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Synthesis of indole-fused heteroacenes by cascade cyclisation involving rhodium(II)-catalysed intramolecular C–H amination

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Heteroacenes are potentially important materials for organic electronics and their syntheses are of topical interest. Herein we report the development of a catalytic, redox-neutral reaction for the synthesis of the 5,10-dihydroindolo[3,2-*b*]indole class of heteroacene. 2-[(2-Azidophenyl)ethynyl]anilines undergo cascade cyclisation by gold(I)/rhodium(II) relay catalysis. Control experiments show that gold(I) is an effective catalyst for the first indole cyclisation with the aniline moiety, while the second cyclisation, which involves the azide moiety, is catalysed by rhodium(II). This protocol delivers a variety of *N*-substituted *N*′-unsubstituted dihydroindoloindoles. 2-[(2-Azidophenyl)ethynyl]phenols are also converted into 10*H*-benzofuro[3,2-*b*]indoles through base-promoted benzofuran cyclisation followed by rhodium(II)-catalysed C–H amination. A related cascade cyclisation reaction of a 2-[(2-azidophenyl)ethynyl]biphenyl is also reported.

Introduction

Fascinating electronic and photophysical properties, which are consequences of their ladder π-electron systems, have led to acenes and heteroacenes becoming the subjects of intensive research.[1] The potential applications of these acene-based molecules in organic electronics, such as light-emitting diodes, field-effect transistors and photovoltaic cells, have gained considerable attention. Therefore, the development of new reactions for the preparation of acenes and heteroacenes, especially those with 6-5-5-6 ring systems, has been a highly active research area.[2,3,4,5] The cascade cyclisation reaction involving *ortho*,*ortho*-difunctionalised diphenylacetylenes has been employed as a straightforward and efficient method for the synthesis of these tetracyclic heteroacenes.[2,3]

Sequential twofold C–N bond formations in bis(2-aminophenyl)acetylene derivatives were reported by Jin and Du in 2016.[2] This cascade cyclisation process uses copper(II) salts as stoichiometric oxidants to afford 5,10-dihydroindolo[3,2-*b*]indoles[4,6,7] in which both nitrogen atoms are substituted. Herein, we report the catalytic, redox-neutral cascade cyclisation of 2-[(2-azidophenyl)ethynyl]anilines for the syntheses of *N*-substituted *N*′-unsubstituted 5,10-dihydroindolo[3,2-*b*]indoles in which cyclisation is achieved through gold(I)/rhodium(II) relay catalysis.[8] The analogous cascade cyclisation of 2-[(2-azidophenyl)ethynyl]phenols are also reported.

Results and discussion

2-[(2-Azidophenyl)ethynyl]-*N*-tosylaniline (**1a**), which was prepared through the Sonogashira coupling of 1-azido-2-iodobenzene with 2-ethynyl-*N*-tosylaniline, was treated with 2.5 mol% (IPr)AuNTf$_2$[9] in DCE[9] at 80 °C (Table 1). The desired product, 5-tosyl-5,10-dihydroindolo[3,2-*b*]indole (**2a**),[10] was obtained in only 23% yield, accompanied by a large amount of 2-(2-azidophenyl)-1-tosylindole (**3a**) as a byproduct (entry 1). Solvent screening revealed that **3a** was the exclusive product when the reaction was performed in toluene (entries 2–4). The highest yield of **3a** was achieved with (SPhos)AuNTf$_2$[9] instead of (IPr)AuNTf$_2$ (entry 5). Given that **3a** was obtained in excellent yield using (SPhos)AuNTf$_2$, we modified our plan such that each cyclisation step was executed with a different catalyst. Hence, when the reaction of **1a** was performed in the presence of (SPhos)AuNTf$_2$ and Rh$_2$(O$_2$CC$_3$F$_7$)$_4$, tetracyclic product **2a** was obtained in 50% yield together with 27% yield of indole **3a** (entry 6). Gratifyingly, **2a** was obtained in excellent yield as the sole product using the (SPhos)AuNTf$_2$/Rh$_2$(esp)$_2$[9] system (entry 7); the catalyst system with 1 mol% Au(I) and 3 mol% Rh(II) was sufficient to achieve similar results (entry 8).

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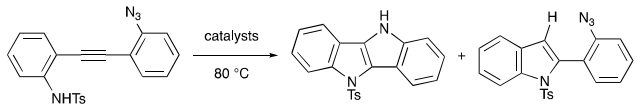
Table 1 Optimising the reaction conditions for the cascade cyclisation of **1a**



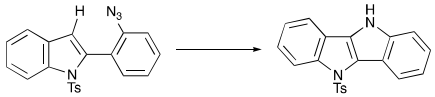
1a **2a** **3a**

Entry	Catalyst I (mol%)	Catalyst II (mol%)	Solvent	Time (h)	**2a**/%Yield[a]	**3a** %Yield[a]
1	(IPr)AuNTf$_2$ (2.5)	–	DCE	3	23	41
2	(IPr)AuNTf$_2$ (2.5)	–	THF	3	7	63
3	(IPr)AuNTf$_2$ (2.5)	–	CH_3CN	3	8	50
4	(IPr)AuNTf$_2$ (2.5)	–	Toluene	3	–[b]	81
5	(SPhos)AuNTf$_2$ (2.5)		Toluene	3	–[b]	87
6	(SPhos)AuNTf$_2$ (2.5)	$Rh_2(O_2CC_3F_7)_4$ (5)	Toluene	16	50	27
7	(SPhos)AuNTf$_2$ (2.5)	$Rh_2(esp)_2$ (5)	Toluene	16	75	–[c]
8	(SPhos)AuNTf$_2$ (1)	$Rh_2(esp)_2$ (3)	Toluene	24	81	–[c]

[a] Isolated yield. [b] Trace. [c] Not detected.

To gain insight into the reaction mechanism, we conducted some control experiments. Substrate **1a** did not cyclise when the reaction was performed in the presence of the rhodium(II) catalyst alone, which highlights the essential role that the gold(I) catalyst plays in the present cascade cyclisation process. The cyclisation of 2-(2-azidophenyl)indole **3a** was next examined (Table 2). Although the Au(I)–IPr catalyst exhibited modest activity toward the second cyclisation involving the azide group (entry 1), the Au(I)–SPhos catalyst was found to be inactive (entry 2). As expected, the Rh(II) catalyst was suitable for this transformation,[11] yielding **2a** in 87% yield (entry 3). Based on the above results, we propose a possible mechanism for the Au(I)/Rh(II)-catalysed cascade cyclisation of **1a** (Scheme 1). Firstly, Au(I) induces cyclisation with the tosylamino group to form indole **3a**,[12] after which intramolecular C–H amination with the azide group, facilitated by Rh(II), furnishes the dihydroindoloindole **2a**.

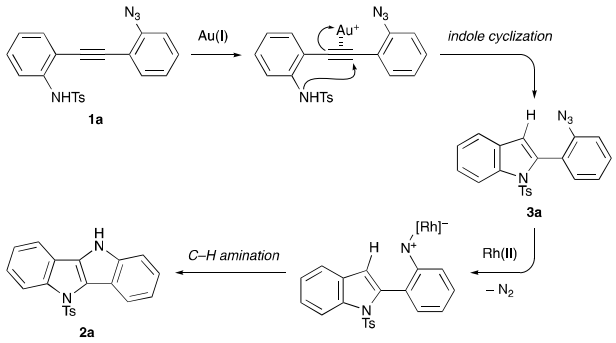
Table 2 Cyclisation of **3a**



3a **2a**

Entry	Catalyst (mol%)	Conditions	Yield (%)
1	(IPr)AuNTf$_2$ (2.5)	DCE, 80 °C, 24 h	35[a,b]
2	(SPhos)AuNTf$_2$ (2.5)	Toluene, 80 °C, 12 h	trace
3	$Rh_2(esp)_2$ (5)	Toluene, 80 °C, 12 h	87[a]

[a] Isolated yield. [b] **3a** was recovered in 48% yield.



Scheme 1 Proposed mechanism for the cascade cyclisation of **1a**

With the optimised conditions in hand, we sought to explore the scope and limitations of this cascade cyclisation protocol (Table 3). Reactions of **1b**–**g**, composed of phenyl rings bearing methyl, methoxy and chloro groups, afforded the corresponding substituted dihydroindoloindoles **2b**–**2g** in yields of 33–72%. Under the standard conditions, the reaction of **1g**, bearing the 2-azido-5-chlorophenyl group, gave a complex mixture of products, but the desired product **2g** was obtained in 34% yield when the reaction was conducted in the presence of (IPr)AuNTf$_2$ alone. The 1-naphthylamine derivative **1h** delivered pentacyclic heteroacene **2h**, albeit in low yield. The reaction was tested with respect to substrates **1i**–**m** that bear different substituents on their aniline nitrogens; they gave the corresponding products **2i**–**m** in yields of 62–71%. However, reactions with substrates bearing free amino and *N*-acetylamino groups resulted in the formation of complex mixtures of products under these reaction conditions.

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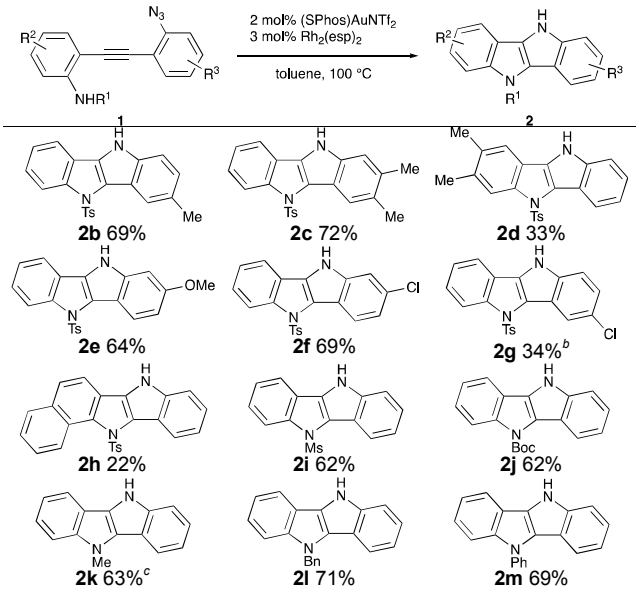
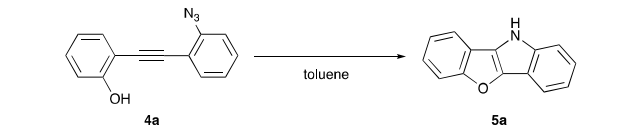
Table 3 Cascade cyclisations of 2-[(2-azidophenyl)ethynyl]anilines **1**[a]



[a] Reaction conditions: **1**, (SPhos)AuNTf$_2$ (2 mol%) and Rh$_2$(esp)$_2$ (3 mol%) in toluene (0.10 M) under N_2 at 100 °C for 12–18 h, unless otherwise noted. [b] 2.5 mol% (IPr)AuNTf$_2$, DCE, 80 °C, 5 h. [c] 1 mol% (SPhos)AuNTf$_2$ instead of 2 mol%.

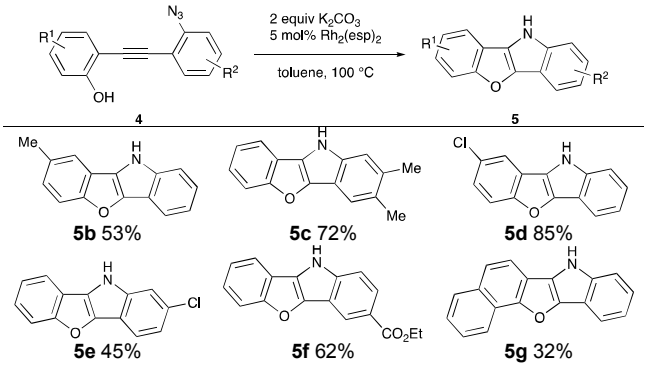
Similar to 2-alkynylanilines, 2-alkynylphenols are also known to readily undergo intramolecular cyclisations.[13] Hence, 2-[(2-azidophenyl)ethynyl]phenol (**4a**) was subjected to the reaction conditions that were optimised for the cyclisation of **1** (Scheme 2). However, the Au(I)/Rh(II) system failed to catalyse the cyclisation of **4a**, resulting in the formation of a complex mixture of products instead. To our delight, we were able to find suitable reaction conditions for this cyclisation; the reaction of **4a** proceeded efficiently in the presence of two equivalents of K_2CO_3 and 5 mol% Rh$_2$(esp)$_2$ at 100 °C in toluene, to afford 10*H*-benzofuro[3,2-*b*]indole (**5a**) in 79% yield through base-promoted benzofuran cyclisation followed by rhodium(II)-catalysed intramolecular C–H amination.[14,15]



Scheme 2 Cascade cyclisation of **4a**

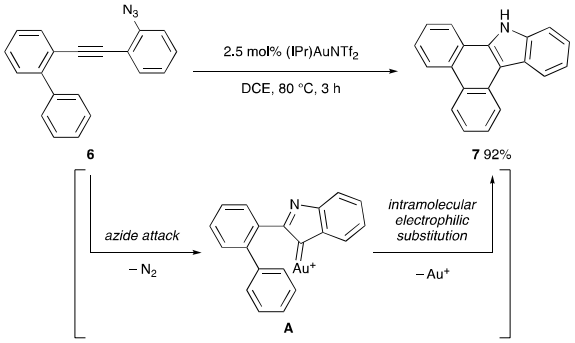
The reaction conditions for the formation of benzofuroindole **5a** were applied to several 2-[(2-azidophenyl)ethynyl]phenols **4b**–**f** bearing methyl, chloro and ester groups on the benzene rings, resulting in the formation of substituted benzofuroindoles **5b**–**f** in yields of 45–85% (Table 4). Pentacyclic naphthofuroindole **5g** was also synthesised by cascade cyclisation.

Table 4 Cascade cyclisation of 2-[(2-azidophenyl)ethynyl]phenols **4**[a]



[a] Reaction conditions: **4**, K_2CO_3 (2 equiv) and Rh$_2$(esp)$_2$ (5 mol%) in toluene (0.10 M) under N_2 at 100 °C for 12–18 h.

Finally, we demonstrated the related cascade cyclisation reaction involving a 2-azidophenylalkyne. 2-[(2-Azidophenyl)ethynyl]biphenyl (**6**) was cyclised in the presence of the Au(I)–IPr catalyst to afford dibenzocarbazole **7** in 92% yield (Scheme 3).[8,14,16] In contrast to the cascade cyclisation of the 2-[(2-azidophenyl)ethynyl]anilines and -phenols that require rhodium(II) catalysts to afford products in acceptable yields, the reaction of azide **6** proceeded efficiently in the absence of a rhodium(II) catalyst. Based on these results, we propose that the reaction of **6** proceeds via intermediate **A**, which is formed through initial azide attack, rather than phenyl attack, on the alkyne moiety.[17]



Scheme 3 Cascade cyclisation of 2-[(2-azidophenyl)ethynyl]biphenyl (**6**)

Conclusions

In conclusion, we developed a cascade cyclisation protocol for 2-[(2-azidophenyl)ethynyl]anilines and -phenols that affords indole-fused tetra- and pentacyclic heteroacenes. The reaction of an aniline derivative proceeds through the intermediate 2-(2-azidophenyl)indole by gold(I)/rhodium(II) relay catalysis. On the other hand, the reactions of phenol derivatives proceed in the presence of a base and a rhodium(II) catalyst.

Experimental

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General procedure for the gold(I)/rhodium(II)-catalysed cascade cyclisation of 2-[(2-azidophenyl)ethynyl]anilines 1. A Schlenk tube containing a magnetic stirring bar was charged with 2-[(2-Azidophenyl)ethynyl]aniline **1** (0.100 mmol), (SPhos)AuNTf$_2$ (1.8 mg, 2.0 μmol, 2.0 mol%) and Rh$_2$(esp)$_2$ (2.3 mg, 3.0 μmol, 3.0 mol%) under nitrogen atmosphere. Toluene (1.0 mL) was added via a syringe through the septum, and the mixture was stirred at 80 °C or 100 °C for 12–18 h. After completion, the reaction mixture was filtered through a plug of Florisil® eluting with hexane–AcOEt (1:1~3:1). The filtrate was concentrated, and the residue was purified by preparative thin-layer chromatography (hexane–AcOEt) to give 5,10-dihydroindolo[3,2-*b*]indole **2**.

General procedure for the base-promoted rhodium(II)-catalysed cascade cyclisation of 2-[(2-azidophenyl)ethynyl]phenols 4. A Schlenk tube containing a magnetic stirring bar was charged with 2-[(2-azidophenyl)ethynyl]phenol **4** (0.100 mmol), Rh$_2$(esp)$_2$ (3.8 mg, 50 μmol, 5.0 mol%) and K_2CO_3 (27.6 mg, 0.200 mmol, 2.0 equiv) under nitrogen atmosphere. Toluene (1.0 mL) was added via a syringe through the septum, and the mixture was stirred at 80 °C for 12–18 h. After completion, the reaction mixture was filtered through a plug of Florisil® eluting with hexane–AcOEt (2:1~3:1). The filtrate was concentrated, and the residue was purified by preparative thin-layer chromatography (hexane–AcOEt or toluene–hexane) to give 10*H*-benzofuro[3,2-*b*]indole **5**.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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9 Abbreviations: IPr = 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene; DCE = 1,2-dichloroethane; SPhos = 2-dicyclohexylphosphino-2′,6′-dimethoxybiphenyl; esp = 3,3′-(1,3-phenylene)bis(2,2-dimethylpropanoate).

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