Chemical Science

ROYAL SOCIETY OF CHEMISTRY

EDGE ARTICLE

View Article Online
View Journal | View Issue

Cite this: *Chem. Sci.*, 2024, **15**, 2205

All publication charges for this article have been paid for by the Royal Society of Chemistry

Received 2nd October 2023
Accepted 3rd January 2024

DOI: 10.1039/d3sc05210a

rsc.li/chemical-science

Efficient construction of functionalized pyrroloindolines through cascade radical cyclization/intermolecular coupling†

Yonggang Jiang,[a] Dongxiang Liu,[a] Lening Zhang,[a] Cuirong Qin,[a] Hui Li,[a] Haitao Yang,[a] Patrick J. Walsh *[b] and Xiaodong Yang *[a]

Pyrroloindolines are important structural units in nature and the pharmaceutical industry, however, most approaches to such structures involve transition-metal or photoredox catalysts. Herein, we describe the first tandem SET/radical cyclization/intermolecular coupling between 2-azaallyl anions and indole acetamides. This method enables the transition-metal-free synthesis of C3a-substituted pyrroloindolines under mild and convenient conditions. The synthetic utility of this transformation is demonstrated by the construction of an array of C3a-methylamine pyrroloindolines with good functional group tolerance and yields. Gram-scale sequential one-pot synthesis and hydrolysis reactions demonstrate the potential synthetic utility and scalability of this approach.

Introduction

Nitrogen-containing heterocycles are among the most fundamental structural motifs in organic compounds.[1–7] Among N-heterocycles, pyrroloindoline alkaloids (also termed hexahydropyrrolo[2,3-*b*]indoles), particularly C3a-substituted pyrroloindolines, are an important subclass in nature and the pharmaceutical industry (such as alline, physostigmine, flustramide B and F, gllocladin C, folicanthine, Fig. 1).[8–12] These molecules have gained interest owing to their extensive biological activities, including antitumor, antimicrobial, antinematodal, vasodilating activities, as well as inhibitory activities against cholinesterases and topoisomerases.[13,14] Consequently, the efficient and straightforward construction of functionalized pyrroloindolines remains in demand.

The classical approach to C3a-substituted pyrroloindolines involves the transition-metal-catalyzed cyclization (Scheme 1a). For example, MacMillan's group developed the copper-catalyzed arylation/cyclization cascade of indole acetamides with diaryliodonium salts to access enantioenriched C3a-aryl pyrroloindolines,[15] while You reported an elegant iridium-catalyzed allylation of tryptamines with *Z*-cinnamyl acetate to obtain Z-retentive C3a-allyl pyrroloindolines.[16] Recently, visible-light-mediated radical cyclizations have emerged as potent approaches for the construction of heterocycles,[17–27] as presented in the representative illustrations in Scheme 1b. Knowles developed a $Ir(ppy)_3$ photocatalytic proton-coupled electron transfer reaction for synthesis of C3a-TEMPO-substituted pyrroloindolines,[28] and Wang reported a eosin Y visible-light-induced radical cascade reaction of indole acetamides to access C3a-hydroxypyrroloindolines.[29] Most of these protocols, however, involve transition-metal catalysts or photoredox catalysts.

Since the pioneering studies by Murphy,[30–32] super electron donors (SEDs), that is neutral and anionic organic compounds that exhibit strong reducing tendencies through single-electron

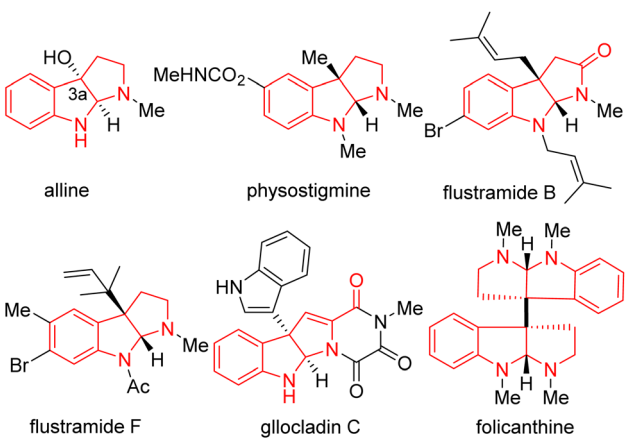
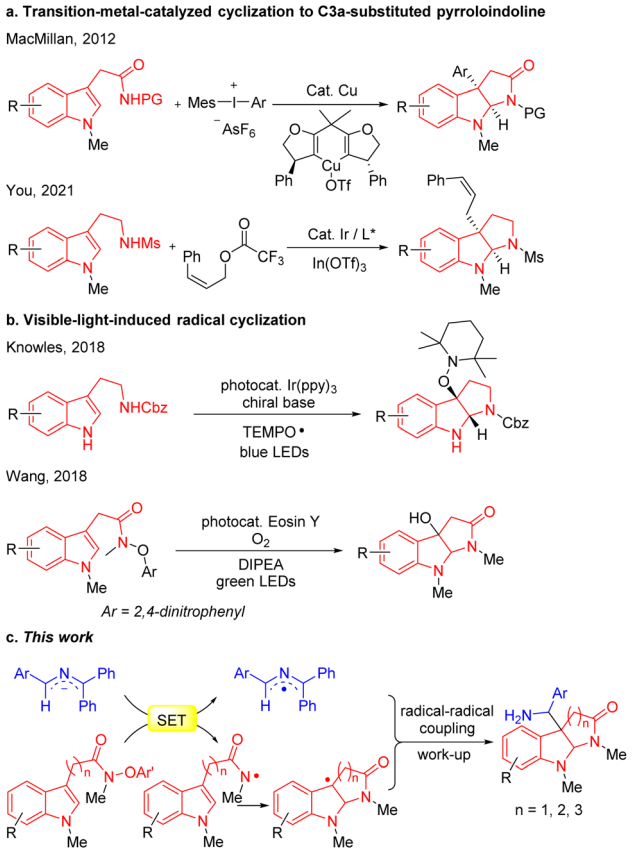


Fig. 1 Representative C3a-substituted pyrroloindoline natural products.

[a]*Key Laboratory of Medicinal Chemistry for Natural Resources, Ministry of Education, Yunnan Provincial Center for Research & Development of Natural Products, School of Pharmacy, Yunnan University, Kunming 650091, P. R. China. E-mail: xdyang@ynu.edu.cn*

[b]*Roy and Diana Vagelos Laboratories, Penn/Merck Laboratory for High-Throughput Experimentation, Department of Chemistry, University of Pennsylvania, 231 South 34th Street, Philadelphia, Pennsylvania 19104, USA*

† Electronic supplementary information (ESI) available. CCDC 2293492 and 2293493. For ESI and crystallographic data in CIF or other electronic format see DOI: https://doi.org/10.1039/d3sc05210a



Scheme 1 (a) Transition-metal-catalyzed cyclization to C3a-substituted pyrroloindoline. (b) Visible-light-induced radical cyclization to C3a-OH pyrroloindoline. (c) SED 2-azaallyl anions enable synthesis of C3a-substituted pyrroloindolines (this work).

transfer (SET), have emerged as an effective partner in radical–radical couplings to form C–C bonds. In particular, 2-azaallyl anions, which possess the ability to behave as strong single electron reducing agents, have attracted attention in the synthetic community.[33–37] Based on the SED properties of 2-azaallyl anions, our team developed a series of tandem cyclization reactions to construct benzofuran, isochromene and isoquinoline derivatives,[38–40] among others. We further employed 2-azaallyl anions to develop a series of radical C(sp^3)–C(sp^2) and C(sp^3)–C(sp^3) coupling strategies.[41–47]

In view of the medicinal value of pyrroloindolines, we felt compelled to apply this radical coupling approach to the synthesis of C3a-substituted pyrroloindolines. Based on our prior generation of amidyl radicals,[48] we hypothesized that SET between the 2-azaallyl anions and indole *N*-aryloxy acetamides would generate 2-azaallyl radicals and amidyl radicals, the latter of which would trigger a radical cyclization to furnish C3a-pyrroloindoline radicals. Finally, coupling between 2-azaallyl radicals and pyrroloindoline radicals was expected to afford C3a-methylamine pyrroloindoline derivatives (Scheme 1c).

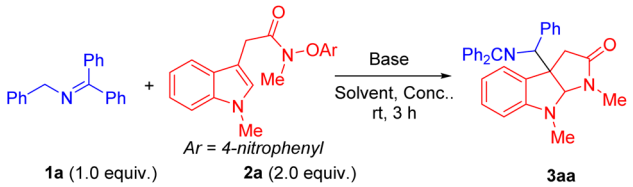
Herein, we describe the first tandem SET/radical cyclization/intermolecular coupling between 2-azaallyl anions and indole acetamides, which enables the synthesis of C3a-substituted pyrroloindolines under mild and convenient conditions. The synthetic utility of this transformation is demonstrated by the construction of an array of C3a-methylamine pyrroloindolines with good functional group tolerance and yields (33 examples, up to 88% yield).

Results and discussion

We initiated the reaction optimization by choosing indole *N*-aryloxy acetamide **2a** as the model substrate. Reaction of **2a** was performed with *N*-benzylketimine **1a** in the presence of base in DMSO at room temperature for 3 h. Initially, a series of bases including LiO^{t}Bu, NaO^{t}Bu, KO^{t}Bu, LiN($SiMe_3$)$_2$, NaN($SiMe_3$)$_2$ and KN($SiMe_3$)$_2$ were evaluated (Table 1, entries 1–6). Among them, NaN($SiMe_3$)$_2$ generated the radical cyclization/coupling product **3aa** in 89% assay yield (AY, as determined by ^{1}H NMR integration against an internal standard) and 86% isolated yield (dr = 1.2 : 1, entry 5), while the other five bases led to product **3aa** in 56–65% AY. Next, we then turned our attention to probe the effect of solvent and concentration. Using NaN($SiMe_3$)$_2$ as base, we examined a range of solvents [THF, DMF, CPME, MTBE (methyl *tert*-butyl ether) and MeCN]. Surprisingly, no desired products formed in these solvents (entries 7–11). Furthermore, decreasing the concentration to 0.1 M or 0.05 M led to a reduction in the AY to 78% and 68% (entries 12 and 13). When the equiv of base was increased from 1.5 to 2.0 equiv, a decrease in the AY to 72% (entry 14) was observed. Finally, increasing the reaction temperature to 60 °C or decreasing it to 0 °C resulted in a decrease in the AY to 22% or 8%, respectively (entries 15 and 16).

With the optimized conditions in hand (Table 1, entry 5), we next focused our attention on exploring the scope of *N*-benzyl ketimines. As shown in Table 2, in general, we found that *N*-benzyl ketimines **1** bearing various substituted *N*-benzyl or *N*-alkyl groups provided C3a-substituted pyrroloindolines in moderate to good yields (48–88%) as a mixture of diastereomers. *N*-Benzyl groups bearing electron-donating substituents 4-OMe (**1b**) and 3,4-methylenedioxy (**1c**) generated cyclization products **3ba** and **3ca** in 56% and 60% yields, respectively. *N*-Benzyl ketimines decorated with electronegative and electron-withdrawing groups, such as 4-F (**1d**), 4-Cl (**1e**), 4-Br (**1f**), 2,4-di-F (**1g**) and 4-CF_3 (**1h**) afforded products **3da**, **3ea**, **3fa**, **3ga**, **3ha** in 80%, 76%, 66%, 63% and 73% yields, respectively. The structures of products **3ga′** and **3ga″**, which were separable by column chromatography and HPLC, were confirmed by X-ray crystallography (CCDC 2293492 and 2293493). The sterically hindered 2-tolyl (**1i**) and 1-naphthyl (**1j**) *N*-benzyl derivatives provided cyclization products **3ia** and **3ja** in 56% and 68% yields, respectively. Notably, this approach also proved tolerant of medicinally relevant heterocyclic derivatives. *N*-benzyl groups decorated with 3-pyridyl (**1k**), 2-furanyl (**1l**) and 2-thiophenyl (**1m**) substituents furnished the corresponding products **3ka**, **3la** and **3ma** in 62%, 48% and 56% yields, respectively. Furthermore, switching *N*-benzyl ketimine with *N*-(9*H*-fluoren-9-yl)alkylanimine, we could expand the scope of imine substrates to those with *N*-alkyl groups. Methyl (**1n**), *i*-Pr (**1o**), isobutyl (**1p**), cyclobutyl (**1q**), cyclopentyl (**1r**) and cyclohexyl (**1s**) were also suitable substituents, giving the corresponding

Table 1 Optimization of coupling of ketimine **1a** and amide **2a** [a,b]



1a (1.0 equiv.) **2a** (2.0 equiv.) **3aa**

Entry	Base (equiv.)	Solvent	Conc. [M]	Yield (%)[b]
1	LiO^{t}Bu (1.5)	DMSO	0.2	56 (dr = 1 : 1)
2	NaO^{t}Bu (1.5)	DMSO	0.2	61 (dr = 1 : 1)
3	KO^{t}Bu (1.5)	DMSO	0.2	65 (dr = 1.3 : 1)
4	LiHMDS (1.5)	DMSO	0.2	59 (dr = 1 : 1)
5	NaHMDS (1.5)	DMSO	0.2	89 (86)[c] (dr = 1.2 : 1)
6	KHMDS (1.5)	DMSO	0.2	65 (dr = 1 : 1)
7	NaHMDS (1.5)	THF	0.2	0
8	NaHMDS (1.5)	DMF	0.2	0
9	NaHMDS (1.5)	CPME	0.2	0
10	NaHMDS (1.5)	MTBE	0.2	0
11	NaHMDS (1.5)	MeCN	0.2	0
12	NaHMDS (1.5)	DMSO	0.1	78 (dr = 1 : 1)
13	NaHMDS (1.5)	DMSO	0.05	68 (dr = 1 : 1)
14	NaHMDS (2.0)	DMSO	0.2	72 (dr = 1 : 1)
15[d]	NaHMDS (1.5)	DMSO	0.1	22 (dr = 1 : 1)
16[e]	NaHMDS (1.5)	DMSO/THF = 1 : 1	0.1	8 (dr = 1 : 1)

[a] Reaction conditions: **1a** (0.1 mmol, 1.0 equiv), **2a** (0.2 mmol, 2.0 equiv), base, rt., 3 h. [b] Assay yield (AY) determined by ^{1}H NMR spectroscopy of the crude reaction mixture using $C_2H_2Cl_4$ as an internal standard. [c] Isolated yield after chromatographic purification. [d] 60 °C. [e] 0 °C.

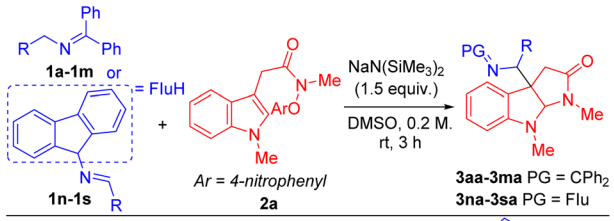
products (**3na-3sa**) in 72–88% yields, respectively. Meanwhile, when imines bearing tetraphenyl ketimine and alpha-substituted benzyl amines were employed, the radical cyclization/intermolecular coupling did not take place, likely due to increased steric interactions.

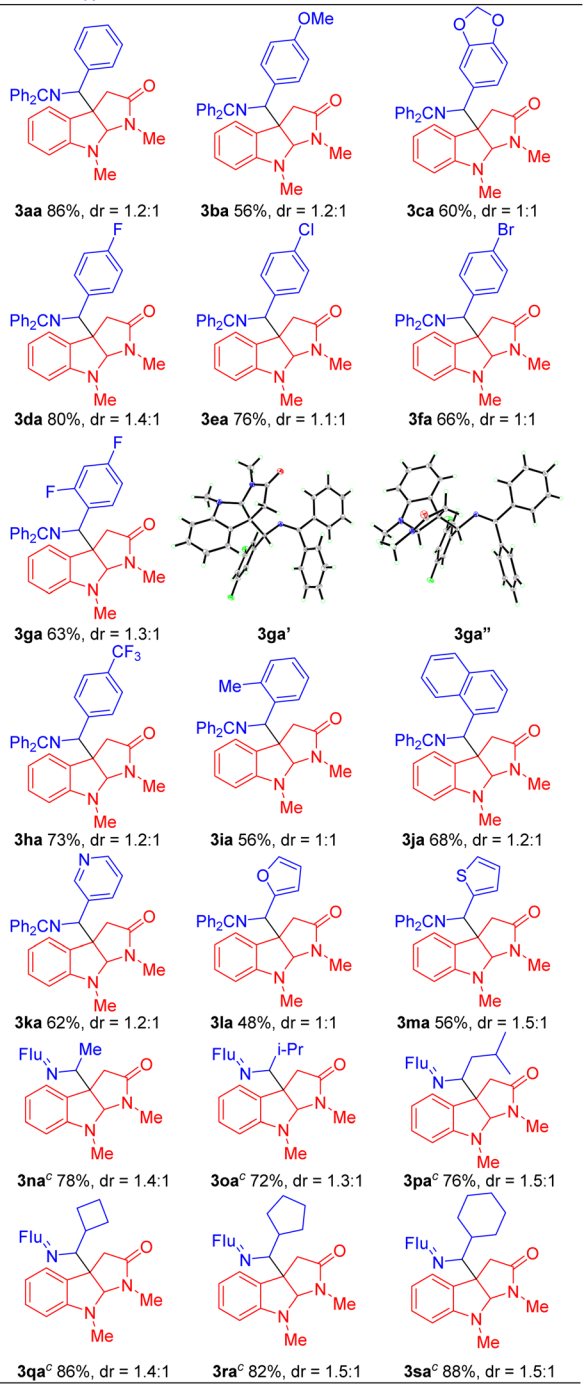
Next, we evaluated the scope of the indole acetamides **2**, which were easily synthesized using the method of Wang[29,49] (see ESI for details†). A wide range of indole *N*-aryloxy acetamides bearing various groups were all compatible with our method, generating the pyrroloindoline products in moderate to good yields (46–78%, Table 3). For instance, indole derivatives with electron-donating substituents, such as 7-Me (**2b**), 5-OMe (**2c**) and 5-OBn (**2d**), afforded cyclization products **3ab**, **3ac** and **3ad** in 63%, 65% and 60% yields, respectively. Indole acetamides with electronegative substituents, such as 5-F (**2e**) and 5-Br (**2f**), provided the corresponding products **3ae** and **3af** in 58% and 60% yields. It is noteworthy that indole derivatives with a heterocyclic piperonyl group (**2g**) and sterically hindered naphthyl group (**2h**) led to coupling products **3ag** and **3ah** in 78% and 72% yields, respectively. In addition, we explored a range of indole *N*-aryloxy acetamide substrates. Gratifyingly, when we extended the alkyl chain of indole acetamides to two or three methylenes, the corresponding six- and seven-member ring products **3ai** and **3aj** were obtained in 52% and 46% yields, respectively. Furthermore, we introduced steric hindrance at the C2 position of indole substrates [2-methyl (**2k**) and 2-ethyl (**2l**)], leading to cyclization products **3ak** and **3al** in 56% and 65% yields. Next, we use indole derivatives bearing benzyl (**2m**), allyl (**2n**) and Boc (**2o**) substituents, which afforded cyclization products **3sm**, **3sn** and **3so** in 67, 70 and 56% yields, respectively.

To demonstrate the utility and scalability of our cascade radical cyclization/intermolecular coupling reaction, a gram-scale sequential one-pot synthesis and product hydrolysis were conducted. A telescoped gram-scale experiment was performed by employing benzylamine and diphenyl methyl imine in THF at 50 °C for 12 h, followed by solvent removal to afford imine **1a**. The unpurified **1a** was coupled with indole *N*-aryloxy acetamide **2a** under the standard reaction conditions. The product **3aa** was obtained in 74% yield (1.40 g, Scheme 2a). Subsequently, imine hydrolysis of the cyclization product **3aa** under mildly acidic conditions furnished the free C3a-methylamine pyrroloindoline derivative **4aa** in excellent yield (92%, Scheme 2b).

Finally, to gain some information on the reaction mechanism, we carried out control experiments. First, the experiment with the addition of 2.0 equiv of radical scavenger 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) was conducted under the standard conditions. However, no desired product **3aa** was detected, only affording TEMPO trapping compounds **5aa** and **6aa** in 70% and 10% yields (Scheme 3a). A control experiment with 2.0 equiv of TEMPO in the absence of *N*-benzyl ketimine **1a** was carried out under the standard conditions, and radical coupling product **5aa** was not observed (Scheme 3b). The lack of

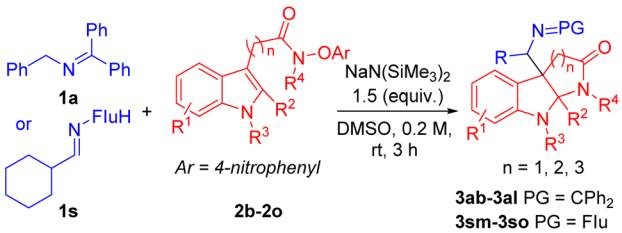
Table 2 Scope of Ketimines 1[a,b]

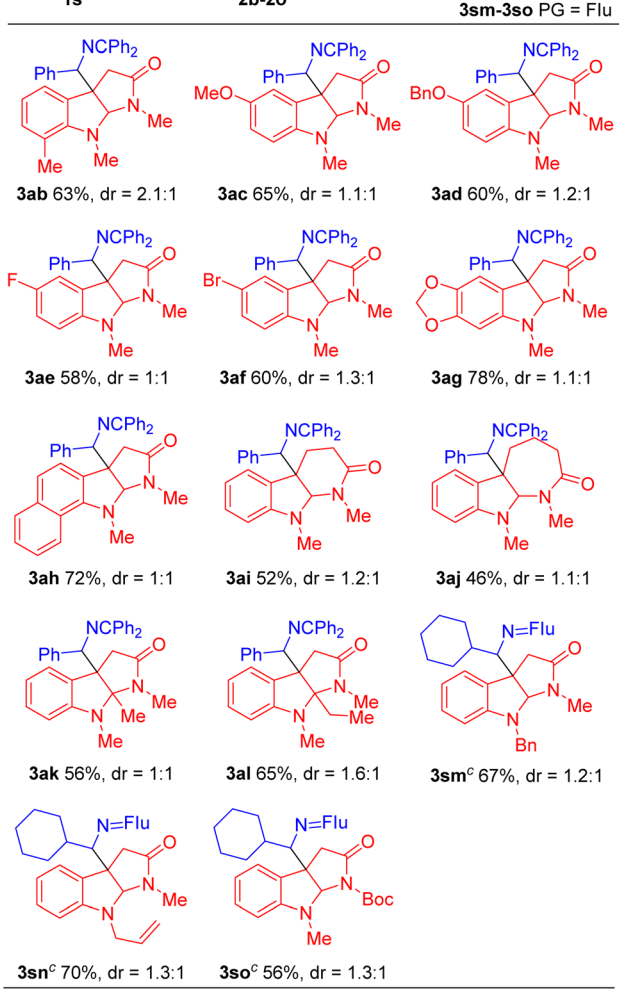




[a] Reactions conducted on 0.4 mmol scale using 1 equiv of **1a–1s** and 2 equiv of **2a**. [b] Isolated yield after chromatographic purification, Flu = 9-fuorenyl. PG = protect group. [c] *N*-(9*H*-Fluoren-9- yl)alkylanimine as the 2-azaallyl precursor.

Table 3 Scope of indole acetamides 2 [a,b]

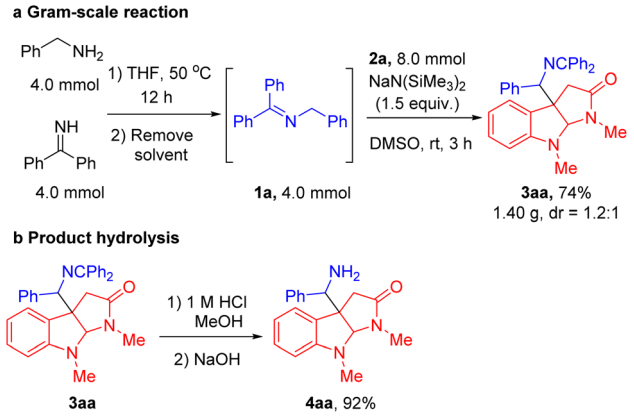




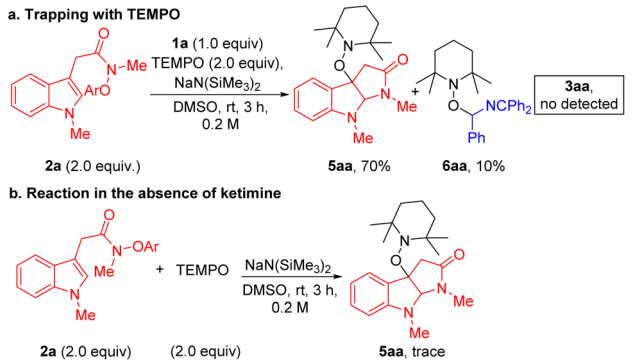
[a] Reactions conducted on 0.4 mmol scale using 2 equiv of **2b–2o**, and 1 equiv of **1a** or **1s**. [b] Isolated yield after chromatographic purification, Flu = 9-fuorenyl. PG = protect group. [c] *N*-(9*H*-Fluoren-9- yl)alkylanimine as the 2-azaallylprecursor.

product formation indicates that $NaN(SiMe_3)_2$ is not the active reductant in this chemistry. Together, these results suggest that the reaction proceeds *via* a radical pathway, supporting the key SET/radical cyclization/coupling pathway proposed in Scheme 1c.

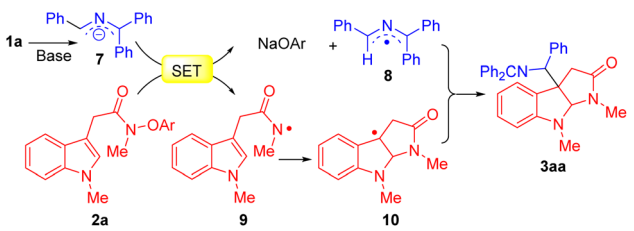
A plausible mechanism for the reaction is outlined in Scheme 4. Ketimine **1a** is deprotonated by the $NaN(SiMe_3)_2$ to afford the 2-azaallyl anion **7**. Next, SED **7** undergoes an SET process with acetamides **2a** to form azaallyl radical **8** and *N*-centered radical **9**. The amidyl radical **9** initiates a radical cyclization to generate C3a-pyrroloindoline radical **10**. Finally,



Scheme 2 (a) Gram-scale sequential one-pot synthesis. (b) Hydrolysis of the product imine.



Scheme 3 Control experiments. (a) Radical trapping experiment. (b) Reaction in the absence of ketimine.



Scheme 4 Proposed reaction pathway.

pyrroloindoline radical **10** couples with 2-azaallyl radical **8** to obtain coupling product **3aa**.

Conclusions

In summary, we have developed a unique strategy for constructing functionalized pyrroloindolines in a single synthetic step. Unlike many previous reports, which generally involve transition-metal catalysts or photoredox catalysts, this chemistry utilizes readily generated SED, 2-azaallyl anions. In this transformation, the tandem SET/radical cyclization/intermolecular coupling between 2-azaallyl anions and indole *N*-aryloxy acetamides provides the functionalized pyrroloindolines related to biologically active compounds by simple combination of base and DMSO at room temperature. A gram-scale sequential one-pot synthesis and hydrolysis reaction demonstrate the potential synthetic utility and scalability of this approach. It is noteworthy that this method includes a multi-step tandem reaction with a rapid increase in molecular complexity. The sustainability of this method enhances its potential utility in the pharmaceutical industry.[50]

Data availability

All experimental data, procedures for data analysis, and pertinent data sets are provided in the ESI.†

Author contributions

X. Y. and Y. J. conceived of the project. X. Y. and P. J. W. designed the experiments. Y. J., D. L., L. Z., C. Q., H. L. and H. Y. performed the research. X. Y. and P. J. W. wrote the manuscript.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was supported by grants from the National Key R&D Program of China (2019YFE0109200), NSFC (22361050), NSF of Yunnan (202207AA110007, 202207AB110002), Ling-Jun Scholars Yunnan Province (202005AB160003), Program for Xingdian Talents (Yun-Ling Scholars), IRTSTYN and Yunnan University Professional Degree Graduate Student Practice and Innovation Fund (H. L.). P. J. W. thanks the US National Science Foundation (CHE-2154593) for financial support.

Notes and references

1 M. E. Welsch, S. A. Snyder and B. R. Stockwell, *Curr. Opin. Cell Biol.*, 2010, **14**, 347–361.
2 C. Lamberth, *Pest Manage. Sci.*, 2013, **69**, 1106–1114.
3 E. Vitaku, D. T. Smith and J. T. Njardarson, *J. Med. Chem.*, 2014, **57**, 10257–10274.
4 R. V. Patel, Y.-S. Keum and S. W. Park, *Eur. J. Med. Chem.*, 2015, **97**, 649–663.
5 K. Chaudhari, S. Surana, P. Jain and H. M. Patel, *Eur. J. Med. Chem.*, 2016, **124**, 160–185.
6 R. Kaur, L. Dahiya and M. Kumar, *Eur. J. Med. Chem.*, 2017, **141**, 473–505.
7 J. Davies, T. D. Svejstrup, D. F. Reina, N. S. Sheikhb and D. Leonori, *J. Am. Chem. Soc.*, 2016, **138**, 8092–8095.
8 A. Huang, J. J. Kodanko and L. E. Overman, *J. Am. Chem. Soc.*, 2004, **126**, 14043–14053.
9 S. Tadano, Y. Mukaeda and H. Ishikawa, *Angew. Chem., Int. Ed.*, 2013, **52**, 7990–7994.
10 B. D. Joshi and J. D. Chisholm, *Tetrahedron Lett.*, 2021, **77**, 153256.

11 J. J. Kodanko and L. E. Overman, *Angew. Chem., Int. Ed.*, 2003, **42**, 2528–2531.
12 A. Steven and L. E. Overman, *Angew. Chem., Int. Ed.*, 2007, **46**, 5488–5508.
13 P. Ruiz-Sanchis, S. A. Savina, F. Albericio and M. Alvarez, *Chem.–Euro. J.*, 2011, **17**, 1388–1408.
14 C. Sun, W. Tian, Z. Lin and X. Qu, *Nat. Prod. Rep.*, 2022, **39**, 1721–1765.
15 S. Zhu and D. W. MacMillan, *J. Am. Chem. Soc.*, 2012, **134**, 10815–10818.
16 R. Jiang, L. Ding, C. Zheng and S.-L. You, *Science*, 2021, **371**, 380–386.
17 J. R. Chen, X. Q. Hu, L. Q. Lu and W. J. Xiao, *Chem. Soc. Rev.*, 2016, **45**, 2044–2056.
18 S. Fukuzumi and K. Ohkubo, *Org. Biomol. Chem.*, 2014, **12**, 6059–6071.
19 L. Furst, J. M. Narayanam and C. R. Stephenson, *Angew. Chem., Int. Ed.*, 2011, **50**, 9655–9659.
20 M. N. Hopkinson, B. Sahoo, J. L. Li and F. Glorius, *Chem.–Euro. J.*, 2014, **20**, 3874–3886.
21 M. D. Karkas, J. A. Porco, Jr. and C. R. Stephenson, *Chem. Rev.*, 2016, **116**, 9683–9747.
22 D. A. Nicewicz and T. M. Nguyen, *ACS Catal.*, 2013, **4**, 355–360.
23 C. K. Prier, D. A. Rankic and D. W. MacMillan, *Chem. Rev.*, 2013, **113**, 5322–5363.
24 N. A. Romero and D. A. Nicewicz, *Chem. Rev.*, 2016, **116**, 10075–10166.
25 J. Xuan and W. J. Xiao, *Angew. Chem., Int. Ed.*, 2012, **51**, 6828–6838.
26 T. P. Yoon, *ACS Catal.*, 2013, **3**, 895–902.
27 D. P. Hari and B. Konig, *Chem. Commun.*, 2014, **50**, 6688–6699.
28 E. C. Gentry, L. J. Rono, M. E. Hale, R. Matsuura and R. R. Knowles, *J. Am. Chem. Soc.*, 2018, **140**, 3394–3402.
29 K. Wu, Y. Du, Z. Wei and T. Wang, *Chem. Commun.*, 2018, **54**, 7443–7446.
30 J. P. Barham, G. Coulthard, K. J. Emery, E. Doni, F. Cumine, G. Nocera, M. P. John, E. Leonard, A. Berlouis, T. McGuire, T. Tuttle and J. A. Murphy, *J. Am. Chem. Soc.*, 2016, **138**, 7402–7410.
31 J. P. Barham, S. E. Dalton, M. Allison, G. Nocera, A. Young, M. P. John, T. McGuire, S. Campos, T. Tuttle and J. A. Murphy, *J. Am. Chem. Soc.*, 2018, **140**, 11510–11518.
32 J. A. Murphy, *J. Org. Chem.*, 2014, **79**, 3731–3746.
33 Y. Lei, J. Yang, R. Qi, S. Wang, R. Wang and Z. Xu, *Chem. Commun.*, 2018, **54**, 11881–11884.
34 S. Tang, X. Zhang, J. Sun, D. Niu and J. J. Chruma, *Chem. Rev.*, 2018, **118**, 10393–10457.
35 Q. Wang, M. Poznik, M. Li, P. J. Walsh and J. J. Chruma, *Adv. Synth. Catal.*, 2018, **360**, 2854–2868.
36 B. Wang, M. Li, G. Gao, A. Sanz-Vidal, B. Zheng and P. J. Walsh, *J. Org. Chem.*, 2022, **87**, 8099–8103.
37 G. B. Panetti, P. J. Carroll, M. R. Gau, B. C. Manor, E. J. Schelter and P. J. Walsh, *Chem. Sci.*, 2021, **12**, 4405–4410.
38 G. Deng, M. Li, K. Yu, C. Liu, Z. Liu, S. Duan, W. Chen, X. Yang, H. Zhang and P. J. Walsh, *Angew. Chem., Int. Ed.*, 2019, **58**, 2826–2830.
39 K. Yu, M. Li, G. Deng, C. Liu, J. Wang, Z. Liu, H. Zhang, X. Yang and P. J. Walsh, *Adv. Synth. Catal.*, 2019, **361**, 4354–4359.
40 Q. Zi, M. Li, J. Cong, G. Deng, S. Duan, M. Yin, W. Chen, H. Jing, X. Yang and P. J. Walsh, *Org. Lett.*, 2022, **24**, 1786–1790.
41 M. Li, S. Berritt, L. Matuszewski, G. Deng, A. Pascual-Escudero, G. B. Panetti, M. Poznik, X. Yang, J. J. Chruma and P. J. Walsh, *J. Am. Chem. Soc.*, 2017, **139**, 16327–16333.
42 M. Li, O. Gutierrez, S. Berritt, A. Pascual-Escudero, A. Yesilcimen, X. Yang, J. Adrio, G. Huang, E. Nakamaru-Ogiso, M. C. Kozlowski and P. J. Walsh, *Nat. Chem.*, 2017, **9**, 997–1004.
43 Z. Liu, M. Li, G. Deng, W. Wei, P. Feng, Q. Zi, T. Li, H. Zhang, X. Yang and P. J. Walsh, *Chem. Sci.*, 2020, **11**, 7619–7625.
44 G. Deng, S. Duan, J. Wang, Z. Chen, T. Liu, W. Chen, H. Zhang, X. Yang and P. J. Walsh, *Nat. Commun.*, 2021, **12**, 3860.
45 S. Duan, G. Deng, Y. Zi, X. Wu, X. Tian, Z. Liu, M. Li, H. Zhang, X. Yang and P. J. Walsh, *Chem. Sci.*, 2021, **12**, 6406–6412.
46 S. Duan, Y. Zi, L. Wang, J. Cong, W. Chen, M. Li, H. Zhang, X. Yang and P. J. Walsh, *Chem. Sci.*, 2022, **13**, 3740–3747.
47 L. Zhang, Z. Liu, X. Tian, Y. Zi, S. Duan, Y. Fang, W. Chen, H. Jing, L. Yang and X. Yang, *Org. Lett.*, 2021, **23**, 1714–1719.
48 Y. Jiang, D. Liu, M. E. Rotella, G. Deng, Z. Liu, W. Chen, H. Zhang, M. C. Kozlowski, P. J. Walsh and X. Yang, *J. Am. Chem. Soc.*, 2023, **145**, 16045–16057.
49 K. Wu, Y. Du and T. Wang, *Org. Lett.*, 2017, **19**, 5669–5672.
50 C. E. Garrett and K. Prasad, *Adv. Synth. Catal.*, 2004, **346**, 889–900.