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Silver-Nanoparticle-Catalyzed Dearomatization of Indoles toward 3-Spiroindolenines via a 5-*exo*-dig Spirocyclization

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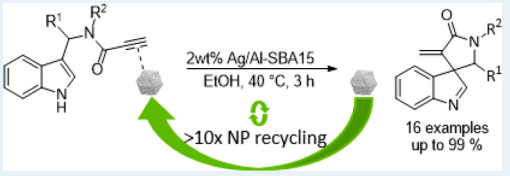
Supporting Information

ABSTRACT: We present a supported silver-nanoparticle-catalyzed dearomatization of 3-substituted indoles toward 3-spiroindolenines. Two scaffolds were investigated for this transformation. The yields range from moderate to high. In the case of chiral reactants (Ugi four-component reaction adducts), the process is diastereoselective with a diastereomeric excess between 75% and 92%. The catalyst was characterized by transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS). Metal leaching was investigated using hot-filtration and inductively coupled plasma-atomic emission spectroscopy (ICP-AES) experiments. An apparent turnover frequency (TOF) was determined.



KEYWORDS: *dearomatization, heterogeneous catalysis, silver nanoparticles, spiroindolenines, spirocyclization*

INTRODUCTION

The synthetic exploration of the chemical space, in order to generate molecular complexity with resemblance to pharmaceutically relevant molecules or natural products, is a hot topic among the synthetic community.[1] As potential bioactive compounds, spiroindolines have attracted significant attention during the past years, because of their presence in various natural products and druglike molecules (Figure 1).[2] In our previous research on the synthesis of spiroindolines from indoles, employing homo- and heterogeneous catalysis in batch[2f,3,2h] as well as in flow,[2g] we were able to isolate and characterize spiroindolenines (Scheme 1a). This was remarkable, because, under acidic or thermal conditions, spiroindolenines normally undergo facile 1.2-migration, restoring aromaticity. For the first time, decent quantities of spiroindolenines were generated via a 5-*exo* dig process (Scheme 1a).[3] These spiroindolenines are interesting scaffolds commonly seen in several natural products (Figure 1).[4]

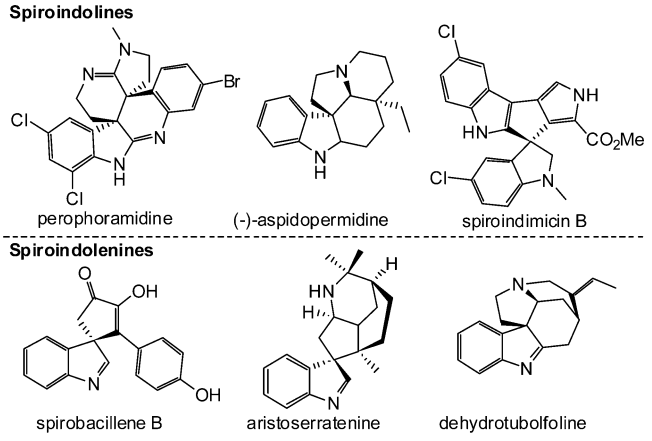


Figure 1. Naturally occurring polycyclic spiroindolines and spiroindolenines.

Based on these initial findings, we decided to further explore a synthetic methodology toward spiroindolenines employing solid supported transition-metal catalysts. Previously, multiple methods have been developed producing 3,3′-spiroindolenines mainly via three different pathways:[5] interrupted Fisher indolization,[6] condensation,[7] and dearomatization.[8a,3,8b−i] Recently, Taylor, Unsworth, and co-workers successfully developed a 5-*endo*-dig process employing homogeneous Ag catalysis for the generation of these spiroindolenines (Scheme 1b).[8e,d,9] An example that does not involve the electrophilic activation of triple bonds, but does involve the application of iridium catalysis is shown in Scheme 1c. Herein, we report the development of an efficient 5-*exo*-dig process for the formation of spiroindolenines employing novel Ag nanoparticles (NPs) (Scheme 1d).

The application of heterogeneous catalysis for complex organic reactions offers various advantages, such as easy

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Scheme 1. Comparison with Previous Related Research: (a) Van der Eycken and Co-workers;[3] (b) Taylor, Unsworth, and Co-workers;[8d] (c) Zheng, You, and Co-workers;[8g] and (d) Current Work

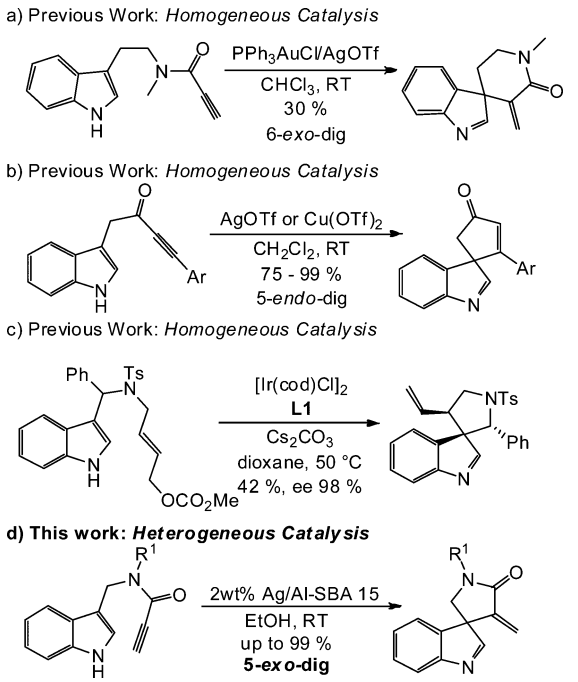
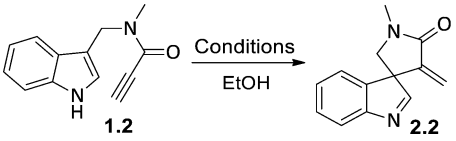


Table 1. Optimization of Reaction Conditions for the Ag Nanoparticle (NP)-Catalyzed Spiroindolenine Formation



entry[a]	catalyst[b] (mol %)	temperature, T (°C)	time, t (min)	% conversion[c] (% yield)
1	1 Au	110	30	92 (61)
2	5 Au	110	20	100 (98)
3	5 Au	80	60	94 (92)
4	5 Au	60	120	31 (27)
5	2.5/2.5 Au/Ag	60	60	100 (99)
6	2.5/2.5 Au/Ag	25	60	82 (79)
7	5 Ag	60	60	100 (99)
8	5 Ag	40	60	100 (99)
9	**5 Ag**	**28**	**60**	**100 (99)**
10	1 Ag	28	60	52 (51)
11	2.5 Ag	28	60	87 (85)
12	blank	60	60	

[a]All reactions were performed with 0.047 mmol starting material in 1 mL of solvent. [b]Au = 2 wt % Au/Al-SBA 15; Au/Ag = 2 wt % Au + 2 wt % Ag/Al-SBA 15; Ag = 2 wt % Ag/Al-SBA 15. [c]Conversion and yield were determined via an NMR integration method, using 2,4,6-trimethoxybenzaldehyde as an internal standard.

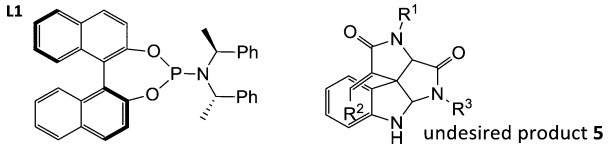
handling of the catalyst,[2g,h] recycling, and transferability into microflow technology,[11,2g] even though the actual nature of the catalytically active species is still under debate.[12] In this work, we were able to apply a heterogeneous Ag catalyst in ethanol as a sustainable and efficient system for the generation of these important class of compounds. Besides the detailed catalyst characterization via TEM and XPS, we also determined the leaching behavior of the Ag catalyst. The use of the Ugi-4CR allows the generation of diversity by assembling simple starting materials into a complex spirocyclic scaffold in a one-pot reaction.[10]

RESULTS AND DISCUSSION

For the screening of the heterogeneous catalyst, we found that a mixed Au/Ag catalyst outperformed the pure Au NPs for the synthesis of spiroindolenines (see Table 1, entries 5 and 6). After careful optimization, we finally determined that a pure Ag catalyst (1.9 wt % Ag/Al-SBA 15 determined by ICP-OES; see the Supporting Information) was superior to all others (Table 1, entries 7−11). Moreover, we did not witness any 1,2-migration with any of our applied catalyst systems. Ethanol was chosen as the solvent, because it is considered to be *green* and has already been proven to be beneficial.[2g,h] For our optimization studies, compound **1.2** was chosen as the model substrate. The terminal alkyne was initially preferred, as it is known that the cyclization would work under milder reaction conditions,[13] which could be ascribed to less sterical hindrance of the triple bond.

Under these optimized reaction conditions (Table 1, entry 9), we investigated the scope of this protocol (Figure 2).[14] Substrates bearing terminal alkynes (R^2 = H) show good to excellent reactivity with our catalyst (compounds **2.1**−**2.7**, except compound **2.5**), resulting in high yields for the spiroindolenine formation, independent from the substituent on the nitrogen. However, as observed previously, internal alkynes ($R^2 \neq$ H) only cyclize slowly to the desired product (compounds **2.8**−**2.10**). The reaction time and temperature must be extended dramatically, as well as the amount of catalyst, to almost equimolar amounts. Although the cyclization works well, to our surprise, we also found that the 6-*endo*-dig products were formed. We have not previously observed this type of process, not even for Ugi adducts with substituents on the triple bond.[2g] Unfortunately, we were not able to separate the mixtures of *endo* and *exo* products. The electronic impact of the substituents at the C5- and C6-positions of the indole core was investigated via the introduction of electron-withdrawing and electron-donating substituents. Although the influence via the C5-position is negligible, a chlorine at the C6-position appears to have a deteriorating impact on the yield (Figure 2, 26% for compound **2.5**).

In order to introduce a higher degree of diversity, we investigated the cyclization of the aforementioned Ugi adducts **3** (Figure 3). However, employing our optimized reaction conditions, we could not isolate satisfying amounts of the desired product **4** as the reaction proceeded directly to the tetracyclic spiroindoline via trapping of the intermediate imine. After having carefully optimized the temperature, time and catalyst we were able to maximize the yield of the desired spiroindolenine **4** (see Table S2 in the Supporting Information). The applied catalyst plays a crucial role for this transformation, because any type of activation of the generated imine would lead to trapping by the amide, resulting in the formation of the spiroindoline **5**:



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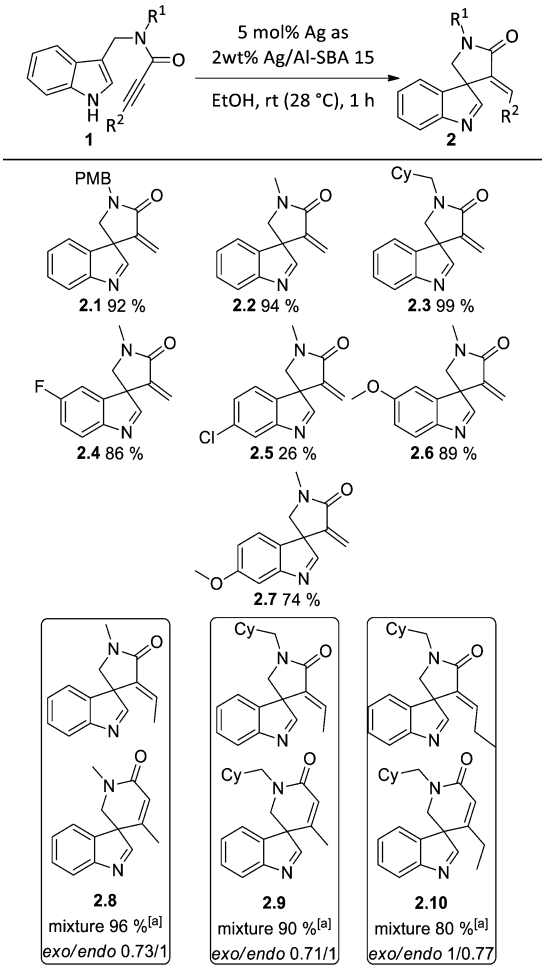

Figure 2. Reaction scope for scaffold **4**. All reactions were performed with 50 mg of starting material. The symbol "[a]" in the framed structures at the bottom of the figure denote the following conditions: 60 °C, 50 mol % Ag as 2 wt % Ag/Al-SBA 15, 3 h.

We found that Ag NPs most probably have a lower affinity for the imine nitrogen (where the metal acts as a Lewis acid and the nitrogen acts as a Lewis base), compared to the Au NPs, which are considered to act as a soft Lewis acid. The temperature was optimized to 40 °C and the reaction time to 3 h. The optimization was done with a substrate bearing R^1 = *para*-methoxy benzyl, R^2 = H, and R^3 = *t*-Bu (substrate **3.1**).

The isolated yields for substrates bearing terminal alkynes are generally high, with the formation of very minor amounts of the undesired tetracyclic product **5** (thin layer chromatography (TLC) analysis). Substituents at the C5- or C6-position of the indole (compounds **4.8**, **4.9**, **4.10**, **4.12**, and **4.13**) seem to perform equally well. However, a nitro-substituent in the C4-position (compound **4.11**) decreased the yield to a meager 23% and no diastereoselectivity was observed. To our surprise, a less sterically demanding R^3-substituent, such as butyl, caused a severe drop in the yield to 11% (compound **4.14**). Employing the optimized conditions, compound **4.6** was not formed because no reaction occurred. This is consistent with our previous observations that substrates bearing internal alkynes require much higher temperatures and larger amounts of catalyst.[13,2g,h] However, in our case, this leads to trapping of the imine, which results in the formation of the undesired tetracyclic product **5**.

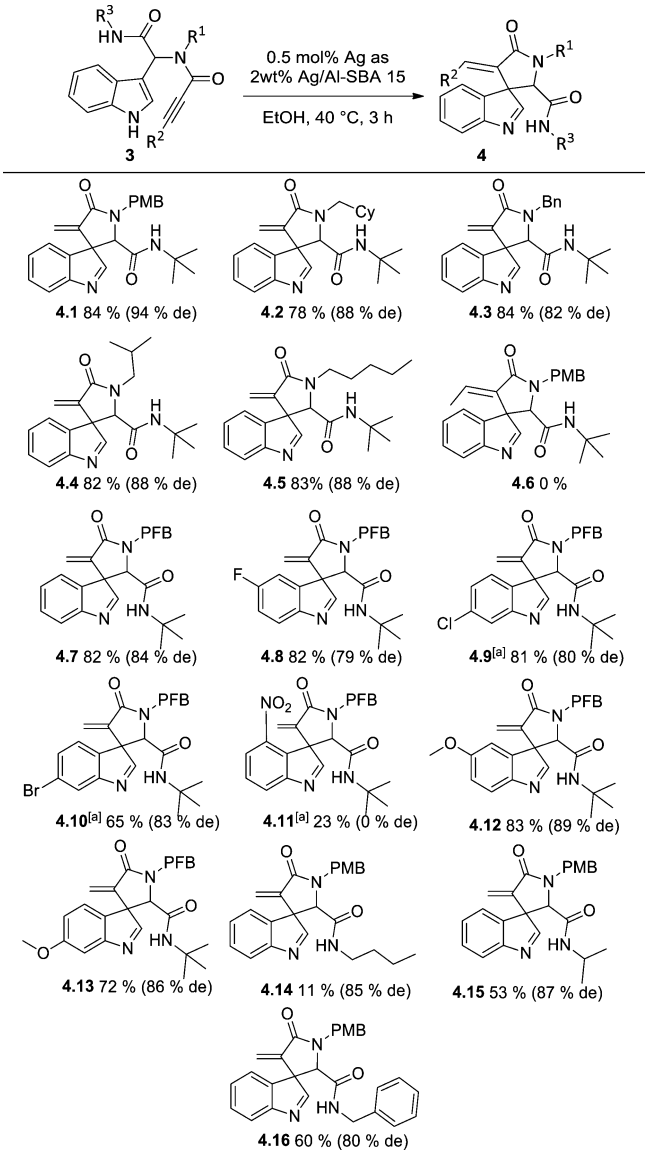

Figure 3. Reaction scope for Ugi adducts (PFB = *para*-fluorobenzyl and PMB = *para*-methoxybenzyl; all reactions were performed with 100 mg of starting material). The symbol "[a]" denotes that, for the noted structure, the reaction time was increased to 9 h.

The catalyst was characterized by X-ray photoelectron spectroscopy (XPS) and transmission electron microscopy (TEM). The Ag/Al-SBA 15 samples show interesting behavior when inside the TEM instrument. We could show that the samples are extremely beam-sensitive, with regard to material destruction. Furthermore, we found that the metal NPs can disappear from the support material when exposed to intensive beams (see Figure 4, top left and top right). Static charge might be a reason for this phenomenon, which leads to empty-appearing support material. From the accumulated data, we obtained a representative NP size distribution (Figure 4, bottom left and bottom right; more details are given in the Supporting Information). The histogram in Figure 5a shows a mean NP diameter of 5 nm. We measured the apparent turnover frequency (TOF) of the catalyst, and a value of TOF = 22 s^{-1} was observed (see the Supporting Information). The apparent TOF only considers the absolute amount of metal and neither the number of NPs nor the surface area of the NPs.

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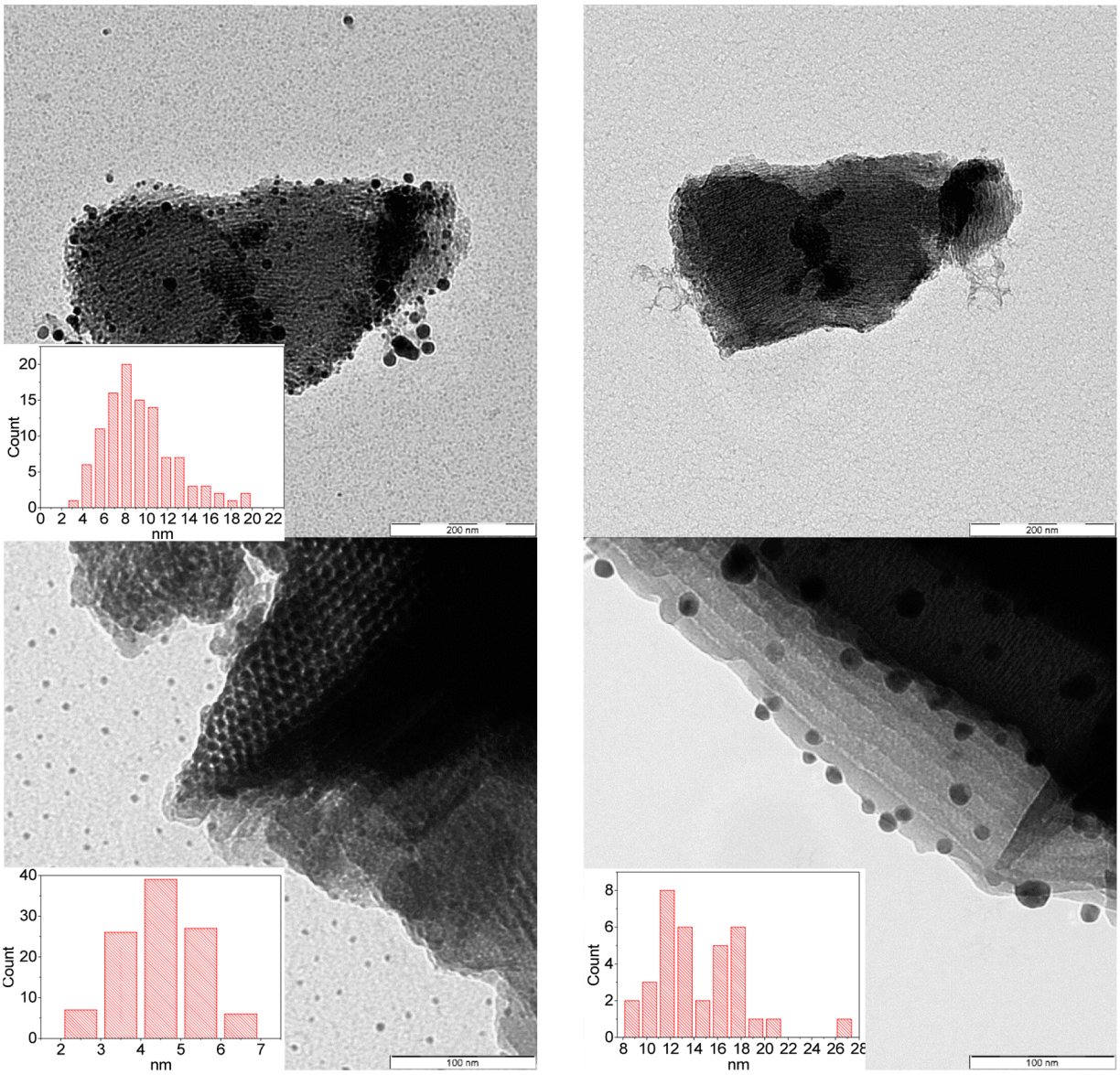

Figure 4. TEMs showing metal NPs before (top, left) and the empty support after (top, right) irradiating with an intensive electron beam. Catalyst samples not affected by an electron beam [bottom, left (24 h at 40 °C) and right (24 h at 80 °C)].

Furthermore, we investigated the reusability of the catalyst and found that it performs unchanged through 10 cycles of reactions. The isolated yields were always ~98%. We could not witness decreasing activity under the optimized conditions from Figure 2 (conditions: 5 mol % catalyst, ethanol, RT, 1 h). Investigating the catalyst stability, we checked under which conditions our used catalyst system shows no increasing size of the NPs. The TEM micrographs of the materials exposed to temperatures of 40, 60, and 80 °C for 24 h in ethanol under stirring (500 rpm) are shown in the Supporting Information. The size distribution curves can be seen in Figure 5b. This experiment leads us to conclude that the catalyst system is stable up to 40 °C and that crystal ripening starts to occur at some point between 40 °C and 60 °C.

In order to determine the leaching behavior of the catalyst system, we performed a hot-filtration experiment (see the Supporting Information). By filtering off the catalyst under reaction conditions, one can assume that any metal that leached from the support would still be in the reaction mixture after the filtration. The leached metal then would still catalyze the cycloisomerization. After 10 min of stirring before removal of the catalyst, we found 12.1% conversion to the product. After removal of the catalyst by filtration, the reaction virtually stopped. Stirring for another 18 h, the conversion remained as low as 13.4%. This also gives a good indication that the process is heterogeneous. If we assume that (i) a steady state of metal desorbing and readsorbing from and onto the support exists and (ii) the leached metal would actually be responsible for the catalysis, we would find a reaction rate similar to that previously observed by removing the catalyst. Using ICP-AES, we found that only an extremely small amount of metal is leached (0.35% leaching of the original silver).

In the XP spectrum of a pristine Ag/Al-SBA 15 sample in Figure 5c (see the full spectrum in the Supporting Information), we found two peaks, corresponding to the Ag $3d_{5/2}$ and Ag $3d_{3/2}$ peaks at 369.2 and 375.2 eV. Determination of the oxidation state of silver is dependent on the shape of the peaks (asymmetry) and the full widths at half maximum

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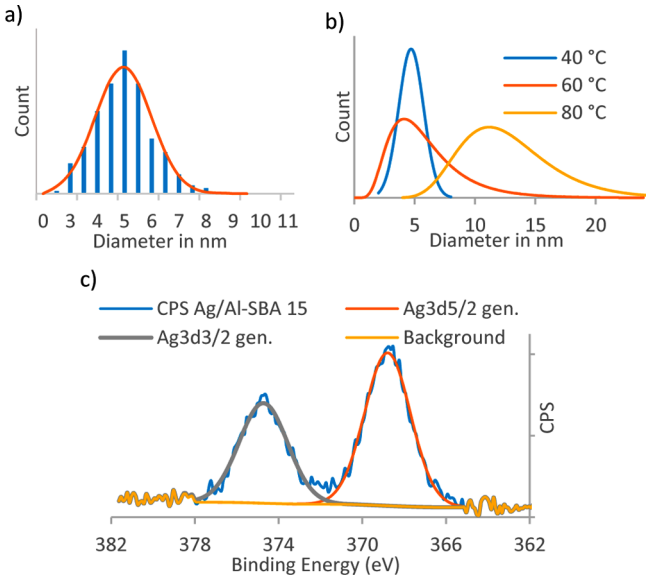

Figure 5. (a) Histogram showing the NP size distribution of the 2 wt % Ag/Al-SBA 15 catalyst; (b) size distribution curves for temperature-dependent NP size; and (c) XPS data of an unused Ag/Al-SBA 15 sample.

(fwhms) they display, rather than their binding energy.[15] The peaks we found show an fwhm in the same range as the C and Si peaks in the same spectrum. A similar result was found for a silver foil sample, except that all peaks were slightly narrower, in comparison with our catalyst sample. Therefore, we can carefully conclude that the Ag NPs in the catalyst samples are mainly metallic and not oxidic. The very low metal loading (1.9 wt % from ICP-AES) and the resulting low signal-to-noise ratio particularly must be taken into account. However, the question for the catalytically active species still remains and we can only assume that, by adsorbing and/or binding of the NP to the support, a cationic charge might be generated, which could act as the active species.

CONCLUSION

We successfully managed to apply heterogeneous silver catalysis in the dearomatizing 5-*exo*-dig cycloisomerization of indol derivatives toward spiroindolenines. Even the cycloisomerization of substrates with internal nucleophiles such as the Ugi adducts could be interrupted at the imine state. The obtained yields of the two processes are good to excellent and the diastereoselectivities are satisfying. Ethanol could be applied as a *green* solvent, and the reusability of the catalyst was found to be excellent under the optimized conditions. The catalyst characterization by TEM and XPS showed NPs with a mean diameter of 5 nm and mostly metallic silver. Furthermore, we found, during the stability study, that, while exposing the catalyst for 24 h to different temperatures, the NPs show no crystal ripening under our optimized conditions. Using hot-filtration and ICP-AES analyses, we determined that (i) the catalyst only shows extremely low leaching and (ii) the process is heterogeneous. The apparent TOF of the catalyst was determined to be 22 s^{-1}. Once more, we could show that heterogeneous catalysis can be a powerful tool in organic synthesis, opening the pathway for the application of flow chemistry to these scaffolds.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.6b02443.

Experimental procedures, TEM micrographs, XPS spectra, ^{1}H NMR and ^{13}C NMR spectra (PDF)

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Author Contributions

F.S., U.K.S., and M.M. performed the experiments; F.D. and D.P.D. are responsible for the TEM and XPS analysis; R.L. provided the catalytic systems; F.S. and E.V.V.dE. conceived the idea and wrote the manuscript. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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