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Article

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[Silver(I)(Pyridine-Containing Ligand)] complexes as unusual catalysts for A^3-coupling reactions

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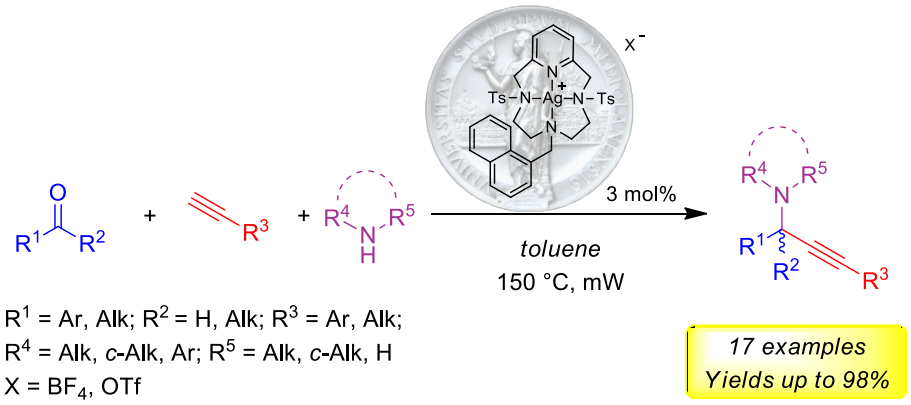
Graphical Abstract



R^1 = Ar, Alk; R^2 = H, Alk; R^3 = Ar, Alk;
R^4 = Alk, *c*-Alk, Ar; R^5 = Alk, *c*-Alk, H
X = BF_4, OTf

Abstract

Two original macrocyclic silver(I)(pyridine-containing ligand) complexes [Ag(I)(*Pc*-L)] were synthesized and characterized. Their ability to catalyze the coupling among aldehydes, terminal alkynes and amines (A^3-coupling) was demonstrated. The reaction could be performed under conventional as well as dielectric heating. The catalysts were effective in both cases, but dielectric heating allowed a lower catalyst loading and reduced ratio among reaction partners in shorter reaction times. The reaction scope was broad, including aryl/alkyl aldehydes, aryl/alkyl acetylenes and secondary aliphatic amines. Some unprecedented propargylamines have been prepared. The new catalytic system was also tested with more challenging coupling partners such as aniline and ketones.

Introduction

Multicomponent reactions (MCR'S) enable the synthesis of complex molecules starting from more than two simple building blocks in a single operative step.[1] These strategies allow reducing the overall time required to obtain the desired product, beside a valuable solvents and energy saving, and the reduction of waste production. The advantages from the ecological and economic point of view are significant. In this context, the transition-metal catalyzed three-component reaction of an aldehyde, an amine and an alkyne, better

known as A^3-coupling,[2] represents a worthwhile approach to propargylamines, which are recurrent moieties in biologically active compounds and valuable intermediates for the synthesis of more complex nitrogen-containing molecules. Starting from the pioneering works of Dax[3] and Dyatkin,[4] the most popular procedures for A^3-coupling are based on copper(I) catalysis.[5] Moreover, the other coinage metals, silver[6] and gold,[7] gave valuable results[8] too, and some other metals such as iron,[9] indium,[10] zinc,[11] nickel,[12] cobalt[13] and mercury[14] demonstrated their skill to catalyze this transformation. In particular, regarding silver based catalysts, it is worth noting that the catalytic systems most frequently used are simple silver(I) salts (e.g., AgX,[6,15] Ag_2O,[16] or $Ag_3PW_{12}O_{40}$[17]) occasionally as acetonitrile complexes[18] or (*N*-heterocyclic carbene)Ag(I) complexes.[19] Interestingly, when this MCR was endeavoured in the presence of phosphine-based Ag(I) complexes, a switch of activity was observed, and surprisingly the simple propargyl alcohol originated from aldehyde-alkyne coupling was obtained.[20] On the other hand, the asymmetric version of the A^3-coupling (the so-called AA^3-coupling) is absolutely dominated by Cu-based complexes,[21] and to the best of our knowledge no examples have been already reported with any other transition metal.[22]

In connection with our ongoing interest in the study of metal catalyzed domino[23] and multicomponent[24] processes involving alkynes, carbonyl compounds and ammonia/amines, we are pleased to report a microwave enhanced synthesis of propargylamines, catalyzed by well-defined Ag(I) complexes which are characterised by the presence of an original tetraaza-macrocyclic ligand. Macrocyclic ligands display a series of peculiar properties, when compared with their non-cyclic analogues, which render their coordination chemistry and the catalytic activity of their complexes an interesting field of inquiry. These includes kinetic (resistance to ligand exchange), thermodynamic (large formation constants), spectral (high ligand field strengths), and structural effects.[25] A few years ago, we introduced a new class of 12-membered macrocyclic ligands, called *Pc*-L (Pyridine containing Ligands), which can be synthesised in good yields, starting from commercially available reagents, even in enantiopure form. These macrocycles were firstly synthetized by the group of research of Stetter in 1981,[26] and some years later they have been rediscovered as ligands for the coordination of lanthanide ions in MRI contrasting agents.[27] By appropriate choice of the starting materials in the target macrocycle synthesis, we reasoned that the presence of a pyridine ring fused to the macrocycle could provide an enhanced conformational preorganization to the molecule, binding strongly to the metal atom while still allowing for the coordination of other molecules directly involved in the desired reaction. With the optimized reaction conditions, a small library of *Pc*-Ls has been obtained, including enantiomerically pure stereoisomers, and their copper and silver complexes demonstrated to be effective in catalysis. The cyclopropanation reaction of alkenes,[28] and the Henry reaction[29] were successfully catalyzed by some original copper based (*Pc*-L) complexes. Very recently, the addition/cycloisomerization reaction of 2-alkynylbenzaldehydes and alcohols under mild reaction conditions was effectively promoted by some new [Ag(I)(Pc-L)] complexes.[30]

Results and discussion

As mentioned above, we recently reported on the synthesis of some well-defined $[Ag(I)(Pc\text{-}L)]^+X^-$ complexes ($X = BF_4$, OTf, $N(Tf)_2$) characterized by the presence of a benzyl group on N6, capable to catalyze in good yield the one pot addition/cycloisomerization reaction of 2-alkynylbenzaldehdehydes and alcohols to yield 3-substituted-1-alkoxyisochromenes (Figure 1, A).[30] These silver complexes were quite stable, versatile and could be used without the need of a protective atmosphere, but they have the disposition to soak moisture from air to form mono-acquo species (Figure 1, B). We have already shown recently that the presence of a 1-(naphthyl)methyl substituent on the N6 of the macrocycle confers a good stability to the metal

complexes of these Pc-Ls (i.e., copper(I) complexes),[28b] by providing a further coordination site for the metal atom (Figure 1, C). This additional coordination site provided by the naphthyl group works as a "protecting cap" for the metal center, so avoiding the formation of undesirable pentacoordinated species with adventitious solvents or water. On the other hand, a suitable more electron-rich molecule in the reaction environment could easily displace the naphthyl cap (Figure 1, D).

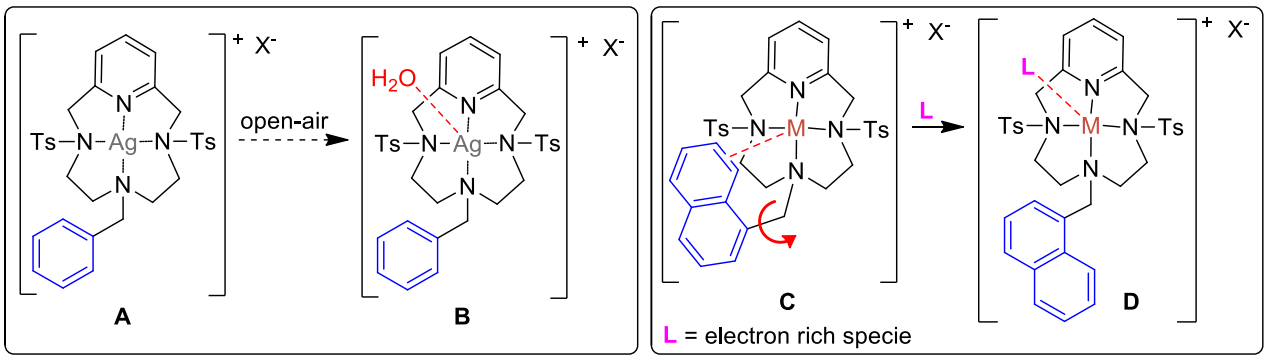
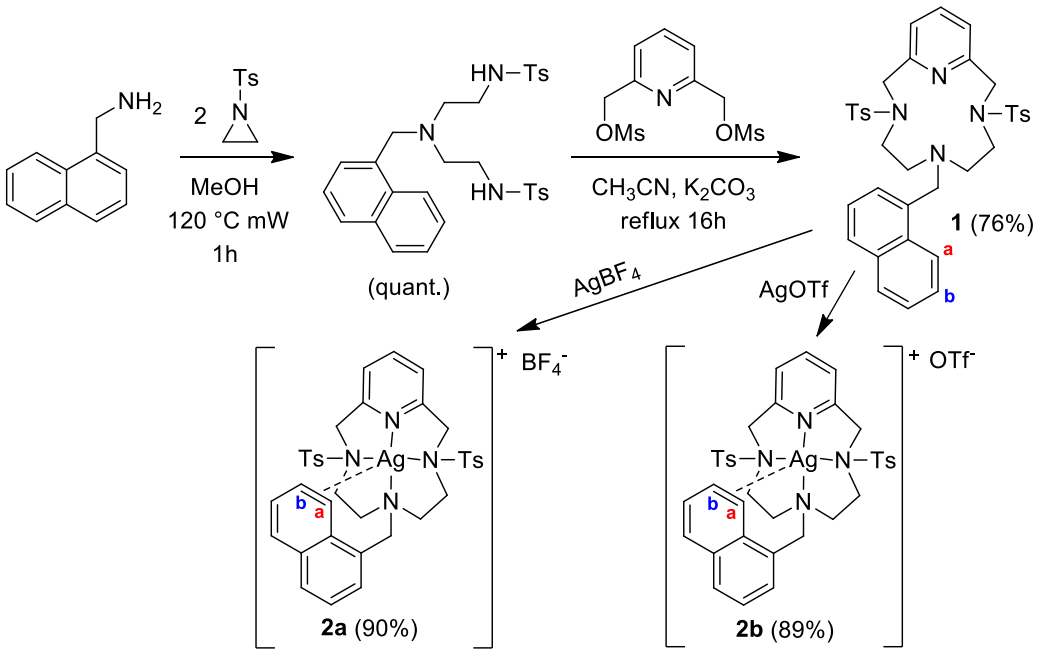


Figure 1. $[M(Pc\text{-}L)]^{+}X^{-}$ complexes used in the synthesis of isochromenes (**A**) and in this work (**C**).

For that reason in the present study we turned our attention to the use of the 1-(naphthyl)methyl substituted Pc-L, **1**, that can be obtained in good overall yield from commercially available starting materials according to Scheme 1.[28b] The synthetic strategy involved the nucleophilic ring opening of 1-tosylaziridine by naphthalen-1-ylmethanamine to give the corresponding 1,7-ditosyl-4-(naphthalen-1-ylmethyl)-1,4,7-triazaheptane in quantitative yields. The approach has been improved by the use of dielectric heating, that not only allowed an overall increase of the yield in shortened reaction times, but moreover the product obtained was sufficiently pure to be used in the macrocyclization step, without need of further purification. Thus, the so obtained *bis*-protected triamine was directly reacted with 2,6-pyridinedimethanol 2,6-dimesylate in refluxing anhydrous acetonitrile in the presence of anhydrous K_2CO_3, to yield the macrocycle **1** in 76% yield.

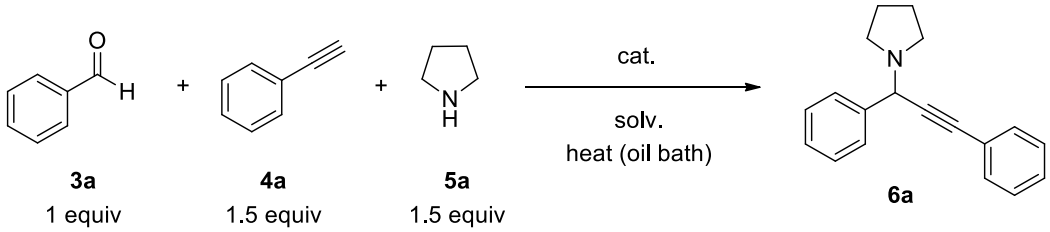


Scheme 1. Synthesis of pyridine-containing ligand 1 and its silver complexes 2a-b

The silver(I) complexes **2a-b** were synthesized in good yields by simple reaction in 1,2-dichloroethane of macrocyclic ligand with the proper silver salts.[30] In the step of formation of the complex, the silver salts and all silver containing solutions were kept in the dark and under protective atmosphere until the isolation of the final products. The silver complexes were collected as white powder from *n*-hexane and once isolated showed a remarkable stability in open air. They have been fully characterized by NMR, IR and UV-vis spectroscopies and electrospray ionization mass spectrometry (ESI-MS) analyses. As already observed for copper complexes,[28b] also the new silver complexes **2a-b** displayed the η^2 coordination of the naphthyl substituent (Scheme 1) as established by ^{1}H and ^{13}C NMR studies in $CDCl_3$ solution. In both ^{13}C NMR spectra of complexes **2a-b** (that showed a very close signals pattern) a significant shift to lower frequencies of the carbon **a** involved in the η^2 bond with silver was observed, precisely from 125.1 ppm in the free ligand **1** to 112.3 and 112.4 ppm in the silver complexes **2a-b**, respectively (see supporting information). Moreover, in ^{13}C NMR APT (attached-proton test) experiments, the signal around 112 ppm appeared broadened, probably due to the coupling with the silver atom. An opposite effect could be observed in the ^{1}H NMR, where the proton directly bound to carbon **a** experienced a higher frequencies shift (i.e., from 8.13 ppm in the free ligand **1**, to 9.16 and 9.18 in complexes **2a** and **2b**, respectively). A similar high frequency shift, although to a lesser extent, is observed also for the proton bound to carbon **b** (from 7.45 ppm in **1**, to 7.90 and 7.92, respectively, in the metal complexes **2a-b**). The observed coupling constant $^1J_{C\text{-}H}$ of 157 Hz for carbon **a** in complex **2b** provided a hint of a partial re-hybridization state from sp^2 to sp^3. A ^{1}H-^{19}F HOESY (heteronuclear Overhauser effect spectroscopy) spectrum of complex **2a** in deuterated chloroform showed that the tetrafluoborate anion has weak proximity interactions only with the pyridine ring (see supporting information). A comparison between the UV spectra of the ligand **1** and of the metal complexes **2a-b** showed that the shape of the absorption bands did not change upon complexation, and only modest differences in the intensities were observed. The measured bands in the near UV were thus attributed to ligand-centered transitions and were consistent with the absence of colour of the complexes **2a** and **2b**.

We started our study testing the $[Ag(I)(Pc\text{-}L)]^+ BF_4^-$ complex **2a** on a model reaction involving simple and easily available starting materials, i.e., benzaldehyde **3a**, phenylacetylene **4a** and pyrrolidine **5a**. The results are reported in table 1. In a first experiment, we tried the reaction in 0.5 mmol scale using the ratio among reagents, the temperature, and the catalyst loading more frequently reported in the literature for A^3-couplings (i.e., ratio aldehyde/amine/alkyne = 1 : 1.5 : 1.5, T = 100 °C, cat. 3 mol %). Under these typical reaction conditions, we briefly explored the effect of some different solvents with decreasing relative polarity[31] (Table 1, entries 1-5). We were pleased to find that complex **2a** was able to catalyze the reaction in all solvent tested. Higher yields were obtained performing the reaction in water, methanol and in toluene (Table 1, entries 1, 2 and 5). It is interesting to note that, despite the low solubility in water of the catalyst **2a** and reactants **3a**, **4a** and **5a**, the reaction however took place with fair yields (Table 1, entry 1), although at the end of the reaction a great amount of free metallic silver(0) was observed in the bottom of the test tube. A similar behaviour was detected when the reaction was performed in methanol (Table 1, entry 2), whereas in toluene only traces of Ag(0) as silver mirror were observed on the internal surface of the test tube (Table 1, entry 5), so this solvent was chosen to optimize the conditions. The addition of a small amount of 3 Å molecular sieve did not strongly influence the reaction yields in both best solvents (i.e., methanol and toluene, Table 1, entries 6 and 7). Decreasing the temperature to rt the reaction became extremely sluggish and the yield was poor (Table 1, entry 8). Conversely, increasing the catalyst loading to 6 mol % a improvement in yield up to 87% was observed (Table 1, entry 9). Moreover, changing the counter ion of the complex from BF_4^- (**2a**) to the slightly more coordinating[32] TfO^- (**2b**) an additional rise in yield was observed (Table 1, entry 10).

Table 1. Exploring the best reaction conditions under conventional heating[a]



3a 1 equiv | **4a** 1.5 equiv | **5a** 1.5 equiv | **6a**

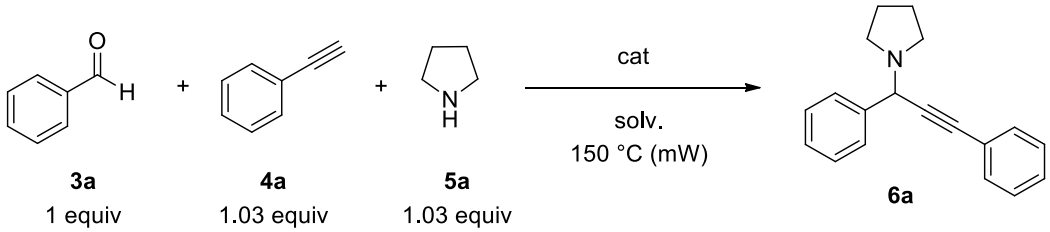
entry	cat. (mol %)	solv.	molecular sieves 4 Å	*T* (°C)	*t* (h)	**6a** (yield[b] %)
1	**2a** (3)	Water	-	100	4	65
2	**2a** (3)	MeOH	-	100	4	62
3	**2a** (3)	DMF	-	100	4	26
4	**2a** (3)	DCE	-	100	4	22
5	**2a** (3)	Ph-Me	-	100	4	60
6	**2a** (3)	MeOH	yes	100	3	57
7	**2a** (3)	Ph-Me	yes	100	3	54
8	**2a** (3)	Ph-Me	yes	rt	90	31
9	**2a** (6)	Ph-Me	-	100	5.5	87
10	***2b*** *(6)*	*Ph-Me*	*-*	*100*	*4.5*	*96*

[a] Reaction conditions: 3a (0.53 mmol), 4a (0.80 mmol), 5a (0.80 mmol), solvent (1 mL), cat., screw capped tube, oil bath, 100 °C. [b] Yields of pure isolated product.

In spite of the remarkable results obtained, the approach suffers for the relatively long reaction times (4-5 h) and quite high catalyst loading (6 mol %). To improve the efficiency of the approach we decide to change the energy source. The ability of dielectric heating to promote different type of Cu(I) catalyzed A^3-coupling has been well established and described by Leadbeater,[33] Tu[34] and Van der Eycken,[35] so we decide to proceed our study under microwave irradiation (Table 2). It is well known that the efficiency of dielectric heating is strongly related to the nature and the polarity of the solvent.[36] For this reason we repeated the solvent screening (Table 2, entries 1-6) and, somewhat surprisingly, we found that also under microwave heating toluene demonstrated to be the best solvent (Table 2, entry 5); the reaction was complete in 15 min with excellent yield. Moreover, we found that the ratio among reaction partners could be advantageously reduced to 1 : 1.03 : 1.03 without loss of efficiency. Furthermore, we tried to reduce also the catalyst loading (Table 2, entries 7 and 8) and we found that 3 mol % of the catalyst was sufficient to obtain excellent results (Table 2, entry 7) whereas in the presence of 1 mol % of catalyst the yield drop-out to 67% (Table 2, entry 8). Also the reaction time can be reduced to 10 min without appreciable loss of efficiency (Table 2, entry 9), whereas 5 min resulted in slightly lower yield (Table 2, entry 10). Finally, we performed two control experiments under the optimized reaction conditions in the presence of simple silver triflate as catalyst (Table 2, entries 11 and 12). Though the model reaction in the presence of 3 mol % of AgOTf gave the product **6a** in very good yield, the activity of complex **2b** appeared superior (Table 2, cf. entry 7 and 11) – in particular when the catalyst loading was reduced to 1 mol % (Table 2, cf. entry 8 and 12) – thus confirming a certain ligand effect. To be sure that also under this relatively harsh reaction conditions, the active catalytic species were actually the Ag[Pc-L] complexes and not degradation products or an in situ generated silver nanoparticles, we made two additional experiments. The complex **2a** was heated at 150 °C in toluene (complex **2a** is slightly soluble in toluene at rt, but dissolves at 150 °C) by dielectric heating for 10 min. Despite at the end of the heating we observed a small amount of dark

precipitate in the test tube, the ^{1}H NMR of the solution revealed that the silver(I) complex was still intact. Moreover, we performed the model reaction under conventional heating at 120 °C in the presence of a drop of mercury as np-inhibitor:[37] after two hours, we obtain the desired propargylamine **6a** in 36 % yield.

Table 2. Exploring the best reaction conditions under microwave heating[a]



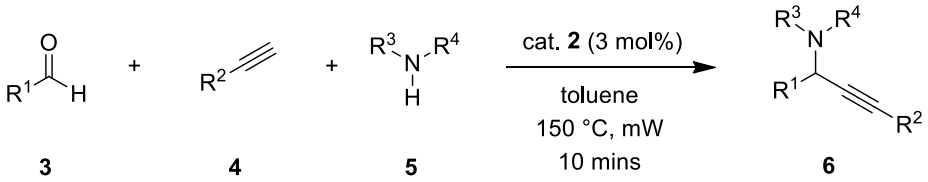
3a 1 equiv | **4a** 1.03 equiv | **5a** 1.03 equiv | **6a**

entry	cat. (mol %)	solvent	*t* (min)	**6a** (yield[b] %)
1	**2b** (6)	MeOH	15	46
2	**2b** (6)	Me-CN	15	62
3	**2b** (6)	DCE	15	68
4	**2b** (6)	Dioxane	15	9
5	**2b** (6)	Ph-Me	15	96
6	**2b** (6)	Cyclohexane	15	61
7	**2b** (3)	Ph-Me	15	95
8	**2b** (1)	Ph-Me	15	67
9	***2b** (3)*	*Ph-Me*	*10*	*96*
10	**2b** (3)	Ph-Me	5	93
11	AgOTf (3)	Ph-Me	15	88
12	AgOTf (1)	Ph-Me	15	52

[a] Reaction conditions: 3a (0.53 mmol), 4a (0.55 mmol), 5a (0.55 mmol), solvent (1 mL), cat., microwave screw capped tube, mW, 150 °C. [b] Yields calculated via ^{1}H NMR using dimethyl terephthalate (DMT) as internal standard.[38]

With the best conditions in hands, we explored scope and limitation of the reaction. In particular, our target was to verify the ability of our catalysts to promote the reaction among partners of different nature, such as substituted aliphatic and aromatic aldehydes, alkynes substituted with alkyl or aryl moieties, and secondary amines. The results are reported in table 3. EWGs and EDGs on arylalkyne partner were in general well-tolerated (Table 3, entries 2, 3, 11-13), except for strongest EWG such as nitro group (Table 3, entry 4). Benzaldehyde derivatives bearing EWGs or EDGs in any position of the ring gave satisfying results (Table 3, entries 6-8) as well as cyclohexanecarbaldehyde (Table 3, entries 9 and 11). Nevertheless, also in this case lower yields were obtained when the aldehyde was characterized by an acyclic alkyl substitution (Table 3, entry 10). The nature of the amine seemed to be the more critical feature. Cyclic secondary amines such as pyrrolidine and piperidine gave best results (Table 3, entries 1-3, 6-9, 11-13), whereas acyclic secondary amines (Table 3, entries 15, 16), and less basic cyclic amines as morpholine (Table 3, entry 14) gave only fair to good reaction yields.

Table 3. Scope of (*Pc*-L)-Ag(I) catalyzed A^3-coupling with secondary amines



3 **4** **5** **6**

		aldehyde **3**	alkyne **4**	amine **5**		
entry[a]	cat.	R^1	R^2	R^3	R^4	**6** (yield[b] %)
1	**2b**	**3a**: Ph-	**4a**: Ph-	**5a**: -$(CH_2)_4$-		**6a** 96
2	**2b**	**3a**: Ph-	**4b**: *p*-MeO-Ph-	**5a**: -$(CH_2)_4$-		**6b** 75
3	**2b**	**3a**: Ph-	**4c**: *m*-F-Ph-	**5a**: -$(CH_2)_4$-		**6c** 83
4	**2b**	**3a**: Ph-	**4d**: *p*-NO_2-Ph-	**5a**: -$(CH_2)_4$-		-
5	**2b**	**3a**: Ph-	**4e:** *n*-Pr-	**5a**: -$(CH_2)_4$-		**6d** 53[c]
6	**2b**	**3b**: *p*-MeO-Ph-	**4a**: Ph-	**5a**: -$(CH_2)_4$-		**6e** 78[c]
7	**2a**	**3c**: *m*-Cl-Ph-	**4a**: Ph-	**5a**: -$(CH_2)_4$-		**6f** 79
8	**2b**	**3d**: *o*-OH-Ph-	**4a**: Ph-	**5a**: -$(CH_2)_4$-		**6g** 83
9	**2b**	**3e**: Cy-	**4a**: Ph-	**5a**: -$(CH_2)_4$-		**6h** 98 (81)[d]
10	**2a**	**3f**: *n*-Bu-	**4a**: Ph-	**5a**: -$(CH_2)_4$-		**6i** 61 (62)[e]
11	**2b**	**3e**: Cy-	**4b**: *p*-MeO-Ph-	**5a**: -$(CH_2)_4$-		**6j** 89
12	**2b**	**3a**: Ph-	**4b**: *p*-MeO-Ph-	**5b**: -$(CH_2)_5$-		**6k** 91
13	**2b**	**3e**: Cy-	**4c**: *m*-F-Ph-	**5b**: -$(CH_2)_5$-		**6l** 96
14	**2b**	**3a**: Ph-	**4a**: Ph-	**5c**: -$(CH_2)_2O(CH_2)_2$-		**6m** 59[c]
15	**2b**[f]	**3a**: Ph-	**4a**: Ph-	**5d**: Et-	Et-[g]	**6n** 57[c] (61)[e]
16	**2b**	**3a**: Ph-	**4a**: Ph-	**5e**: Bn-	Bn-	**6o** 61[c]

[a] Reaction conditions: 3a (0.53 mmol), 4a (0.55 mmol), 5a (0.55 mmol), toluene (1 mL), cat. (3 mol%), microwave screw capped tube, mW, 150 °C, 10 min. [b] Yields of pure isolated products. [c] Reaction time: 20 min. [d] With AgOTf as cat. (calculated as indicated in footnote e). [e] Yields calculated via ^{1}H NMR using dimethyl terephthalate (DMT) as internal standard. [f] Cat. loading = 6 mol %. [g] Equiv of amine = 2.

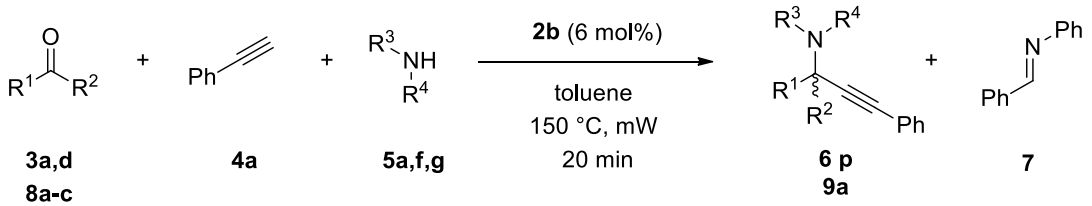
It is well known that the A^3-coupling process was mainly optimized with aliphatic secondary amines for the synthesis of tertiary propargylamines. Considerable work has been done also with anilines for the synthesis of secondary *N*-arylpropargylamines, but it is difficult to find a single catalytic system capable to efficiently catalyze both the transformations.[34] Moreover, primary alkyl amines as well as ketones were generally considered to be very difficult substrates. With the aim to broaden the scope of our approach, we tested our [Ag(I)(*Pc*-L)] catalysts with some of these more challenging substrates, in particular aromatic amines and ketones. A number of examples of A^3-coupling reactions with anilines as amine partners have been reported in the literature, mainly catalyzed by Cu(I) salts and complexes,[21d,e, 39] or else Ru(III)-Cu(I),[40] $AuCl_3$-CuBr,[41] and $InBr_3$,[10b] but only a single reaction catalyzed by a simple silver catalyst (silver iodide) was published.[42] On the other side, in the literature are reported some examples of that variant of A^3-coupling, called KA^2-coupling, that involves the use of a ketone instead of an aldehyde to yield propargylamines bearing a quaternary carbon. In most cases these reactions were performed with copper(I/II)[43] salts as catalysts, but also isolated examples catalyzed by gold(III)[44] and Ti(IV)/Cu(II)[45] salts were reported. However, to the best of our knowledge, no examples of Ag catalyzed KA^2-coupling have been already reported.

The results of our exploratory study with more challenging substrates are summarized in table 4. The first

attempt was performed with benzaldehyde **3a**, phenylacetylene **4a** and aniline **5f**. The reaction conditions were slightly modified: the catalyst loading and the reaction time were increased to 6 mol % and 20 min, respectively (Table 4, entry 1). Under these conditions, the corresponding propargylamine **6p** was obtained in a modest 28 % yield, beside a 68 % yield of the imine **7**. Also in this case, the addition of molecular sieve did not improve the yield of the desired product (Table 4, entry 2). Slightly better results were obtained by increasing the amount of alkyne **4a**, but also in these cases the imine **7** remained the main product (Table 4, entries 3 and 4). Conversely, the use of a three-fold excess of amine and aldehyde partners was unsuccessful (Table 4, entry 5). Based on these results we argued that the low yields obtained were not related to the imine formation stage, but probably to a more difficult addition of the activated alkyne on the less electrophilic carbon of the imine intermediate. With the aim to obtain a more reactive aryl-iminium intermediate we tested the reaction with diphenylamine **5g**, as secondary arylamine[5a] but in these cases the reactions totally failed (Table 4, entries 6 and 7), and complex mixtures of unidentified products were obtained.

Concerning the KA^2-coupling, we briefly tested the reactivity of 2-pentanone **8a**, phenylacetylene **4a** and pyrrolidine **5a** in the reaction conditions adopted for the A^3-couplings with aniline (i.e., toluene, 6 mol % of catalyst, microwave heating, 150°C, 20 min), and different molar ratio between reactants were tested (Table 4, entries 8-10). With the aim to facilitate the formation of the keto-iminium cation, 4Å molecular sieves were added to the reaction mixture. Unfortunately, also in these cases the reaction yields were unsatisfactory. Probably, the reaction is low yielding due to the intrinsic lower reactivity of ketones more hindered and less electrophilic than aldehydes. This hypothesis was also supported by the complete failure of the reaction with the less reactive acetophenone **8b** and benzophenone **8c** (table 4, entries 11 and 12).

Table 4. Study of the reaction with more challenging substrates

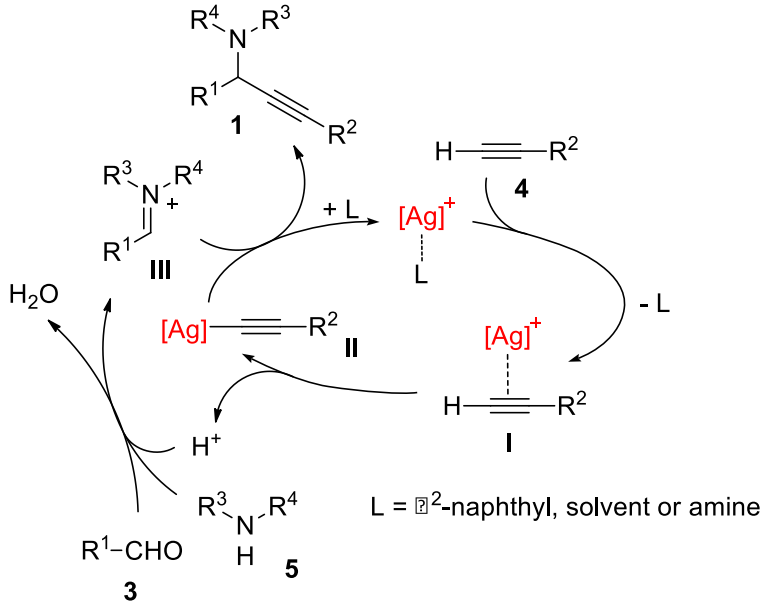


3a,d **8a-c** | **4a** | **5a,f,g** | **6 p** **9a** | **7**

entry	R^1	R^2	R^3	R^4	ratio **3** or **8** : **4** : **5**	molecular sieves 4 Å	**6** or **9** (Yield[a] %)	**7** (Yield[a] %)
1	**3a**: Ph-	H-	**5f**: Ph-	H-	1 : 1.03 : 1.03	-	**6p**: 28	68
2	**3a**: Ph-	H-	**5f**: Ph-	H-	1 : 1.03 : 1.03	yes	**6p**: 24	74
3	**3a**: Ph-	H-	**5f**: Ph-	H-	1.03 : 2 : 1	-	**6p**: 34	58
4	**3a**: Ph-	H-	**5f**: Ph-	H-	1 : 3 : 1.03	-	**6p**: 42	55
5	**3a**: Ph-	H-	**5f**: Ph-	H-	3 : 1 : 3	-	**6p**: 30	74[b]
6	**3a**: Ph-	H-	**5g**: Ph-	Ph-	1 : 1.03 : 1.03	-	-	-
7	**3e**: Cy-	H-	**5g**: Ph-	Ph-	1 : 1.03 : 1.03	-	-	-
8	**8a**: *n*-Pr-	Me-	**5a**: -$(CH_2)_4$-		1 : 1.03 : 1.03	yes	**9a:** 30	
9	**8a**: *n*-Pr-	Me-	**5a**: -$(CH_2)_4$-		2 : 1 : 2	yes	**9a:** 32	
10	**8a**: *n*-Pr-	Me-	**5a**: -$(CH_2)_4$-		1 : 2 : 1	yes	**9a:** 36[c] (33)[d]	
11	**8b**: Ph-	Me-	**5a**: -$(CH_2)_4$-		1 : 1.03 : 1.03	yes	**9b:** -	
12	**8c**: Ph-	Ph-	**5a**: -$(CH_2)_4$-		1 : 1.03 : 1.03	yes	**9c:** -	

[a] Yields calculated via ^{1}H NMR using dimethyl terephthalate (DMT) as internal standard with respect to limiting reagent. [b] With respect to aniline. [c] Under conventional heating at 100 °C for 1.5 h. [d] Isolated yield.

^{1}H NMR experiments in $CDCl_3$ at room temperature showed no interaction between the metal complexes and the aldehyde, while a remarkable shift, especially for the signals originally involved in the η^2 coordination of the naphthyl moiety to the silver atom were observed upon addition of both the phenylacetylene **4a** or pyrrolidine **5a**. In the absence of any base, however, complex **2a** reacts very easily with a terminal alkyne to give the silver acetylide. This liberates acid, which protonates the ligand causing partial decomplexation. This decomplexation does not happen in the presence of a stoichiometric amount of pyrrolidine. Based on the experimental results and taking in mind the literature findings,[6, 19c] a tentative mechanism was proposed: first the catalyst form the π-complex (**I**) with the alkyne **4** (an equilibrium with the silver complex coordinated to the amine cannot be however ruled out). This increase the acidity of acetylenic hydrogen which is removed by the amine (or more probably by the emiaminal intermediate resulted from the reaction between the amine **5** and the aldehyde **3**) to give silver acetylide **II**. The proton assisted condensation between the amine **5** and the aldehyde **3** generate a molecule of water and the iminium halide **III**, which reacts with the silver acetylide **II** to afford the desired propargylamine **6** and regenerate the catalyst (Scheme 2).



Scheme 2. Tentative mechanism proposed

Conclusions

In conclusion, we have synthesized and in depth characterized two original Ag(I)(*Pc*-L) complexes and their catalytic activity was tested in A^3-coupling MCR. We optimized the reaction conditions both under conventional and microwave heating. The catalysts were effective in both cases, but dielectric heating allowed a lower catalyst loading and a reduced ratio among reaction partners in shorter reaction times. The reaction scope was broad when secondary aliphatic amines were used and some unprecedented propargylamines have been prepared. This work represent the first example of A^3-coupling catalyzed by tetraaza-macrocyclic silver complexes. Moreover, some explorative experiments demonstrated that the new catalysts worked with more challenging reaction partners such as aromatic amines and ketones too, although the results, in these cases, are only modest. Current efforts are now devoting to design and

synthesize some new chiral [Pc-L]* ligands characterized by a well-planned chiral profile able to induce stereoselectivity in this valuable MCR.

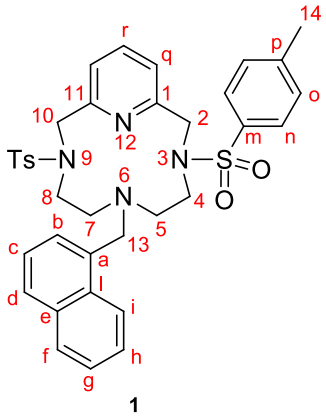
EXPERIMENTAL SECTION

General Experimental Details. All of the reactions that involved the use of reagents sensitive to oxygen or hydrolysis were carried out under an inert atmosphere. The glassware was previously dried in an oven at 110 °C and was set with cycles of vacuum and nitrogen. Also syringes, used to transfer reagents and solvents, were previously set under a nitrogen atmosphere. The syntheses of the silver complexes were carried out under a nitrogen atmosphere by employing standard Schlenk techniques. All chemicals and solvents were commercially available and were used after distillation or treatment with drying agents. The chromatographic column separations were performed by a flash technique, using silica gel (pore size 60 Å, particle size 230−400 mesh, Merck grade 9385). For TLC, silica was used on TLC Alu foils with fluorescent indicator (254 nm) and the detection was performed by irradiation with UV light (λ = 254 nm or 366 nm). ^{1}H NMR analyses were performed with 200, 300, or 400 MHz spectrometers at room temperature. The coupling constants (*J*) are expressed in hertz (Hz), and the chemical shifts (δ) in ppm. ^{13}C NMR analyses were performed with the same instruments at 50.3, 75.5, and 100 MHz, and attached proton test (APT) sequence was used to distinguish the methine and methyl carbon signals from those arising from methylene and quaternary carbon atoms. All ^{13}C NMR spectra were recorded with complete proton decoupling. The ^{1}H NMR signals of the ligand described in the following have been attributed by correlation spectroscopy (COSY) and nuclear Overhauser effect spectroscopy (NOESY) techniques. Assignments of the resonance in ^{13}C NMR were made using the APT pulse sequence and heteronuclear single quantum correlation (HSQC) and heteronuclear multiple bond correlation (HMBC) techniques. The ^{15}N NMR signals of the compound described have been attributed by HMBC technique. Low resolution MS spectra were recorded with instruments equipped with electron ionization (EI), ESI/ion trap (using a syringe pump device to directly inject sample solutions), or fast atom bombardment (FAB) (for Pc-L and metal complexes) sources. The values are expressed as mass−charge ratio and the relative intensities of the most significant peaks are shown in brackets. High resolution MS spectra were recorded with an instrument equipped with an electrospray source and a ion cyclotron resonance-Fourier transform mass spectroscopy (ICR-FTMS) analyzer. UV−vis spectra of the ligand and its silver complexes were recorded in $CHCl_3$. The melting points of the solid products are uncorrected. Microwave promoted reactions were performed with a single-mode Personal Chemistry microwave synthesizer “Emrys Creator,” using sealed glass vessels. The temperature was detected with an infrared sensor.

Synthesis of 1,7-ditosyl-4-(naphthalen-1-ylmethyl)-1,4,7-triazaheptane. A solution of tosyl aziridine (0.769 g, 3.90 mmol) and 1-naphthylmethylamine (0.283 g, 1.80 mmol) in MeOH (15 mL) was stirred and heated by microwave irradiation for 1 h at 120 °C. The mixture was dried and used without any further purification. Yield quantitative (0.993 g, 1.80 mmol). ^{1}H NMR (300 MHz, $CDCl_3$, δ): 8.14 (d, *J* = 8.3 Hz, 1H, H_{ar}), 7.86 (d, *J* = 8.3 Hz, 1H, H_{ar}), 7.78 (m, 1H, H_{ar}), 7.54 (d, *J* = 8.0 Hz, 4H, H_{ar}) overlapping with 7.61-7.49 (m, 2H, H_{ar}), 7.42-7.32 (m, 2H, H_{ar}), 7.19 (d, *J* = 8.0 Hz, 4H, H_{ar}), 4.83 (bs, 2H, NH), 4.00 (s, 2H, CH_2), 2.90 (m, 4H, CH_2), 2.66 (m, 4H, CH_2), 2.38 (s, 6H, CH_3). The spectral data are consistent with those previously reported.[28b]

Synthesis of 6-(naphthalen-1-ylmethyl)-3,9-ditosyl-3,6,9,15-tetraazabicyclo[9,3,1]pentadeca-1(15),11,13-triene 1. A solution of 1,7-ditosyl-4-(naphthalen-1-ylmethyl)-1,4,7-triazaheptane (2.053 g, 3.731 mmol), 2,6-*bis*(methanesulfonyloxymethyl)pyridine (1.101 g, 3.731 mmol) and micronized anhydrous potassium

carbonate (1.547 g, 11.19 mmol) in freshly distilled acetonitrile (110 mL) was stirred and heated under reflux for 16 h. The mixture was washed with water (150 mL) and extracted with ethyl acetate (3 x 80 mL). The organic layers were dried with sodium sulphate and then evaporated to dryness under reduced pressure. The crude product was then dissolved in hot ethyl acetate (60 mL), filtered while hot and layered with *n*-hexane (35 mL). After cooling at 0 °C an amorphous yellowish solid fell out from the solution. The solid was filtered off and the mothers liquors were evaporated to dryness, yielding a white solid. Yield = 1.857 g, 76%. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.14 (d, *J* = 8.1 Hz, 1H, H^{i}), 7.91 (d, *J* = 7.8 Hz, 1H, H^{d} o H^{f}),7.87 (d, *J* = 8.1 Hz, 1H, H^{d} o H^{f}), 7.78 (t, *J* = 7.8 Hz, 1H, H^{r}), 7.50 (d, *J* = 8.2 Hz, 4H, H^{n}) overlapping with 7.51-7.45 (m, 3H, H_{ar}), 7.39 (d, *J* = 7.8 Hz, 2H, H^{q}), 7.35 (d, *J* = 6.9 Hz, 1H, H^{b}), 7.19 (d, *J*= 8.2 Hz, 4H, H^{o}), 4.31 (s, 4H, CH_2^{2} and CH_2^{10}), 3.93 (s, 2H, CH_2^{13}), 3.07 (m, 4H, CH_2^{4} and CH_2^{8}), 2.40 (s, 6H, CH_3^{14}), overlapping with 2.36 (m, 4H, $CH_2^{5}$and CH_2^{7}). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 155.3 (C^{1}), 143.7 (C^{p}), 139.2 ($C^{r}H$), 136.2 (C^{m}), 134.9 (C), 134.3 (C), 132.8 (C), 130.1 ($C^{o}H$), 128.8 ($C^{Ar}H$), 128.5 ($C^{Ar}H$), 127.7 ($C^{Ar}H$), 127.4 ($C^{n}H$), 126.04 ($C^{Ar}H$), 125.98 ($C^{Ar}H$), 125.7 ($C^{Ar}H$), 125.1 ($C^{i}H$), 124.4 ($C^{q}H$), 58.5 ($C^{13}H_2$), 54.7 ($C^{2}H_2$), 50.9 ($C^{5}H_2$), 44.7 ($C^{4}H_2$), 21.9 ($C^{14}H_3$). ^{15}N NMR (40 MHz; $CDCl_3$, δ): 312 (N^{12}), 95 (N-Ts), 32 (N^{6}). MS (FAB): *m/z* (%) = 655 (100) $[MH]^+$, 499 (34) $[MH–Ts]^+$. UV/vis (5.2 10^{-5} mol L^{-1}, $CHCl_3$ in 1-cm cuvettes): λ_{max} [nm] = 242, 264, 283, 296 nm.



1

General procedure for the synthesis of silver complexes 2a-b. The silver salt and all silver-containing solutions were kept in the dark until the final isolation of the product. The ligand **1** was dissolved in 1,2-dichloroethane, the silver salt (weighed under a nitrogen atmosphere) was added and the mixture stirred for one hour, then filtered to remove any unreacted solid. The solvent was evaporated to dryness, then *n*-hexane was added and the product recovered by filtration in open air.

2a: **1** (MW = 654.84; 0.137 g; 0.209 mmol), $AgBF_4$ (MW = 194.67; 0.041 g; 0.21 mmol), $C_2H_4Cl_2$ (10 mL), *n*-hexane (20 mL). Yield 0.161 g (MW = 849.51) 90 %. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 9.16 (d, *J* = 8.1 Hz, 1H, H^{i}), 8.12 (d, *J* = 8.1 Hz, 1H, H^{f}), 7.99 (d, *J* =8.1 Hz, 1H, H^{d}), 7.90 (m, 1H, H^{h}), 7.81 (t, *J* = 7.9 Hz, 1H, H^{r}), 7.72 (m, 1H, H^{b}), 7.67-7.59 (m, 2H, H^{c} and H^{g}) overlapping with 7.59 (d, *J* = 7.8 Hz, 4H, H^{n}), 7.41 (d, *J* = 7.8 Hz, 4H, H^{o}), 7.24 (d, *J* = 7.9 Hz, 2H, H^{q}), 4.89 (d, *J* = 15.0 Hz, 2H, CH_2^{2} and CH_2^{10}), 4.35 (br s, 2H, CH_2^{13}), 3.50 (d, *J* = 15.0 Hz, 2H, $CH_2^{2'}$ and $CH_2^{10'}$) overlapping with 3.51-3.48 (m, 2H, CH_2), 2.81 (m, 2H, CH_2), 2.59 (m, 2H, CH_2), 2.49 (s, 6H, CH_3^{14}), 2.13 (m, 2H, CH_2).^{13}C NMR (75 MHz, $CDCl_3$, δ): 154.0 (C^{1}), 146.0 (C^{p}), 141.0 ($C^{r}H$), 135.3 (C^{m}), 133.8 (C), 133.2 (C), 132.5 ($C^{f}H$), 131.1 (C), 130.8 ($C^{o}H$), 130.7 ($C^{b}H$), 130.0 ($C^{d}H$), 128.6 ($C^{n}H$), 127.1 ($C^{h}H$), 126.4 ($C^{Ar}H$), 125.8 ($C^{Ar}H$), 125.3 ($C^{q}H$), 112.3 ($C^{i}H$), 56.4 ($C^{13}H_2$), 56.3 ($C^{2}H_2$ and $C^{10}H_2$), 54.7 (CH_2), 48.3 (CH_2), 22.1 ($C^{14}H_3$). ^{19}F NMR (282 MHz, $CDCl_3$, δ): -152.8. MS (FAB): *m/z* (%) = 761/763 (90/100) $[M – BF_4]^+$, 655 (37) $[MH – AgBF_4]^+$. UV/vis (5.2 10^{-5} mol L^{-1}, $CHCl_3$ in 1-cm cuvettes): λ_{max} [nm] = 242, 264, 284, 295 nm. Anal. Calcd for $C_{36}H_{38}AgBF_4N_4O_4S_2$: C, 50.90; H, 4.51; N, 6.60. Found: C, 50.75; H, 4.61; N, 6.43.

2b: **1** (MW = 654.84; 0.867 g; 1.32 mmol), AgOTf (MW = 256.94; 0.340 g; 1.32 mmol), $C_2H_4Cl_2$ (26 mL); *n*-hexane (15 mL), Yield 1.077 g (MW = 911.78) 89 %. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 9.18 (d, *J* = 8.4 Hz, 1H, H^{i}), 8.12 (d, *J* = 8.4 Hz, 1H, H^{f}), 8.00 (d, *J* =8.1 Hz, 1H, H^{d}), 7.92 (m, 1H, H^{h}), 7.84 (t, *J* = 7.7 Hz, 1H, H^{r}), 7.73 (m, 1H,H^{b}), 7.69-7.62 (m, 2H, H^{c} and H^{g}), 7.59 (d, *J* = 8.2 Hz, 4H, H^{n}), 7.41 (d, *J* = 8.2 Hz, 4H, H^{o}), 7.26 (d, *J* = 7.7 Hz, 2H, H^{q}), 4.88 (d, *J* = 15.0 Hz, 2H, CH_2^{2} and CH_2^{10}), 4.36 (br s, 2H, CH_2^{13}), 3.59 (d, *J* = 15.0 Hz, 2H, $CH_2^{2'}$ and $CH_2^{10'}$) overlapping with 3.57-3.49 (m, 2H, CH_2), 2.84 (m, 2H, CH_2), 2.74 (m, 2H, CH_2), 2.50 (s, 6H, CH_3^{14}), 2.26 (m, 2H, CH_2). ^{13}C NMR (75 MHz, $CDCl_3$, δ): 154.1 (C^{1}), 146.0 (C^{p}), 141.0 ($C^{r}H$), 135.3 (C^{m}), 133.7 (C), 133.2 (C), 132.7 ($C^{f}H$), 131.2 (C), 130.8 ($C^{o}H$) overlapping with 130.8 ($C^{b}H$), 130.1 ($C^{d}H$), 128.6 ($C^{n}H$), 127.1 ($C^{h}H$), 126.5

($C^{Ar}H$), 125.9 ($C^{Ar}H$), 125.4 ($C^{q}H$), 112.4 ($C^{i}H$, J ^{1}H-^{13}C = 156.8 Hz), 56.6 ($C^{13}H_2$), 56.4 ($C^{2}H_2$ and $C^{10}H_2$), 54.8 (CH_2), 48.3 (CH_2), 22.1 ($C^{14}H_3$). ^{19}F NMR (282 MHz, $CDCl_3$): δ = -78.5. MS (FAB): *m/z* (%) = 761/763 (90/100) $[M - CF_3SO_3]^+$, 655 (35) $[MH - AgCF_3SO_3]^+$. Anal. Calcd for $C_{37}H_{38}AgF_3N_4O_7S_3$: C, 48.74; H, 4.20; N, 6.14. Found: C, 48.41; H, 4.52; N, 6.02.

General procedure for the A^3-coupling under conventional heating. The reaction were performed in a 0.5 mmol scale in open air. The catalyst (**2a** or **2b**, 0.03 mmol) was dissolved in dry toluene (1 mL) in a screw-cap test tube equipped with a stirring bar. The suitable aldehyde (0.5 mmol), amine (0.75 mmol) and alkyne (0.75 mmol) were added to the stirred solution, according to this order. The mixture was stirred and heated with an oil-bath at 100 °C (for reaction times see table 1). The reaction mixture was diluted with ethyl acetate (20 mL) and the organic layer was washed with water (20 mL) and brine (20 mL). The organic layer was dried over sodium sulphate, and the solvent was evaporated under reduced pressure. The reaction crude was purified by flash column chromatography over a silica gel column with gradients of *n*-hexane/ethyl acetate as eluent. For reaction yields see table 1.

General procedure for the A^3-coupling under dielectric heating. The reaction were performed in a 0.5 mmol scale in open air. The catalyst (**2a** or **2b**, 0.015 mmol) was dissolved in dry toluene (1 mL) in a sealed microwave vial equipped with a stirring bar. The suitable aldehyde (0.5 mmol), amine (0.515 mmol) and alkyne (0.515 mmol) were added to the stirred solution, according to this order. The mixture was heated in a single-mode microwave oven at 150 °C for 15 min. The reaction mixture was diluted with ethyl acetate (20 mL) and the organic layer was washed with water (20 mL) and brine (20 mL). The organic layer was dried over sodium sulphate, and the solvent was evaporated under reduced pressure. The reaction crude was purified by flash column chromatography over a silica gel column with gradients of *n*-hexane/ethyl acetate as eluent. (When the reaction yields were calculated by ^{1}H NMR with the internal standard, a precise amount of DMT (around 45 mg) was added to the reaction crude before the work-up, and the ^{1}H NMR was recorded with a prolonged delay time (d1 = 10)).

1-(1,3-Diphenylprop-2-yn-1-yl)pyrrolidine **6a**.[7d] Pale yellow oil. Yield: 96% (125 mg). ^{1}H NMR (200 MHz, $CDCl_3$, δ): 7.61 (dd, J = 7.8, 1.7 Hz, 2H, H_{Ar}), 7.53–7.44 (m, 2H, H_{Ar}), 7.42–7.27 (m, 6H, H_{Ar}), 4.89 (s, 1H, CH), 2.69 (pt, J = 6.7 Hz, 4H, N–CH_2), 1.98–1.61 (m, 4H, CH_2). Spectral data are in good agreement with literature values.

1-(3-(4-Methoxyphenyl)-1-phenylprop-2-yn-1-yl)pyrrolidine **6b**. Pale yellow oil. Yield: 75% (109 mg). ^{1}H NMR (200 MHz, $CDCl_3$, δ): 7.60 (dd, J = 7.8, 1.2 Hz, 2H, H_{ar}), 7.42 (d, J = 8.9 Hz, 2H, H_{ar}), 7.37–7.27 (m, 3H, H_{ar}), 6.84 (d, J = 8.9 Hz, 2H, H_{ar}), 4.86 (s, 1H, CH), 3.81 (s, 3H, O–CH_3), 2.68 (pt, J = 6.6 Hz, 4H, N–CH_2), 1.83–1.75 (m, 4H, CH_2). ^{13}C NMR (50.3 MHz, $CDCl_3$, δ): 159.7 (C_q), 139.9 (C_q), 133.4 (CH_{ar}), 128.54 (CH_{ar}), 128.46 (CH_{ar}), 127.8 (CH_{ar}), 115.6 (C_q), 114.2 (CH_{ar}), 87.0 (C_{sp}), 85.3 (C_{sp}), 59.4 (CH), 55.5 (O–CH_3), 50.5 (N–CH_2), 23.8 (CH_2). MS ESI(+): m/z (%) = 292.1 (4) $[M + H]^+$, 221.2 (100) $[M - pyrrolidine]^+$. HRMS ESI $(M + H)^+$ calcd for $C_{20}H_{22}NO^+$, 292.1696; found, 292.1701.

1-(3-(3-Fluorophenyl)-1-phenylprop-2-yn-1-yl)pyrrolidine **6c**. Pale yellow oil. Yield: 83% (116 mg). ^{1}H NMR (200 MHz, $CDCl_3$, δ): 7.67–7.53 (m, 2H, H_{ar}), 7.44–7.23 (m, 6H), 7.23–7.13 (m, 1H), 7.11–6.90 (m, 1H), 4.91 (s, 1H, CH), 2.71 (pt, J = 6.6 Hz, 4H, N–CH_2), 1.88–1.76 (m, 4H, CH_2). ^{13}C NMR (50.3 MHz, $CDCl_3$, δ): 162.6 (d, $^{1}J_{C-F}$ = 246.4 Hz, C_q), 139.3 (C_q), 130.0 (d, $^{3}J_{C-F}$ = 8.7 Hz, CH_{ar}), 128.54 (CH_{ar}), 128.47 (CH_{ar}), 127.92 (CH_{ar}), 127.89 (d, $^{4}J_{C-F}$ = 3.2 Hz, CH_{ar}), 125.3 (d, $^{3}J_{C-F}$ = 9.5 Hz, C_q), 118.8 (d, $^{2}J_{C-F}$ = 22.7 Hz, CH_{ar}), 115.7 (d, $^{2}J_{C-F}$ = 21.2 Hz, CH_{ar}), 88.5 (C_{sp}), 86.0 (d, $^{4}J_{C-F}$ = 3.3 Hz, C_{sp}), 59.3 (CH), 50.5 (N–CH_2), 23.7 (CH_2). MS ESI(+): m/z (%) =

280.2 (100) $[M + H]^+$, 209.4 (48) $[M – pyrrolidine]^+$. HRMS ESI $(M + H)^+$ calcd for $C_{19}H_{19}FN^+$, 280.1496; found, 280.1493.

1-(1-Phenylhex-2-yn-1-yl)pyrrolidine **6d**. Pale yellow oil. Yield: 53% (60 mg). ^{1}H NMR (200 MHz, $CDCl_3$, δ): 7.53 (dd, *J* = 7.5, 1.5 Hz, 2H, H_{ar}), 7.44–7.19 (m, 3H, H_{ar}), 4.60 (t, *J* = 2.0, 1H, CH), 2.59 (pt, *J* = 6.2 Hz, 4H, N–CH_2), 2.26 (dt, *J* = 7.1, 2.0 Hz, 2H, CH_2), 1.79–1.73 (m, 4H, CH_2), 1.58 (ses, *J* = 7.1 Hz, 2H, CH_2), 1.02 (t, *J* = 7.2 Hz, 3H, CH_3). ^{13}C NMR (50.3 MHz, $CDCl_3$, δ): 140.3 (C_q), 128.5 (CH_{ar}), 127.6 (CH_{ar}), 87.2 (C_{sp}), 77.3 (C_{sp}), 59.0 (CH), 50.4 (N–CH_2), 23.7 (CH_2), 22.7 (CH_2), 21.0 (CH_2), 13.8 (CH_3). MS ESI(+): m/z (%) = 228.1 (100) $[M + H]^+$. HRMS ESI $(M + H)^+$ calcd for $C_{16}H_{22}N^+$, 228.1747; found, 228.1750.

1-(1-(4-Methoxyphenyl)-3-phenylprop-2-yn-1-yl)pyrrolidine **6e**.[46] Pale yellow oil. Yield: 78% (114 mg). ^{1}H NMR (200 MHz, $CDCl_3$, δ): 7.46–7.54 (m, 4H, H_{ar}), 7.29–7.32 (m, 3H, H_{ar}), 6.89 (d, *J* = 8.6 Hz, 2H), 6.84 (d, *J* = 8.9 Hz, 1H, H_{ar}), 4.82 (s, 1H, CH), 3.81 (s, 3H, CH_3), 2.71–2.64 (m, 4H, N–CH_2), 1.82–1.76 (m, 4H, CH_2). Spectral data are in good agreement with literature values.

1-(1-(3-Chlorophenyl)-3-phenylprop-2-yn-1-yl)pyrrolidine **6f**.[47] Pale yellow oil. Yield: 79% (117 mg). ^{1}H NMR (200 MHz, $CDCl_3$, δ): 7.63 (s, 1H, H_{ar}), 7.58–7.41 (m, 3H), 7.40–7.20 (m, 5H), 4.91 (s, 1H, CH), 2.84–2.60 (m, 4H, N–CH_2), 1.96–1.67 (m, 4H, CH_2). ^{13}C NMR (50.3 MHz, $CDCl_3$, δ): 141.9 (C_q), 134.4 (C_q), 132.0 (CH_{ar}), 129.7 (CH_{ar}), 128.6 (CH_{ar}), 128.5 (CH_{ar}), 128.5 (CH_{ar}), 128.0 (CH_{ar}), 126.6 (CH_{ar}), 123.2 (C_q), 87.7 (C_{sp}), 85.9 (C_{sp}), 58.7 (CH), 50.3 (N–CH_2), 23.79 (CH_2). MS ESI(+): m/z (%) = 298.1/296.1 (30/100) $[M + H]^+$. Spectral data are in good agreement with literature values.

2-(3-Phenyl-1-(pyrrolidin-1-yl)prop-2-yn-1-yl)phenol **6g**.[48] Pale yellow oil. Yield: 83% (115 mg). ^{1}H NMR (200 MHz, $CDCl_3$, δ): 7.57–7.50 (m, 3H, H_{ar}), 7.41–7.32 (m, 3H, H_{ar}), 7.29–7.17 (m, 1H, H_{ar}), 6.95–6.79 (m, 2H, H_{ar}), 5.29 (s, 1H, CH), 2.96–2.75 (m, 4H, N–CH_2), 1.96–1.82 (m, 4H, CH_2). Spectral data are in good agreement with literature values.

1-(1-Cyclohexyl-3-phenylprop-2-yn-1-yl)pyrrolidine **6h**.[6] Colorless oil. Yield: 98% (131 mg). ^{1}H NMR (200 MHz, $CDCl_3$, δ): 7.48–7.38 (m, 2H, H_{ar}), 7.35–7.22 (m, 3H, H_{ar}), 3.36 (d, *J* = 8.4 Hz, 1H, CH), 2.80–2.60 (m, 4H, N–CH_2), 2.12–1.92 (m, 2H, $C_{sp3}H$), 1.85–1.52 (m, 8H, $C_{sp3}H$), 1.30–1.05 (m, 5H, CH_2). ^{13}C NMR (50.3 MHz, $CDCl_3$, δ): 131.9 (CH_{ar}), 128.4 (CH_{ar}), 127.9 (CH_{ar}), 123.9 (C_q), 88.1 (C_{sp}), 86.0 (C_{sp}), 61.5 (CH), 50.3 (N–CH_2), 41.6 (CH), 30.9 (CH_2), 30.5 (CH_2), 26.9 (CH_2), 26.5 (CH_2), 23.8 (CH_2). MS ESI(+): m/z (%) = 268.2 (100) $[M + H]^+$. Spectral data are in good agreement with literature values.

1-(1-Phenylhept-1-yn-3-yl)pyrrolidine **6i**.[6] Colorless oil. Yield: 61% (74 mg). ^{1}H NMR (200 MHz, $CDCl_3$, δ): 7.45–7.40 (m, 2H), 7.31–7.26 (m, 3H, H_{ar}), 3.67 (dd, *J* = 7.9, 6.7 Hz, 1H, CH, H_{ar}), 2.78–2.67 (m, 4H, N–CH_2), 1.84–1.26 (m, 10H, CH_2), 0.93 (t, *J* = 7.0 Hz, 3H, CH_3). ^{13}C NMR (50.3 MHz, $CDCl_3$, δ): 131.9 (CH_{ar}), 128.4 (CH_{ar}), 127.9 (CH_{ar}), 123.8 (C_q), 88.7 (C_{sp}), 85.4 (C_{sp}), 55.4 (CH), 49.9 (N–CH_2), 35.1 (CH_2), 30.9 (CH_2), 29.1 (CH_2), 23.7 (CH_2), 22.7 (CH_2), 14.2 (CH_3). MS ESI(+): m/z (%) = 242.1 (100) $[M + H]^+$, 171.2 (12) $[M – pyrrolidine]^+$. Spectral data are in good agreement with literature values.

1-(1-Cyclohexyl-3-(4-methoxyphenyl)prop-2-yn-1-yl)pyrrolidine **6j**. Colorless oil. Yield: 89% (132 mg). ^{1}H NMR (200 MHz, $CDCl_3$, δ): 7.36 (d, *J* = 8.9 Hz, 2H, H_{ar}), 6.82 (d, *J* = 8.9 Hz, 2H, H_{ar}), 3.80 (s, 1H, O–CH_3), 3.32 (d, *J* = 8.3 Hz, 1H, CH), 2.77–2.57 (m, 4H, N–CH_2), 2.10–1.90 (m, 2H, $C_{sp3}H$), 1.83–1.49 (m, 8H, $C_{sp3}H$), 1.28–1.04 (m, 5H, CH_2). ^{13}C NMR (75.5 MHz, $CDCl_3$, δ): 159.6 (C_q), 133.4 (CH_{ar}), 116.3 (C_q), 114.2 (CH_{ar}), 86.7 (C_{sp}), 85.9 (C_{sp}), 61.7 (O–CH_3), 55.7 (CH), 50.4 (N–CH_2), 41.8 (CH), 31.1 (CH_2), 30.7 (CH_2), 27.1 (CH_2), 26.6 (CH_2), 23.9 (CH_2). HRMS ESI $(M + H)^+$ calcd for $C_{20}H_{28}NO^+$, 298.2165; found, 298.2162.

1-(3-(4-Methoxyphenyl)-1-phenylprop-2-yn-1-yl)piperidine **6k**.[49] Pale yellow oil. Yield: 91% (139 mg). ^{1}H NMR (200 MHz, $CDCl_3$, δ): 7.66–7.60 (m, 2H, H_{ar}), 7.45 (d, *J* = 8.9 Hz, 2H, H_{ar}), 7.40–7.28 (m, 3H, H_{ar}), 6.86 (d, *J* = 8.9 Hz, 2H, H_{ar}), 4.77(s, 1H, CH), 3.82 (s, 3H, CH_3), 2.55 (pt, *J* = 5.2 Hz, 4H, N–CH_2), 1.66–1.53 (m, 4H, CH_2), 1.50–1.40 (m, 2H, CH_2). Spectral data are in good agreement with literature values.

1-(1-Cyclohexyl-3-(3-fluorophenyl)prop-2-yn-1-yl)piperidine **6l**.[50] Pale yellow oil. Yield: 96% (144 mg). ^{1}H NMR (200 MHz, $CDCl_3$, δ): 7.32–7.18 (m, 2H, H_{ar}), 7.17–7.09 (m, 1H), 7.04–6.92 (m, 1H), 3.10 (d, *J* = 9.9 Hz, 1H, CH), 2.68–2.55 (m, 2H, N–CH_2), 2.44–2.32 (m, 2H, N–CH_2), 2.11–1.99 (m, 2H, CH_2), 1.80–1.38 (m, 10H, CH_2), 1.33–0.88 (m, 5H, CH_2). Spectral data are in good agreement with literature values.

4-(1,3-Diphenylprop-2-yn-1-yl)morpholine **6m**.[51] Colorless oil. Yield: 59% (82 mg). ^{1}H NMR (200 MHz, $CDCl_3$, δ): 7.68–7.63 (m, 2H, H_{ar}), 7.57–7.50 (m, 2H), 7.44–7.31 (m, 6H), 4.81 (s, 1H, CH), 3.80–3.71 (m, 4H, O–CH_2), 2.74–2.59 (m, 2H, N–CH_2). ^{13}C NMR (50.3 MHz, $CDCl_3$, δ): 138.1 (C_q), 132.0 (CH_{ar}), 128.8 (CH_{ar}), 128.53 (CH_{ar}), 128.45 (CH_{ar}), 128.0 (CH_{ar}), 123.3 (C_q), 88.7 (C_{sp}), 85.3 (C_{sp}), 67.4 (O–CH_2), 62.3 (CH), 50.2 (N–CH_2) (one signal obscured). MS ESI(-): m/z (%) = 276.5 (100) $[M - H]^-$, 191.4 (75) [M – morpholine]$^-$. Spectral data are in good agreement with literature values.

N,*N*-Diethyl-1,3-diphenylprop-2-yn-1-amine **6n**. Colorless oil. Yield: 57% (75 mg). ^{1}H NMR (200 MHz, $CDCl_3$, δ): 7.73 (dd, *J* = 7.4, 0.8 Hz, 2H, H_{ar}), 7.57–7.52 (m, 2H, H_{ar}), 7.43–7.30 (m, 6H, H_{ar}), 5.09 (s, 1H, CH), 2.71–2.53 (m, 4H, N–CH_2), 1.11 (t, *J* = 7.1 Hz, 6H, CH_3). ^{13}C NMR (75.5 MHz, $CDCl_3$, δ): 140.2 (C_q), 132.0 (CH_{ar}), 128.6 (CH_{ar}), 128.5 (CH_{ar}), 128.3 (CH_{ar}), 127.5 (CH_{ar}), 126.7 (C_q), 87.7 (C_{sp}), 86.4 (C_{sp}), 57.3 (CH), 44.8 (N–CH_2), 13.9 (CH_3) (one signal obscured). MS ESI(+): m/z (%) = 264.0 (100) $[M + H]^+$, 191.4 (20) [M – diethylamine]$^+$. HRMS ESI $(M + H)^+$ calcd for $C_{19}H_{22}N^+$, 264.1747; found, 264.1744.

N,*N*-Dibenzyl-1,3-diphenylprop-2-yn-1-amine **6o**.[7a] Colorless oil. Yield: 61% (118 mg). ^{1}H NMR (200 MHz, $CDCl_3$, δ): 7.77 (d, *J* = 7.5 Hz, 2H, H_{ar}), 7.67 (dd, *J* = 6.0, 2.6 Hz, 2H, H_{ar}), 7.52–7.20 (m, 16H, H_{ar}), 4.98 (s, 1H, CH), 3.84 (d, *J* = 13.5 Hz, 2H, N–CH_2), 3.58 (d, *J* = 13.5 Hz, 2H, N–CH_2). Spectral data are in good agreement with literature values.

1-(3-methyl-1-phenylhex-1-yn-3-yl)pyrrolidine **9a**. Colorless oil. Yield: 33% (40 mg). ^{1}H NMR (200 MHz, $CDCl_3$, δ): 7.447–7.39 (m, 2H, H_{ar}), 7.31–7.27 (m, 3H, H_{ar}), 2.79 (t, *J* = 5.9 Hz, 4H, N–CH_2), 1.88–1.48 (m, 8H, CH_{sp3}), 1.43 (s, 3H, CH_3), 0.96 (t, *J* = 7.1 Hz, 3H, CH_3). ^{13}C NMR (75.5 MHz, $CDCl_3$, δ): 132.0 (CH_{ar}), 128.4 (CH_{ar}), 127.9 (CH_{ar}), 123.9 (C_q), 91.7 (C_{sp}), 84.6 (C_{sp}), 58.2 (C_q), 48.0 (N–CH_2), 44.1 (CH_2), 26.1 (CH_3), 23.9 (CH_2), 18.0 (CH_2), 14.8 (CH_3). MS ESI(+): m/z (%) = 264.1 (10) $[M + Na]^+$, 242.1 (75) $[M + H]^+$, 171.0 (100) [M – pyrrolidine]$^+$. HRMS ESI $(M + H)^+$ calcd for $C_{17}H_{24}N^+$, 242.1903; found, 242.1899.

Supporting information

Copies of ^{1}H and ^{13}C NMR, spectra of ligand **1**, Ag complexes **2a–b**, and propargylamines **6b,c,d,f,h,i,j,m,n** and **9a**. ^{1}H NMR spectra of propargylamines **6a,e,g,k,l,o**. HOESY spectrum of complex **2a** and HSQC NMR experiments for the free ligand *1* and complex **2b**. ^{1}H NMR spectra of the reaction with aniline with internal standard. This material is available free of charge via the Internet at http://pubs.acs.org.

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