

I₂/TBHP-Catalyzed Chemoselective Amination of Indoles

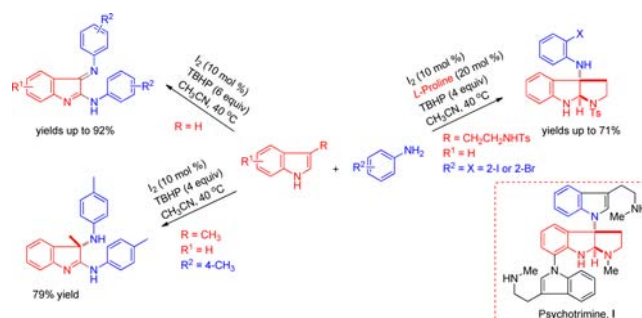
Zhong-Jian Cai, Shun-Yi Wang,* and Shun-Jun Ji*

Key Laboratory of Organic Synthesis of Jiangsu Province, College of Chemistry,
Chemical Engineering and Materials Science, Soochow University, Suzhou 215123, China

shunyi@suda.edu.cn; shunjun@suda.edu.cn

Received August 20, 2013

ABSTRACT



A novel I₂/TBHP-mediated direct oxidative diamination reaction of indoles with anilines was developed. The reaction proceeded smoothly under aqueous and open air reaction conditions. This protocol provides a practical synthetic method for the synthesis of Tryptanthrin and the construction of N–C3 linked pyrrolidinoindolines which is the core structure of Psychotrimine.

Indole is the core structure of many clinical drugs¹ and natural products,² which has attracted the exploration of

methods for direct indole functionalization.³ There are a series of reports on the direct C–C bond functionalization of indole derivatives;⁴ however, investigations on the direct C–N bond functionalization of indole derivatives remain rare,⁵ especially for direct diamination at the C2 and C3 positions in one step. The pyrrolidinoindolines are an important class of indole derivatives and widely exist in pharmacologically important compounds and natural products.⁶

(1) (a) Sundberg, R. J. *Indoles*; Academic: New York, 1996. (b) Katritzky, A. R.; Pozharskii, A. F. *Handbook of Heterocyclic Chemistry*; Pergamon Press: Oxford, 2000. (c) Takayama, H.; Tsutsumi, S. I.; Kitajima, M.; Santiarworn, D.; Liawruangrath, B.; Aimi, N. *Chem. Pharm. Bull.* **2003**, *51*, 232. (d) Humphrey, G. R.; Kuethe, J. T. *Chem. Rev.* **2006**, *106*, 2875.

(2) (a) Sundberg, R. J. In *Comprehensive Heterocyclic Chemistry II*; Katritzky, A. R., Rees, C. W., Scriven, E. F. V., Bird, C. W., Eds.; Pergamon Press: Oxford, U.K., 1996; Vol. 2, pp 119–206. (b) Gribble, G. W. In *Comprehensive Heterocyclic Chemistry II*; Katritzky, A. R., Rees, C. W., Scriven, E. F. V., Eds.; Pergamon: Oxford, 1996; Vol. 2, p 207. (c) Joule, J. A. In *Science of Synthesis—Houben–Weyl Methods of Molecular Transformations*; Thomas, E. J., Ed.; Thieme: Stuttgart, 2000; Vol. 10, p 361. (d) Somei, M.; Yamada, F. *Nat. Prod. Rep.* **2005**, *22*, 73. (e) Lebsack, A. D.; Link, J. T.; Overman, L. E.; Stearn, B. A. *J. Am. Chem. Soc.* **2002**, *124*, 9008. (f) Movassaghi, M.; Schmidt, M. A. *Angew. Chem., Int. Ed.* **2007**, *46*, 3725.

(3) (a) Cacchi, S.; Fabrizi, G. *Chem. Rev.* **2005**, *105*, 2873. (b) Seregin, I. V.; Gevorgyan, V. *Chem. Soc. Rev.* **2007**, *36*, 1173. (c) Bandini, M.; Eichholzer, A. *Angew. Chem., Int. Ed.* **2009**, *48*, 9608. (d) Shiri, M. *Chem. Rev.* **2012**, *112*, 3508. (e) Ball, C. J.; Willis, M. C. *Eur. J. Org. Chem.* **2013**, *425*.

(4) (a) Zhang, G. Z.; Catalano, V. J.; Zhang, L. M. *J. Am. Chem. Soc.* **2007**, *129*, 11358. (b) Nakamura, I.; Yamagishi, U.; Song, D.; Konta, S.; Yamamoto, Y. *Angew. Chem., Int. Ed.* **2007**, *46*, 2284. (c) Shen, M. H.; Leslie, B. E.; Driver, T. G. *Angew. Chem., Int. Ed.* **2008**, *47*, 1. (d) England, D. B.; Padwa, A. *Org. Lett.* **2008**, *10*, 3631. (e) Pathak, T. P.; Gligorich, K. M.; Welm, B. E.; Sigman, M. S. *J. Am. Chem. Soc.* **2010**, *132*, 7870. (f) Schipper, D. J.; Hutchinson, M.; Fagnou, K. *J. Am. Chem. Soc.* **2010**, *132*, 6910. (g) Ferrer, C.; Echavarren, A. M. *Angew. Chem., Int. Ed.* **2006**, *45*, 1105.

(5) (a) Shuai, Q.; Deng, G.; Chua, Z.; Bohle, D. S.; Li, C.-J. *Adv. Synth. Catal.* **2010**, *352*, 632. (b) Liu, X.-Y.; Gao, P.; Shen, Y.-W.; Liang, Y.-M. *Org. Lett.* **2011**, *13*, 4196. (c) Li, Y.-X.; Ji, K.-G.; Wang, H.-X.; Ali, S.; Liang, Y.-M. *J. Org. Chem.* **2011**, *76*, 744. (d) Li, Y.-X.; Wang, H.-X.; Ali, S.; Xia, X.-F.; Liang, Y.-M. *Chem. Commun.* **2012**, *48*, 2343. (e) Wu, W.-B.; Huang, J.-M. *Org. Lett.* **2012**, *14*, 5832. (f) Prasad, B.; Sreenivas, B. Y.; Rambabu, D.; Krishna, G. R.; Reddy, C. M.; Kumar, K. L.; Pal, M. *Chem. Commun.* **2013**, *49*, 3970. (g) Beaumont, S.; Pons, V.; Retailleau, P.; Dodd, R. H.; Dauban, P. *Angew. Chem., Int. Ed.* **2010**, *49*, 1634. (h) Benkovics, T.; Guzei, I. A.; Yoon, T. P. *Angew. Chem., Int. Ed.* **2010**, *49*, 9153.

(6) (a) Anthoni, U.; Christophersen, C.; Nielsen, P. H. Naturally Occurring Cyclotryptophans and Cyclotryptamines. In *Alkaloids: Chemical & Biological Perspectives*; Pelletier, S. W., Ed.; Pergamon: Oxford, U.K., 1999; Vol. 13, pp 163–236. (b) Julian, P. L.; Pikl, J. *J. Am. Chem. Soc.* **1933**, *55*, 2105. (c) Julian, P. L.; Pikl, J.; Boggess, D. *J. Am. Chem. Soc.* **1934**, *56*, 1797. (d) Julian, P. L.; Pikl, J. *J. Am. Chem. Soc.* **1935**, *57*, 755. (e) Cordell, G. A.; Saxton, J. E. In *The Alkaloids*, Vol. 20; Elsevier: Amsterdam, 1981, p 10. (f) Steven, A.; Overman, L. E. *Angew. Chem., Int. Ed.* **2007**, *46*, 5488. (g) Schmidt, M. A.; Movassaghi, M. *Synlett* **2008**, *313*. (h) Ruiz-Sanchis, P.; Savina, S. A.; Albericio, F.; Alvarez, M. *Chem.—Eur. J.* **2011**, *17*, 1388.

A wide variety of polymeric-tryptamine-related alkaloids containing two to eight pyrrolidinoindoline units show excellent biological activities, such as antifungal, antibacterial, antiviral,⁷ and analgesic properties.⁸ Most polymeric-tryptamine-related alkaloids are linked through C–C bonds to give oligomeric structures. Interestingly, a small amount of polypyrrolidinoindoline alkaloids with a N1–C3 linkage have been isolated in recent decades,

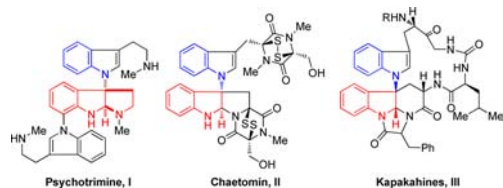


Figure 1. Selected polypyrrolidinoindoline alkaloids with the N1–C3 linkage.

which exhibit fascinating structures and biological functions (Figure 1).⁹ For example, Psychotrimine (Figure 1, I), which had been totally synthesized by Takayama's and Baran's groups independently in 2008, exhibits potent activity against colon and lung cancers.¹⁰ The direct diamination at the C2 and C3 positions of indole was treated as the key

(7) Saad, H. A.; El-Sharkawy, S. H.; Shier, W. T. *Planta Med.* **1995**, *61*, 313.

(8) (a) Amador, T. A.; Verrota, L.; Nunes, D. S.; Elisabetsky, E. *Planta Med.* **2000**, *66*, 770. (b) Verrota, L.; Orsini, F.; Sbacci, M.; Scheidler, M. A.; Amador, T. A.; Elisabetsky, E. *Bioorg. Med. Chem.* **2002**, *10*, 2133. (c) Kodanko, J. J.; Hiebert, S.; Peterson, E. A.; Sung, L.; Overman, L. E.; Linck, V. M.; Goerck, G. C.; Amador, T. A.; Leal, M. B.; Elisabetsky, E. *J. Org. Chem.* **2007**, *72*, 7909. (d) Sanz-Biset, J.; Campos-de-la-Cruz, J.; Epiquién-Rivera, M. A.; Cannigueral, S. *J. Ethnopharmacol.* **2009**, *122*, 333.

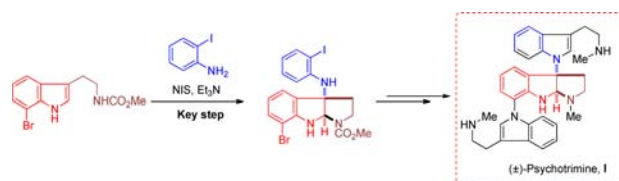
(9) (a) Brewer, D.; McInnes, A. G.; Smith, D. G.; Taylor, A.; Walter, J. A.; Loosli, H. R.; Kis, Z. L. *J. Chem. Soc., Perkin Trans. 1* **1978**, *10*, 1248. (b) McInnes, A. G.; Taylor, A.; Walter, J. A. *J. Am. Chem. Soc.* **1976**, *98*, 6741. (c) Kung, A. L.; Zabudoff, S. D.; France, D. S.; Freedman, S. J.; Tanner, E. A.; Vieira, A.; Cornell-Kennon, S.; Lee, J.; Wang, B.; Wang, J.; Memmert, J.; Naegeli, H.-U.; Petersen, F.; Eck, M. J.; Bair, K. W.; Wood, A. W.; Livingston, D. M. *Cancer Cell* **2004**, *6*, 33. (d) Masashi, H.; Mitsuyoshi, S.; Hiroshi, M.; Yuji, S. *Tennen Yuki Kagobutsu Toronkai Koen Yoshishu* **1994**, *36*, 557. (e) Nakao, Y.; Yeung, B. K. S.; Yoshida, W. Y.; Scheuer, P. J.; Kelly-Borges, M. *J. Am. Chem. Soc.* **1995**, *117*, 8271. (f) Nakao, Y.; Kuo, J.; Yoshida, W. Y.; Kelly, M.; Scheuer, P. J. *Org. Lett.* **2003**, *5*, 1387. (g) Li, G.-Y.; Li, B.-G.; Yang, T.; Yan, J.-F.; Liu, G.-Y.; Zhang, G.-L. *J. Nat. Prod.* **2006**, *69*, 1374. (h) Ding, G.; Jiang, L.; Guo, L.; Chen, X.; Zhang, H.; Che, Y. *J. Nat. Prod.* **2008**, *71*, 1861.

(10) (a) Matsuda, Y.; Kitajima, M.; Takayama, H. *Org. Lett.* **2008**, *10*, 125. (b) Newhouse, T.; Baran, P. S. *J. Am. Chem. Soc.* **2008**, *130*, 10886. (c) Newhouse, T.; Lewis, C. A.; Eastman, K. J.; Baran, P. S. *J. Am. Chem. Soc.* **2010**, *132*, 7119. (d) Foo, K.; Newhouse, T.; Mori, I.; Takayama, H.; Baran, P. S. *Angew. Chem., Int. Ed.* **2011**, *50*, 2716. (e) Takayama, H.; Mori, I.; Kitajima, M.; Aimi, N.; Lajis, N. H. *Org. Lett.* **2004**, *6*, 2945.

(11) (a) Delord, W. J.; Droge, T.; Liu, F.; Glorius, F. *Chem. Soc. Rev.* **2011**, *40*, 4740. (b) Colby, D. A.; Bergman, R. G.; Ellman, J. A. *Chem. Rev.* **2010**, *110*, 624. (c) Armstrong, A.; Collins, J. C. *Angew. Chem., Int. Ed.* **2010**, *49*, 2282. (d) Cho, S. H.; Kim, J. Y.; Kwak, J.; Chang, S. *Chem. Soc. Rev.* **2011**, *40*, 5068. (e) Surry, D. S.; Buchwald, S. L. *Angew. Chem., Int. Ed.* **2008**, *47*, 6338. (f) Hartwig, J. F. *Acc. Chem. Res.* **2008**, *41*, 1534. (g) Ma, D.; Zhang, Y.; Yao, J.; Wu, S.; Tao, F. *J. Am. Chem. Soc.* **1998**, *120*, 12459. (h) Ullmann, F. *Ber. Dtsch. chem. Ges.* **1903**, *36*, 2382. (i) Lam, P. Y. S.; Deudon, S.; Averill, K. M.; Li, R.; He, M. Y.; DeShong, P.; Clark, C. G. *J. Am. Chem. Soc.* **2000**, *122*, 7600. (j) Rao, H.; Fu, H.; Jiang, Y.; Zhao, Y. *Angew. Chem., Int. Ed.* **2009**, *48*, 1114. (k) Armstrong, A.; Collins, J. C. *Angew. Chem., Int. Ed.* **2010**, *49*, 2282.

step in the total synthesis of Psychotrimine reported by Baran (Scheme 1),^{10b} which inspired us to explore new methods for the direct diamination of nonactivated indoles. Most synthetic strategies for the direct C–N bond formations are based on transition-metal catalysis because they are straightforward, efficient, convenient, and highly selected.¹¹ However, the transition-metal-catalyzed direct oxidative aminations have many drawbacks such as the toxicity of catalysts, expensive transition metals or ligands, production of heavy metal byproducts, and requiring harsh reaction conditions. Therefore, it is an interesting challenge to develop a metal-free method from the environmental and economical

Scheme 1. Baran's Synthesis of Psychotrimine



standpoints. Metal-free catalyzed direct amination has attracted intensive attention from both academic and industrial communities, because of the visible advantages of lower cost, less waste, and milder conditions.¹² Herein, we report a novel I₂/TBHP-mediated¹³ intramolecular oxidative diamination of indoles with anilines, which provides an efficient way to construct N–C3 linked pyrrolidinoindolines with high diastereoselectivities under mild conditions.

We started by studying the reaction of 1.0 mmol indole (**1a**) with 3.0 mmol *p*-toluidine (**2a**) in the presence of 6.0 mmol of TBHP (*tert*-butyl hydroperoxide, 70% in water) as the oxidant and 10 mol % of iodine as the catalyst. When the reaction was stirred in CH₃CN (2 mL) at rt for 6 h, *N*-(*p*-tolyl)-3-(*p*-tolylimino)-3*H*-indol-2-amine (**3a**) was obtained in 70% LC-yield (Table 1, entry 1). The structure of **3a** was further confirmed by single-crystal X-ray analysis. To our delight, when the ratio of **1a**:**2a** was changed from 1:3 to 1:4, the yield of the desired product **3a** could increase to 80% (Table 1, entry 2). We next scrutinized the catalyst dosage, which suggested that 10 mol % of iodine could achieve a satisfied result (Table 1, entries 3–4). When the reaction time was prolonged, a similar yield was detected

(12) (a) Joseph, J.; Kim, Y. J.; Chang, S. *Chem.—Eur. J.* **2011**, *17*, 8294. (b) Froehr, T.; Sindlinger, C. P.; Kloeckner, U.; Finkbeiner, P.; Nachtsheim, B. J. *Org. Lett.* **2011**, *13*, 3754. (c) Kim, H. J.; Kim, J.; Cho, S. H.; Chang, S. *J. Am. Chem. Soc.* **2011**, *133*, 16382. (d) Souto, J. A.; Zian, D.; Muniz, K. *J. Am. Chem. Soc.* **2012**, *134*, 7242. (e) Uyanik, M.; Okamoto, H.; Yasui, T.; Ishihara, K. *Science* **2010**, *328*, 1376. (f) Uyanik, M.; Suzuki, D.; Yasui, T.; Ishihara, K. *Angew. Chem., Int. Ed.* **2011**, *50*, 5331. (g) Uyanik, M.; Ishihara, K. *ChemCatChem* **2012**, *4*, 177. (h) Zhang, J. T.; Zhu, D. P.; Yu, C. M.; Wan, C. F.; Wang, Z. Y. *Org. Lett.* **2010**, *12*, 2841. (i) Yan, Y. Z.; Xu, K.; Fang, Y.; Wang, Z. Y. *J. Org. Chem.* **2011**, *76*, 6849. (j) Liu, Z. J.; Zhang, J.; Chen, S. L.; Shi, E. B.; Xu, Y.; Wan, X. B. *Angew. Chem., Int. Ed.* **2012**, *51*, 3231.

(13) (a) Xu, K.; Hu, Y. B.; Zhang, S.; Zha, Z. G.; Wang, Z. Y. *Chem.—Eur. J.* **2012**, *18*, 9793. (b) Wu, Y. Z.; Wang, Z. Y. *Chem. Commun.* **2011**, *47*, 9513. (c) Laman, M.; Prabhu, K. R. *J. Org. Chem.* **2011**, *76*, 7938. (d) Zhang, J. T.; Zhu, D. P.; Yu, C. M.; Wan, C. F.; Wang, Z. Y. *Org. Lett.* **2010**, *12*, 2841. (e) Wan, C. F.; Gao, L. F.; Wang, Q.; Zhang, J. T.; Wang, Z. Y. *Org. Lett.* **2010**, *12*, 3902.

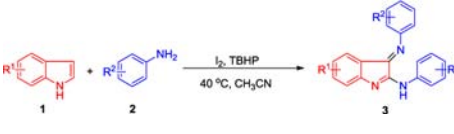
Table 1. Optimization of the Reaction Conditions^a


entry	1a:2a	I ₂ (mol %)	time (h)	solvent (2 mL)	temp (°C)	yield (%) ^a
1	1:3	(10)	6	CH ₃ CN	25	70
2	1:4	(10)	6	CH ₃ CN	25	80
3	1:4	(20)	6	CH ₃ CN	25	80
4	1:4	(5)	6	CH ₃ CN	25	56
5	1:4	(10)	8	CH ₃ CN	25	76
6	1:4	(10)	6	CH ₃ NO ₂	25	80
7	1:4	(10)	6	Tol.	25	78
8	1:4	(10)	6	EtOH	25	74
9	1:4	(10)	6	DMSO	25	13
10	1:4	(10)	6	DMF	25	34
11	1:4	(10)	6	CH ₃ CN	40	85(81) ^b

^a Reaction conditions: **1a** (1 mmol), TBHP (70% in water), solvent (2 mL); the yields were determined by LC analysis using biphenyl as the internal standard. ^b Isolated yield.

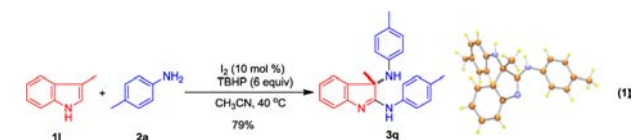
(Table 1, entry 5). Further optimization studies with a variety of solvents such as CH₃NO₂, toluene, and EtOH resulted in good yields (Table 1, entries 6–8). However, when the reaction was treated with DMF or DMSO, poor yields were obtained (Table 1, entries 9 and 10). To increase the reaction yields, we further screened different reaction temperatures. It was found that when the reaction was treated at 40 °C, the desired product **3a** could be produced in 85% LC-yield and 81% isolated yield (Table 1, entry 11). After optimization, optimal reaction conditions were confirmed: 10 mol % iodine as the catalyst, 6.0 equiv of TBHP as the oxidant, CH₃CN as the reaction solvent, and a reaction temperature of 40 °C.

With the optimal reaction conditions in hand, we next investigated the substrate scope of the direct oxidative diamination reactions (Table 2). Various substituted indoles (**1a–j**) were reacted with *p*-toluidine (**2a**) to give the corresponding *N*-phenyl-3-(phenylimino)-3*H*-indol-2-amines (**3a–j**) in good to excellent yields. Substituents on the different positions of the phenyl ring of indoles did not affect the reaction. The halogen-containing indoles could also furnish the desired products in excellent yields under the identical reaction conditions, which offer possibilities for further functionalizations (Table 2, entries 4–5 and 7–9). Unfortunately, when 5-nitro-1*H*-indole (**3k**) bearing a strong electron-withdrawing group was treated to this transformation, only trace product was detected (Table 2, entry 11). Reactions of a variety of substituted anilines **2** with indole **1a** were also surveyed. It was found that substrates **2c** and **2d** possessing the –OCH₃ and –OC₂H₅ substituent at the 4-position of the aryl ring provided the desired products **3m** and **3n** in 84% and 60% yields, respectively (Table 2, entries 13 and 14). However, when 4-bromoaniline was subjected to the reaction, the yield of

Table 2. Reactions with Various Indoles and Anilines^a


entry	R ¹	R ²	product	yield (%) ^a
1	H (1a)	4-CH ₃ (2a)	3a	81
2	5-CH ₃ (1b)	4-CH ₃	3b	90
3	5-OCH ₃ (1c)	4-CH ₃	3c	83
4	5-F (1d)	4-CH ₃	3d	89
5	5-Br (1e)	4-CH ₃	3e	85
6	6-CH ₃ (1f)	4-CH ₃	3f	92
7	6-F (1g)	4-CH ₃	3g	91
8	6-Cl (1h)	4-CH ₃	3h	85
9	6-Br (1i)	4-CH ₃	3i	85
10	7-CH ₃ (1j)	4-CH ₃	3j	91
11	5-NO ₂ (1k)	4-CH ₃	3k	trace
12	H (1a)	H (2b)	3l	51
13	H	4-OCH ₃ (2c)	3m	84
14	H	4-OC ₂ H ₅ (2d)	3n	60
15	H	4- <i>t</i> -Bu (2e)	3o	71
16	H	4-Br (2f)	3p	34

^a Reaction conditions: **1** (1 mmol), **2** (4 mmol), I₂ (0.1 mmol), TBHP (70% in water) (6 mmol), solvent (2 mL), 40 °C, 6 h.

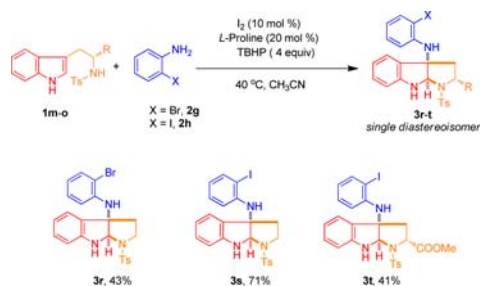
Scheme 2. Reaction of **1l** with **2a**

the desired product **3p** was decreased to 34% (Table 2, entry 15).

When 3-methyl-1*H*-indole **1l** was applied to this reaction instead of **1a** under the optimized reaction conditions, the diamination product **3q** with a single N–C3 bond could also be obtained in 79% yield (Scheme 2, eq 1). This promising result suggested the possibility of constructing N–C3 linked pyrrolidinoindolines in one step under similar reaction conditions.

Herein, *N*-(2-(1*H*-indol-3-yl)ethyl)-4-methylbenzenesulfonamide (**1m**) was treated with 2-bromoaniline (**2g**) under the optimized reaction conditions. However, the desired product **3r** could only be obtained in a poor yield. In order to improve the yield of **3r**, we further screened some additives such as Lewis acids and amino acids. Fortunately, the yield could be increased to 43% when 20 mol % L-proline was added as the additive, and only a single diastereoisomer was observed. The structure of **3r** was further confirmed by X-ray analysis (Scheme 3). When 2-iodoaniline **2h** instead of **2g** was subjected to the reaction with **1m** in the presence of 20 mol % L-proline, the desired

Scheme 3. Construction of N–C3 Linked Pyrrolidinoindolines^a



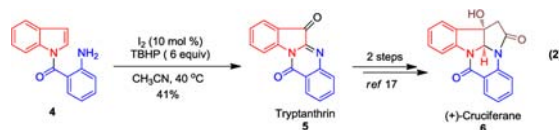
^a Reaction conditions: **3m–o** (0.5 mmol), **2g–h** (1 mmol), I_2 (0.05 mmol), L-proline (0.1 mmol), TBHP (70% in water) (2 mmol), solvent (2 mL), 40 °C, 24 h.

pyrrolidinoindoline **3s** could be obtained in 71% yield. Furthermore, the optically active **3t** could be formed in 43% yield as a single diastereoisomer by the reaction of (*R*)-methyl 3-(1*H*-indol-3-yl)-2-(4-methylphenylsulfonamido)-propanoate **1o** with **2h** under identical reaction conditions (Scheme 3).

In order to explore the possibility of intramolecular amination of indole, we further explored the reaction of (2-aminophenyl)(1*H*-indol-1-yl)methanone **4** under the I_2 /TBHP conditions. To our delight, the reaction proceeded smoothly to furnish the corresponding product Tryptanthrin **5** in 41% yield (Scheme 4, eq 2), which is an interesting synthetic target¹⁴ and exhibits remarkable pharmacological and biological activity against cancer cells.¹⁵ In addition, alkaloid (+)-Cruciferane **6**, which possesses a wide array of biological properties,^{6h,16} could be synthesized from Tryptanthrin **5** over two steps.¹⁷

In conclusion, we have developed a metal-free direct oxidative diamination reaction of indoles with anilines under

Scheme 4. Intramolecular Amination of **4**



mild conditions. This transformation displays many advantages, such as use of aqueous solvent and being air-tolerant, inexpensive, less toxic, and environmentally benign. This protocol provides a practical synthetic method for the construction of 3-amido-substituted pyrrolidinoindolines which can be treated as precursors of Psychotrimine. Meanwhile, this reaction is applicable to the synthesis of Tryptanthrin which is found in many kinds of plants. Further investigations are ongoing in our laboratory to understand the mechanism of this reaction and to apply it to other organic reactions.

Acknowledgment. We gratefully acknowledge the Natural Science Foundation of China (No. 21172162), the Young National Natural Science Foundation of China (No. 21202111), the Young Natural Science Foundation of Jiangsu Province (BK2012174), PAPD, and Soochow University for financial support.

Note Added after ASAP Publication. In the version published ASAP September 12, 2013 there were errors in the structures of natural psychotrimine and compound **3t**. The abstract graphic, Figure 1, Scheme 1, and Scheme 3 have been revised to show the correct structures and reposted September 17, 2013.

Supporting Information Available. Experimental procedures; CIF files for **3a**, **3q**, **3r**, and **3t**; and full spectroscopic data for all new compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

(17) (a) Vaidya, S. D.; Argade, N. P. *Org. Lett.* **2013**, *15*, 4006. (b) Gahtory, D.; Chouhan, M.; Sharma, R.; Nair, V. A. *Org. Lett.* **2013**, *15*, 3942.

The authors declare no competing financial interest.

(14) (a) Wang, C.; Zhang, L. P.; Ren, A. N.; Lu, P.; Wang, Y. G. *Org. Lett.* **2013**, *15*, 2982. (b) Lee, E. S.; Park, J. G.; Jahng, Y. *Tetrahedron Lett.* **2003**, *44*, 1883. (c) Batanero, B.; Barba, F. *Tetrahedron Lett.* **2006**, *47*, 8201.

(15) Jao, C. W.; Lin, W. C.; Wu, Y. T.; Wu, P. L. *J. Nat. Prod.* **2008**, *71*, 1275.

(16) (a) Shoji, N.; Umeyama, A.; Saito, N.; Arihara, S. *J. Nat. Prod.* **1989**, *52*, 1160. (b) Chen, M.; Gan, L.; Lin, S.; Wang, X.; Li, L.; Li, Y.; Zhu, C.; Wang, Y.; Jiang, B.; Jiang, J.; Yang, Y.; Shi, J. *J. Nat. Prod.* **2012**, *75*, 1167.