88–7.84 (m, 3H), 7.78–7.69 (m, 5H), 5.60 (d, J = 16.5 Hz, 1H), 5.52 (d, J = 16.5 Hz, 1H), 3.65–3.60 (m, 2H), 3.46–3,41 (m, 1H), 0.90 (s, 9H); ^{13}C NMR ($(CD_3)_2SO$): δ 164.5, 143.5, 133.0, 131.6, 130.7, 130.6, 130.5, 127.5, 127.1, 125.1, 114.2, 113.6, 60.3, 60.0, 49.1, 33.6, 26.9. HRMS (ESI^+) calcd for $C_{21}H_{26}N_3O_2^+$: 352.2019, found 352.2012.

*4.3.13. 3-[2-{[(1S)-1-(Hydroxymethyl)-2,2-dimethylpropyl]amino}-2-oxoethyl]-1-(4-nitrophenyl)-1H-benzimidazolium chloride (**28**)*

Light yellow solid (yield: 17%); ^1H NMR ($(CD_3)_2SO$): δ 10.55 (s, 1H), 8.63 (d, J = 9.6 Hz, 1H), 8.58 (d, J = 9.2 Hz, 2H), 8.20 (d, J = 9.2 Hz, 2H), 8.14 (d, J = 7.3 Hz, 1H), 7.96–7.94 (m, 1H), 7.80–7.73 (m, 2H), 5.62 (d, J = 16.0 Hz, 1H), 5.53 (d, J = 16.0 Hz, 1H), 4.70 (t, J = 5.7 Hz, 1H), 3.66–3.59 (m, 2H), 3.46–3.38 (m, 1H), 0.90 (s, 9H); ^{13}C NMR ($(CD_3)_2SO$): δ 164.3, 148.1, 144.0, 138.0, 131.7, 130.4, 127.7, 127.3, 126.6, 125.7, 114.4, 113.6, 60.3, 59.9, 49.3, 33.6, 26.9. Anal. Calc. for $C_{21}H_{25}ClN_4O_4 \cdot 0.5H_2O \cdot 0.5CH_2Cl_2$: C, 53.31; H, 5.62; N, 11.57. Found: C, 52.99; H, 5.53; N, 11.86%. M.p. 230.7–230.9 °C.

*4.3.14. 3-[2-{[(1S)-1-(Hydroxymethyl)-2,2-dimethylpropyl]amino}-2-oxoethyl]-1-(2,4,6-trimethylphenyl)-1H-benzimidazolium chloride (**29**)*

White solid (yield: 44%); ^1H NMR ($CDCl_3$): δ 10.24 (s, 1H), 8.91 (d, J = 8.7 Hz, 1H), 8.16 (d, J = 8.2 Hz, 1H), 7.68 (t, J = 7.8 Hz, 1H), 7.56 (t, J = 7.8 Hz, 1H), 7.21 (d, J = 8.2 Hz, 1H), 7.07 (s, 2H), 6.12 (d, J = 16.0 Hz, 1H), 5.87 (d, J = 16.0 Hz, 1H), 4.56 (br, 1H), 3.79–3.73 (m, 1H), 3.71–3.70 (m, 2H), 2.39 (s, 3H), 2.02 (s, 3H), 1.99 (s, 3H), 0.92 (s, 9H); ^{13}C NMR ($CDCl_3$): δ 165.6, 143.8, 141.5, 135.6, 135.4, 131.8, 131.2, 129.9, 129.9, 128.0, 127.6, 127.6, 114.5, 112.6, 61.1, 60.9, 50.0, 33.7, 26.9, 21.1, 17.5, 17.4. HRMS (ESI^+) calcd for $C_{24}H_{32}N_3O_2^+$: 394.2489, found 394.2493.

*4.3.15. 3-[2-{[(1S)-1-Cyclohexyl-2-hydroxyethyl]amino}-2-oxoethyl]-1-phenylmethyl-1H-benzimidazolium chloride (**31**)*

White solid (yield: 74%); ^1H NMR ($(CD_3)_2SO$): δ 10.05 (s, 1H), 8.59 (br, 1H), 7.99–7.95 (m, 2H), 7.68–7.61 (m, 2H), 7.51–7.49 (m, 2H), 7.42–7.34 (m, 3H), 5.85 (s, 2H), 5.44 (d, J = 16.0 Hz, 1H), 5.36 (d, J = 16.0 Hz, 1H), 4.77 (br, 1H), 3.60–3.53 (m, 1H), 3.46–3.43 (m, 2H), 1.70–1.47 (m, 6H), 1.21–0.89 (m, 5H); ^{13}C NMR ($(CD_3)_2SO$): δ 164.3, 143.6, 134.0, 131.7, 130.5, 129.0, 128.7, 128.2, 126.8, 126.7, 113.9, 113.7, 60.8, 56.0, 49.8, 48.7, 37.9, 29.4, 28.2, 26.0, 25.8, 25.7. Anal. Calc. for $C_{24}H_{30}ClN_3O_2 \cdot 0.3H_2O \cdot 0.3CH_2Cl_2$: C, 63.61; H, 6.85; N, 9.16. Found: C, 64.00; H, 6.45; N, 9.38%. M.p. 119.7–120.0 °C.

*4.3.16. 3-{2-[(1S)-1-Cyclohexylethylamino]-2-oxoethyl}-1-phenylmethyl-1H-benzimidazolium chloride (**32**)*

White solid (yield: 65%); ^1H NMR ($(CD_3)_2SO$): δ 10.02 (s, 1H), 8.69 (d, J = 8.6 Hz, 1H), 8.00–7.93 (m, 2H), 7.69–7.62 (m, 2H), 7.51–7.49 (m, 2H), 7.43–7.34 (m, 3H), 5.85 (s, 2H), 5.40 (d, J = 16.3 Hz,

1H), 5.33 (d, J = 16.3 Hz, 1H), 3.66–3.57 (m, 1H), 1.72–1.58 (m, 5H), 1.34–1.26 (m, 1H), 1.17–1.08 (m, 3H), 1.04 (d, J = 6.8 Hz, 3H), 0.96–0.87 (m, 2H); ^{13}C NMR ($(CD_3)_2SO$): δ 163.7, 143.6, 134.1, 131.7, 130.5, 129.0, 128.8, 120.2, 126.8, 126.7, 114.0, 113.7, 49.8, 49.5, 48.6, 42.4, 28.7, 28.7, 26.0, 25.8, 25.7, 17.5. Anal. Calc. for $C_{24}H_{30}ClN_3O\cdot H_2O$: C, 67.04; H, 7.50; N, 9.77. Found: C, 66.95; H, 7.24; N, 9.81%. M.p. 144.4–144.8 °C.

*4.3.17. 3-[2-{[(1S)-2-Hydroxy-1-methylethyl]amino}-2-oxoethyl]-1-phenylmethyl-1H-benzimidazolium chloride (**33**)*

White solid (yield: 48%); ^{1}H NMR ($(CD_3)_2SO$): δ 10.06 (s, 1H), 8.80 (br, 1H), 8.03–7.92 (m, 2H), 7.66–7.35 (m, 7H), 5.85 (s, 2H), 5.37 (s, 2H), 4.90 (br, 1H), 3.79–3.76 (m, 1H), 3.38–3.36 (m, 2H), 1.07 (d, J = 7.6 Hz, 3H); ^{13}C NMR ($(CD_3)_2SO$): δ 164.0, 143.6, 134.0, 131.8, 130.4, 129.0, 128.7, 128.2, 126.8, 126.7, 113.9, 113.8, 64.1, 59.8, 49.8, 48.7, 16.9. Anal. Calc. for $C_{19}H_{22}ClN_3O_2\cdot 0.5H_2O$: C, 61.87; H, 6.28; N, 11.39. Found: C, 61.48; H, 6.03; N, 11.21%. M.p. 205.1–205.4 °C.

*4.3.18. 3-[2-{[(1S)-1-Methylpropyl]amino}-2-oxoethyl]-1-phenylmethyl-1H-benzimidazolium chloride (**34**)*

White solid (yield: 26%); ^{1}H NMR ($(CD_3)_2SO$): δ 10.11 (s, 1H), 8.90 (d, J = 7.8 Hz, 1H), 7.99–7.97 (m, 2H), 7.67–7.60 (m, 2H), 7.52–7.50 (m, 2H), 7.42–7.34 (m, 3H), 5.86 (s, 2H), 5.43 (d, J = 16.5 Hz, 1H), 5.37 (d, J = 16.5 Hz, 1H), 3.71–3.64 (m, 1H), 1.45–1.40 (m, 2H), 1.07 (d, J = 6.9 Hz, 3H), 0.83 (t, J = 7.3 Hz, 3H); ^{13}C NMR ($(CD_3)_2SO$): δ 163.7, 143.6, 134.0, 131.7, 130.4, 129.0, 128.7, 128.2, 126.8, 126.6, 113.9, 113.6, 49.8, 48.6, 46.6, 28.7, 20.0, 10.4. HRMS (ESI^+) calcd for $C_{20}H_{24}N_3O_2^+$: 322.1919, found 322.1920.

*4.3.19. 3-[2-{[(1S)–2-Methoxyl-1-methylethyl]amino}-2-oxoethyl]-1-phenylmethyl-1H-benzimidazolium chloride (**35**)*

White solid (yield: 42%); ^{1}H NMR ($(CD_3)_2SO$): δ 10.21 (br, 1H), 9.14 (br, 1H), 8.00–7.96 (m, 2H), 7.68–7.62 (m, 2H), 7.53–7.51 (m, 2H), 7.42–7.36 (m, 3H), 5.88–5.87 (br, 2H), 5.42–5.38 (br, 2H), 3.98–3.92 (m, 1H), 3.40–3.23 (m, 5H), 1.09 (d, J = 6.9 Hz, 3H); ^{13}C NMR ($(CD_3)_2SO$): δ 163.9, 143.6, 134.0, 131.6, 130.4, 128.9, 128.7, 128.2, 126.7, 126.6, 113.9, 113.7, 74.7, 58.2, 49.7, 48.6, 44.7, 17.1. HRMS (ESI^+) calcd for $C_{20}H_{24}N_3O_2^+$: 338.1868, found 338.1863.

4.4. General procedure for the AAA reaction catalyzed by well defined amidate/NHC–Pd(II) complex

Dimethyl malonate (**6**) (0.6 mmol, 79 mg) was added slowly to a stirring suspension of NaH 60% w/w dispersion in mineral oil (0.57 mmol, 22.8 mg) in 1,2-dichloroethane (1 mL). Once gas evolution had caused (5 min), this solution was added to the solution of 1,3-diphenylprop-3-en-1-yl acetate (**5**) (0.2 mmol, 50 mg) and amidate/NHC–Pd(II) complex (5 mol %, 0.01 mol) in 1,2-dichloroethane (2 mL). The resulting reaction mixture was stirred at 80 °C. After 15 h, the reaction was quenched with water (ca. 2 mL) and extracted with diisopropyl ether (ca. 2 mL). The product yield was determined by GLC using an internal standard method. Enantiomeric excess of the product was measured by HPLC using OD chiral stationary phase and 99:1 hexane–^{i}PrOH as eluent, flow = 1 mL/min.

*4.5. Procedure for the AAA reaction catalyzed by in situ generated NHC–Pd(II) complex derived from azolium salt **9** and $[Pd(allyl)Cl]_2$*

A flask was charged with azolium salt **9** (0.01 mmol, 3.8 mg), silver(I) oxide (0.005 mmol, 1.2 mg) and CH_2Cl_2 (1 mL), and the resulting mixture was stirred at room temperature for 1 h in the dark. Then, $[Pd(allyl)Cl]_2$ (0.005 mmol, 1.9 mg) was added to the reaction vessel. The resulting mixture was stirred at room temperature for an additional 16 h in the dark, filtered through a membrane filter, and evaporated to dryness in vacuo. To the resulting flask containing yellow solid of unpurified NHC-Pd(II) complex, a solution of **5** (0.2 mmol, 50 mg) in CPME (2 mL), and then subsequently a solution of $NaCH(COOMe)_2$ (1 mmol) in CPME (1 mL) were added. After stirring at 80 °C for 15 h, the reaction was quenched with water (ca. 2 mL) and extracted with diisopropyl ether (ca. 2 mL).

*4.6. One-pot synthesis of $[Pd(allyl)(NHC)_2]Cl$ **30** from azolium salt **1** and $[Pd(allyl)Cl]_2$*

A suspension of azolium salt **1** (0.2 mmol, 62 mg) and silver(I) oxide (0.1 mmol, 23 mg) in CH_2Cl_2 (10 mL) was stirred in the dark at room temperature. After 16 h, $[Pd(allyl)Cl]_2$ (0.05 mmol, 18 mg) was added to a suspension of the resulting silver complex in the dark at room temperature. Then, the resulting suspension was stirred for 24 h and filtered through a plug of glass fiber filter paper. The filtrate was evaporated to dryness in vacuo. The crude residue was purified by column chromatography (SiO_2, CH_2Cl_2/MeOH: 9/1) to yield $[Pd(allyl)(NHC)_2]Cl$ **30** as white solid (50 mg, 67% yield). **30**: ^{1}H NMR (CD_3OD): δ 7.59 (d, J = 7.8 Hz, 2H), 7.44–7.31 (m, 6H), 5.69–5.59 (m, 1H), 5.20 (d, J = 16.9 Hz, 2H), 5.15 (d, J = 16.9 Hz, 2H), 4.17 (d, J = 7.3 Hz, 2H), 4.01 (s, 6H), 3.51–3.43 (m, 4H), 3.39–3.34 (m, 2H), 3.00 (d, J = 13.3 Hz, 2H), 1.78–1.70 (m, 2H), 0.86 (d, J = 6.9 Hz, 6H), 0.83 (d, J = 6.9 Hz, 6H); ^{13}C NMR (CD_3OD): δ 191.2, 168.5, 136.7, 136.2, 124.7, 122.0, 111.9, 111.8, 62.8, 62.4, 58.6, 51.9, 35.8, 30.2, 19.9, 19.1. Anal. Calc. for $C_{33}H_{47}ClN_6O_4Pd\cdot 0.3CHCl_3\cdot 2H_2O$: C, 49.65; H, 6.42; N, 10.43. Found: C, 49.25; H, 6.10; N, 10.83%.

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Appendix A. Supplementary data

CCDC 739455 contains the supplementary crystallographic data for **3c**. This data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Appendix B. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jorganchem.2012.12.015.

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