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FULL PAPER

"Golden" Cascade Cyclization to Benzo[*c*]-Phenanthridines

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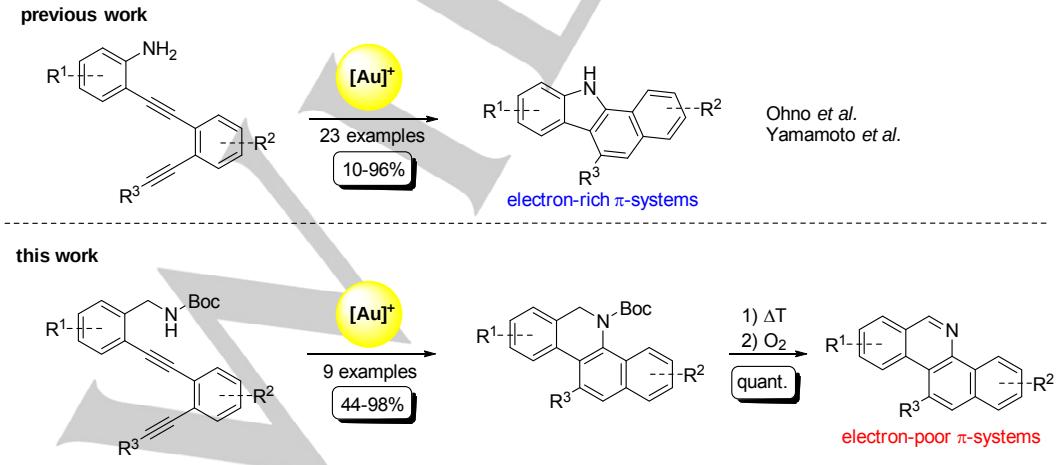
+ Crystallographic investigation

Abstract: Herein we describe a gold-catalyzed cascade cyclization of Boc-protected benzylamines bearing two tethered alkyne moieties via a domino reaction initiated by a 6-*endo*-*dig* cyclization. The reaction was screened intensively and the scope was explored, resulting in nine new Boc-protected dihydrobenzo[*c*]phenanthridines with yields of up to 98%; even a π-extension and two bidirectional approaches were successful. Furthermore, a thermal cleavage of the Boc-group and subsequent oxidation was possible to obtain substituted benzo[*c*]phenanthridines in up to quantitative yields. Two bidirectional approaches were successful using the optimized conditions and the resulting π-extended molecules were tested as organic semiconductors in organic thin-film transistors.

Introduction

Homogeneous gold catalysis went through an impressive evolution during the last decades.[1] Not only for scientific reasons, but also for applications - e.g. natural product synthesis[2] or materials science,[3] gold catalysis became a versatile tool in organic chemistry. In 2010, Ohno *et al.* published a cascade cyclization covering an innovative expansion of Utimoto's indole cyclization.[4] In the following years this methodology was even extended to up to five tethered alkynes, which in some cases even gave access to helically chiral compounds.[5] Due to their ability to create complex molecular structures in only a few steps, cascade reactions became a powerful synthetic strategy in the recent time.[6] While in literature many examples for the cyclization of anilines to indole derivatives are reported (Scheme 1),[7] examples for a corresponding cyclization of benzylamines to six-membered *N*-heterocycle derivatives are rare[8] and Ohno-like cascade cyclizations of tethered alkynes are completely missing. We envisioned that such a process might deliver benzo[*c*]phenanthridines, which are useful intermediates in organic synthesis and important subunits of various pharmaceutically important alkaloids.[9] In this context, we herein wanted to present our studies on a gold-catalyzed cascade cyclization of benzylamines for the formation of benzo[*c*]phenanthidine derivatives, which strategically complements other synthetic approaches like different palladium-catalyzed variations[10], light , or *tert*-butoxide-promoted variants.[11,12]



Scheme 1. Comparable previous cascade cyclizations of anilines and our benzylamine approach.

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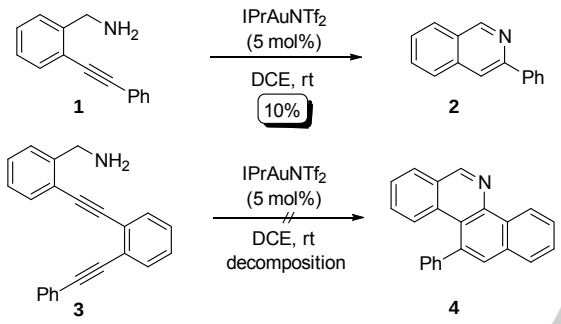
Results and Discussion

Our first approach started with the cyclization of the primary benzylamine **1** as model substrate. To the best of our knowledge only one gold-catalyzed cyclization for a similar substrate was conducted until now.[13] Interestingly, besides not identified side products, 10% of the already oxidized isoquinoline **2** could be obtained when **1** was treated with 5 mol% of commercially available $IPrAuNTf_2$. But the low yield could not be improved, even when the reaction was conducted under an oxygen atmosphere. The first effort to achieve a cascade cyclization with primary amine **3** only led to an unselective decomposition of the starting material instead of the desired formation of benzo[*c*]phenanthridine **4** (Scheme 2).



Scheme 2. First evaluations for the synthesis of isoquinoline **2** and benzo[*c*]phenanthridine **4**.

Based on these results and preceding work of Takemoto *et al.*, who successfully screened the cyclization of Boc protected benzylamines to isoquinoline derivatives,[14] benzylamine **3** was protected with a Boc group (= **5a**). This addressed first cyclization step of our sequence (for the mechanism, compare Scheme 6). Catalan and co-workers had demonstrated that for similar Boc-protected benzylamine substrates a 6-*endo-dig* cyclization is preferred over a 5-*exo-dig* cyclization, the latter is dominating for substrates bearing an electron-withdrawing group (e.g. CF_3) in the benzylic position.[15]

Scheme 3. Gold-catalyzed cascade cyclization of Boc-protected diyne **5a**.

Thus, the Boc-protected diyne **5a** was treated with 5 mol% of $IPrAuNTf_2$, yielding the expected product **6a** in 52% (Scheme 3).

Next, we focused on the optimization of this gold-catalyzed step (Scheme 4). With $IPrAuNTf_2$, a 2.5 mol% catalyst loading turned out to be most suitable (for more details see Supporting Information). Then, $AgSbF_6$, $PtCl_2$ and $Pd(OAc)_2$ were tested, but no product formation was observed with these metal salts (Table 1, entries 1-3). For the screening of the counter anion,[16] IPrAuCl was activated with different silver salts in $CDCl_3$, before the in situ formed catalyst was added to the reaction mixture (entries 5-7). SbF_6^- turned out to be the best counter ion. The same procedure was carried out for the screening of the ligand (Figure 1). Besides the sterically more hindered NHC ligand IPr* (9, entry 8), also some phosphane-based ligands were tested (9-12), of which the JohnPhos ligand showed the highest yield. Noticeable is the slightly higher yield for the pre-activated $JohnPhosAu(MeCN)SbF_6$ complex (entry 13) in comparison to the *in situ* activated catalyst. Interestingly, for some cases also the intermediate **7a** could be observed. Especially for the SPhos ligand (entry 9), the reaction seems to stop at **7a** of the sequence, the observed yield of **7a** was almost ten times higher than the yield of **6a**. Next, temperature variations and different solvents were tested. The reaction in deuterated DCM or DCE at 50 °C increased the yields to 96% - in just 1 h reaction time. Surprisingly, the reaction seems to be highly dependent on the solvent. Even after 5 h at 50 °C in deuterated benzene and acetonitrile the conversion is rather low and remarkable amounts of intermediate **7a** could be observed.

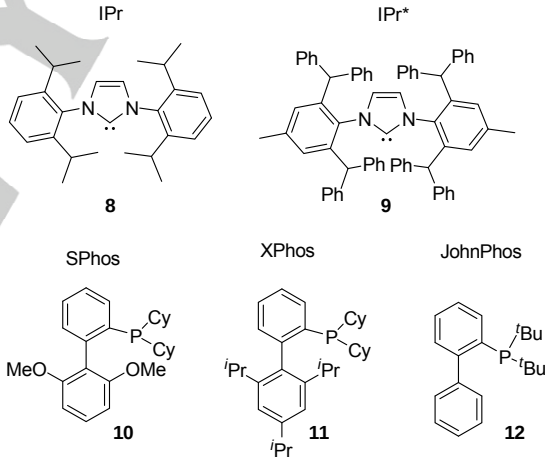


Figure 1. Chemical structure of some ligands used for the screening.

Scheme 4. Screened reaction of diyne **5a** to **6a** via intermediate **7a**.

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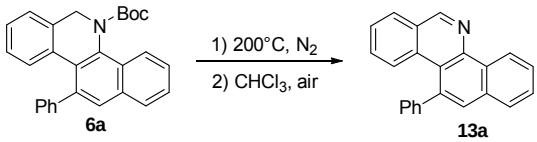
Table 1. Overview of the catalyst systems and conditions for the NMR screening.

Entry	Catalyst	Solvent	Temperature	Time [h]	Conversion	Yield **7a**[a]	Yield **6a**[a]
1	$AgSbF_6$	$CDCl_3$	rt	5	-	-	-
2	$PtCl_2$	$CDCl_3$	rt	5	-	-	-
3	$Pd(OAc)_2$	$CDCl_3$	rt	5	3%	-	-
4	$IPrAuNTf_2$	$CDCl_3$	rt	2	75%	3%	56%
5	$IPrAuCl/AgBF_4$	$CDCl_3$	rt	2	100%	3%	64%
6	$IPrAuCl/AgPF_6$	$CDCl_3$	rt	2	100%	2%	65%
7	$IPrAuCl/AgSbF_6$	$CDCl_3$	rt	2	100%	-	67%
8	$IPr^*AuCl/AgSbF_6$	$CDCl_3$	rt	5	7%	1%	3%
9	$SPhosAuCl/AgSbF_6$	$CDCl_3$	rt	5	27%	19%	2%
10	$PPh_3AuCl/AgSbF_6$	$CDCl_3$	rt	5	11%	2%	1%
11	$XPhosAuCl/AgSbF_6$	$CDCl_3$	rt	2	99%	-	86%
12	$JohnPhosAuCl/AgSbF_6$	$CDCl_3$	rt	2	100%	-	87%
13	$JohnPhosAu(MeCN)SbF_6$	$CDCl_3$	rt	2	100%	-	92%
14	$JohnPhosAu(MeCN)SbF_6$	$CDCl_3$	0 °C	1	52%	4%	39%
15	$JohnPhosAu(MeCN)SbF_6$	$CDCl_3$	0 °C	5	94%	29%	51%
16	$JohnPhosAu(MeCN)SbF_6$	$CDCl_3$	50 °C	1	100%	-	94%
17	$JohnPhosAu(MeCN)SbF_6$	CD_2Cl_2	50 °C	1	100%	-	**96%**
18	$JohnPhosAu(MeCN)SbF_6$	CD_3CN	50 °C	5	76%	26%	40%
19	$JohnPhosAu(MeCN)SbF_6$	C_6D_6	50 °C	5	53%	41%	3%
20	$JohnPhosAu(MeCN)SbF_6$	d_4-DCE	50 °C	1	100%	-	**96%**

[a] NMR yield.

Our mechanistic proposal is shown in Scheme 6. We assume that a similar sequence as published for the indole cascade cyclization from Ohno is operating.[5a] The nucleophilic attack of the Boc-protected secondary amino group to the gold-activated triple bond (**A**) forms the vinyl gold species (**B**), which first undergoes protodeauration, followed by a second nucleophilic attack of the newly formed double bond to the tethered alkyne (**C**). The observation of **7a** in the catalyst screenings and isolation of **7j** (compare Table 1 and Table 2) further support this mechanism. Final protodeauration of vinyl gold species **D** furnishes product **6a**. After optimization of the gold-catalyzed step we focused on the cleavage of the Boc-protecting group. Besides common ways like acid-mediated deprotection methods,[17] an approach of Cava from 1985[18] looked promising, which we already successfully used for indolocarbazoles.[3a] This solvent-free thermal deprotection, originally used for pyrrole-based substances, was also effective for our Boc-protected product **6a**. For this step our substrate was heated to 200 °C under a nitrogen atmosphere for about 3 h. In a very efficient way the oxidized benzo[*c*]phenanthridine **13a** was directly obtained by bubbling air through a chloroform solution of the residue after the thermal treatment. The final product was obtained after removing the solvent under reduced pressure without the need of any further purification (Scheme 5).



Scheme 5. Conditions for the thermal Boc-deprotection and subsequent oxidation to benzo[*c*]phenanthridine **13a**.

Even though this procedure already was very simple, we tried to further simplify it by applying a semi-one-pot synthesis of the gold catalysis and the deprotection. In a test reaction first the gold catalysis with **5a** was conducted as described, but instead of the work up, the crude product was directly used for the thermal deprotection after removing the solvent under reduced pressure. After complete conversion, it was dissolved in chloroform. Then air was bubbled through the solution for the oxidation, followed by flash column chromatography. However, this semi-one pot variant

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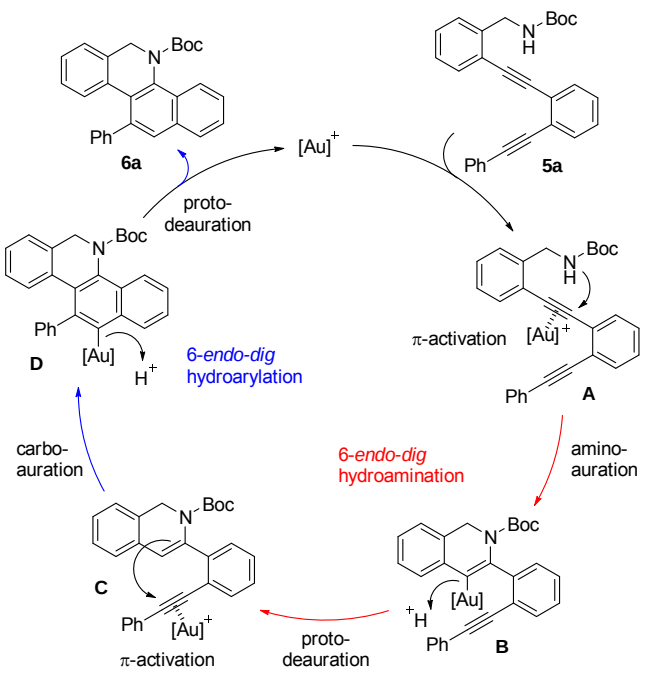
resulted only in a 74% yield, compared to a 95% combined yield for the two step method.

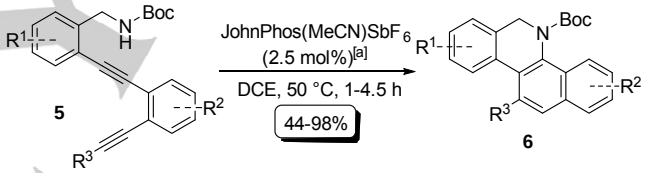


Scheme 6. Proposed mechanism.

Once, the gold-catalyzed step and the cleavage of the Boc group were optimized, we explored the scope of this new method (Scheme 7 and Table 2). For synthesizing the corresponding alkyne systems **5**, different synthetic strategies involving sequences of Sonogashira cross couplings, were used (see SI for more details). First, we installed an electron-withdrawing (R^1 = F, **5b**) and an electron-donating group (R^1 = two OMe groups, **5c**) in the backbone of the benzyl moiety. For **6b** an isolated yield of 90% was obtained, whereas the yield for the electron-rich **6c** dropped to 44%.

Next, the aryl group connecting the two alkynes was varied. Besides an electron-withdrawing (R^2 = F, **5d**) and an electron-donating group (R^2 = Me, **5e**), also an attempt for a π-extended naphthalene backbone (**5f**) was conducted. In contrast to the upper trend a fluoro substituent at this position (**6d**) led to a drop in yield to 67% while **6e** bearing the slightly electron-donating methyl group furnished the corresponding product in 96% yield. An excellent yield was also obtained for the π-extended **6f** (90%). For this substrate, the thermal treatment for the cleavage of the Boc protecting group was not quantitative, but needed a further purification step. A short column chromatography resulted in 39% yield of **13f**.

Lastly, different substituents on the alkyne moiety were tested (**5g-j**). Substrate **5g**, bearing an alkyl group instead of an aryl substituent, with 98% delivered the highest yield among all substrates investigated here. With sterically hindered substituents like TMS- (**5h**) or *tert*-butyl (**5j**) groups only intermediates **7h** and **7j** were formed which can be explained by the steric repulsion for the second cyclization step. After its isolation, **5j** was again treated with 2.5 mol% gold catalyst in DCE at higher reaction temperatures. But even at 80 °C and 100 °C no conversion could be observed. A possible 5-*exo-dig* cyclization was not observed as well. Surprisingly the terminal alkyne **5i** did not convert at all.



Scheme 7. Conditions for the scope of the reaction.[a]For **5c** additional 2.5 mol% catalyst were used.

Table 2. Overview of all examined structures including yields of the gold catalysis and deprotection/oxidation.

Starting material	Diyne **5a-l**	Cyclization product **6a-l**	Yield	Oxidation product **13a-l**	Yield
5a		**6a** 95%		**13a** quant.	
5b		**6b** 90%		**13b** quant.	
5c		**6c** 44%[b]		**13c** quant.	
5d		**6d** 67%[b]		**13d** quant.	

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5e		**6e** 96%	**13e** quant.
5f		**6f** 90%	**13f** 39%[c]
5g		**6g** 98%	**13g** quant.
5h		**7h** 76%[d]	-
5i	-	-	-
5j		**7j** 87%	-
5k		**6k** 65%[f]	**13k** 77%
5l		**6l** -[g]	**13l** 33%[h]

[a] Yield for an one-pot approach. [b] Yields were reproduced by a second independent attempt. [c] An additional purification step in form of a short column chromatography was needed. [d] NMR yield. [e] No conversion was observed. [f] Combined yields for two isomers (see SI). [g] **6l** was not isolated properly and therefore directly used for the next step. [h] Yield over two steps.

To further expand the possibilities of this powerful cascade reaction, also two bidirectional approaches were established (**5k** and **5l**). Unfortunately, the non-aromatized intermediates of **6k** and **6l** of the bidirectional gold catalysis could not be isolated and characterized properly. This might be due to the fact that different stereoisomers can be formed. The strong twisted *N*-heterocycle, in combination with the steric demanding Boc protection group could form diasteromers, which is also manifested in the X-ray structure of **6c** (Figure 2, left).[19] Nevertheless, the structure of **6k** showing a "trans"-conformation of the two Boc groups was confirmed by X-ray analysis (Figure 3, left and right top).

In order to estimate the rotational barrier of the Boc groups as well as the phenyl rings attached to the aromatic core, relaxed scans were performed on the PBE0-D3/aug-pcseg-1 level of theory as implemented in the TeraChem software package (for more information see SI). The barrier for the rotation of the Boc group is 20.7 kcal/mol, whereas a rotational barrier of 12.6 kcal/mol for the phenyl group turned out to be lower. Interestingly, in NMR experiments a coalescence temperature of 318 K between the two structures can be observed.

Due to the mentioned difficulties the products of the gold catalysis were directly used for the next step. The deprotection procedure was similar to the mono directional method, but needed an additional workup in form of column chromatography and subsequent recrystallization (see SI for more information). This resulted in moderate yields over two steps of 36% (for **13k**) and 27% (for **13l**), respectively. Both structures, **13k** and **13l**, were also confirmed by X-ray crystallography.

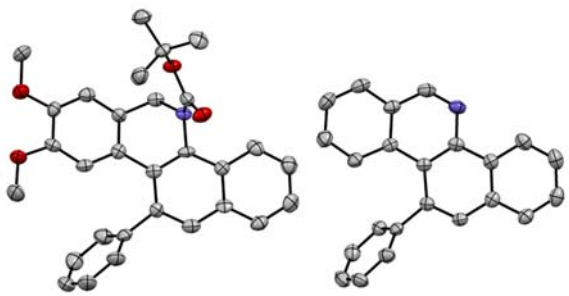

Figure 2. Solid state molecular structures of **6c** (left) and **13a** (right).

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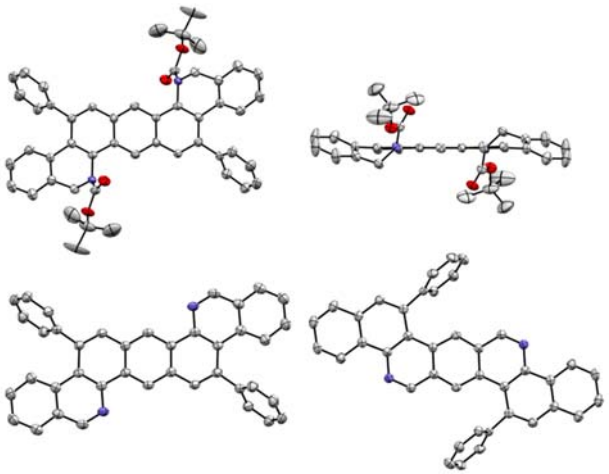

Figure 3. Solid state molecular structures of compounds generated in a bidirectional manner. Left, top: **6k**; Right, top: side view of **6k** (the Ph-substituents are omitted for clarity); Left, bottom: **13k**; Right, bottom: **13l**.

Due to the large π-system of both bidirectionally obtained phenanthridines, **13k** and **13l** are potentially interesting as organic semiconductors for materials science. Thus, their optical properties (UV/Vis and fluorescence spectra can be found in SI) and their potential charge-transport properties were evaluated. Both molecules are fluorescent and show two local maxima, with **13l** exhibiting a bathochromic shift of about 14 nm. The same trend is observed for the absorption spectra, with an onset of 423 nm for **13k** and 438 nm for **13l**. Using both materials, we attempted the fabrication of thin-film transistors (TFTs) in the inverted staggered (bottom-gate, top-contact) device architecture on heavily doped silicon substrates using different gate dielectrics and by deposition of the organic semiconductors by thermal sublimation in vacuum.[20] However, we were unable to measure any appreciable drain current or field effect with either **13k** or **13l**. Atomic force microscopy (AFM) and scanning electron microscopy (SEM) images (see SI) indicate that **13l** did not form a closed (or even percolated) film on any of the substrates, which explains the lack of charge transport. Compound **13k** appears to form a closed film, so the reason for the lack of charge transport remains unclear. The fact that we were not able to fabricate functional transistors by vacuum deposition of **13k** and **13l** does not mean that these materials may not form well-ordered films with good charge-transport properties when processed from solution or produced in the form of single-crystals.

Conclusion

We present a highly effective new cascade cyclization using gold catalysis. It was possible to optimize the gold-catalyzed step from initially 52% up to 96% NMR yield by screening different catalysts and reaction conditions. Overall seven differently substituted Boc-protected dihydrobenzo[*c*]phenanthridines were synthesized showing the dependence of electron-drawing and electron withdrawing substituents on different positions of the molecule as well as steric effects. This reaction pattern was then transferred successfully to bidirectional variants enabling the formation of large *N*-heterocyclic π-systems. It was further possible to thermally cleave the Boc-group and to oxidize the cyclization products in a semi one-pot strategy to furnish benzo[*c*]phenanthridine derivatives. Lastly, two bidirectional approaches were successfully conducted and tested as organic semiconductor in thin-film transistors. The presented reaction enables an elegant way for the synthesis of highly substituted six-membered *N*-heterocycles. This synthetic strategy is especially interesting for materials science, but could also be used for the synthesis of pharmaceutically important alkaloids.

Acknowledgements

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Keywords: Homogeneous gold catalysis • cascade reactions • benzylamines • benzo[*c*]phenanthridines

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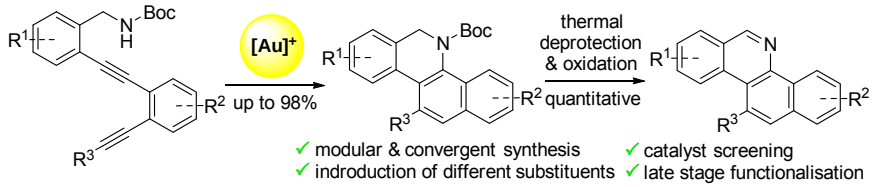

The synthesis of substituted benzo[*c*]phenanthridines using gold catalysis is reported. The applied cascade reaction using different substituted alkyne systems as starting materials, furnished the corresponding benzo[*c*]phenanthridines in very high overall yields. In addition, two π-extended molecules were studied as organic semiconductors in organic thin-film transistors.