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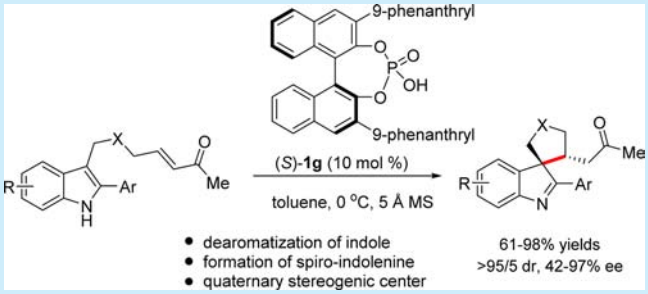
Chiral Phosphoric Acid Catalyzed Intramolecular Dearomative Michael Addition of Indoles to Enones

Yong Zhou, Zi-Lei Xia, Qing Gu, and Shu-Li You*

State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 345 Lingling Lu, Shanghai 200032, China

Supporting Information

ABSTRACT: An enantioselective intramolecular dearomative Michael addition of indolyl enones is presented. In the presence of catalytic amount of chiral phosphoric acid, various enantioenriched spiro-indolenines bearing a quaternary stereogenic center were obtained with good yields and enantioselectivity (up to 97% ee) under mild reaction conditions.



The dearomatization of indoles is a class of important and straightforward transformations leading directly to a variety of heterocyclic systems.[1] Over the past several years, extensive efforts have been devoted to the selective C3 functionalization of 3-substituted indoles through a dearomatization process to construct polycyclic indolines in an enantioselective manner.[2] One representative class is the cascade reaction which undergoes asymmetric dearomatization by reacting at the C3 position of indole and subsequent nucleophilic addition to the resulting indolenium. In addition, spiro-indolenine is also an important scaffold widely found in natural alkaloids, biologically active compounds, and important intermediates in total synthesis (Figure 1).[3] Therefore, quite a few excellent approaches mostly by transition-metal catalysis have been developed to construct thermodynamically unstable indolenines, staying at the stage of the first dearomatization step.[4−6] For example, in 2006, Trost and Quancard reported palladium-catalyzed enantioselective intermolecular C3-allylation of 3-substituted indoles with allylic alcohols in the presence of a bulky boron reagent, providing indolenines bearing a quaternary stereogenic center.[4] In comparison, construction of spiro-indolenine by an intramolecular design represents a great challenge due to steric congestion and the energetic barrier encountered during the dearomatization process. In 2010, we reported an iridium-catalyzed intramolecular asymmetric allylic reaction of indole-3-yl allyl carbonates, affording a variety of highly enantioenriched spiro-indolenines.[5] Despite this recent progress, highly efficient construction of structurally diverse indolenine skeleton remains desirable.

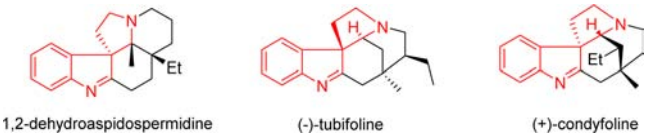
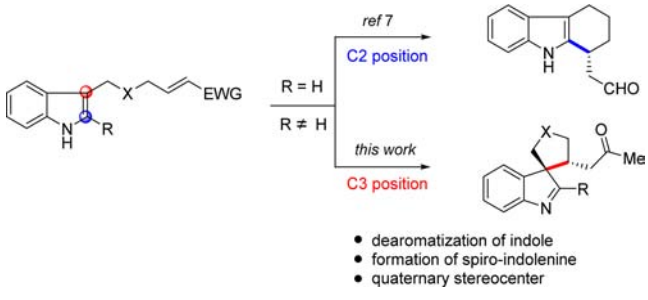


Figure 1. Selected alkaloids containing a spiro-indolenine core.

In 2011, Xiao and co-workers reported an asymmetric intramolecular Friedel−Crafts reaction of ω-indolyl α, β-unsaturated aldehyde, and this elegant approach delivered C2 alkylative product.[7] With our continuing interest in catalytic asymmetric dearomatization (CADA) reactions,[1] we envisaged that spiro-indolenine might be accessed via chiral phosphoric acid catalyzed dearomative Michael addition of indolyl enone (Scheme 1).[8,9] Herein, we report our results from this study.

We began our studies by examining chiral phosphoric acids with **2a** as a model substrate. In this case, a substrate bearing a substituent at the C2 position was employed to avoid migration from the C3 to the C2 position in spiro-indolenine under acidic conditions.[5b,c] In the presence of 10 mol % chiral phosphoric acid (*S*)-**1a**, we were delighted to find that this dearomative

Scheme 1. Asymmetric Intramolecular Michael Addition Reaction at the C2 and C3 Positions of the Indole Ring



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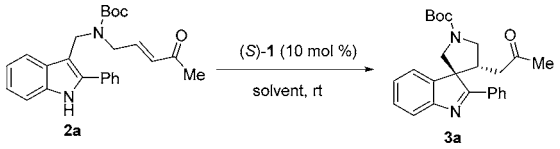
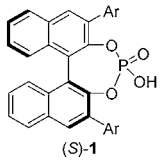
Michael addition reaction proceeded smoothly at room temperature to afford the desired spirocyclic product in 53% yield and 53% ee (Table 1, entry 1). Further evaluation of chiral

Table 1. Optimization of the Reaction Conditions[a]





1a, Ar = 2,4,6-(*i*-Pr)$_3$-C$_6$H$_2$
1b, Ar = 3,5-(CF$_3$)$_2$-C$_6$H$_3$
1c, Ar = 4-NO$_2$-C$_6$H$_4$
1d, Ar = 1-naphthyl
1e, Ar = 2-naphthyl
1f, Ar = 9-anthryl
1g, Ar = 9-phenanthryl
1h, Ar = 4-biphenyl
1i, Ar = SiPh$_3$
1j, Ar = 2,4,6-tricyclohexylphenyl

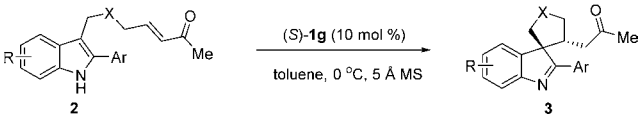
entry	1	solvent	time (h)	yield[b] (%)	ee[c] (%)
1	**1a**	DCM	60	53	53
2	**1b**	DCM	20	76	63
3	**1c**	DCM	37	72	64
4	**1d**	DCM	20	99	57
5	**1e**	DCM	19	98	64
6	**1f**	DCM	24	98	58
7	**1g**	DCM	20	98	67
8	**1h**	DCM	19	98	61
9	**1i**	DCM	60	45	19
10	**1j**	DCM	40	62	56
11	**1g**	toluene	13	92	75
12	**1g**	*o*-xylene	18	65	53
13	**1g**	PhCl	10	98	61
14	**1g**	PhF	15	98	68
15	**1g**	THF	13	22[d]	nd
16	**1g**	Et$_2$O	13	36	44
17[e]	**1g**	toluene	3.5	98	83
18[e,f]	**1g**	toluene	24	83	92

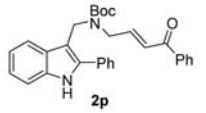
[a]Reaction conditions: (*S*)-**1** (10 mol %), **2a** (0.1 mmol) in solvent (2 mL) at room temperature. [b]Isolated yield. [c]Determined by HPLC analysis. [d]Determined by ^{1}H NMR of crude mixture. [e]50 mg of 5 Å MS was added. [f]Reaction at 0 °C.

phosphoric acids bearing different substituents indicated that all of the reactions occurred smoothly to give the desired product. As summarized in Table 1, the substituent of the catalyst had a great influence on the enantioselectivity of the reaction. Chiral phosphoric acid **1g** bearing 9-phenanthryl groups gave the best results in terms of yield and enantioselectivity (Table 1, entry 7, 98% yield, 67% ee). Encouraged by these results, we further investigated the effect of solvents and additive with (*S*)-**1g** as the optimal catalyst. Various weakly polar solvents such as toluene, *o*-xylene, PhCl, and PhF could be well tolerated, affording spiro-indolenine (**3a**) in good yields and enantioselectivity (Table 1, entries 11−14), while the reactions in polar solvents such as THF and Et$_2$O were sluggish (Table 1, entries 15 and 16). To our great delight, the addition of 5 Å MS could further increase the enantiomeric excess of the product when the reaction was performed at 0 °C (Table 1, entry 18, 83% yield, 92% ee).

With the optimized reaction conditions (10 mol % (*S*)-**1g**, 5 Å MS as the additive in toluene at 0 °C) in hand, we then examined the substrate scope of this reaction. The results are summarized in Table 2. The reaction of substrates with varied protecting group on the linking *N* atom (Boc, Ts, Cbz) all gave

Table 2. Substrate Scope[a]



entry	2, Ar, R, X	time (h)	3, yield (%)[b]	dr[c]	ee (%)[d]
1	**2a**, Ph, H, NBoc	24	**3a**, 83	>95/5	92
2	**2b**, Ph, H, NTs	24	**3b**, 67	>95/5	88
3	**2c**, Ph, H, NCbz	16	**3c**, 69	>95/5	75
4[e]	**2d**, Ph, H, C(CO$_2$Me)$_2$	24	**3d**, 95	>95/5	82
5	**2e**, 4-CH$_3$C$_6$H$_4$, H, NBoc	16	**3e**, 98	>95/5	82
6	**2f**, 4-ClC$_6$H$_4$, H, NBoc	20	**3f**, 82	>95/5	89
7	**2g**, 4-FC$_6$H$_4$, H, NBoc	20	**3g**, 90	>95/5	92
8[e]	**2h**, Ph, 4-CH$_3$, NBoc	12	**3h**, 61	>95/5	88
9[e]	**2i**, Ph, 4-Cl, NBoc	72	**3i**, 65	>95/5	94
10[e]	**2j**, Ph, 5-F, NBoc	48	**3j**, 93	>95/5	94
11	**2k**, Ph, 5-MeO, NBoc	16	**3k**, 95	>95/5	93
12	**2l**, Ph, 5-Me, NBoc	24	**3l**, 97	>95/5	85
13	**2m**, Ph, 6-F, NBoc	72	**3m**, 85	>95/5	63
14	**2n**, Ph, 6-Me, NBoc	24	**3n**, 93	>95/5	75
15	**2o**, Ph, 7-Me, NBoc	16	**3o**, 77	>95/5	76
16[f]	 **2p**	120	**3p**, 56	>95/5	79
17	**2q**, 2-MeOC$_6$H$_4$, H, NBoc	21	**3q**, 71	>95/5	97
18	**2r**, 3-MeOC$_6$H$_4$, H, NBoc	26	**3r**, 77	>95/5	95
19	**2s**, Ph, 6-MeO, NBoc	26	**3s**, 80	>95/5	42

[a]Reaction conditions: (*S*)-**1g** (10 mol %), **2** (0.1 mmol), 5 Å MS (50 mg) in toluene (2 mL) at 0 °C. [b]Isolated yield. [c]Determined by ^{1}H NMR of crude mixture. [d]Determined by HPLC analysis. [e]20 mol % of (*S*)-**1g**. [f]Reaction at room temperature.

their corresponding spiro-indolenine products with good yields, enantioselectivity, and diastereoselectivity (Table 2, entries 1−3). The reaction of carbon-tethered substrate **2d** occurred well in the presence of 20 mol % (*S*)-**1g** (Table 2, entry 4, 95% yield, > 95/5 dr, 82% ee). Besides a phenyl group at the C2 position of indole, substrates bearing a different aryl group (4-MeC$_6$H$_4$, 4-ClC$_6$H$_4$, 4-FC$_6$H$_4$, 2-MeOC$_6$H$_4$, 3-MeOC$_6$H$_4$) are all compatible under the optimized reaction conditions (Table 2, entries 5−7, 17, and 18). These NBoc-tethered substrates with either an electron-withdrawing group (4-Cl, 5-F, 6-F) or an electron-donating group (4-CH$_3$, 5-MeO, 5-Me, 6-Me, 6-MeO, 7-Me) on the indole ring all led to the formation of their desired dearomatized products in 61−97% yields, 42−94% ee, and excellent dr (Table 2, entries 8−15 and 19). In some cases, 20 mol % catalyst was required to obtain a reasonable yield. The dearomatization reaction of the substrate **2p** bearing a

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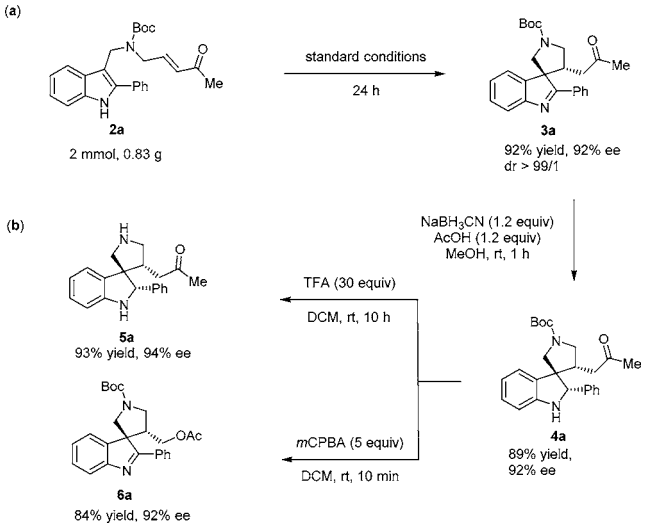
phenyl enone moiety could also occur under optimized reaction conditions, affording the desired spiroindolenine **3p** in 56% yield and with 79% ee (Table 2, entry 16). The stereochemistry of the products was determined as (3*S*,4′*R*) by X-ray structural determination of enantiopure **3d**.[10] A working model of the enantioselectivity-determining transition state was also proposed. The chiral phosphoric acid acts as a bifunctional catalyst in which the P═O and the acidic proton of the catalyst interact with NH of indole ring and carbonyl group, respectively (see the Supporting Information for details).

To test the practicality of the new methodology, a gram-scale reaction was carried out. The intramolecular dearomative Michael addition reaction of indole derivative **2a** in 2 mmol scale gave the spiro-indolenine product in 92% yield, 92% ee, and up to 95/5 dr (Scheme 2a). Furthermore, several straightforward transformations of product **3a** were carried out. As illustrated in Scheme 2b, selective reduction of the imine moiety of **3a** by $NaBH_3CN$ in the presence of AcOH at room temperature afforded **4a** containing three contiguous stereogenic centers with high diastereoselectivity in 89% yield. N-Boc protecting group of **4a** could be easily removed by TFA, providing **5a** in 93% yield (see the Supporting Information for NOE experiments of **5a**). Interestingly, treatment of spiroindoline **4a** with *m*-CPBA afforded indolenine ester **6a** in 84% yield. It should be noted that in all cases no loss of enantiomeric purity was observed during the transformation (Scheme 2b).

Scheme 2. Gram-Scale Reaction and Transformations of Product 3a



In conclusion, we have developed an efficient chiral phosphoric acid catalyzed intramolecular dearomative Michael addition of indolyl enones. A variety of spiro-indolenines bearing a chiral quaternary carbon center were obtained in good yield and enantioselectivity under mild conditions.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.6b03610.

Synthesis of substrates, copies of ^1H and ^{13}C NMR spectra, and HPLC chromatographs of all compounds described (PDF)

X-ray crystallographic data of (R_p,*S*)-**3d** (CIF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: slyou@sioc.ac.cn.

ORCID

Shu-Li You: 0000-0003-4586-8359

Notes

The authors declare no competing financial interest.

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