ACES Asian Chemical Editorial Society

DOI: 10.1002/asia.201600013

CHEMISTRY AN ASIAN JOURNAL Communication

Asymmetric Synthesis

Hydrogen-Bonding Network Promoted [3+2] Cycloaddition: Asymmetric Catalytic Construction of Spiro-pseudoindoxyl Derivatives

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Abstract: The enantioselective construction of a spirocyclic quaternary stereogenic carbon center at the C2 position of indole has long been an elusive problem in organic synthesis. Herein, by employing a rationally designed hydrogen-bonding network activation strategy, for the first time, 2,2′-pyrrolidinyl-spirooxindole, which is a valuable and prevalent indole alkaloid scaffold, was directly obtained through a catalytic asymmetric [3+2] cycloaddition reaction with high yields and excellent stereoselectivities.

The spiro-pseudoindoxyl scaffold has been found in a wide range of indole alkaloids.[1] In particular, as shown in Figure 1, some alkaloids incorporating a spiro ring fusion at the 2-position of the oxindole skeleton with a pyrrolidinyl moiety, such as mitragynine pseudoindoxyl,[2] fluorocurine,[3] diketopiperazine,[4] and rauniticine,[5] display important and diverse biological properties.[6] For instance, mitragynine pseudoindoxyl was found to have potent opioid agonistic activity, anti-viral and anti-cancer properties.[2,7] To date, the established approaches to spiro-pseudoindoxyl skeleton are mainly racemic syntheses and oxidative rearrangement of indole derivatives has been employed as the primary strategy to construct this structural unit.[2b,3b,8] Among these significant advances, Glorius and coworkers elegantly developed an enantioselective *N*-heterocyclic carbene (NHC)-catalyzed annulation of enals with azaaurones to synthesize spiro-pseudoindoxyl (Figure 2).[9] Considering the remarkable achievements in the construction of 3,3′-pyrrolidinyl-spirooxindole alkaloids that also show promising biological activities,[10] it will naturally be an ideal and direct method for the asymmetric synthesis of spiro-[pseudoindoxyl-2,3′-pyrrolidine] through 1,3-dipolar cycloadditions of azomethine ylides[11] with azaaurone. However, to our surprise, despite numerous efforts towards constructing spiro-pseudoindoxyl, the catalytic asymmetric approach to valuable spiro-[pseudoindoxyl-2,3′-pyrrolidine] derivatives is still not available (Figure 2). This can be attributed to two reasons: 1) the special structure and low reactivity of azaaurone,[12] which can be recognized as a combination of electron-donating enamine and electron-withdrawing α,β-unsaturated ketones; and 2) the difficulty of constructing a spiro quaternary C2 carbon center with a pyrrolidinyl moiety. In this context, the development of a new activation strategy for catalytic asymmetric synthesis of spiro-[pseudoindoxyl-2,3′-pyrrolidine] has been a highly desirable yet challenging task.

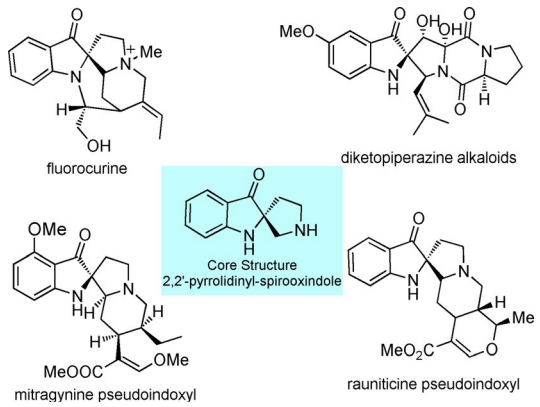

Figure 1. Indole alkaloids containing the 2,2′-pyrrolidinyl-spirooxindole core structure.

Design Plan: Recently, we have developed a series of methods involving cycloaddition reactions and cascade reactions for the efficient synthesis of complex molecules and construction of diverse scaffolds.[13] In continuing with our research program, we then questioned whether or not it is possible to develop a direct [3+2] cycloaddition reaction of azaaurone with azomethine ylides for the synthesis of spiro-[pseudoindoxyl-2,3′-pyrrolidine]. Indeed, in the presence of representative catalyst, cinchona-thiourea **4a**, the reaction of aromatic aldimine **1′** with (*Z*)-1-acetyl-2-benzylideneindolin-3-one **2a** was unsuccessful in toluene at room temperature even after 120 h (Scheme 1). By considering the special structure and low reactivity of azaaurone, it is expected that the construction of the pyrrolidinyl moiety incorporated spiro quaternary carbon center is not trivial. When methanol was used as the solvent,

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Supporting information for this article can be found under http://dx.doi.org/10.1002/asia.201600013.

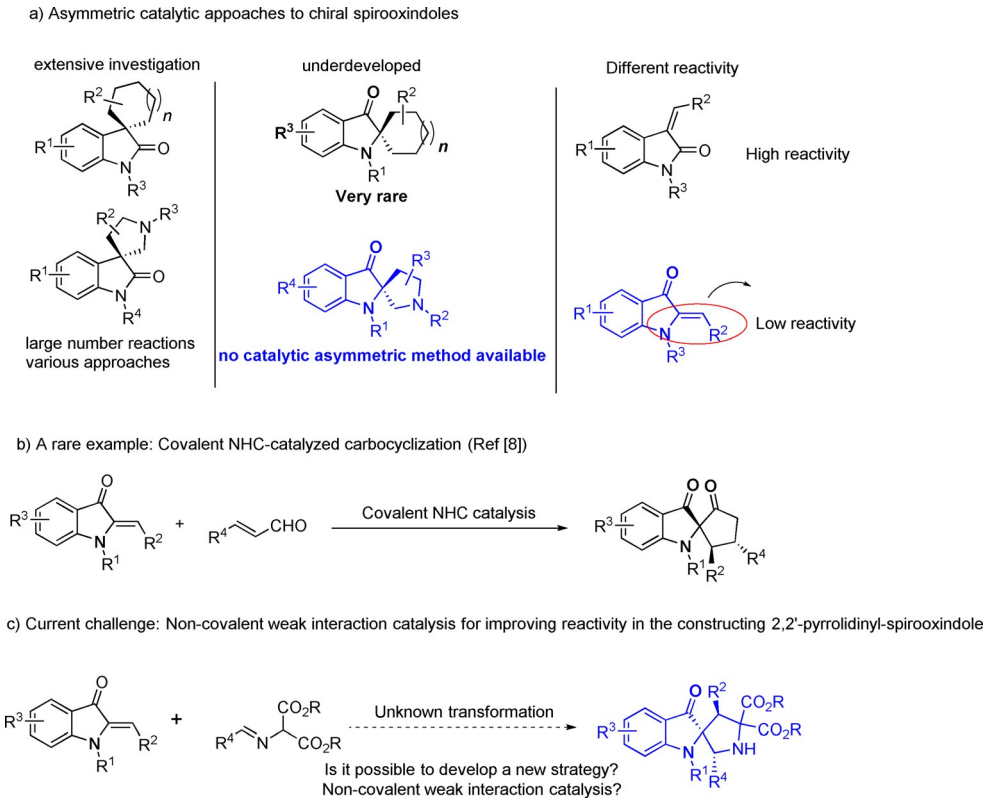
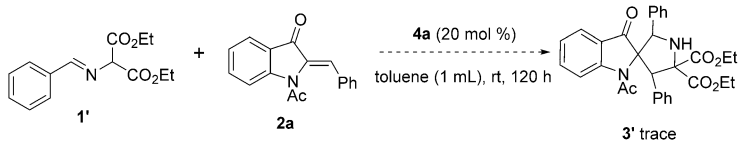


Figure 2. Different approaches and proposed method for the synthesis of spirooxindole.



Scheme 1. Initial attempt.

the desired product was obtained albeit with only 11% yield. We realized that extra hydrogen-bonding with the substrate is critical to the success of the designed [3+2] cycloaddition.[14] Phenols have been demonstrated to be a unique component in assembling some supramolecular catalysts, which showed remarkably new reactivity through noncovalent interactions.[15] We envisioned that the introduction of a phenol group in the substrate for assembling a hydrogen-bonding network would significantly activate the whole catalytic system (Figure 3).

To our delight, the corresponding product was obtained as expected with 68% yield and moderate enantioselectivity in toluene (Table 1, entry 1). Encouraged by this positive result, we then screened a series of bifunctional catalysts in toluene at room temperature. As shown in Table 1, all of the catalysts **4a**–**4g** could give the desired product **3a** with moderate-to-high yields. However, only low-to-moderate enantioselectivities were obtained (Table 1, entries 1–7). Further screening revealed that catalyst **4i** could afford the desired product with 79% yield and good stereoselectivities (>20:1 dr; 89% *ee*) (Table 1, entry 9). Upon reducing the catalyst loading to 10 mol%, nearly the same good result was obtained. However, the use of 5 mol% catalyst **4i** led to a significant decrease in reaction yield (Table 1, entries 10 and 11). The optimization of solvent showed that 1,2-dichloroethane (DCE) was the optimal selection (Table 1, entries 12–16). The enantioselectivity decreased dramatically when methanol and THF

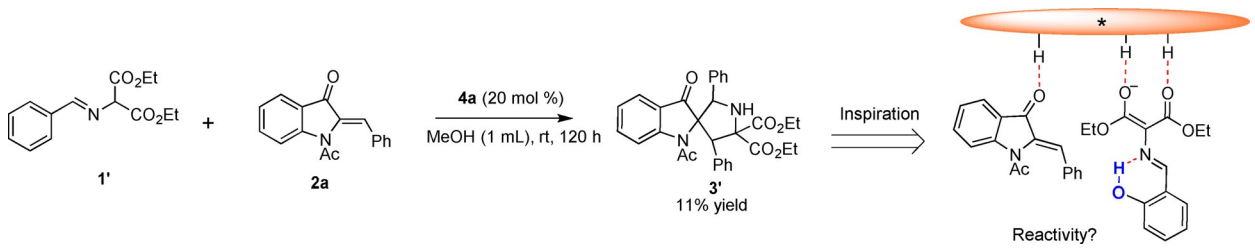
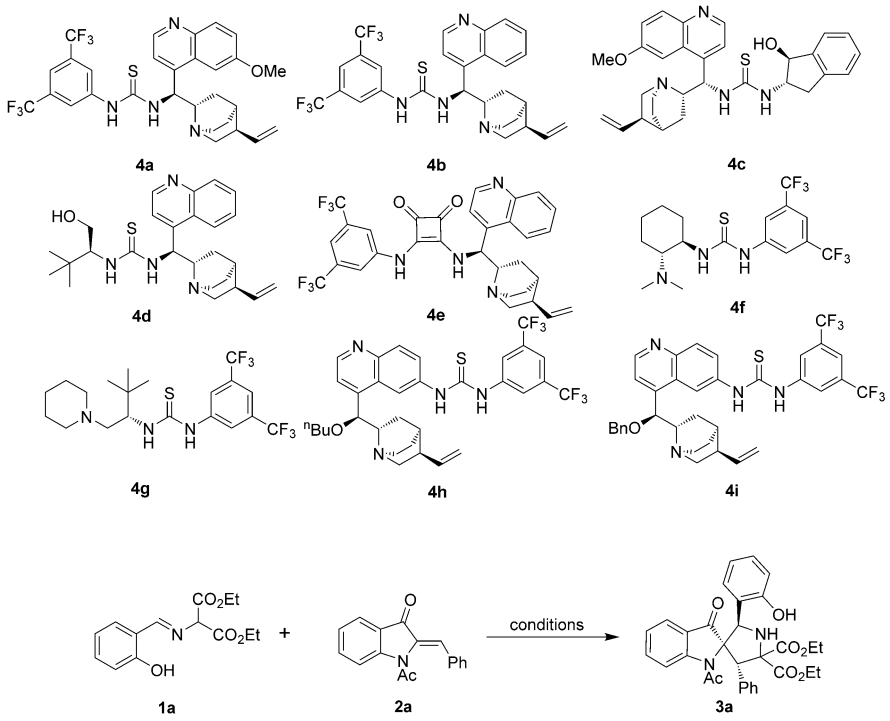


Figure 3. Design of the reaction.

Table 1. Optimization of the reaction conditions.[a]



Entry	Catalyst	Catalyst [mol%]	Sovlent	*t* [h]	Yield [%][b]	d.r.[c]	*ee* [%][d]
1	**4a**	20	toluene	72	68	>20:1	45
2	**4b**	20	toluene	72	82	13:1	51
3	**4c**	20	toluene	72	23	>20:1	15
4	**4d**	20	toluene	72	38	>20:1	21
5	**4e**	20	toluene	72	58	1:1	9
6	**4f**	20	toluene	72	81	>20:1	13
7	**4g**	20	toluene	72	76	>20:1	67
8	**4h**	20	toluene	72	73	>20:1	87
9	**4i**	20	toluene	72	79	>20:1	89
10	**4i**	10	toluene	72	80	>20:1	89
11	**4i**	5	toluene	72	56	>20:1	90
12	**4i**	10	DCM	72	78	>20:1	91
13	**4i**	10	DCE	72	83	>20:1	92
14	**4i**	10	THF	96	16	>20:1	45
15	**4i**	10	CH_3CN	96	26	>20:1	66
16	**4i**	10	CH_3OH	48	90	4:1	21

[a] Unless otherwise noted, all reactions were performed using **1a** (0.1 mmol) and **2a** (0.12 mmol) in solvent (1.0 mL) at room temperature. [b] Isolated yield. [c] Determined by 1H NMR spectroscopy. [d] Determined by HPLC using a chiral stationary phase.

were used (Table 1, entries 14 and 16). This observation is consistent with our design plan as these solvents could affect the hydrogen-bonding network between catalyst and substrates. Based on the above results, it is the optimal choice to conduct the reaction in DCE at room temperature in the presence of catalyst **4i**.

With the optimized reaction conditions, the substrate scope of the reaction was then explored (Table 2). In general, good-to-excellent yields and diastereo- and enantioselectivities were achieved with a variety of electron-donating or electron-withdrawing substituents on the phenyl ring (up to 84% yield, >20:1 d.r. and 95% *ee*; Table 2, entries 1–12). With azaaurones possessing a furan or piperonyl aldehyde substituent, the desired products were obtained with good yields albeit with lower enantioselectivities (Table 2, entries 13 and 14). Furthermore, substituted *o*-hydroxy aromatic aldimines could be applied to this reaction and products were obtained with good yields and stereoselectivities (Table 2, entries 17 and 18). The absolute configuration of the product was determined by X-ray crystallographic analysis of **3l** (see the Supporting Information).[16]

As shown in Scheme 2, in the presence of 20 mol% para-toluenesulfonic acid (*p*-TSA), **3a** reacted with paraformaldehyde to afford polycyclic compound **5** in moderate yield with excellent diastereoselectivity and enantioselectivity (64% yield, >20:1 d.r. and 94% *ee*, see the Supporting Information).

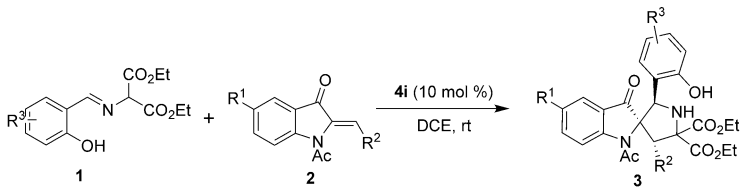
When pure (*Z*)-azaaurone was used as the substrate, we observed that there was an equilibrium between (*Z*)- and (*E*)-azaaurone in the reaction system. Then we performed control experiments using pure (*Z*)- and (*E*)-azaaurone, respectively (Scheme 3 and see the Supporting Information).[17] The results revealed that under the optimal reaction conditions, the same product **3a** was formed with similar yield and stereoselectivity (Scheme 2). In the presence of catalyst **4i**, substarte **1a**, and (*Z*)- or (*E*)-azaaurone form complex **TS-1** and **TS-2**, respectively. Due to steric interaction, **TS-2** is favored and product **3a** was generated.

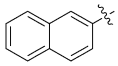
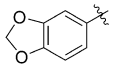
In summary, by employing a hydrogen-bonding network activation strategy, 2,2′-pyrrolidinyl-spirooxindole for the first time could be directly obtained through a catalytic asymmetric [3+2] cycloaddition reaction. The desired products containing three stereocenters including one spiro quaternary chiral center at the C2 position of indoles were generally obtained with high yields and excellent stereoselectivities. This finding is an important advancement for the synthesis of spirooxindoles.

Experimental Section

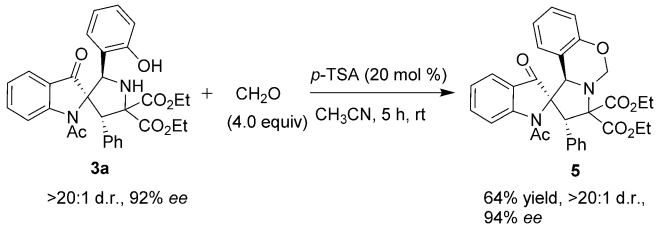
Chemicals and solvents were either purchased from commercial suppliers or purified by standard techniques. Analytical thin-layer chromatography (TLC) was performed on silicycle silica gel plates with F-254 indicator and the compounds were visualized by irradiation with UV light. Flash chromatography was carried out utilizing

Table 2. Scope of the cycloaddition reaction.[a]



Entry	R^1	R^2	R^3	*t* [h]	3	Yield [%][b]	d.r.[c]	*ee* [%][d]
1	H	3-BrPh	H	68	**3b**	79	>20:1	90
2	H	4-BrPh	H	72	**3c**	81	>20:1	95
3	H	4-ClPh	H	72	**3d**	81	>20:1	93
4	H	4-FPh	H	72	**3e**	82	>20:1	92
5	H	4-CNPh	H	32	**3f**	70	>20:1	92
6	H	4-CF_3Ph	H	72	**3g**	79	>20:1	90
7	H	2-MePh	H	72	**3h**	64	>20:1	86
8	H	3-MePh	H	64	**3i**	80	>20:1	91
9	H	4-MePh	H	72	**3j**	81	>20:1	94
10	H	4-MeOPh	H	72	**3k**	64	>20:1	93
11[e]	H	4-$C(CH_3)_3$Ph	H	72	**3l**	81	>20:1	90
12	H		H	72	**3m**	84	>20:1	93
13[f]	H	2-furyl	H	72	**3n**	76	>20:1	80
14	H		H	72	**3o**	80	>20:1	77
15	Cl	Ph	H	60	**3p**	77	>20:1	80
16	Me	Ph	H	58	**3q**	84	>20:1	92
17	H	Ph	5-Cl	38	**3r**	83	>20:1	90
18	H	Ph	4-MeO	72	**3s**	84	>20:1	87

[a] The reaction was carried out with **1** (0.1 mmol), ***Z*-2** (0.12 mmol), and **4i** (10 mol%) in DCE (1.0 mL) at room temperature. [b] Isolated yield. [c] Determined by ^{1}H NMR spectroscopy. [d] Determined by HPLC analysis using a chiral stationary phase. [e] The starting material was used as an *Z/E* mixture (17:1). [f] The starting material was used as an *Z/E* mixture (1:1).



Scheme 2. Synthetic transformation.

silica gel 200–300 mesh. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AM-400 spectrometer (400 MHz ^{1}H NMR, 100 MHz ^{13}C). The spectra were recorded in $CDCl_3$ as solvent at room temperature, ^{1}H and ^{13}C NMR chemical shifts are reported in ppm relative to either the residual solvent peak or internal standard (TMS = trimethylsilyl). Data for ^{1}H NMR are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, q = quartet, dd = doublet), integration, coupling constant (Hz) and assignment. Data for ^{13}C NMR are reported as chemical shift. IR spectra were recorded using Nicolet NEXUS 670 FT-IR instrument and are reported in wave numbers (cm^{-1}). HRMS were performed on Bruker Apex II mass instrument (ESI). HPLC (Waters 600 Delta or Agilent 1100) analysis was conducted on a ID-H column delta eluting with DCM and *n*-hexane or AD-H column delta eluting with *i*PrOH and n-hexane solution. Optical rotation was measured on the PerkinElmer 341 polarimeter with $[\alpha]^D$ values reported in degrees; concentration (c) is reported in g 100 mL^{-1}.

General procedure for the synthesis of products 3

The solution of organocatalyst **4i** (0.01 mmol, 10 mol%), azaaruone **2** (0.12 mmol, 1.2 equiv), *o*-hydroxy aromatic aldimine **1** (0.1 mmol, 1.0 equiv) in dry DCE (1.0 mL) was prepared and stirred at room temperature. After **1** disappeared, as monitored by TLC, the crude mixture was purified by flash chromatography on silica gel to afford product **3**.

Synthesis of compound 5

To a solution of **3a** (54.2 mg, 0.1 mmol, 1.0 equiv) and paraformaldehyde (12 mg, 0.4 mmol, 4.0 equiv) in CH_3CN (1.0 mL) was added *p*-TSA (3.4 mg, 20 mol%) and the reaction was stirred at room temperature for five hours (monitored by TLC). After evaporation of the solvent in vacuo, the residue was purified via flash column chromatography (silica gel, pentane/ethyl acetate = 4:1 as eluent) to afford the product **5**.

Acknowledgements

We are grateful to the NSFC (21172097, 21202070, 21302075 and 21372105), the International S&T Cooperation Program of China (2013DFR70580), the National Natural Science Foundation from Gansu Province of China (no. 1204WCGA015), and the "111" program from MOE of P. R. China.

Keywords: [3+2] cycloaddition · azomethine ylides · hydrogen bonding · quaternary carbons · spiro-pseudoindoxyl

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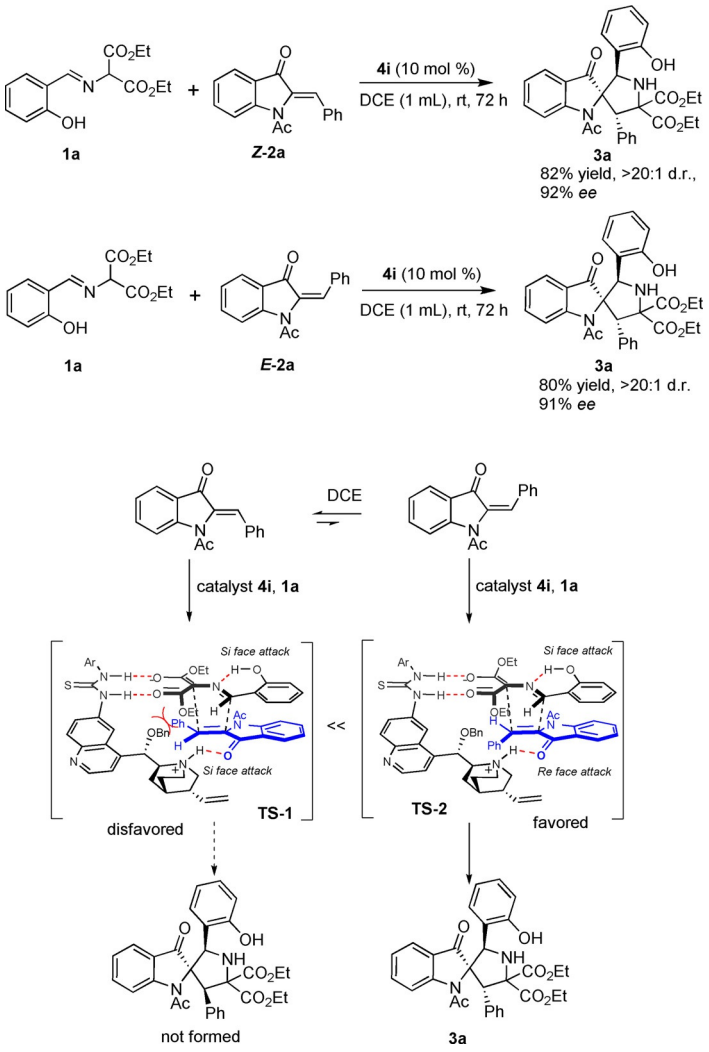

Scheme 3. Proposed mechanism for the [3+2] cycloaddition.

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Manuscript received: January 5, 2016
Accepted Article published: January 26, 2016
Final Article published: February 16, 2016