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Synthesis of Structurally Diverse 2,3-Fused Indoles via Microwave-Assisted AgSbF₆-Catalysed Intramolecular Difunctionalization of *o*-Alkynylanilines

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2,3-Fused indoles are found in numerous natural products and drug molecules. Although several elegant methods for the synthesis of this structural motif have been reported, long reaction times and harsh conditions are sometimes required, and the yields tend to be low. Herein, we report a microwave method for straightforward access to various types of 2,3-fused indoles via AgSbF₆-catalysed intramolecular difunctionalization of *o*-alkynylanilines. AgSbF₆ played a role in both the hydroamination step and the imine-formation step. This method, which exhibited excellent chemoselectivity (no ring-fused 1,2-dihydroquinolines were formed), was used for formal syntheses of the natural products conolidine and ervaticine and the antihistamine drug latrepirdine.

Ring-fused indoles in general, and 2,3-fused indoles in particular, are found in numerous natural products and drug molecules (Fig. 1)^{1–8}. Hexahydro-1*H*-azocino[4,3-*b*]indole is the core motif of numerous natural products, such as (+)-condylocarpine⁹, (+)-uleine¹⁰, conolidine and ervaticine¹¹, (–)-actinophyllic acid¹², and (–)-strychnine¹³. In addition, the clinical antihistamine drug latrepirdine contains a tetrahydro-1*H*-pyrido[4,3-*b*]indole skeleton (also known as γ -carboline)¹⁴. 2,3-Fused indoles have synthetically challenging structures and interesting biological activities, and much attention has been paid to the development of new approaches to the synthesis of this structural motif^{15–19}. However, a practical method for the efficient synthesis of 2,3-fused indoles in a single operation is lacking.

Intramolecular difunctionalization of *o*-alkynylanilines is widely used to construct ring-fused indoles^{20–22}, but this method, and other conventional synthetic methods, suffer from long reaction times, harsh conditions, and low yields. Microwave-assisted organic synthesis, which was first reported by Gedye *et al.* and Giguere *et al.* in 1986^{23,24}, can be used to increase product yields and dramatically reduce reaction times compared to those of conventional synthetic methods^{25,26}. Therefore, we wondered whether microwave-assisted intramolecular difunctionalization could be used to construct 2,3-fused indoles efficiently.

Results

To evaluate this possibility, we initially carried out the reaction of *o*-alkynylaniline **1a** and benzaldehyde (2 equiv) with 10 mol% Sc(OTf)₃ as a catalyst in 1,2-dichloroethane for 1.5 h at 80 °C at a microwave power of 100 W. These reaction conditions yielded indole **3aa'** as the sole product in 10% yield (Table 1, entry 1), and bicyclization product **3aa** was still not obtained when In(OTf)₃ or Cu(OAc)₂ was used

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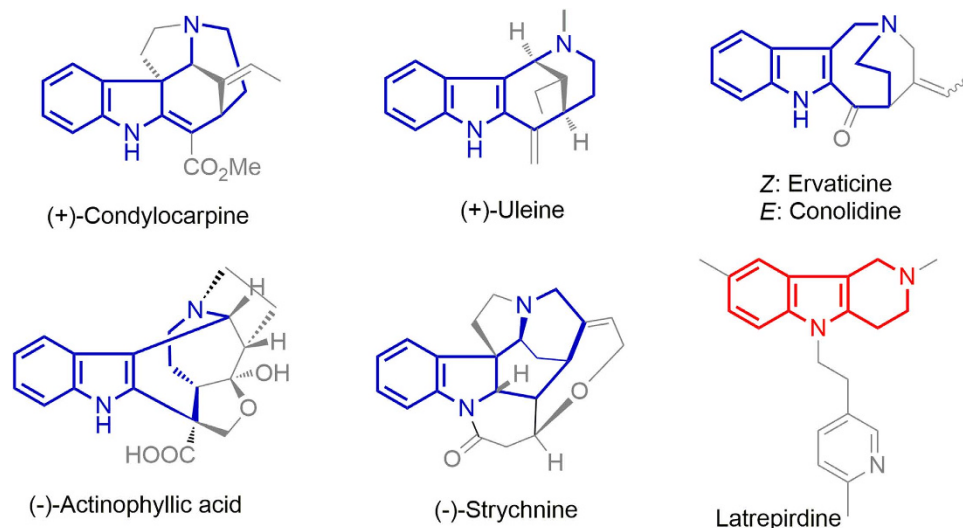


Figure 1. Representative compounds with 2,3-fused indole motifs.

Entry	Catalyst	Solvent	T (°C)	t (h)	3aa Yield (%) ²	3aa' Yield (%) ²
1	Sc(OTf) ₃	DCE	80	1.5	0	10
2	In(OTf) ₃	DCE	80	1.5	0	10
3	Cu(OAc) ₂	DCE	80	1.5	0	40
4	AgSbF₆	DCE	80	1.5	94	0
5	AgSbF ₆	1,4-dioxane	80	1.5	0	65
6	AgSbF ₆	acetonitrile	80	1.5	0	30
7	AgSbF ₆	toluene	80	1.5	54	46
8	AgSbF ₆	DCE	60	1.5	50	50
9	AgSbF ₆	DCE	80	0.5	0	95
10	AgOTf	DCE	80	1.5	70	20
11	AgOAc	DCE	80	1.5	0	0
12	AgBF ₄	DCE	80	1.5	30	60
13 ^c	AgSbF ₆	DCE	80	36	86	5

Table 1. Optimization of reaction conditions^a. ^aThe reaction was conducted with **1a** (1 equiv) and **2a** (1.2 equiv) in the presence of catalyst (10 mol%) under microwave conditions in 1,2-dichloroethane (DCE) for 1–3 h at 80 °C, unless otherwise stated. Ts = 4-methylphenylsulfonyl. ^bThe yields given are isolated yields. ^cThis reaction was conducted without microwave assistance.

instead of Sc(OTf)₃ (entries 2 and 3). However, **3aa** was obtained in 94% yield when AgSbF₆ was used as the catalyst (entry 4). The nature of the solvent greatly influenced the outcome of the reaction. No **3aa** formed when the solvent was 1,4-dioxane or acetonitrile, and the yield was only 54% in toluene (entries 5–7, respectively). Neither lowering the reaction temperature (entry 8) nor shortening the reaction time (entry 9) provided any benefit. Other silver(I) catalysts gave no better results than AgSbF₆ (entries 10–12), and in the absence of microwaves, more than 30 h was required to give **3aa** in 86% yield (entry 13). These preliminary results indicated that the optimal reaction conditions were as follows: 10 mol% AgSbF₆ in 1,2-dichloroethane at 80 °C (entry 4). This reaction exhibited excellent chemoselectivity: no ring-fused 1,2-dihydroquinoline **3aa''** was obtained²⁷.

We then used the optimal conditions to investigate the substrate scope of the reaction (Fig. 2). First, we carried out reactions of **1a** with various substituted benzaldehydes (**2a–2i**). The corresponding

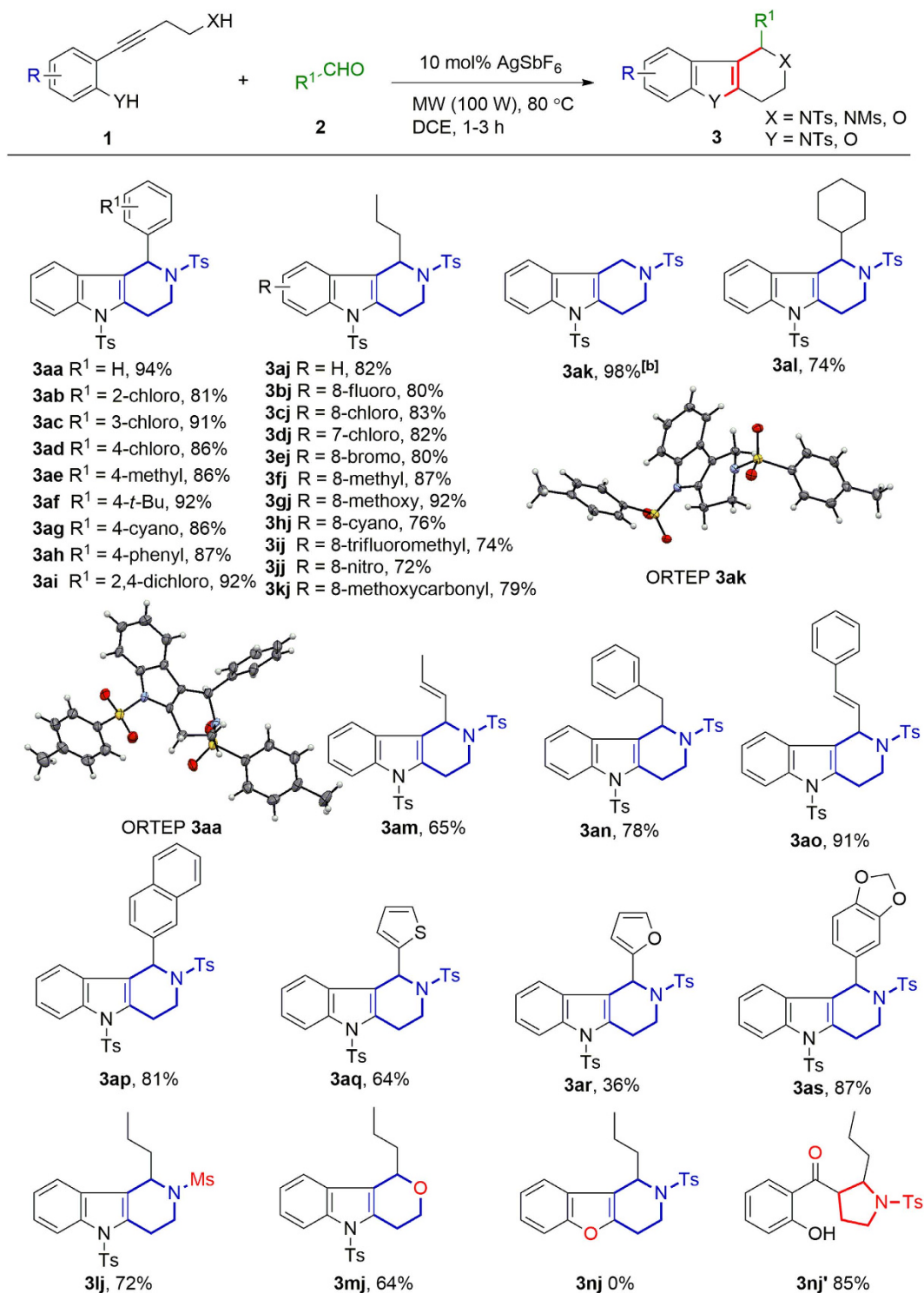


Figure 2. Synthesis of tetrahydro-1H-pyrido[4,3-*b*]indole and tetrahydropyrano[4,3-*b*]indole by intramolecular difunctionalization^[a]. ^[a]The yields given are isolated yields. DCE = 1,2-dichloroethane, Ts = 4-methylphenylsulfonyl, Ms = methanesulfonyl, MW = microwave. ^[b]The reaction was conducted with **1a** (1 equiv) in the presence of AgSbF₆ (10 mol%) in DCE at a MW power of 100 W for 1 h at 80 °C. Then **2k** (2 equiv) and CF₃COOH (1.5 equiv) were added, and the mixture was reacted under the same conditions for 3 h.

difunctionalization products (**3aa–3ai**) were obtained in more than 80% yield, indicating that neither the position nor the electronic properties of the substituents had a marked effect on the reaction outcome. We evaluated the electronic effects of substituents (R) on the benzene ring of **1** by carrying out

reactions of **1a–1k** with **2j**. Substrates with no substituents, a weakly electron-withdrawing substituent (**1a–1e**), or an electron-donating substituent (**1f–1g**) afforded desired compounds **3aj–3gj** in more than 80% yield. Substrates with a strongly electron-withdrawing group, such as a cyano, trifluoromethyl, nitro, or methoxycarbonyl group, could also be converted to the desired products (**3hj–3kj**), albeit in slightly lower yields. Difunctionalization products **3ak–3ao** were obtained in moderate to good yields when **1a** was allowed to react with aliphatic aldehydes **2k–2o**, and the structures of **3aa** and **3ak** were confirmed by X-ray diffraction analysis²⁸. Substrate **1a** reacted with aromatic aldehydes 2-naphthaldehyde (**3ap**, 81%), thiophene-2-carbaldehyde (**3aq**, 64%), furan-2-carbaldehyde (**3ar**, 36%), and piperonyl aldehyde (**3as**, 87%).

We also evaluated various nucleophilic moieties. The reaction worked well when the methylphenylsulfonyl group (XH = NHTs) was changed to a methanesulfonyl group (**3lj**, 72%), and tetrahydropyrano[4,3-*b*]indole (**3mj**) was obtained in 64% when XH was OH rather than NHTs. However, when YH was OH, intramolecular difunctionalization product **3nj** was not obtained, owing to the poor nucleophilicity of the phenolic hydroxyl group; instead, 5-*endo-trig* product **3nj'** resulting from a reaction in which water acted as a nucleophile was the sole product.

We also investigated ring-closure reactions to form ring systems of various sizes (Fig. 3). Substrate **1o** ($n = 1$) reacted both with aromatic aldehydes (**2a**, **2d**, **2e**, and **2q**) and with aliphatic aldehydes (**2j**, **2l**, and **2n**) to afford the corresponding hexahydro-1*H*-azocino[4,3-*b*]indoles. We investigated both a one-pot method (Method A) and a stepwise method (Method B) and found that the latter gave higher yields. When CF₃COOH was added to the reaction mixture (Method C), indoles fused to seven- to nine-membered-rings (**3ok**, **3pk**, and **3ql**) were obtained; **3pk** (hexahydro-1*H*-azocino[4,3-*b*]indole) is the core skeleton of many natural products (Fig. 1). The structures of **3pk** and **3oq** were confirmed by X-ray diffraction analysis²⁸.

Plausible pathways for the difunctionalization reactions between *n*-butanal and **1a** (YH = NHTs) and **1n** (YH = OH) are depicted in Fig. 4a. Pathway **1** involves initial closure of the B ring to form **3aa'** via an AgSbF₆-catalysed hydroamination reaction. Subsequently, AgSbF₆ promotes the formation of imine **A**²⁹, which is further transformed to target compound **3aj** via a 6-*endo-trig* cyclization. In this pathway, AgSbF₆ catalyses both the hydroamination step and the formation of imine **A**. In pathway 2, an initial AgSbF₆-catalysed imination reaction results in the formation of imine **B**, which can undergo two possible cyclizations: (1) 6-*endo-trig* cyclization leading to intermediate **C**, which can then be transformed to **3aj** or (2) 5-*endo-trig* cyclization (when YH = OH) leading to intermediate **D**, which can afford pyrrolidine **3nj'** by means of the addition of water. A third reaction pathway, leading to ring-fused 1,2-dihydroquinoline **3aa''** via 5-*endo-dig* cyclization, is also possible; however, no **3aa''** was obtained from the reaction.

To determine which of these pathways occurred under our reaction conditions, we monitored the formation of **3aj** over time by means of ¹H NMR spectroscopy (Fig. 4b). The ¹H NMR spectrum of **1a** exhibited a triplet at $\delta = 2.61$ ppm and a quartet at $\delta = 3.17$ ppm. After 10 min of reaction under the optimal conditions (Table 1, entry 4), a new singlet ($\delta = 6.38$ ppm), attributable to the hydrogen at the 3-position of indole **3aa'** (Fig. 2a), was observed, along with a new triplet ($\delta = 3.22$ ppm) and a new quartet ($\delta = 3.38$ ppm), which are attributable to the two CH₂ protons of **3aa'**. Note also that at this stage, the triplet and quartet attributable to **1a** shifted from 2.61 and 3.17 ppm to 2.80 and 3.10 ppm, respectively, owing to the formation of a complex between **1a** and AgSbF₆. At 30 min, all of the complex had been transformed to **3aa'**. As the reaction progressed, the signals for **3aa'** disappeared gradually, and signals due to **3aj** appeared and increased in intensity. The reaction was almost complete after 60 min. These ¹H NMR spectroscopy results suggest that the intramolecular difunctionalization reaction of **1a** occurred via pathway **1** in Fig. 4a.

Because our intramolecular difunctionalization method efficiently gave hexahydro-1*H*-azocino[4,3-*b*]indole **3pk**, we used the method for the rapid formal synthesis of the natural products ervaticine and conolidine as follows (Fig. 5a). Reaction of 2-iodoaniline with Ts-protected hex-5-yn-1-amine gave the corresponding coupled product, which reacted with 4-methylbenzene-1-sulfonyl chloride to give **1p** in 72% yield for the two steps²⁷. Exposure of **1p** to the optimal difunctionalization reaction conditions afforded **3pk** in 73% yield. Removal of the *N*-tosyl group with sodium and naphthalene³⁰ followed by protection with Boc₂O provided **5pk** in 81% over two steps, and subsequent oxidation with SeO₂ afforded **6pk** (56% yield)³¹, which has been converted to ervaticine and conolidine as described previously³².

We also used our method for a formal synthesis of latrepirdine as follows (Fig. 5b). Compound **1f** was obtained by Sonogashira coupling and subsequent protection of the primary amine with 4-methylbenzene-1-sulfonyl chloride in 67% yield for the two steps. Reaction between **1f** and formaldehyde by means of the method described for the synthesis of **3ak** (Fig. 2) gave **3fk** in 95% yield. Removal of the *N*-tosyl group³⁰ and subsequent reductive amination³³ afforded **5fk** (81% yield over two steps), which could be converted to latrepirdine as reported in the literature³⁴.

In summary, we developed a straightforward method for accessing various 2,3-fused indoles via microwave-assisted AgSbF₆-catalysed intramolecular difunctionalization of *o*-alkynylanilines. The reaction exhibited excellent chemoselectivity: no ring-fused 1,2-dihydroquinolines were formed. In addition to indoles fused to six-membered rings, indoles fused to saturated medium-sized *N*-containing rings could also be constructed. We used the method for efficient formal syntheses of the indole alkaloids ervaticine and conolidine and the antihistamine drug latrepirdine.

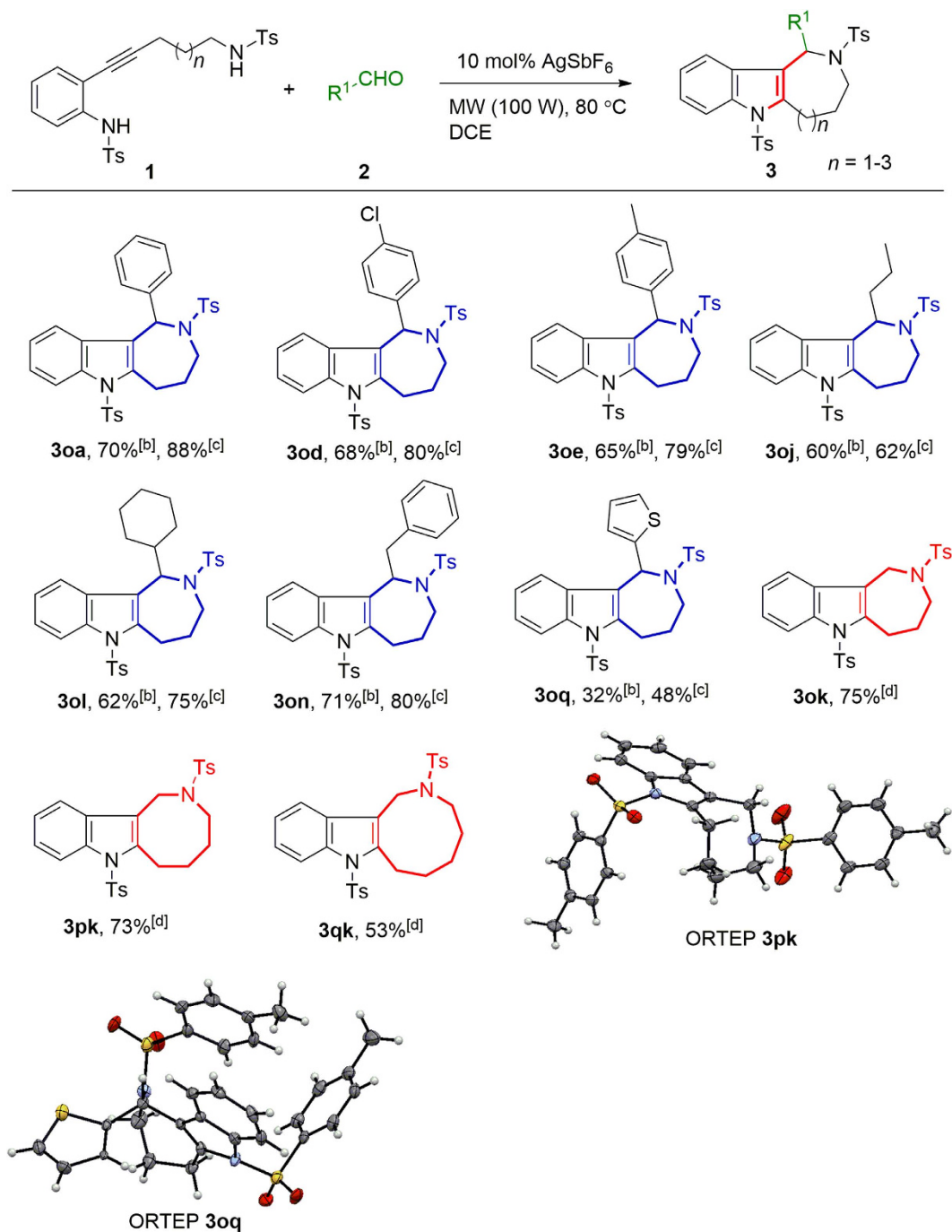


Figure 3. Synthesis of indoles fused to saturated medium-sized *N*-containing rings by means of intramolecular difunctionalization^[a]. ^[a]The yields given are isolated yields. DCE = 1,2-dichloroethane, MW = microwave. ^[b]Method A: The reaction was conducted with **1** (1 equiv) and **2** (2 equiv) in the presence of AgSbF_6 (10 mol%) at a MW power of 100 W in DCE for 6 h at 80 °C. ^[c]Method B: The reaction was conducted with **1** (1 equiv) in the presence of AgSbF_6 (10 mol%) at a MW power of 100 W in DCE for 3 h at 80 °C. Then **2** (2 equiv) was added, and the mixture was allowed to react under the same conditions for another 3 h. ^[d]Method C: Similar to method B, except that CF_3COOH (1.5 equiv) was added along with **2** (2 equiv) in the second step.

Methods

One-pot synthesis of 3aa. A microwave vessel was charged with *o*-alkynylaniline **1a** (98.5 mg, 0.21 mmol, 1 equiv), AgSbF_6 (7.1 mg, 0.021 mmol, 0.1 equiv), aldehyde **2a** (26.7 mg, 0.25 mmol, 1.2 equiv), and DCE (5.0 mL); and the mixture was heated at a microwave power of 100 W at 80 °C for 1.5 h. After the reaction mixture cooled to room temperature, CH_2Cl_2 (10 mL) and H_2O (10 mL) were added. The

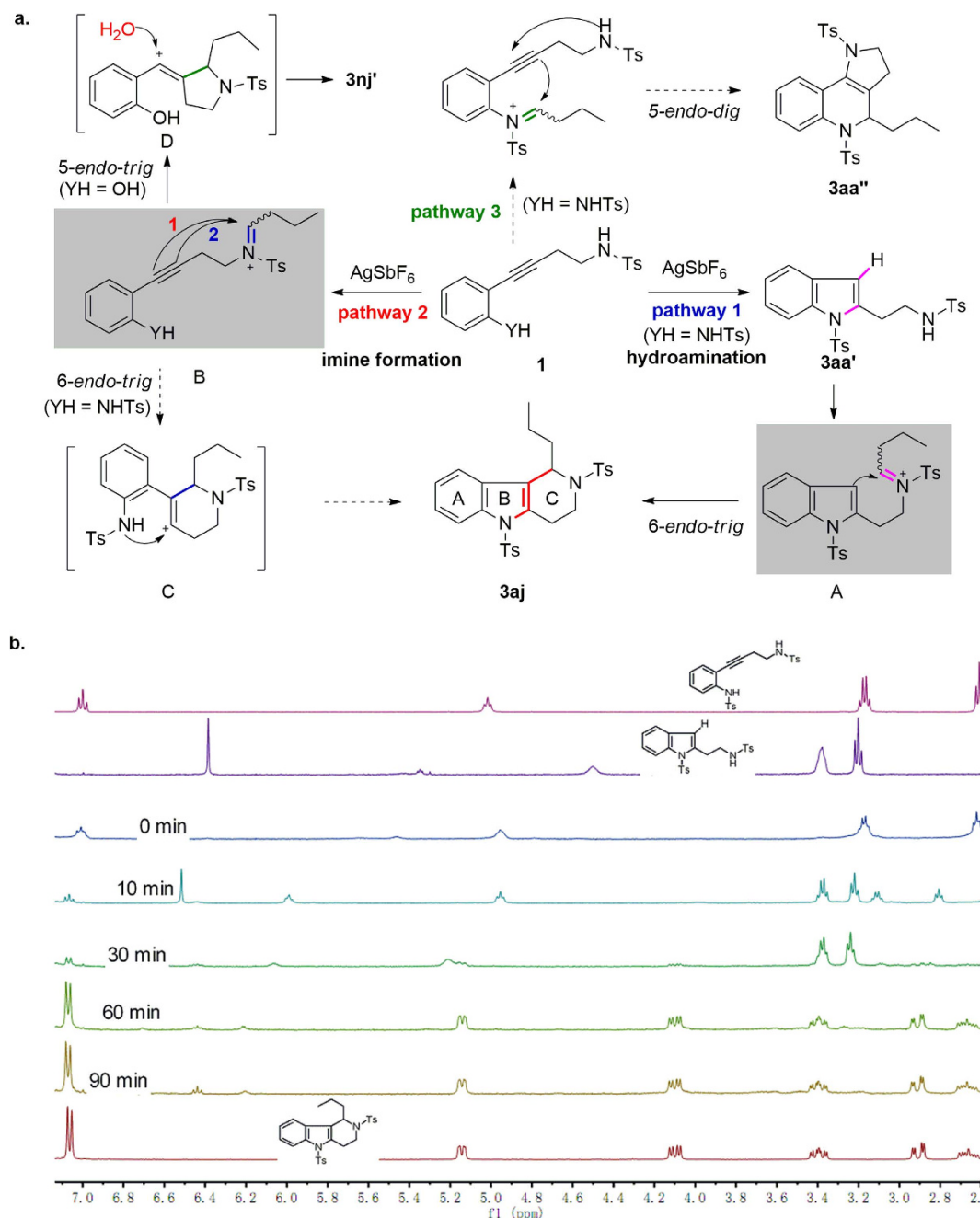


Figure 4. (a) Plausible reaction pathways and (b) time course of ^1H NMR spectra measured during synthesis of **3aj**.

organic layer was separated, dried over anhydrous Na_2SO_4 , and filtered. The filtrate was evaporated, and the residue was purified by silica gel chromatography with 10:1 (v/v) petroleum ether/ethyl acetate as the eluent to afford **30a** (110.0 mg, 94%) as a white solid (see Supplementary Information).

Stepwise synthesis of 3pk. A microwave vessel was charged with **1p** (100.0 mg, 0.20 mmol, 1 equiv), AgSbF_6 (6.8 mg, 0.02 mmol, 0.1 equiv), and DCE (5.0 mL) in that order; and the mixture was heated at a microwave power of 100 W at 80 °C for 3 h. Then **2k** (40% formaldehyde, 30.0 mg, 0.40 mmol, 2.0 equiv) and CF_3COOH (34.2 mg, 0.30 mmol, 1.5 equiv) were added, and the mixture was allowed to react under the same conditions for another 1 h. CH_2Cl_2 (10 mL) and H_2O (10 mL) were added to the resulting mixture. The organic layer was separated, dried over anhydrous Na_2SO_4 , and filtered. The filtrate was evaporated, and the residue was purified by silica gel chromatography with 10:1 (v/v) petroleum ether/ethyl acetate as the eluent to afford **3pk** (74.2 mg, 73%) as a white solid.

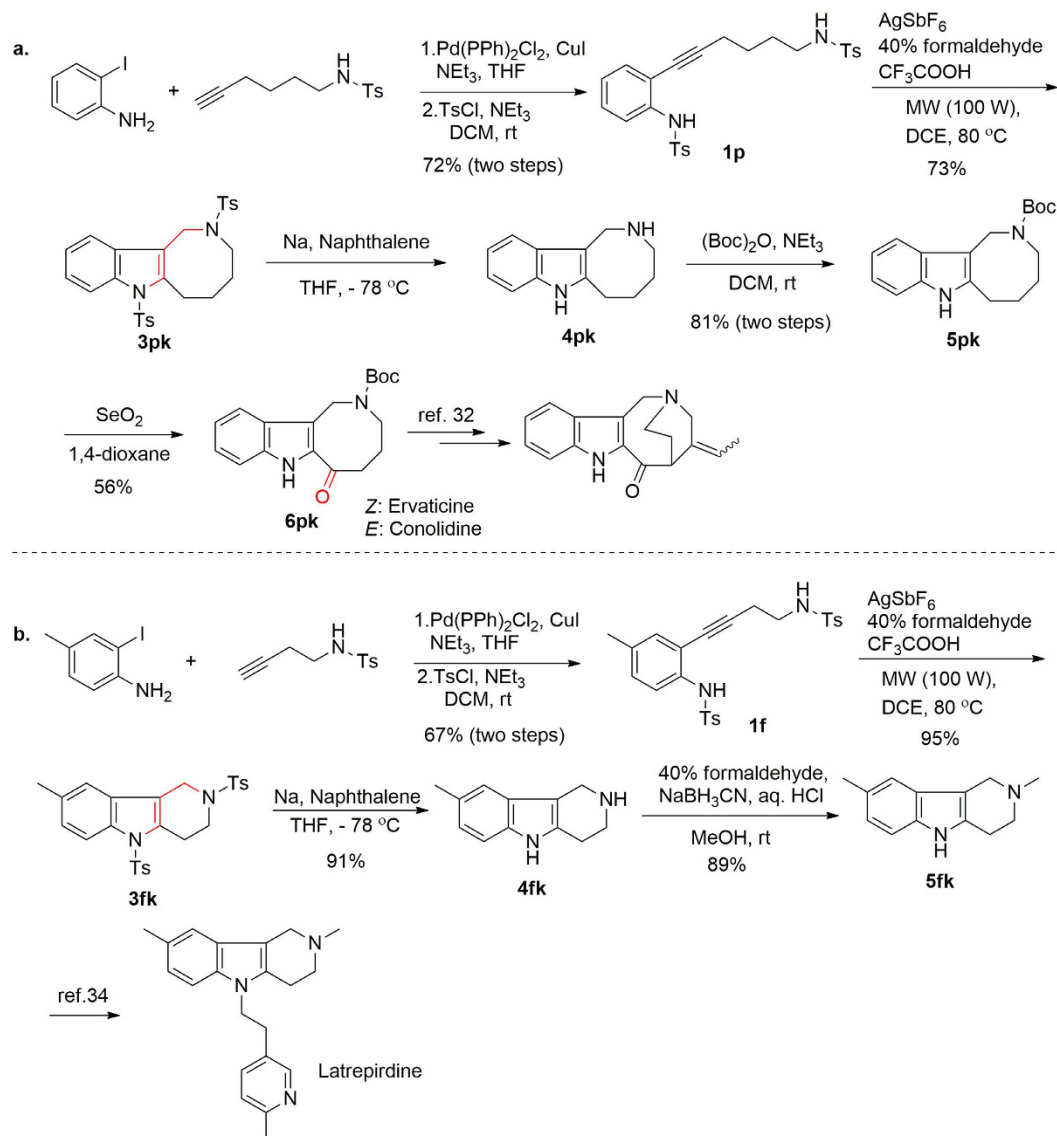


Figure 5. Formal syntheses of (a) ervaticine and conolidine and (b) latrepirdine.

References

- Inman, M. & Moody, C. J. Indole synthesis—something old, something new. *Chem. Sci.* **4**, 29–41 (2013).
- Cannon, J. S. & Overman, L. E. Is there no end to the total syntheses of strychnine? Lessons learned in strategy and tactics in total synthesis. *Angew. Chem. Int. Ed.* **51**, 4288–4311 (2012).
- Mercado-Marin, E. V. *et al.* Total synthesis and isolation of citrinalin and cyclopiamine congeners. *Nature* **509**, 318–324 (2014).
- Mizoguchi, H., Oikawa, H. & Oguri, H. Biogenetically inspired synthesis and skeletal diversification of indole alkaloids. *Nature Chem.* **6**, 57–64 (2014).
- Baran, P. S., Guerrero, C. A., Ambhaikar, N. B. & Hafenstein, B. D. Short, enantioselective total synthesis of stephacidin A. *Angew. Chem., Int. Ed.* **44**, 606–609 (2005).
- Ishikawa, H. *et al.* Total synthesis of vinblastine, vincristine, related natural products, and key structural analogues. *J. Am. Chem. Soc.* **131**, 4904–4916 (2009).
- Qin, H., Xu, Z. R., Cui, Y. X. & Jia, Y. X. Total synthesis of (±)-decursivine and (±)-serotobine: A Witkop photocyclization/elimination/O-Michael addition cascade approach. *Angew. Chem., Int. Ed.* **50**, 4447–4449 (2011).
- Bhat, V., Allan, K. M. & Rawal, V. H. Total synthesis of *N*-methylwelwitindolinone D isonitrile. *J. Am. Chem. Soc.* **133**, 5798–5801 (2011).
- Martin, C. L., Nakamura, S., Otte, R. & Overman, L. E. Total synthesis of (+)-condylocarpine, (+)-isocondylocarpine, and (+)-tubotaiwine. *Org. Lett.* **13**, 138–141 (2011).
- Büchi, G., Gould, S. J. & Näf, F. Stereospecific syntheses of uleine and epiuleine. *J. Am. Chem. Soc.* **93**, 2492–2501 (1971).
- Tarselli, M. A. *et al.* Synthesis of conolidine, a potent non-opioid analgesic for tonic and persistent pain. *Nature Chem.* **3**, 449–453 (2011).
- Martin, C. L., Overman, L. E. & Rohde, J. M. Total Synthesis of (±)- and (–)-actinophyllic acid. *J. Am. Chem. Soc.* **132**, 4894–906 (2010).
- Jones, S. B., Simmons, B., Mastracchio, A. & MacMillan, D. W. C. Collective synthesis of natural products by means of organocascade catalysis. *Nature* **475**, 183–188 (2011).
- Matveeva, I. A. Action of dimebon on histamine receptors. *Farmakologiya i Toksikologiya.* **46**, 27–29 (1983).

15. England, D. B. & Padwa, A. Gold-catalyzed cycloisomerization of *N*-propargylindole-2-carboxamides: application toward the synthesis of lavendamycin analogues. *Org. Lett.* **10**, 3631–3634 (2008).
16. Wang, L., Xie, X. & Liu, Y. H. Facile synthesis of fully substituted dihydro- β -carbolines via Brønsted acid promoted cascade reactions of α -indolyl propargylic alcohols with nitrones. *Org. Lett.* **14**, 5848–5851 (2012).
17. Pumphrey, A. L., Dong, H. J. & Driver, T. G. RhII-catalyzed synthesis of α -, β -, or δ -carbolines from aryl azides. *Angew. Chem., Int. Ed.* **51**, 5920–5923 (2012).
18. Xia, G. Q., Han, X. L. & Lu, X. Y. Pd(II)-Catalyzed one-step construction of cycloalkane-fused indoles and its application in formal synthesis of (\pm)-aspidospermidine. *Org. Lett.* **16**, 2058–2061 (2014).
19. Nissen, F., Richard, V., Alayrac, C. & Witulski, B. Synthesis of β - and γ -carbolines via ruthenium and rhodium catalysed [2+2+2] cycloadditions of yne-ynamides with methylcyanoformate. *Chem. Commun.* **47**, 6656–6658 (2011).
20. Yao, B., Wang, Q. & Zhu, J. P. Palladium(II)-catalyzed intramolecular diamination of alkynes under aerobic oxidative conditions: Catalytic turnover of an iodide ion. *Angew. Chem., Int. Ed.* **51**, 5170–5174 (2012).
21. Song, H. J., Liu, Y. X., Liu, Y. X. & Wang, Q. M. Self-induced stereoselective *in situ* trifluoromethylation: Preparation of spiro[indoline-3,3'-quinoline] via palladium-catalyzed cascade reaction. *Org. Lett.* **16**, 3240–3243 (2014).
22. Song, H. J., Liu, Y. X. & Wang, Q. M. Cascade electrophilic iodocyclization: Efficient preparation of 4-iodomethyl substituted tetrahydro- β -carbolines and formal synthesis of oxopropaline G. *Org. Lett.* **15**, 3274–3277 (2013).
23. Gedye, R. *et al.* The use of microwave ovens for rapid organic synthesis. *Tetrahedron Lett.* **27**, 279–282 (1986).
24. Giguere, R. J., Bray, T. L., Duncan, S. M. & Majetich, G. Application of commercial microwave ovens to organic synthesis. *Tetrahedron Lett.* **27**, 4945–4948 (1986).
25. Kingston, H. M. & Haswell, S. J. *Microwave-enhanced chemistry. Fundamentals, sample preparation and applications* (American Chemical Society, Washington, DC, 1997).
26. Gawande, M. B., Shelke, S. N., Zboril, R. & Varma, R. S. Microwave-assisted chemistry: synthetic applications for rapid assembly of nanomaterials and organics. *Acc. Chem. Res.* **47**, 1338–1348 (2014).
27. Zhu, C. & Ma, S. M. Sc(OTf)₃-catalyzed bicyclization of *o*-alkynylanilines with aldehydes: Ring-fused 1,2-dihydroquinolines. *Angew. Chem., Int. Ed.* **53**, 13532–13535 (2014).
28. CCDC 1402996 (**3aa**), 1402995 (**3ak**), 1402986 (**3pk**) and 1402998 (**3oq**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
29. When isolated **3aa'** was allowed to react with *n*-butanal under the optimal reaction condition but in the absence of AgSbF₆, no difunctionalization product was obtained.
30. Mori, M., Nakanishi, M., Kajishima, D. & Sato, Y. A novel and general synthetic pathway to strychnos indole alkaloids: Total syntheses of (–)-tubifoline, (–)-dehydrotubifoline, and (–)-strychnine using palladium-catalyzed asymmetric allylic substitution. *J. Am. Chem. Soc.* **125**, 9801–9807 (2003).
31. Bonjoch, J., Casamitjana, N., Gràcia, J. & Bosch, J. A stereoselective total synthesis of dasycarpidan alkaloids: (\pm)-dasycarpidone, (\pm)-dasycarpidol and (\pm)-nordasycarpidone. *J. Chem. Soc., Chem. Commun.* **1991**, 1687–1688 (1991).
32. Yu, J. M., Liao, X. B. & Cook, J. M. Stereospecific, enantiospecific total synthesis of the sarpagine indole alkaloids (*E*)-16-epiaffinisine, (*E*)-16-epinormacusine B, and dehydro-16-epiaffinisine. *Org. Lett.* **4**, 4681–4684 (2002).
33. Butler, K. V. *et al.* Rational design and simple chemistry yield a superior, neuroprotective HDAC6 inhibitor, tubastatin A. *J. Am. Chem. Soc.* **132**, 10842–10846 (2010).
34. Dong, H. J., Latka, R. T. & Drive, T. G. Ruthenium-catalyzed γ -carbolinium ion formation from aryl azides; synthesis of dimebolin. *Org. Lett.* **13**, 2726–2729 (2011).

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Author Contributions

Q.M.W. and H.J.S. conceived the concept and directed the project. Y.Q.H. and Y.Y. designed the synthetic route and performed all of the synthesis and standard characterization. The manuscript was co-written by H.J.S. and Y.X.L. All authors discussed the results and commented on the manuscript.

Additional Information

Supplementary information accompanies this paper at <http://www.nature.com/srep>

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