Chemical Science

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: Y. Kawada, S. Ohmura, M. Kobayashi, W. Nojo, M. Kondo, Y. Matsuda, J. Matsuoka, S. Inuki, S. Oishi, C. WANG, T. Saito, M. Uchiyama, T. Suzuki and H. Ohno, *Chem. Sci.*, 2018, DOI: 10.1039/C8SC03525C.

ROYAL SOCIETY OF CHEMISTRY

rsc.li/chemical-science

View Article Online
DOI: 10.1039/C8SC03525C

ROYAL SOCIETY OF CHEMISTRY View Article Online
DOI: 10.1039/C8SC03525C

Journal Name

COMMUNICATION

Direct synthesis of aryl-annulated [*c*]carbazoles by gold(I)-catalysed cascade reaction of azide-diynes and arenes†

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Yuiki Kawada,[a,‡] Shunsuke Ohmura,[a,‡] Misaki Kobayashi,[a] Wataru Nojo,[b] Masaki Kondo,[c,d] Yuka Matsuda,[a] Junpei Matsuoka,[a] Shinsuke Inuki,[a] Shinya Oishi,[a] Chao Wang,[c,d] Tatsuo Saito,[c] Masanobu Uchiyama,*[c,d] Takanori Suzuki,*[b] and Hiroaki Ohno*[a]

The gold-catalysed annulation of conjugated alkynes bearing an azido group with arenes gave annulated [*c*]carbazoles. Using benzene, pyrrole, and indole derivatives as the nucleophile, benzo[*c*]-, pyrrolo[2,3-*c*]-, and indolo[2,3-*c*]carbazoles were produced, respectively. The reaction proceeded through pyrrole and benzene ring construction accompanied by the formation of two carbon-carbon and one carbon-nitrogen bonds and the cleavage of two aromatic C-H bonds. The mechanism of the reaction with pyrrole was investigated by density functional theory calculations. An *N*,*N*'-dimethylated indolo[2,3-*c*]carbazole showed dual ultraviolet-visible-near-infrared and fluorescence spectra changes upon electrolysis.

Introduction

Carbazoles are an important structural motif that is found in a variety of organic molecules of current interest (Fig. 1).[1] Benzo[*c*]carbazoles are commonly used in organic light-emitting diodes (OLEDs) owing to their charge-transport properties and thermal stability.[2] Heteroaryl-annulated [*c*]carbazoles are core structures of various bioactive natural products, such as eustifoline-D (furo[2,3-*c*]carbazole), arcyriaflavin A and dictyodendrins (pyrrolo[*c*]carbazole), and asteropusazole A (indolo[3,2-*c*]carbazole).[1a] Thus, the development of efficient synthetic methods for preparing benzo[*c*]carbazoles and their heteroaromatic congeners from readily accessible starting materials is an active pursuit in organic chemistry.

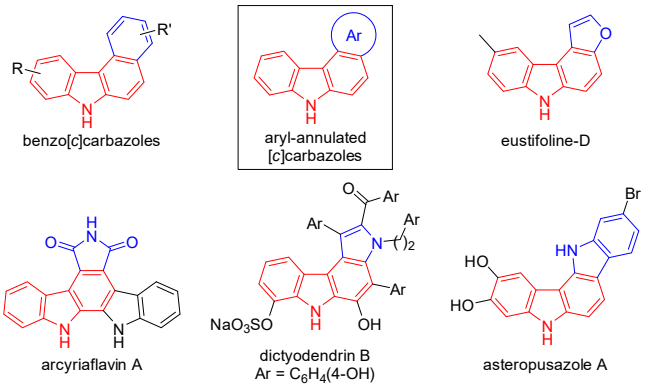
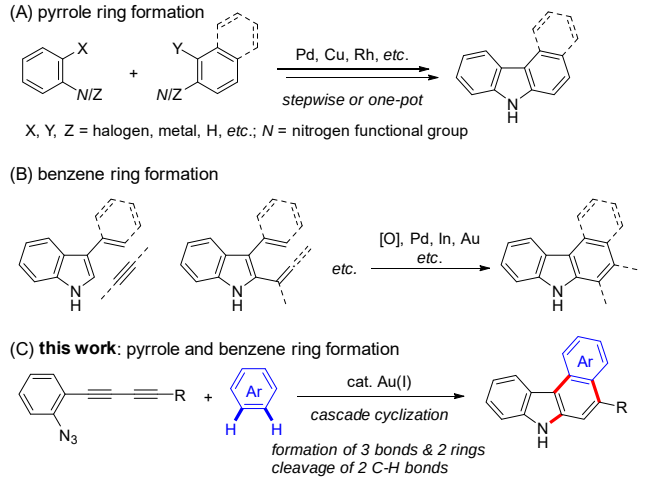


Fig. 1 Aryl-annulated [*c*]carbazoles.



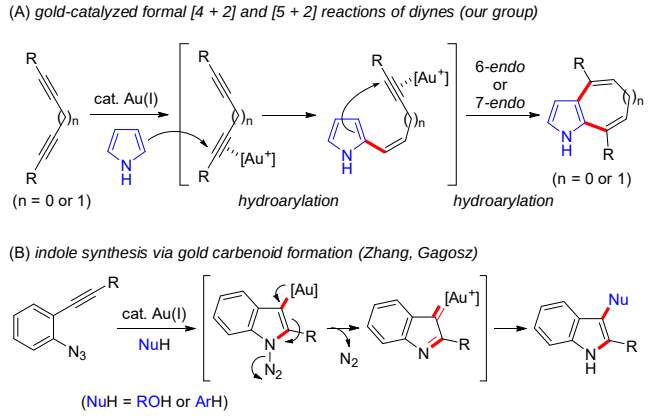
Scheme 1 General synthetic approaches to carbazoles including aryl-annulated carbazoles and this work

The general synthetic approaches to carbazoles including aryl-annulated [*c*]carbazoles are shown in Scheme 1A and 1B.[1a,3] Pyrrole ring formation based on a combination of carbon-

[a] *Graduate School of Pharmaceutical Sciences, Kyoto University, Sakyo-ku, Kyoto 606-8501 (Japan).*
[b] *Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo 060-0810, Japan*
[c] *Graduate School of Pharmaceutical Sciences, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, Japan*
[d] *Cluster of Pioneering Research (CPR), Advanced Elements Chemistry Laboratory, RIKEN, 2-1 Hirosawa, Wako, Saitama 351-0198, Japan.*
† *Electronic Supplementary Information (ESI) available: Experimental details and spectral data are provided. CCDC 1860899 (**6aF-Me$_2$**), 1860901 (**7aF-Me$_2$**) and 1860904 (**11D-Me$_2$**). See DOI: 10.1039/x0xx00000x*
‡ *Y. K. and S.O. contributed equally.*

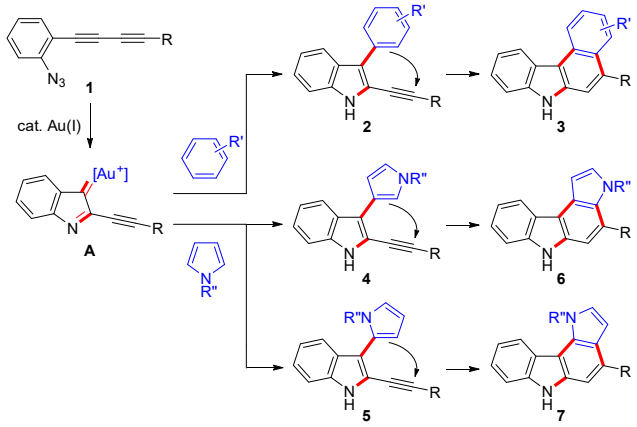
nitrogen and carbon-carbon bond formation provides an efficient route to carbazoles (Scheme 1A).[4,5] Reliable coupling reactions such as the Suzuki-Miyaura, Buchwald, and oxidative coupling reactions can be employed for this purpose. Benzene ring formation using vinyl- or aryl-substituted indoles including Diels-Alder-type reactions,[6] hydroarylation,[7] and related reactions[8] leads to various carbazoles including aryl-annulated carbazoles (Scheme 1B). However, the double cyclisation approach for synthesising aryl-annulated [*c*]carbazoles has not been investigated until recently.[9-11] We expected that the gold carbenoid-based cascade cyclisation of conjugated diynes would directly provide aryl-annulated [*c*]carbazoles in a single operation via the sequential cleavage of two aromatic C-H bonds (Scheme 1C).

Homogenous gold catalysis has emerged as a powerful tool for atom-economical transformations.[12] The π-acidity of gold catalysts enables the activation of C–C multiple bonds to promote various transformations. Recent investigations using diynes in gold-catalysed reactions have revealed that both conjugated and unconjugated diynes are useful precursors of complex molecules.[13] For example, we recently reported a gold-catalysed formal [4 + 2] reaction between 1,3-diynes and pyrroles for synthesising 4,7-disubstituted indoles (Scheme 2A, n = 0).[14a] This reaction proceeded through a double hydroarylation cascade involving the initial intermolecular hydroarylation of a 1,3-diyne at the 2-position of a pyrrole, followed by an intramolecular hydroarylation. When using skipped diynes as the substrates, the formal [5 + 2] reaction efficiently proceeded to produce 1,6-dihydrocyclohepta[*b*]pyrrole derivatives,[14b] which can be considered as homologs of 4,7-disubstituted indoles (Scheme 2A, n = 1).



Scheme 2 Related works

We then turned our attention to synthesising aryl-annulated [*c*]carbazole based on gold-carbenoid formation[15] using conjugated diynes. In 2011, Gagosz[16a] and Zhang[16b] independently reported the gold(I)-catalysed synthesis of indoles bearing an electron-donating group at the 3-position (Scheme 2B).[17] The reaction can be rationalised by the formation of a gold carbenoid intermediate followed by nucleophilic reaction at the carbenoid moiety. As the coupling partner, alcohol and arenes can be used for the reaction to produce 3-substituted indoles. We envisaged that incorporating gold carbenoid chemistry to the diyne cyclisation would provide direct access to aryl-annulated [*c*]carbazoles (Scheme 3). Thus, gold(I)-mediated nucleophilic attack of the azido group of diyne **1** to the proximal alkyne followed by elimination of nitrogen would produce gold carbenoid species **A**. The electrophilic aromatic substitution of benzene-type arenes with **A** would produce the intermediate **2**. Finally, the intramolecular hydroarylation toward alkynes[18] would occur to produce the benzo[*c*]carbazole **3**. The challenge of this strategy is controlling the regioselectivity when using pyrrole-type heteroarenes as the coupling partner: whereas the first nucleophilic attack at the pyrrole 3 position would produce pyrrolo[2,3-*c*]carbazole **6**, the first nucleophilic attack at the pyrrole 2 position would give pyrrolo[3,2-*c*]carbazole **7**, through 3-pyrrolylindole intermediates **4** and **5**, respectively. Attention should also be given to the regioselectivity in the second arylation in the reaction with the benzene-type nucleophile (**2** to **3**).

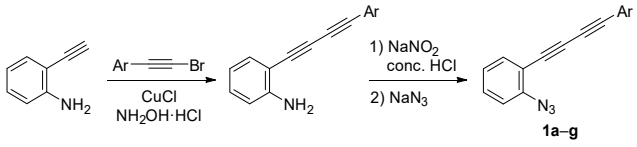


Scheme 3 Possible reaction pathways

Herein, we report a full account of our study on the direct synthesis of aryl-annulated [*c*]carbazoles by regioselective gold-catalysed annulation of conjugated diynes and arenes such as benzene, pyrrole, and indole derivatives.[19] Computational investigations for elucidating the mechanism as well as redox and fluorescence properties of the pyrrolo[2,3-*c*]carbazoles are also presented.

Results and discussion

Reaction with benzene derivatives. The azido-substituted diynes **1** were easily prepared through Cadiot–Chodkiewicz coupling[20] between 2-ethynyaniline and bromoalkynes (Scheme 4). The resulting anilines bearing a conjugated diyne moiety were converted to **1a**–**g** via the Sandmeyer reaction with sodium azide (see Supplementary Information).



Scheme 4 Preparation of azide-diynes

View Article Online
DOI: 10.1039/C8SC03525C

We initially screened a variety of different gold catalysts (5 mol %) for the synthesis of benzo[*c*]carbazole using diyne **1a** and anisole **8A** (10 equiv.) (Table 1, entries 1–5). $Ph_3PAuSbF_6$ in 1,2-dichloroethane (DCE) did not promote even the first arylation of the desired transformation (entry 1). IPr, XPhos, and BrettPhos (Fig. 2) were ineffective ligands for bis-cyclisation; however, the 3-phenylindole intermediate **2aA** was formed in 36–65% yields (entries 2–4). Fortunately, the annulation reaction was promoted by JohnPhosAu(MeCN)SbF_6 (entry 5) to provide the desired fused carbazole **3aA** in 44% yield. Next, we examined the choice of reaction solvent using JohnPhosAu(MeCN)SbF_6 as the catalyst. The reaction using benzene, propan-2-ol, and 1,4-dioxane gave the monocyclisation product **2aA** (63–87% yields) without forming the carbazole **3aA** (entries 6–8). Carrying out the reaction in 1,1,2,2-tetrachloroethane (TCE) at 140 °C increased the yield of **3aA** to 55% (entry 9). In this case, decomposition of JohnPhosAu(MeCN)SbF_6 at high reaction temperature was anticipated. Thus, the first arylation was conducted at 80 °C and, after the disappearance of starting material and formation of **2aA** (monitored by TLC), the reaction temperature was raised to 140 °C for the second arylation, giving rise to higher yield of the fused carbazole **3aA** (75% yield, entry 10). Finally, examination of the stoichiometry revealed that the reaction using excess anisole (as solvent) and 5 mol % BrettPhosAu(MeCN)SbF_6 at 140 °C improved the yield to 86% (entry 12), whereas the reaction at 80 °C did not reach completion (entry 11). Thus, we used the conditions shown in entry 10 (10 equiv. of arene, condition A) and entry 12 (arene as the solvent, condition B) for further investigations for benzo[*c*]carbazole synthesis.

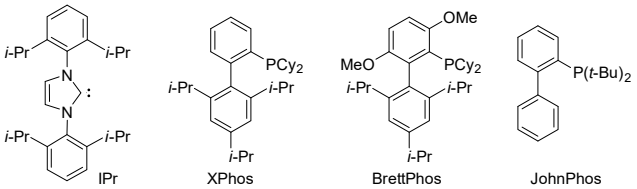
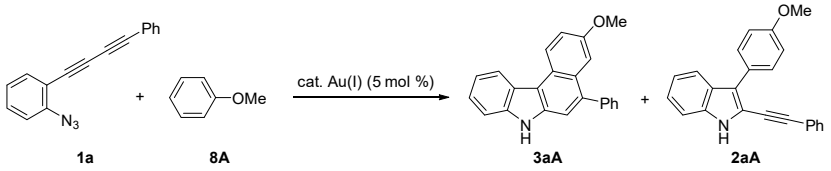


Fig. 2 Structures of screened ligands.

Using these optimised reaction conditions, we then explored the scope of the reaction. Variation of the substitution on the aryl moiety of the nucleophile **8** was initially investigated (Table 2). 1,2-Dimethoxybenzene (**8B**) and 1,3-dimethoxybenzene (**8C**) served as suitable nucleophiles for the gold-catalysed annulation when used as the solvent (condition B), to give the benzo[*c*]carbazoles **3aB** (quant) and **3aC** (95%) in excellent yields. In these cases, the reaction using 10 equiv. of nucleophile (condition A) also permitted 70% and 40% yields of **3aB** and **3aC**, respectively. The reaction with benzodioxole (**8D**) afforded pentacyclic benzo[*c*]carbazole (**3aD**) in 76% yield. Less

Table 1. Reaction optimization using anisole [a]



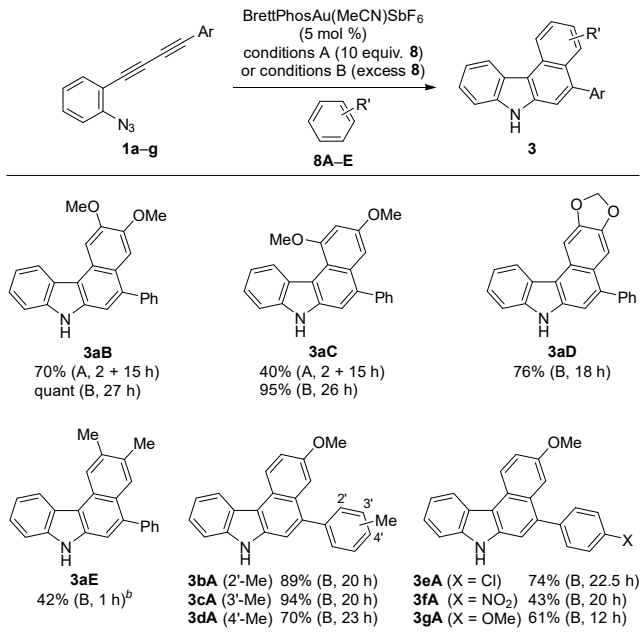
1a 8A 3aA 2aA

Entry	Catalyst [b]	Solvent [c]	Temperature (time)	Yield [d] (%)	
				3aA	**2aA**
1	$Ph_3PAuCl/AgSbF_6$	DCE	80 °C (44 h)	0	0
2	$IPrAuNTf_2$	DCE	80 °C (24 h)	0	36
3	$XPhosAuCl/AgNTf_2$	DCE	80 °C (21 h)	0	57
4	BrettPhosAu(MeCN)SbF_6	DCE	80 °C (30 h)	0	65
5	JohnPhosAu(MeCN)SbF_6	DCE	80 °C (26 h)	44	26
6	JohnPhosAu(MeCN)SbF_6	benzene	80 °C (10 h)	0	78
7	JohnPhosAu(MeCN)SbF_6	propan-2-ol	80 °C (10 h)	0	63
8	JohnPhosAu(MeCN)SbF_6	1,4-dioxane	80 °C (10 h)	0	87
9	JohnPhosAu(MeCN)SbF_6	TCE	140 °C (13 h)	55	0
10	**JohnPhosAu(MeCN)SbF_6**	**TCE (condition A)**	**80 °C** (1 h), **140 °C** (16 h)	**75**	0
11	BrettPhosAu(MeCN)SbF_6	anisole	80 °C (15 h)	13	28
12	**BrettPhosAu(MeCN)SbF_6**	**anisole (condition B)**	**140 °C** (19.5 h)	**86**	0

[a] Reactions were carried out using **1a** (1 equiv.), **8A** (10 equiv.), gold catalyst (5 mol %). [b] The ligand structures are shown in Fig. 2. BrettPhosAu(MeCN)SbF_6, JohnPhosAu(MeCN)SbF_6, and $IPrAuNTf_2$ were prepared in advance. The other catalysts were prepared *in-situ* by mixing AuCl·ligand with $AgNTf_2$ or $AgSbF_6$. [c] DCE = 1,2-dichloroethane, TCE = 1,1,2,2-tetrachloroethane. [d] Isolated yields.

nucleophilic *o*-xylene (**8E**) also gave the corresponding benzo[*c*]carbazole (**3aE**) in moderate yield (42%), although an increased loading of the gold catalyst (20 mol %) was required. Benzene and toluene did not provide the fused carbazoles owing to their lower reactivities. In all cases using arenes **8A**–**E**, the cascade reaction proceeded in a regioselective manner: the first arylation occurred at the *para*-position of the electron-donating substituent of **8**, and the second hydroarylation occurred at the less-sterically-hindered carbon of the introduced aryl group. We next investigated the reaction using various diynes **1b**–**g** under condition B.[21] A methyl substituent at the *ortho*-, *meta*-, or *para*- position of the terminal phenyl group was tolerated, producing the corresponding benzo[*c*]carbazoles (**3bA**–**3dA**) in good to excellent yields (70–94%). Similarly, the reaction of **1e**–**g** bearing an electron-donating or -withdrawing group (Cl, NO_2, or OMe) at the *para* position gave the desired products **3eA**–**3gA** (43–74% yield). The lower yield of the nitro derivative **3fA** can be attributed to the less efficient coordinating ability of the electron-deficient alkyne(s) to the gold catalyst, which would decrease the probability of being activated.

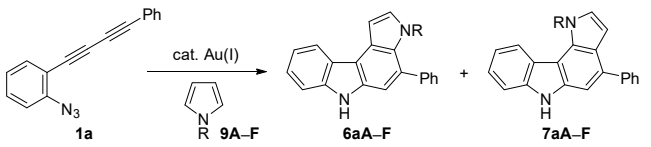
Table 2 Scope of benzo[c]carbazole synthesis [a]



[a] Reaction conditions: **1a**, **8** (excess), and gold catalyst (5 mol %). The reaction conditions employed (condition A or B) and reaction time are shown in parentheses. [b] Catalyst loading was increased to 20 mol %.

Reaction with pyrrole and indole derivatives. Next, we investigated the synthesis of pyrrolocarbazoles by the reaction with pyrroles **9** (Table 3). The gold-catalysed reaction of conjugated diyne **1a** with NH-pyrrole **9A** produced an isomeric mixture of the two annulation products **6aA** and **7aA** in *ca*. 62% yield, along with several unidentified minor products (entry 1). In this case, the pyrrolo[3,2-*c*]carbazole **7aA** was obtained as the major isomer (**6aA**:**7aA** = 25:75). This result can be readily understood by the more nucleophilic nature of the C2 position of NH-pyrrole than that of the C3 position.[22] Expecting that the regioselectivity of nucleophilic attack could be controlled by steric and electronic factors of the pyrrole, we subsequently evaluated the impact of substitution at the pyrrole nitrogen (entries 2–6). As expected, regioselectivity was significantly affected by the *N*-substituent: *N*-Boc pyrrole **9F** showed the highest regioselectivity to produce the pyrrolo[2,3-*c*]carbazole **6aF** (**6**:**7** = 92:8, entry 6), whereas *N*-benzylpyrrole **9B** preferentially produced the corresponding [3,2-*c*]-isomer **7aB** (**6**:**7** = 18:82, entry 2).

Table 3. Optimisation of pyrrole structure [a]



Entry	Pyrrole	R	Time (h)	Yield [b] (%)	Ratio [c] (**6** : **7**)
1	**9A**	H	8	<62%[d]	25 : 75
2	**9B**	Bn	10	62%	18 : 82
3[e]	**9C**	Ts	0.5	34%	58 : 42
4	**9D**	CO_2Me	1.5	62%	81 : 19
5	**9E**	Piv	1.5	60%	82 : 18[f]
6	**9F**	Boc	1.5	60%	92 : 8

[a] Reaction conditions: **9** (5 equiv.), BrettPhosAu(MeCN)SbF_6 (5 mol %), DCE, 80 °C. [b] Combined isolated yields. [c] Determined by ^{1}H NMR spectroscopy. [d] Contained small amounts of impurities. [e] Reaction carried out in TCE at 140 °C using 10 mol % of the catalyst. [f] Separation of the minor isomer from other by-products was difficult.

The structural elucidation of **6aF** and **7aF** was unambiguously made by X-ray crystallographic analyses of the methylation products **6aF-Me$_2$** and **7aF-Me$_2$** (Fig. 3). The pyrrolocarbazole moiety adopted a planer geometry as expected, and the twist angle of the phenyl group was 71.1° (for **6aF-Me$_2$**) or 26.2–44.0° (for **7aF-Me$_2$**).[23] The larger twist angle of the phenyl group in **6aF-Me$_2$** was attributed to the presence of an *N*-methyl group in close proximity to the phenyl group.

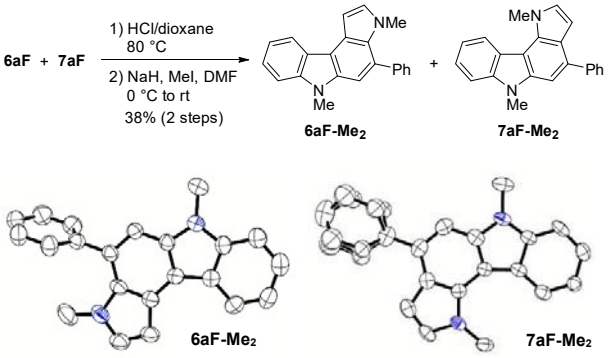
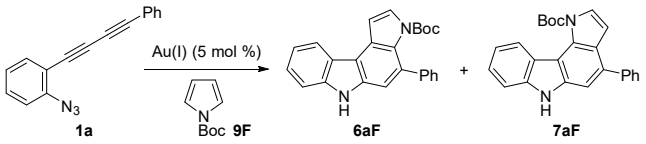


Fig. 3 Synthesis and X-ray structures of dimethylated pyrrolocarbazoles. The phenyl group in the latter adopted two orientations in the crystal structure.

We then optimised the reaction conditions for pyrrolocarbazole formation using diyne **1a**, *N*-Boc-pyrrole **9F** (5 equiv.), and various gold catalysts (5 mol %) (Table 4). Whereas $Ph_3PAuCl/AgNTf_2$ showed low reactivity (<5% yield, entry 1), other gold complexes bearing IPr, JohnPhos, XPhos, or BrettPhos as the ligand resulted in formation of the pyrrolo[2,3-*c*]carbazole **6aF** in sufficient regioselectivities (>91:9) and moderate yields (55–62%, entries 2–5). Using the most efficient ligand BrettPhos in terms of regioselectivity (**6**:**7** = 94:6, entry 5), two other silver salts were tested ($AgSbF_6$ and AgOTf, entries 6 and 7, respectively); however, the regioselectivity was not improved. The use of a gold complex prepared in advance slightly improved the reactivity (reaction completed within 0.5 h) and regioselectivity (**6**:**7** = 95:5, entries 8, 9). The solvent screening and investigations of reaction temperature did not improved the yields and product ratio (see Supplementary Information), whereas the reaction at 80 °C was found to be acceptable (entry 10). From these results, we used the conditions shown in entry 8 (condition C) and entry 10 (condition D) for further studies.

Table 4. Reaction optimisation using *N*-Boc-pyrrole [a]

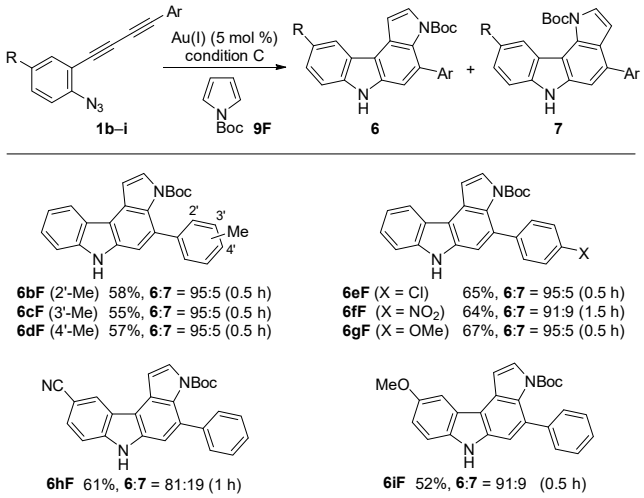


Entry	Catalyst	Time (h)	Yield [b] (%)	Ratio [c] (**6**:**7**)
1	$Ph_3PAuCl/AgNTf_2$	24	<5[d]	87 : 13
2	$IPrAuCl/AgNTf_2$	1	60	91 : 9
3	$JohnPhosAuCl/AgNTf_2$	1	56	92 : 8
4	$XPhosAuCl/AgNTf_2$	1	62	93 : 7
5	$BrettPhosAuCl/AgNTf_2$	1	55	94 : 6
6	$BrettPhosAuCl/AgSbF_6$	3	51	89 : 11
7	BrettPhosAuCl/AgOTf	20	<12[d]	75 : 25
8	$BrettPhosAu(MeCN)SbF_6$, (TCE, 110 °C: **condition C**)	0.5	58	95 : 5
9	$BrettPhosAuNTf_2$	0.5	58	95 : 5
10	$BrettPhosAu(MeCN)SbF_6$ (DCE, 80 °C: **condition D**)[e]	1.5	60	92 : 8

[a] Reaction conditions: **9F** (5 equiv.), gold catalyst (5 mol %), TCE, 110 °C. [b] Combined isolated yields. [c] Determined by ^1H NMR spectroscopy. [d] Contained small amounts of impurities. [e] The reaction was conducted in DCE at 80 °C.

We subsequently investigated the scope of the pyrrolo[2,3-*c*]carbazole formation (Table 5). The conjugated diynes **1b**–**i** bearing electron-donating or -withdrawing substituents on both the aryl groups reacted smoothly with pyrrole **9F** to afford the corresponding carbazoles **6bF**–**6iF** under condition C. The position of a methyl group or introduction of chloro or methoxy substituents to the terminal aryl group did not significantly affect the reaction, and the desired annulation products were efficiently produced (**6**:**7** = 95:5). The regioselectivity was slightly decreased when using electron-deficient diyne **1f** substituted by a nitro group. Diynes **1h** and **1i** substituted by a cyano or methoxy group at the *para*-position to the azido group also showed relatively low selectivities (**6**:**7** = 81:19-91:9).

Table 5 Scope of pyrrolo[2,3-*c*]carbazole synthesis [a]



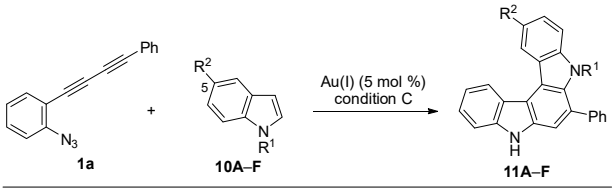
6bF (2'-Me) 58%, **6**:**7** = 95:5 (0.5 h)
6cF (3'-Me) 55%, **6**:**7** = 95:5 (0.5 h)
6dF (4'-Me) 57%, **6**:**7** = 95:5 (0.5 h)
6eF (X = Cl) 65%, **6**:**7** = 95:5 (0.5 h)
6fF (X = NO_2) 64%, **6**:**7** = 91:9 (1.5 h)
6gF (X = OMe) 67%, **6**:**7** = 95:5 (0.5 h)

6hF 61%, **6**:**7** = 81:19 (1 h)
6iF 52%, **6**:**7** = 91:9 (0.5 h)

[a] Reaction conditions: **9F** (5 equiv.), $BrettPhosAu(MeCN)SbF_6$ (5 mol%), TCE, 110 °C (condition C).

We then applied indole derivatives as the nucleophile for the annulation reaction (Table 6). The reactions of azide-diyne **1a** with *N*-protected indoles **10A**–**C** (R^1 = Boc, Piv, or CO_2Et) under condition C regioselectively gave the indolo[2,3-*c*]carbazoles **11A**–**C** as well as several unidentified by-products. The structure of **11A** was confirmed by X-ray analysis after cleavage of the *N*-Boc group and dimethylation,[24] similarly to the cases of **6aF** and **7aF** (Fig. 3). Indoles possess reactive sites other than the desired 2- and 3-positions, which may cause undesired side reactions.[16b] Thus, the introduction of an electron-withdrawing group at the 5-position of indole was examined. As expected, indoles **10D**–**F** bearing a bromo, chloro, or ethoxycarbonyl group at the 5-position reacted more efficiently to afford the indolo[2,3-*c*]carbazoles **11D**–**F** in better yields (50–67%) under condition D.

Table 6 Scope of indolo[2,3-*c*]carbazole synthesis [a]

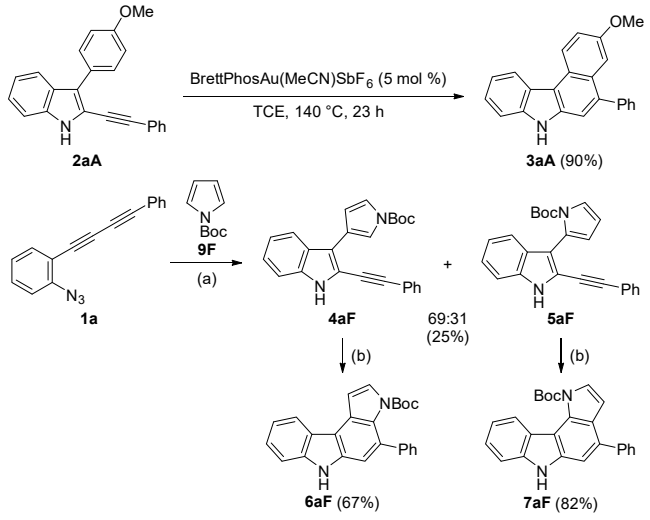


11A (R^1 = Boc) 35% (C, 3 h)
11B (R^1 = Piv) 12% (C, 6.5 h)
11C (R^1 = CO_2Et) 44% (C, 6.5 h)
11D (R^2 = Br) 50% (D, 4.5 h)
11E (R^2 = Cl) 52% (D, 4.5 h)
11F (R^2 = CO_2Et) <67% (D, 7.5 h)[b]

View Article Online DOI: 10.1039/C8SC03525D

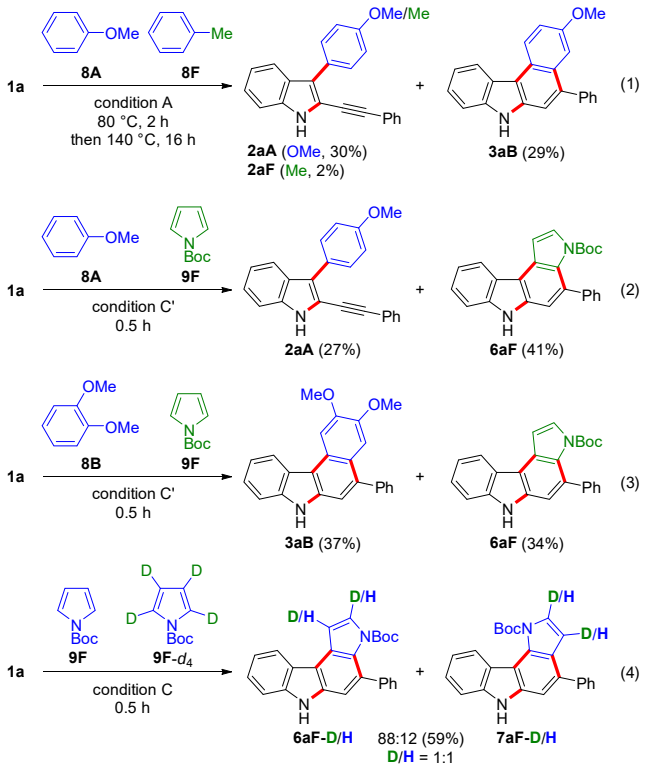
[a] Reaction conditions: **10** (5 equiv.), BrettPhosAu(MeCN)SbF_6 (5 mol%). The reaction conditions employed (condition C or D) and reaction time are shown in parentheses. [b] Contained small amounts of impurities.

Reaction mechanism. Although nucleophilicity of arenes including heteroarenes were well investigated previously, their relative reactivity between *N*-Boc-pyrrole is not well understood.[25] To better understand the reaction mechanism as well as relative reactivities of arenes employed in this study, several further experiments were performed. First, the exposure of **2aA** (obtained during the reaction optimisations shown in Table 1) to the gold-catalysed reaction conditions led to its complete conversion to the corresponding benzo[*c*]carbazole **3aA** in 90% yield (Scheme 5). Second, the reaction of **1a** with the pyrrole **9F** was intentionally stopped before it reached completion, which afforded the alkyne-substituted indoles **4aF** and **5aF** in 25% yield (**4**:**5** = 69:31) along with the recovered starting material. These alkynylindoles were consumed completely under the gold-catalysed reaction conditions to produce the pyrrolocarbazoles **6aF** and **7aF** in 67% and 82% yield, respectively. These results strongly indicated that the reactions proceeded through stepwise nucleophilic attack of the arenes to the gold carbenoid followed by intramolecular hydroarylation, as per our intended reaction pathway.



Scheme 5 Hydroarylation of the monocyclisation Intermediates. Reaction conditions: (a) **9F** (5 equiv.), BrettPhosAu(MeCN)SbF_6 (5 mol%), DCE, 60 °C, 1.5 h. (b) BrettPhosAu(MeCN)SbF_6 (5 mol%), TCE, 110 °C, 0.5 h.

Competition experiments using two different arenes were then carried out (Scheme 6). The gold-catalysed reaction of **1a** with anisole **8A** (5 equiv.) and toluene **8F** (5 equiv.) under condition A gave the anisole-derived products **2aA** (30%) and **3aB** (29%) along with a small amount of the toluene derivative **2aF** (2%) (eq 1 in Scheme 6). Thus, the first arylation was highly dependent on the nucleophilicity of the arene.[25] The competition between anisole **8A** (5 equiv.) and *N*-Boc-pyrrole **9F** (5 equiv.) led to formation of the anisole-derived monocyclised product **2aA** (27%) and pyrrole-derived biscyclised product **6aF** (41%), the latter being the preferred product (eq 2 in Scheme 6). This result suggested that *N*-Boc-pyrrole **9F** was a slightly more efficient partner in the first arylation than anisole **8A**, and that the anisole-derived intermediate **2aA** was significantly less reactive for the second arylation than the pyrrole-derived intermediate. The competition reaction using dimethoxybenzene **8B** and *N*-Boc-pyrrole **9F** gave the biscyclisation products **3aB** (37%) and **6aF** (34%) in comparable yields (eq 3 in Scheme 6). This result suggested that the second arylation was accelerated by the additional methoxy group located at the *para* position to the reacting carbon.[26] We then examined the kinetic isotope effect (eq 4 in Scheme 6). The competition reaction using *N*-Boc-pyrroles **9F** (2.5 equiv.) and **9F**-d_4 (2.5 equiv.) under condition C gave the corresponding pyrrolocarbazoles **6aF** and **7aF**, where the D/H ratios were 1:1 in both products. Thus, deprotonation was not the rate-determining step for formation of these products. This result suggested that electrophilic aromatic substitution was more likely for the first arylation than C-H insertion.[27]



Scheme 6 Competition experiments between different nucleophiles. Condition A: nucleophiles (5 equiv. each), JohnPhosAu(MeCN)SbF_6 (10 mol%), TCE, 80 °C then 140 °C. Condition C/C': nucleophiles (2.5 equiv. each for condition C; 5 equiv. each for condition C'), BrettPhosAu(MeCN)SbF_6 (5 mol%), TCE, 110 °C.

To further elucidate the reaction mechanism, we undertook density functional theory (DFT) calculations. The calculations were conducted at the M06L/6-31G** (for H, C, N, and P) and SDD (for Au) levels using the formation of pyrrolo[2,3-*c*]carbazole from **1a** and *N*-methylpyrrole as the model reaction (Fig. 4A). As previously proposed,[16] the reaction initiates by intramolecular nucleophilic attack of the azide group to the activated alkyne through **TS1/2** to form an indolyl-gold

View Article Online
DOI: 10.1039/C8SC03525C

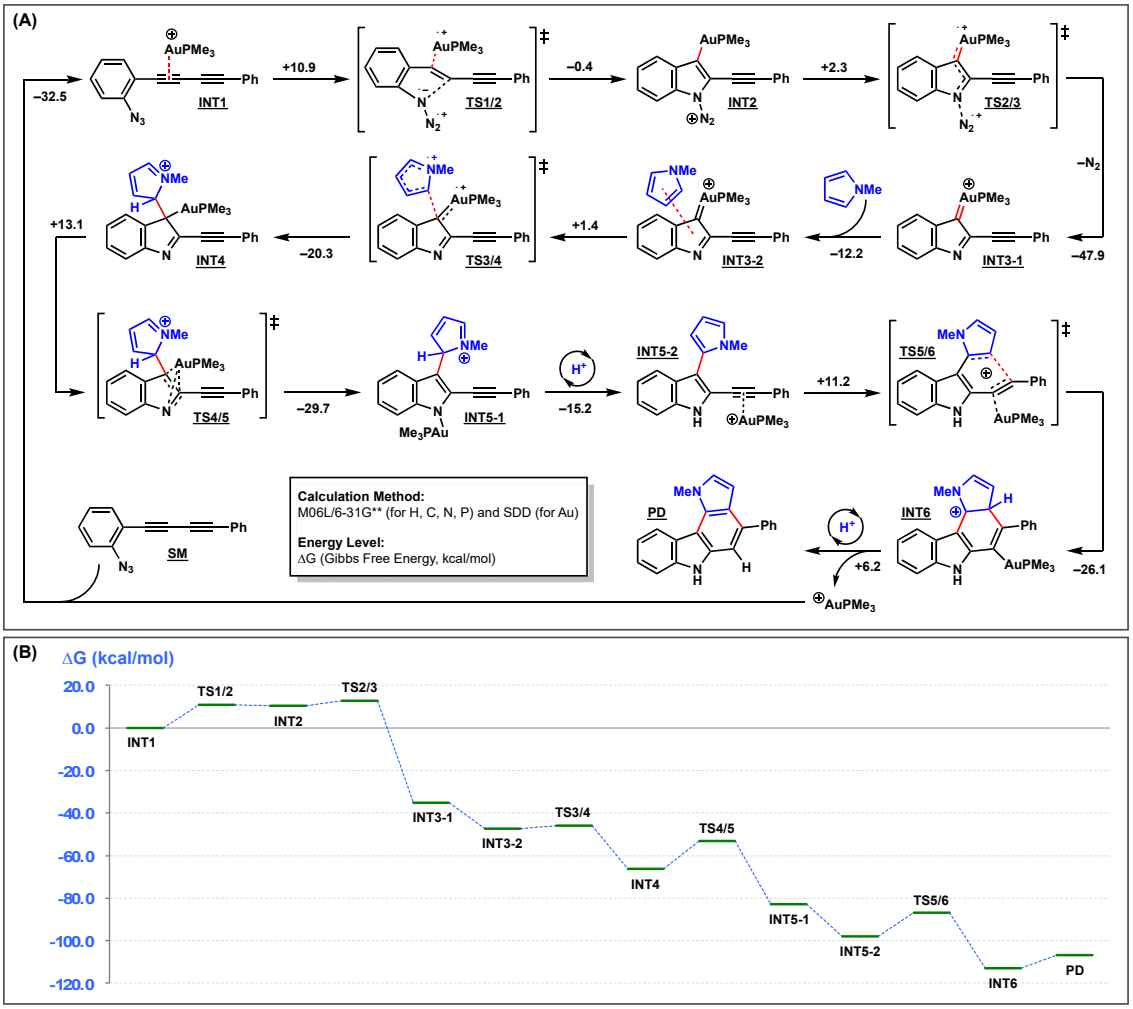


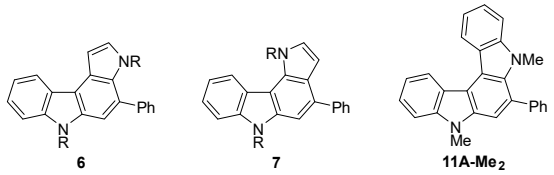
Fig. 4 DFT calculations for cyclisation of 1a with *N*-methylpyrrole [M06L/6-31G**(H, C, N, P)&SDD(Au)].

intermediate **INT2** with a small barrier of 10.9 kcal/mol and a rather large endothermicity (10.5 kcal/mol higher than **INT1**). This unfavourable energy loss is compensated for by successive reaction(s). **INT2** ejects nitrogen to form a gold carbenoid intermediate **INT3-1** with a large stabilisation energy (45.6 kcal/mol). Next, the key arylation step occurs by intermolecular nucleophilic attack of *N*-methylpyrrole to the gold carbenoid **INT3-2** through **TS3/4**, with a small barrier of 1.4 kcal/mol, to produce **INT4**. The gold rearrangement from C to N, with a reasonable barrier of 16.6 kcal/mol, gives an *N*-aurated indole intermediate **INT5-1**. This occurs with the simultaneous re-aromatisation, protodeauration, and re-complexation of the gold catalyst with the internal acetylene, and exothermically provides the pyrrole-substituted indole intermediate **INT5-2**. Finally, 6-*endo-dig* cyclisation of **INT5-2** is promoted by the gold catalyst to produce the pyrrolo[2,3-*c*]carbazole (**PD**), which regenerates the active gold catalyst. The entire reaction profile is illustrated in Fig. 4B. All the transition states have reasonable energy barriers (1.4–13.1 kcal/mol). The overall exothermicity is very large because of the formation of one C–N bond and two C–C bonds, and the formation of two aromatic rings. This provides the driving force for the overall reaction.

Electrochemical investigations of pyrrolo[2,3-*c*]carbazoles. From the viewpoint of electronic structure, pyrrolo[2,3-*c*]carbazoles **6** and indolo[2,3-*c*]carbazoles **11** could be considered as π-fused 1,4-phenylenediamines. Thus, their cation radicals would be generated as persistent species as the π-extended form[9c-e,28] of Wurster's Blue.[29] According to voltammetric analyses in CH_2Cl_2 (Table 7), the oxidation process of pyrrolo[2,3-*c*]carbazole **6aF-H** was irreversible as in the isomer, pyrrolo[3,2-*c*]carbazole **7aF-H**. Substitution with methyl groups at the reactive position (N-H of pyrrole) failed to stabilise the cation radical species, as shown by the irreversible oxidation wave for **6aF-Me$_2$**. This was despite the electron-donating nature of the substituents marginally facilitating the electrochemical oxidation, as indicated by the less positive oxidation potentials. By fusing the benzene nucleus in **6aF-Me$_2$** to furnish the indolo[2,3-*c*]carbazole skeleton, the cation radical species could attain enough persistency. **11A-Me$_2$** underwent

reversible two-stage one-electron oxidation processes, as shown by the voltammogram (Fig. 5). The redox pathway can be postulated as shown in the scheme, similar to that for 1,4-phenylenediamine.

Table 7. Oxidation potentials of pyrrolocarbazoles [a]



Entry	Compound	R	Oxidation potential [a]
1	**6aF-H**	H	+0.85
2	**6aF-Me$_2$**	Me	+0.79
3	**7aF-H**	H	+0.73
4	**7aF-Me$_2$**	Me	+0.75
5	**11A-Me$_2$**	–	+0.80 [b]

[a] E/V vs SCE, CH_2Cl_2 containing 0.1 M Bu_4NPF_6, Pt electrode, 100 mV s^{-1}. $E^{ox} = E^{pa} – 0.03$ V (for entries 1–5). $E(Fc/Fc^+) = +0.53$ V under similar conditions. [b] Reversible redox reaction was observed.

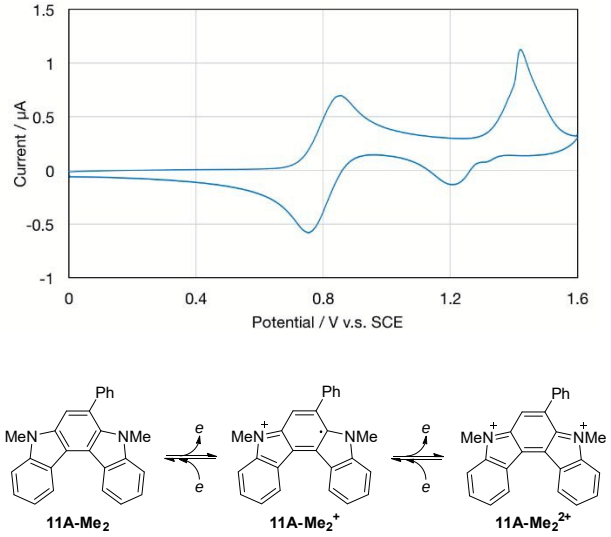


Fig. 5 Cyclic voltammogram of **11A-Me$_2$** in CH_2Cl_2 (upper panel) and possible redox pathway (lower panel). The irregular peak shape for the second oxidation wave may have been related to partial adsorption of the doubly-charged species on the electrode.

Upon electrochemical oxidation of **11A-Me$_2$** in CH_2Cl_2, the colourless solution turned green, which demonstrated its electrochromic nature. A continuous change in ultraviolet-visible-near-infrared (UV-Vis-NIR) absorption was accompanied by several isosbestic points, indicating that **11A-Me$_2$** was cleanly oxidised into the corresponding cation radical species (Fig. 6). Wurster's Blue exhibits absorption only in the Vis region (λ < 700 nm). Thus, the observed red shift was induced through π-extension by fusing of the indole rings. The carbazole skeleton gives rise to fluorescence properties,[30] so the electrolysis of **11A-Me$_2$** also caused a change in the fluorescence (FL) spectrum [λ_{em} 424, 442 (sh) nm in CH_2Cl_2 (λ_{ex} 354 nm)]. The steady decrease in fluorescence with increasing electrochemical oxidation time could be rationalised by the non-fluorescent nature of its cation radical. Such dual electrochromism in which changes occur in both UV-Vis-NIR and FL spectra is rare,[30] but was also realised in our previous study on benzo[*g*]indolo[2,3-*c*]carbazole derivatives,[9c-e] which were synthesised through a different mode of the gold(I)-catalysed cascade reaction.[9a] Thus, the gold-catalysed synthesis of annulated carbazoles is a powerful tool for exploring the little developed category of advanced electrochromic systems.

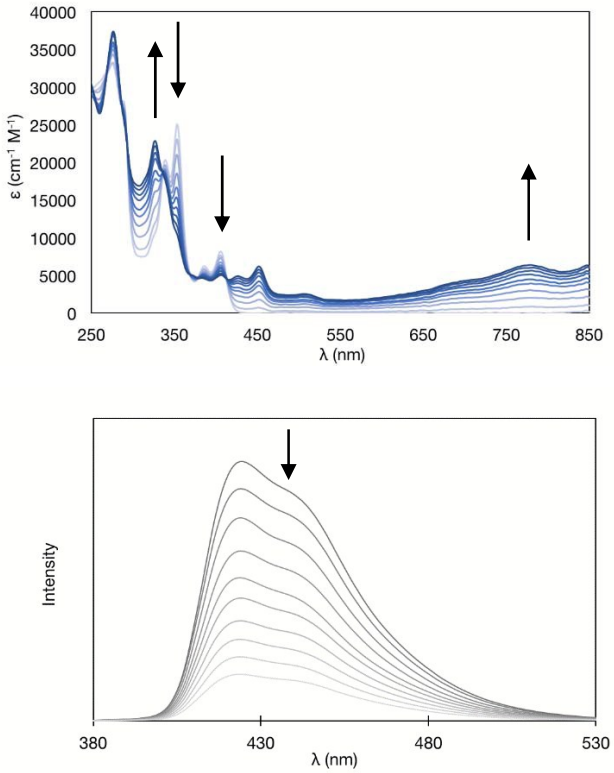


Fig. 6 Continuous changes in UV-Vis-NIR (upper panel) and fluorescence (lower panel) spectra upon constant current electrochemical oxidation of **11A-Me$_2$** [in CH_2Cl_2 (7.1×10^{-6}M) containing 0.05 M Bu_4NPF_6 (20 μA, every 8 min)].

Conclusions

We have developed a strategy for synthesising aryl-annulated [*c*]carbazoles through the gold-catalysed cascade cyclisation of azido-diynes. The reaction with electron-rich benzenes such as anisole and toluene gave benzo[*c*]carbazoles via functionalisation of two benzene C-H bonds. Use of *N*-Boc-pyrrole and indoles as a coupling partner regioselectively produced the corresponding heteroaryl-annulated carbazoles, namely pyrrolo[2,3-*c*]carbazoles and indolo[2,3-*c*]carbazoles, respectively. The reaction proceeded through intramolecular nucleophilic attack of azide to the proximal alkyne to form a

gold carbenoid species, nucleophilic attack of arenes to the carbenoid, and subsequent 6-*endo*-*dig* cyclisation of the introduced arene to the other alkyne. This proposed reaction mechanism was well supported by the results of DFT calculations, competition experiments, and deuterium-labeling experiments. An *N*,*N*′-dimethylated derivative of indolo[2,3-*c*]carbazole showed dual UV-Vis-NIR and fluorescence spectral changes on electrolysis, which demonstrates the potential utility of this reaction in materials chemistry.

Acknowledgements

This work was supported by the JSPS KAKENHI [Grant Numbers JP15KT0061 (HO), 18H04408 (HO), 18H04376 (TK), 17H05430 (MU), 17H06173 (MU)], the Platform Project for Supporting Drug Discovery and Life Science Research (Platform for Drug Discovery, Informatics, and Structural Life Science) from the Japan Agency for Medical Research and Development (AMED), and the Hoansha Foundation. A generous allotment of computational resources (Projects G17022, G18008) from HOKUSAI GreatWave (RIKEN) is gratefully acknowledged.

Conflicts of interest

There are no conflicts to declare.

Notes and references

1 For reviews, see: (*a*) A. W. Schmidt, K. R. Reddy and H.-J. Knölker, *Chem. Rev*., 2012, **112**, 3193−3328; (*b*) J.-P. Lellouche, R. R. Koner and S. Ghosh, *Rev. Chem. Eng*., 2013, **29**, 413−437; (*c*) A. Venkateswararao and K. R. J. Thomas, *Solar Cell Nanotechnology*, 2014, 41−96.

2 For recent examples, see: (*a*) C. Jiao, K.-W. Huang, J. Luo, K. Zhang, C. Chi and J. Wu, *Org. Lett*., 2009, **11**, 4508–4511; (*b*) A. D. Hendsbee, J.-P. Sun, W. K. Law, H. Yan, I. G. Hill, D. M. Spasyuk and G. C. Welch, *Chem. Mater.*, 2016, **28**, 7098–7109; (*c*) S. M. Kim, J. H. Yun, S. H. Han and J. Y. Lee, *J. Mater. Chem. C*, 2017, **5**, 9072–9079.

3 For recent reviews, see: (*a*) N. Yoshikai and Y. Wei, *Asian J. Org. Chem*., 2013, **2**, 466–478; (*b*) J. Roy, A. K. Jana and D. Mal, *Tetrahedron*, 2012, **68**, 6099−6121.

4 For recent examples of aryl-annulated [*c*]carbazole syntheses, see: (*a*) M. E. Budén, V. A. Vaillard, S. E. Martin and R. A. Rossi, *J. Org. Chem*., 2009, **74**, 4490–4498; (*b*) T. Chatterjee, G. Roh, M. A. Shoaib, C.-H. Suhl, J. S. Kim, C.-G. Cho and E. J. Cho, *Org. Lett*., 2017, **19**, 1906–1909.

5 For our recent studies on carbazole synthesis, see: (*a*) T. Watanabe, S. Ueda, S. Inuki, S. Oishi, N. Fujii and H. Ohno, *Chem. Commun*., 2007, 4516–4518; (*b*) T. Watanabe, S. Oishi, N. Fujii and H. Ohno, *J. Org. Chem*., 2009, **74**, 4720–4726; (*c*) T. Takeuchi, S. Oishi, T. Watanabe, H. Ohno, J. Sawada, K. Matsuno, A. Asai, N. Asada, K. Kitaura and N. Fujii, *J. Med. Chem*., 2011, **54**, 4839–4846.

6 (*a*) S. K. Ghosh, B.-C. Kuo, H.-Y. Chen, J.-Y. Li, S.-D. Liu and H. M. Lee, *Eur. J. Org. Chem*., 2015, 4131–4142; (*b*) X.-Q. Feng, F. Zhang, X.-P. He, G.-R. Chen, X.-Y. Wu and F. Sha, *RSC Adv*., 2016, **6**, 75162–75165; (*c*) F. Yu, D. Li, Y. Wei, R.-M. Kang and Q.-X. Guo, *Tetrahedron*, 2018, **74**, 1965–1972.

7 (*a*) Y. Nagase, H. Shirai, M. Kaneko, E. Shirakawa and T. Tsuchimoto, *Org. Biomol. Chem*., 2013, **11**, 1456–1459; (*b*) J. K. Tan, M. Mathiew, S. Nayak and P. W. H. Chan, *Chem. Asian J*., 2017, **12**, 1475–1479.

8 (*a*) R. Y. Huang, P. T. Franke, N. Nicolaus and M. Lautens, *Tetrahedron*, 2013, **69**, 4395–4402; (*b*) P. Raju and A. K. Mohanakrishnan, *Eur. J. Org. Chem*., 2016, 4361–4371.

9 For our studies on annulated [*c*]carbazoles, see: (*a*) K. Hirano, Y. Inaba, K. Takasu, S. Oishi, Y. Takemoto, N. Fujii and H. Ohno, *J. Org. Chem*., 2011, **76**, 9068–9080; (*b*) M. Taguchi, Y. Tokimizu, S. Oishi, N. Fujii and H. Ohno, *Org. Lett*., 2015, **17**, 6250–6253; see also: (*c*) T. Suzuki, Y. Tokimizu, Y. Sakano, R. Katoono, K. Fujiwara, S. Naoe, N. Fujii and H. Ohno, *Chem. Lett*., 2013, **42**, 1001–1003; (*d*) T. Suzuki, Y. Sakano, Y. Tokimizu, Y. Miura, R. Katoono, K. Fujiwara, N. Yoshioka, N. Fujii and H. Ohno, *Chem. Asian J*., 2014, **9**, 1841–1846; (*e*) T. Suzuki, W. Nojo, Y. Sakano, R. Katoono, Y. Ishigaki, H. Ohno and K. Fujiwara, *Chem. Lett*., 2016, **45**, 720–722.

10 Quite recently, synthesis of aryl-annulated [*c*]carbazoles via silver-mediated amination/cyclisation/aromatisation cascade was reported: X. Fan, L.-Z. Yu, Y. Wei and M. Shi, *Org. Lett*., 2017, **19**, 4476–4479.

11 For carbazole syntheses based on rhodium-catalysed [2 + 2 + 2] cycloisomerisation of alkynes, see: B. Witulski and C. Alayrac, *Angew. Chem. Int. Ed*., 2002, **41**, 3281–3284.

12 For selected reviews, see: (*a*) H. Ohno, *Isr. J. Chem.*, 2013, **53**, 869–882; (*b*) R. Dorel and A. M. Echavarren, *Chem. Rev*., 2015, **115**, 9028–9072; (*c*) D. Pflästerer and A. S. K. Hashmi, *Chem. Soc. Rev*., 2016, **45**, 1331–1367; (*d*) Y. Li, W. Li and J. Zhang, *Chem. Eur. J*., 2017, **23**, 467–512.

13 (*a*) A. M. Asiria and A. S. K. Hashmi, *Chem. Soc. Rev*., 2016, **45**, 4471–4503; (*b*) S. M. Abu Sohel and R.-S. Liu, *Chem. Soc. Rev.*, 2009, **38**, 2269–2281.

14 (*a*) Y. Matsuda, S. Naoe, S. Oishi, N. Fujii and H. Ohno, *Chem. Eur. J*., 2015, **21**, 1463–1467; (*b*) N. Hamada, Y. Yoshida, S. Oishi and H. Ohno, *Org. Lett*., 2017, **19**, 3875–3878.

15 For the pioneering work, see: (*a*) D. J. Gorin, N. R. Davis and F. D. Toste, *J. Am. Chem. Soc.*, 2005, **127**, 11260–11261; for a review, see: (b) P. W. Davies and M. Garzón, *Asian J. Org. Chem*., 2015, **4**, 694–708.

16 (*a*) A. Wetzel and F. Gagosz *Angew. Chem. Int. Ed*., 2011, **50**, 7354–7358; (*b*) B. Lu, Y. Luo, L. Liu, L. Ye, Y. Wang and L. Zhang, *Angew. Chem. Int. Ed*., 2011, **50**, 8358–8362.

17 For related studies based on azide-derived gold carbenoids, see: (*a*) Z.-Y. Yan, Y. Xiao and L. Zhang, *Angew. Chem. Int. Ed*., 2012, **51**, 8624–8627; (*b*) C. Gronnier, G. Boissonnat and F. Gagosz, *Org. Lett*., 2013, **15**, 4234–4237; (*c*) N. Li, T. Wang, L. Gong and L. Zhang, *Chem.–Eur. J.*, 2015, **21**, 3585–3588; (*d*) C. Shu, Y.-H. Wang, B. Zhou, X.-L. Li, Y.-F. Ping, X. Lu and L.-W. Ye, *J. Am. Chem. Soc*., 2015, **137**, 9567–9570; (*e*) Y. Wu, L. Zhu, Y. Yu, X. Luo and X. Huang, *J. Org. Chem*., 2015, **80**, 11407–11416; (*f*) N. Li, X.-L. Lian, Y.-H. Li, T.-Y. Wang, Z.-Y. Han, L. Zhang and L.-Z. Gong, *Org. Lett*., 2016, **18**, 4178–4181; (*g*) C. Shu, Y.-H. Wang, C.-H. Shen, P.-P. Ruan, X. Lu and L.-W. Ye, *Org. Lett*., 2016, **18**, 3254–3257; (*h*) G. H. Lonca, C. Tejo, H. L. Chan, S. Chiba and F. Gagosz, *Chem. Commun*., 2017, **53**, 736–739; (*i*) J. Cai, B. Wu, G. Rong, C. Zhang, L. Qiu and X. Xu, *Org. Lett*., 2018, **20**, 2733–2736; for oxidative cyclisation of azido-diynes for synthesis of fused quinolines and indoles, see: (*j*) W.-B. Shen, Q. Sun, L. Li, X. Liu, B. Zhou, J.-Z. Yan, X. Lu and L.-W. Ye, *Nat. Commun*., 2017, **8**, 1748.

18 For pioneering works on gold-catalysed hydroarylation of alkynes, see: (*a*) A. Fürstner and V. Mamane, *J. Org. Chem*., 2002, **67**, 6264–6267; (*b*) V. Mamane, P. Hannen and A. Fürstner, *Chem. Eur. J*., 2004, **10**, 4556–4575; (*c*) E. Soriano and J. Marco-Contelles, *Organometallics*, 2006, **25**, 4542–4553; for recent theoretical study, see: (d) V. M. Lau, W. C. Pfalzgraff, T. E. Markland and M. W. Kanan, *J. Am. Chem. Soc*., 2017, **139**, 4035−4041.

19 A portion of this study for total synthesis of dictyodendrins has been already disclosed as a preliminary communication: J. Matsuoka, Y. Matsuda, Y. Kawada, S. Oishi and H. Ohno, *Angew. Chem. Int. Ed*., 2017, **56**, 7444–7448.

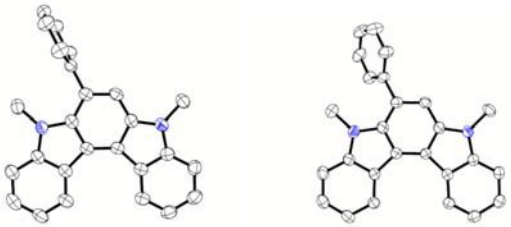
20 (*a*) A. Padwa, D. J. Austin, Y. Gareau, J. M. Kassir and S. L. Xu, *J. Am. Chem. Soc.*, 1993, **115**, 2637–2647; for a recent review, see: (*b*) K. S. Sindhu, A. P. Thankachan, P. S. Sajitha and G. Anilkumar, *Org. Biomol. Chem.*, 2015, **13**, 6891–6905.

21 The substituent effect at the terminal position is a subject of future investigation.

22 For a C2-selective addition of pyrrole in gold-catalyzed reaction of alkynes, see: S. Naoe, Y. Suzuki, K. Hirano, Y. Inaba, S. Oishi, N. Fujii and H. Ohno, *J. Org. Chem*., 2012, **77**, 4907–4916.

23 In single crystals of **7aF'**, two crystallographically independent molecules, both of which were disordered at the phenyl group.

24 Recrystallisation of **11D-Me$_2$** from CH_2Cl_2 gave four crystallographically independent molecules in the single crystal lattices, two of which are shown below. As expected, the indolo[2,3-*c*]carbazole core had a planer structure in all four molecules.



25 (*a*) S. Pratihar and S. Roy, *J. Org. Chem*., 2010, **75**, 4957–4963; (*b*) T. A. Nigst, M. Westermaier, A. R. Ofial and H. Mayr, *Eur. J. Org. Chem*., 2008, 2369–2374; for a nucleophilic reaction of *N*-Boc-pyrrole at the 2-position, see: (*c*) J. Tang, J.-J. Yue, F.-F. Tao, G. Grampp, B.-X. Wang, F. Li, X.-Z. Liang, Y.-M. Shen and J.-H. Xu, *J. Org. Chem*., 2014, **79**, 7572−7582.

26 D. Pflästerer, S. Schumacher, M. Rudolph and A. S. K. Hashmi, *Chem. Eur. J*., 2015, **21**, 11585–11589.

27 The C-H insertion is often observed in gold-carbenoid chemistry, see: (*a*) M. R. Fructos, T. R. Belderrain, P. de Frémont, N. M. Scott, S. P. Nolan, M. M. Díaz-Requejo and P. J. Pérez, *Angew. Chem. Int. Ed*., 2005, **44**, 5284–5288; (*b*) S. Bhunia and R.-S. Liu, *J. Am. Chem. Soc*., 2008, **130**, 16488–16489; (*c*) L. Cui, G. Zhang, Y. Peng and L. Zhang, *Org. Lett*., 2009, **11**, 1225–1228; (*d*) Y. Horino, T. Yamamoto, K. Ueda, S. Kuroda and F. D. Toste, *J. Am. Chem. Soc*., 2009, **131**, 2809–2811; (*e*) A. S. K. Hashmi, I. Braun, P. Nösel, J. Schädlich, M. Wieteck, M. Rudolph and F. Rominger, *Angew. Chem. Int. Ed*., 2012, **51**, 4456–4460; (*f*) L. Ye, Y. Wang, D. H. Aue and L. Zhang, *J. Am. Chem. Soc*., 2012, **134**, 31–34; (*g*) S. Bhunia, S. Ghorpade, D. B. Huple and R.-S. Liu, *Angew. Chem. Int. Ed*., 2012, **51**, 2939–2942; (*h*) F. Pan, S. Liu, R.-K. Lin, Y.-F. Yu, J.-M. Zhou and L.-W. Ye, *Chem. Commun*., 2014, **50**, 10726–10729; (*i*) Y. Wang, M. Zarca, L.-Z. Gong and L. Zhang, *J. Am. Chem. Soc*., 2016, **138**, 7516–7519; (*j*) J. E. M. N. Klein, G. Knizia, L. N. dos Santos Comprido, J. Kästner and A. S. K. Hashmi, *Chem. Eur. J*., 2017, **23**, 16097–16103.

28 (*a*) T. Suzuki, T. Tsuji, T. Ohkubo, A. Okada, Y. Obana, T. Fukushima, T. Miyashi and Y. Yamashita, *J. Org. Chem.*, 2001, **66**, 8954–8960; (*b*) T. Suzuki, Y. Tsubata, Y. Obana, T. Fukushima, T. Miyashi, H. Kawai, K. Fujiwara and K. Akiyama, *Tetrahedron Lett.*, 2003, **44**, 7881–7884.

29 (*a*) C. Wurster and R. Sendtner, *Ber. Dtsch. Chem. Ges.*, 1897, **12**, 1803; (*b*) L. Michaelis, M. P. Shubert and S. Granick, *J. Am. Chem. Soc.*, 1939, **61**, 1981–1992; (*c*) J. R. Bolton, A. Carrington and J. Santos-Veiga, *Mol. Phys*., 1962, **5**, 615–619; (*d*) J. Steigman and W. Cronkright, *J. Am. Chem. Soc*., 1970, **92**, 6736–6743.

30 (*a*) M. Luo, H. Shadnia, G. Qian, X. Du, D. Yu, D. Ma, J. S. Wright and Z. Y. Wang, *Chem. Eur. J*., 2009, **15**, 8902–8908; (*b*) Y. Ishigaki, H. Kawai, R. Katoono, K. Fujiwara, H. Higuchi, H. Kikuchi and T. Suzuki, *Can. J. Chem.*, 2017, **95**, 243–252; (*c*) M. Walesa-Chorab and W. G. Skene, *ACS Appl. Mater. Interfaces*, 2017, **9**, 21524–21531.