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Selective Syntheses of Benzo[*b*]carbazoles and C3-Substituted Indoles *via* Tunable Catalytic Annulations of *β*-Alkynyl Ketones with Indoles

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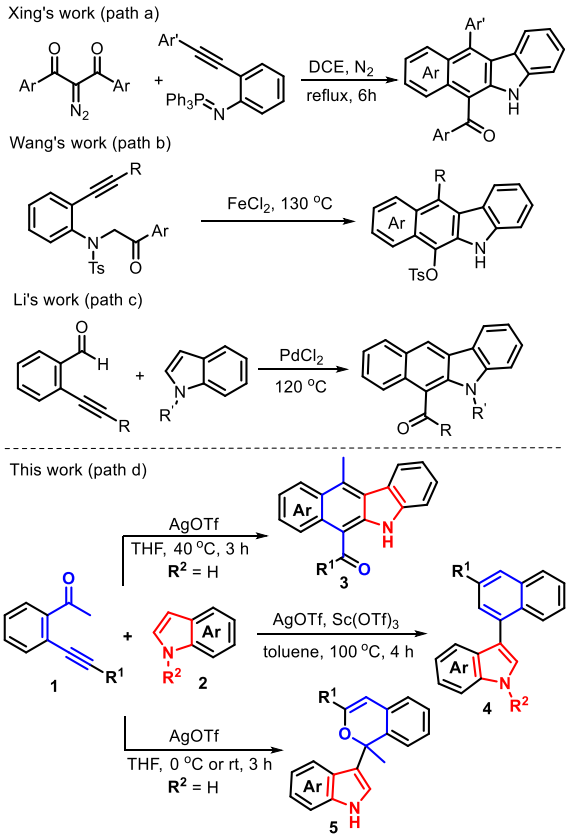
Abstract. Tunable catalytic annulation reactions of *β* alkynyl ketones with indoles have been developed, enabling multiple chemical bond-forming events to selectively access skeletally diverse indole-containing heterocycles with generally good yields. Silver-catalyzed intermolecular benzannulation reaction of *β*-alkynyl ketones with indoles afforded tetracyclic benzo[*b*]carbazoles whereas isochromen-1-yl-substituted indoles could be obtained using the same silver catalysis by lowering the reaction temperature (0 °C or rt). Interestingly, using $Sc(OTf)_3$ and AgOTf as a combined catalytic system led to the formation of C3-naphthylated indoles *via* intramolecular benzannulation reaction.

Keywords: Benzannulation; Benzo[*b*]carbazoles; Chemoselectivity; Isochromenes; *oxo*-Cyclization

Introduction

Benzo[*b*]carbazoles constitute a class of important polycyclic skeletons commonly present in a myriad of naturally occurring alkaloids such as ellipticine B and 9-methoxyellipticine as well as in biologically active substances.[1] These molecules are, due to their co-planar structures and chemiluminescent and optoelectronic properties, widely applied in organic semiconductor and luminescent materials.[2] Therefore, numerous efforts have been made to establish effective methods for producing these targets, with these methods often including cycloaromatization of keteneimines (Scheme 1, path a),[3] intramolecular Diels–Alder cycloaddition reactions (Scheme 1, path b),[4] and benzannulation reactions with indoles (Scheme 1, path c),[5] naphthalenes,[6a,b] or carbazoles.[6c] However, most of these methods suffer from the need to carry out prefunctionalizations of starting materials,[3],[4] use of expensive transition metal catalysts,[5],[6] harsh reaction conditions[3-6] and uneconomical atomic transformations.[3],[4],[6] Therefore, atom-economic approaches are still needed to synthesize benzo[*b*]carbazoles and their derivatives from simple precursors and inexpensive catalysts.

Metal-catalyzed annulation reactions of *β*-alkynyl ketones have been recognized as a versatile tool for the assembly of bioactive cyclic scaffolds in a convergent manner.[7,8] Since the pioneering works reported by Asao, Yamamoto and coworkers,[9] great advances in the metal-catalyzed [4 + 2] cycloadditions of *β*-

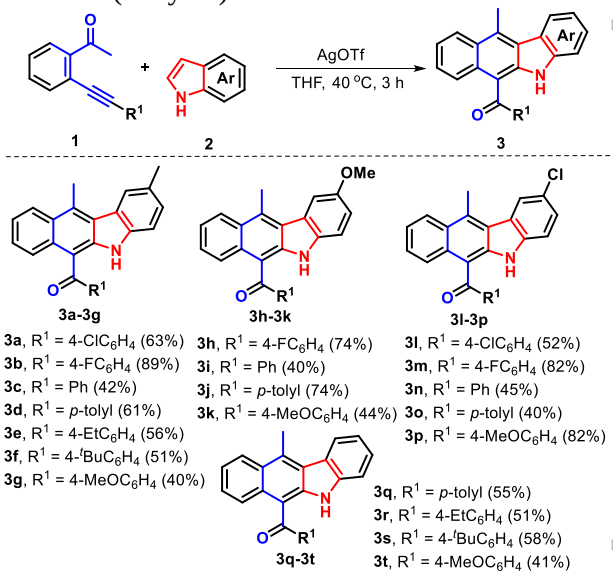


Scheme 1. Profiles for the synthesis of benzo[*b*]carbazoles

alkynyl ketones with alkenes or alkynes have been made, with the key advance here involving the *in situ* generation of benzopyrylium intermediates as 1,4-dipoles.[10] Recently, we developed silver-catalyzed selective dimerizations and trimerizations of β-alkynyl ketones to access functionalized spiro-substituted isochromenes.[11] While carrying out this project, we reasoned that under suitable silver catalysis conditions, benzopyrylium intermediates from *β*-alkynyl ketones could react with indoles, enabling an intermolecular [4 + 2] cycloaddition and oxygen migration process to give benzo[*b*]carbazoles.[5g] In the current work, tunable catalytic annulation reactions of β-alkynyl ketones **1** with indoles **2** could be well controlled by adjusting reaction parameters including the catalyst, solvent and reaction temperature, which allowed for the selective syntheses of benzo[*b*]carbazoles **3**, C3-naphthylated indoles **4** and isochromen-1-yl substituted indoles **5** with generally good yields. i) Silver-catalyzed benzannulations between *β*-alkynyl ketones **1** and indoles **2** in tetrahydrofuran (THF) at 40 °C accessed the benzo[*b*]carbazoles as major products. ii) At 0 °C or rt, the reactions proceeded in a different direction to give isochromen-1-yl-substituted indoles **5**. iii) And, C3-naphthylated indoles **4** were obtained upon carrying out synergistic silver/scandium catalyses of these substrates in toluene at 100 °C (Scheme 1, path d). Herein, we report these three types of catalytic annulation reactions.

Results and Discussion

At the outset of our studies, the preformed β-alkynyl ketone **1a** and 5-methyl-1*H*-indole (**2a**) were chosen as model substrates for the reaction in commercial THF in the presence of silver trifluoroacetate (AgTFA, 10 mol %) as a catalyst at 40 °C under air conditions (Table 1, entry 1). As a result, two different annulation products, namely benzo[*b*]carbazole **3a** and C3-naphthylated indole **4a**, were isolated in 32% and 10% yields, respectively. Next, we aimed to improve the yield of each product by realizing the chemoselectivity of the reaction. Besides AgTFA, several other silver salts such as AgOTf, AgOAc and $AgNO_3$ were screened: AgOTf displayed a better catalytic performance for the formation of product **3a** than did AgTFA, and drove the conversion into **3a** with 63% yield along with a much lower yield of **4a** (entry 2); in contrast, the latter two did not show any improvement in the efficiency of the transformation (entries 3 and 4). Various solvents were tested. The use of aprotic solvents including toluene, dichloromethane (DCM), dimethyl sulfoxide (DMSO), and acetonitrile (CH_3CN) had no positive impact on the yield of **3a** (entries 5-9), but DMSO was beneficial for the generation of product **4a**, albeit with still a relatively low yield, of 26% (entry 5). Unexpectedly, when the temperature was lowered to 0 °C, the reaction generated isochromen-1-yl substituted indole **5a** in almost quantitative yield (98%, entry 10). Then, $Sc(OTf)_3$ as a Lewis acid was added into this reaction system, and was found to clearly suppress the formation of **3a** but to favor the generation of **4a** (entry 11). A similar reaction tendency was observed when elevating the reaction temperature. An increase in the temperature to 80 °C provided an elevated yield of **4a** (37%) along with a reduced yield of **3a** (40%, entry 12). The reaction catalyzed by AgOTf/$Sc(OTf)_3$ in toluene showed an even better yield of **4a** (47%, entry 13). To our satisfaction, this Ag/Sc-co-catalysis only produced **4a** in 60% yield when the reaction temperature was elevated to 100 °C (entry 14). Further increasing the temperature led to a lower conversion into **4a** (entry 15). Without AgOTf, the reaction did not work and the starting materials were recovered (entry 16).



Scheme 2. Substrate scope for the synthesis of **3**.

With these acceptable reaction conditions in hand, we set out to investigate the generality of these controlled catalytic annulation cascades for accessing the three different functionalized indoles **3**, **4** and **5** by examining *β*-alkynyl ketone and indole components (Scheme 2, Scheme 3 and Scheme 4). Under the optimized reaction conditions for forming product **2a** (Table 1, entry 2), 5-methyl-1*H*-indole (**2a**) was first reacted with *β*-alkynyl ketones **1** having either electronically poor, neutral, or rich groups relative to the arylalkynyl moiety (R^1), and gave access to the corresponding benzo[*b*]carbazoles **3b-3g** in 40-89% yields (Scheme 2). Various substituents on **1**, including fluoro (**1b**), methyl (**1d**), ethyl (**1e**), *t*-butyl (**1f**), and methoxy (**1g**, 4-methoxyphenyl = PMP) groups, were observed to tolerate the catalytic conditions well. Representative indoles bearing a methoxy (**2b**) or chloro (**2c**) functionality at the C4-position were appropriate reaction partners; i.e., they reacted with *β*-alkynyl ketones **1** to afford the corresponding products **3h-3p** with yields ranging from 40% to 82%. Unsubstituted indole (**2d**) was also engaged in this benzannulation and furnished the desired products **3q-3t** in 41-58% yields.

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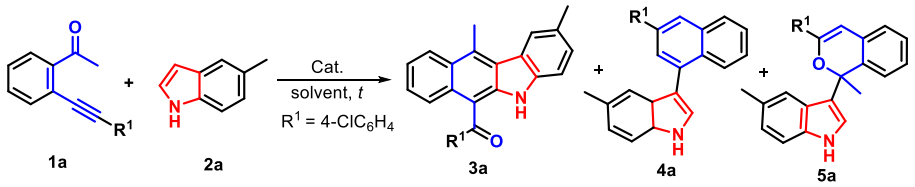
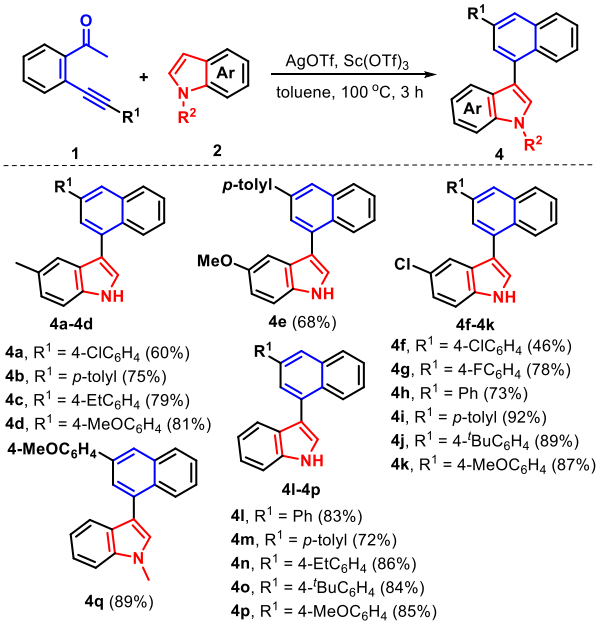
Table 1 Optimization of the reaction conditions for forming **3a**, **4a** and **5a**[a]



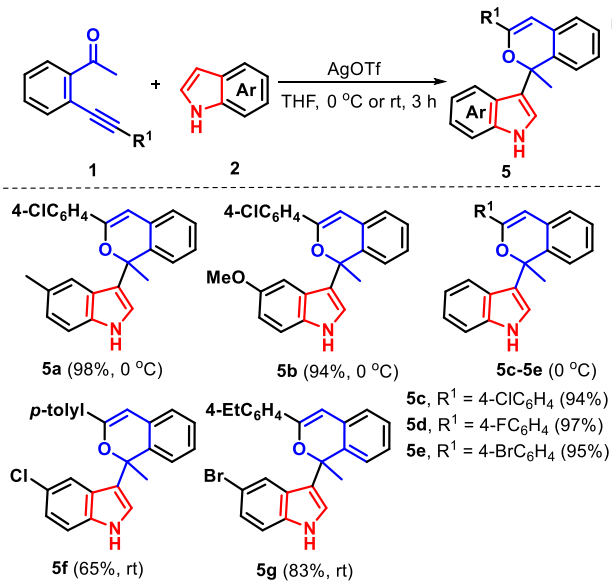
Entry	Cat. (mol%)	Solvent	Temp/°C	Yield[b] (%)
				3a/4a/5a
1	AgTFA (10)	THF	40	32/10/0
2	AgOTf (10)	THF	40	63/8/0
3	AgOAc (10)	THF	40	23/12/0
4	$AgNO_3$ (10)	THF	40	trace/trace/0
5	AgOTf (10)	toluene	40	25/26/0
6	AgOTf (10)	DCM	40	17/12/0
7	AgOTf (10)	DMSO	40	trace/trace/0
8	AgOTf (10)	MeCN	40	trace/trace/0
9	AgOTf (10)	1,4-dioxane	40	trace/trace/0
10	AgOTf (10)	THF	0	trace/0/98
11	AgOTf (10)/$Sc(OTf)_3$ (20)	THF	40	51/28/0
12	AgOTf (10)/$Sc(OTf)_3$ (20)	THF	80	40/37/0
13	AgOTf (10)/$Sc(OTf)_3$ (20)	toluene	80	31/49/0
14	AgOTf (10)/$Sc(OTf)_3$ (20)	toluene	100	trace/60/0
15	AgOTf (10)/$Sc(OTf)_3$ (20)	toluene	110	trace/55/0
16	$Sc(OTf)_3$ (20)	toluene	100	0/0/0

[a] Reaction conditions: 1a (0.5 mmol), 2a (0.75 mmol), catalyst (x mol%), and solvent (3 mL), air conditions, 3 h.
[b] Isolated yield.



Scheme 3. Substrate scope for the synthesis of **4**.

After the successful syntheses of products **3**, we turned our attention to evaluating AgOTf/$Sc(OTf)_3$-co-catalyzed annulation reactions for synthesizing C3-naphthylated indoles **4** by exploiting the optimized reaction conditions (Table 1, entry 14; Scheme 3). *β*-Alkynyl ketones bearing various substituents linked by the arylalkynyl moiety (R^1) with electron-withdrawing (chloro and fluoro), electron-neutral (H) and electron-donating (methyl, ethyl and methoxy) groups were all accommodated, confirming the efficiencies of the benzannulation reactions, as products **4a-4q** were obtained with 46%-92% yields. The reaction proceeded reliably in the presence of different functional groups (methyl, methoxy and chloro) at the C5 position of the indole ring. Similarly, unsubstituted indole (**2d**) was also suitable for this



Scheme 4. Substrate scope for the synthesis of **5**.

reaction. And *N*-methyl indole (**2e**) worked well under the standard conditions, furnishing product **4q** with an 89% yield. Next, we focused on the silver-enabled 6-*endo*-*dig* *oxo*-cyclization/nucleophilic addition cascade of *β*-alkynyl ketones **1** with indoles for the syntheses of isochromen-1-yl-substituted indoles **5**. These reactions proceeded readily under the standard conditions (Table 1, entry 10; Scheme 4), enabling Ag catalysis to offer indole products **5a-5g** in good to excellent yields. As described above, *β*-alkynyl ketones with both electron-withdrawing (fluoro, chloro and bromo) and electron-donating (methyl and ethyl) groups were compatible.

Similar tests were also carried out using indole components. In general, the current controllable tandem annulation strategies represent reliable and chemoselective approaches for the direct constructions of richly decorated indoles and their fused derivatives. The structures of these heterocycles were confirmed using NMR spectroscopy and HRMS. Furthermore, in the cases of **3j** and **5c**, their structures were unambiguously determined using single crystal X-ray diffraction (Figures 1-2).[12]

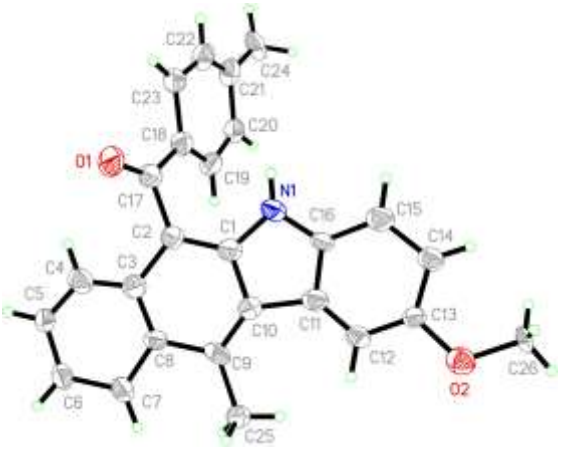
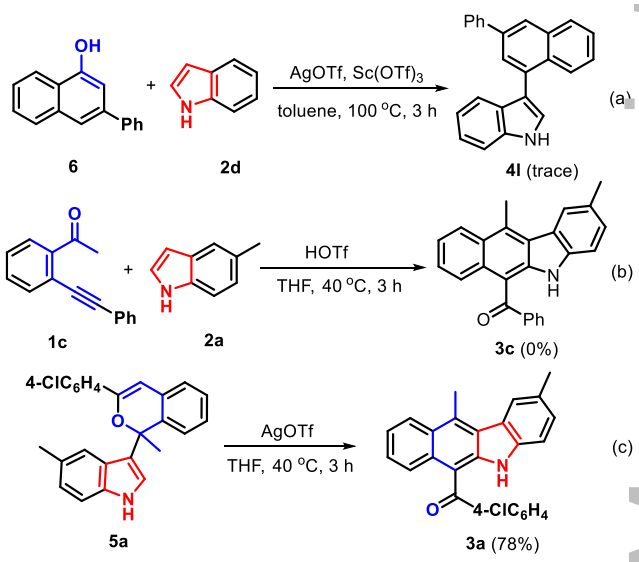


Figure 1. The ORTEP drawing of **3j**.

To gain a mechanistic insight into the formation of **4**, the preformed 3-phenylnaphthalen-1-ol **6** was treated with indole **4d** under the standard conditions (Table 1, entry 14). It did not give the desired product **4l** (Scheme 5a), indicating that 3-phenylnaphthalen-1-ol is not an intermediate for the generation of **4** and the dehydration of a *β*-alkynyl ketone with an indole occurs prior to its carbocyclization. To confirm the role of silver cation, the reaction of **1c** with **2a** was conducted in the presence of HOTf, but the target **3c** was not observed (Scheme 5b), demonstrating that silver cation may activate the carbon-carbon triple bond of *β*-alkynyl ketone **1** to accelerate its further transformation. In order to understand reaction pathway for forming **3**, the resulting product **5a** was subjected with the reaction in THF at 40 °C in the presence of AgOTf, and the corresponding benzo[*b*]carbazole **3a** was obtained in 78% yield. These results may support product **5** to be intermediate for accessing product **3** (Scheme 5c) and the high temperature favors ring-opening of pyran ring and electrocyclization in the presence of Ag catalyst.



Scheme 5. Control experiments.

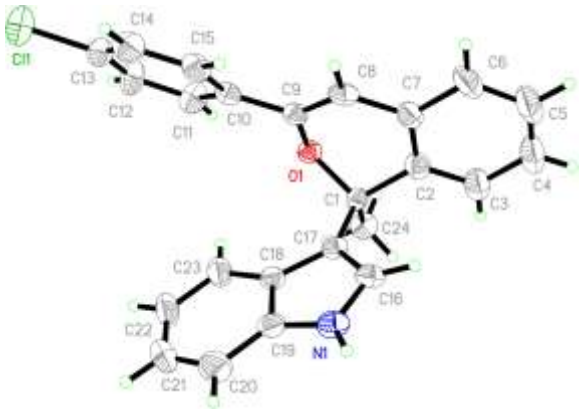
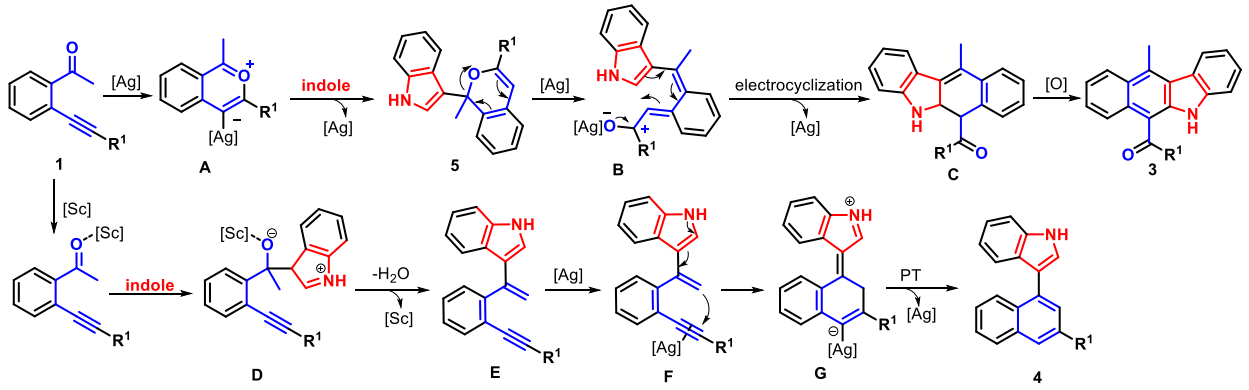


Figure 2. The ORTEP drawing of **5c**.



Scheme 6. Proposal reaction pathways

By combining the above experimental results with literature precedents of silver-catalyzed *oxo*-cyclizations,[7],[8],[9], we derived what appears to be reasonable mechanisms for these three transformations (Scheme 6). According to our proposed mechanisms, first, Ag-catalyzed 6-*endo*-*dig* *oxo*-cyclization of *β*-alkynyl ketone **1** would generate isobenzopyrylium intermediate **A**, which at a reaction temperature of 0 °C apparently prefers to undergo nucleophilic addition with indole to give product **5** and regenerate silver catalyst. At higher temperatures, a ring opening reaction of product **5** yields intermediate **B** in the presence of silver catalyst, and then intermediate **B** undergoes thermal electrocyclization to afford dihydrobenzo[*b*]carbazole intermediate **C**[5g,6c] and release silver catalyst. Subsequent oxidation of **C** by O_2 from air gives final the product **3**. In the presence of AgOTf and $Sc(OTf)_3$,[13] $Sc(OTf)_3$ would, according to the proposed mechanisms, activate carbonyl group of *β*-alkynyl ketone **1**, which would become trapped by indole to form tertiary alcohol anion intermediate **D**, followed by dehydration of **D** and release of $Sc(OTf)_3$ to form 1,5-enyne intermediate **E**.[14] AgOTf would, according to the mechanisms, then activate the carbon-carbon triple bond of **E** to promote intramolecular 6-*endo*-*dig* cyclization,[15] offering intermediate **G** —followed finally by a proton transfer (PT) in G and regeneration of the Ag catalyst to produce **4**.

Conclusion

In conclusion, starting from easily available *β*-alkynyl ketones and indoles, we have established tunable catalytic annulation reactions for the selective syntheses of skeletally diverse benzo[*b*]carbazoles, and C3-substituted indoles with generally good yields under mild conditions. The silver-catalyzed benzannulation reaction between *β*-alkynyl ketones and indoles afforded tetracyclic benzo[*b*]carbazoles. At lower reaction temperatures (0 °C or rt), this silver- catalysis enabled a different route to be followed to isochromen-1-yl-substituted indoles through an *oxo*-cyclization and nucleophilic addition cascade. Notably, by using $Sc(OTf)_3$ and AgOTf as a combined catalytic system, the complete chemoselectivity was achieved and C3-naphthylated indoles were furnished *via* benzannulation reactions. The present transformations provide chemoselective and practical protocols for the collection of skeletally diverse indole-containing heterocycles from the same substrates, opening new avenues for realizing the control of the chemoselectivity.

Experimental Section

General procedure for the synthesis of products 3

Example for the synthesis of **3a**: Under air conditions, CF_3SO_3Ag (12.8 mg, 10 mol %), 5-methyl-1*H*-indole (**2a**, 98.3 mg, 0.75 mmol, 1.5 equiv), 1-(2-((4-chlorophenyl)ethynyl)phenyl)ethan-1-one (**1a,** 127 mg, 0.5 mmol) and THF (3.0 mL) were added into a 10-mL reaction vial. Then the reaction vial was sealed and stirred at 40 °C. Until TLC (petroleum ether: ethyl acetate 5:1) revealed that conversion of the starting material **1a** was complete (3 hours), the reaction mixture was dissolved in acetone. After that, the reaction mixture was concentrated by performing vacuum distillation and was purified by carrying out flash column chromatography (silica gel, mixtures of petroleum ether / acetic ester, 30:1, v/v) to afford the desired pure product **3a** as a yellow solid.

General procedure for the synthesis of products **4**

Example for the synthesis of **4a**: Under air conditions, CF_3SO_3Ag (12.8 mg, 10 mol %), $Sc(SO_3CF_3)_3$ (49.2 mg, 20 mol%), 5-methyl-1*H*-indole (**2a**, 98.3 mg, 0.75 mmol, 1.5 equiv) and dry toluene (2.0 mL) were added into a 10-mL reaction vial. Then, the reaction vial was sealed. After that, 1-(2-((4-chlorophenyl)ethynyl)phenyl)ethan-1-one (**1a**, 127 mg, 0.5 mmol) in dry toluene (1.0 ml) was added into the reaction system at 110 °C *via* a syringe pump the course of 2.0 h. Until TLC (petroleum ether: ethyl acetate 7:1) revealed that conversion of the starting material **1a** was complete (3 hours), the reaction mixture was dissolved in acetone. After that, the reaction mixture was concentrated by performing vacuum distillation and was purified by carrying out flash column chromatography (silica gel, mixtures of petroleum ether / acetic ester, 50:1, v/v) to afford the desired pure product **4a** as a colourless oil.

General procedure for the synthesis of products **5**

Example for the synthesis of **5a**: Under air conditions, CF_3SO_3Ag (12.8 mg, 10 mol %), 5-methyl-1*H*-indole (**2a**, 98.3 mg, 0.75 mmol, 1.5 equiv) and THF (2.0 mL) were added in a 10-mL reaction vial. Then, the reaction vial was sealed. After that, 1-(2-((4-chlorophenyl)ethynyl)phenyl) ethan-1-one (**1a**, 127 mg, 0.5 mmol) in THF (1.0 ml) was added into the reaction system at 0 °C *via* a syringe pump over the course of 1.0 h. The system was stirred at this temperature until TLC (petroleum ether: ethyl acetate 4:1) revealed that conversion of the starting material **1a** was complete (3 hours). The resulting reaction mixture was dissolved in acetone, then concentrated by performing vacuum distillation, and after that was purified by carrying out flash column chromatography (silica gel, mixtures of petroleum ether / acetic ester, 30:1, v/v) to afford the desired pure product **5a** as a white solid.

Acknowledgements

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FULL PAPER

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