Synthetic Methods

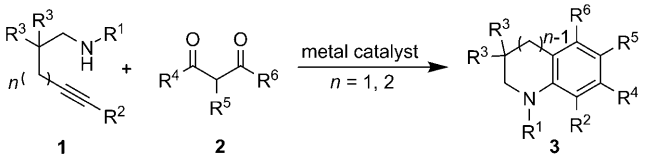
DOI: 10.1002/anie.200805383

Highly Efficient and Regioselective Platinum(II)-Catalyzed Tandem Synthesis of Multiply Substituted Indolines and Tetrahydroquinolines**

*Xin-Yuan Liu and Chi-Ming Che**

Transition-metal-catalyzed tandem cyclization reactions can provide an efficient way to construct polycyclic structures from readily accessible organic compounds.[1] In particular, the use of platinum and gold complexes as catalysts has recently generated a variety of methods for the synthesis of organic compounds. These syntheses exhibit good selectivity, have high atom-economy, and are carried out under mild reaction conditions and at low catalyst loadings.[2]

Following our recent work on the synthesis of substituted 1,2-dihydroquinolines and pyrrolo[1,2-*a*]quinolines from reactions of alkynes with amines or aminoalkynes through gold(I)-catalyzed tandem cyclization,[3] we turned to a more complicated system, that is, the metal-catalyzed reaction of aminoalkynes (**1**) with 1,3-diketones (**2**; see Scheme 1). A wide variety of products could be expected from this reaction based on well-documented metal-catalyzed reactions such as 1) intermolecular addition of **2** to alkynes,[2b,4] 2) condensation of **2** with amines to give β-enaminones,[2a,4c,5] and 3) hydroamination of **1** to generate an enamine intermediate[2a,b,4c] and possible reaction of the enamine with **2** to give a mixture of products.[6] Unexpectedly, we detected neither a β-enaminone nor the product resulting from the intermolecular addition of **2** to the alkynyl moiety of **1,** when **1** and **2** were with the platinum(II) compound as the catalyst. The reaction was found to result in the isolation of indoline or tetrahydroquinoline derivative **3** in up to 99% yield by a highly selective tandem cyclization. This new method for the synthesis of indoline or tetrahydroquinoline derivatives is reported herein (Scheme 1).



Scheme 1. The highly selective formation of indolines or tetrahydroquinolines from metal-catalyzed tandem reactions.

Indoline frameworks are ubiquitous structural motifs in a myriad of biologically active alkaloid natural products[7] and pharmaceutically active compounds.[8] Consequently, there has been continued interest in the development of efficient methods for the syntheses of indolines bearing multiple and diverse substituent patterns. Most of the methods available for the construction of indolines use precursors that already contain the six-membered ring of the indoline bicyclic core.[9] Few methods are known for the assembly of both the six- and five-membered rings (of the indoline core) from acyclic precursors. All of these methods involve an intramolecular [4+2] cycloaddition step.[10] A notable example is the stoichiometric intramolecular [4+2] cycloaddition of ynamides and conjugated enynes—a method that is particularly useful for the construction of indolines bearing multiple substituents on the six-membered ring.[10d] The method reported herein (Scheme 1) is useful for constructing indoline compounds bearing multiple substituents on both the six- and five-membered rings. Also, the method has a very broad substrate scope and can be used to synthesize tetrahydroquinoline derivatives. The indoline or tetrahydroquinoline compounds can be obtained in good to excellent yields and with high regioselectivity and with almost complete chemoselectivity under mild reaction conditions.

To optimize the reaction conditions, we treated 4-methoxy-*N*-(pent-4-ynyl)aniline (**1A**) with 2,4-pentanedione (**2a**) in different solvents and screened a variety of metal catalysts. These catalysts were based on Cu, Co, Ni, Ag, Au, Pd, or Pt compounds and the results are shown in Table S1 of the Supporting Information. These studies revealed that methanol was the solvent of choice, and catalyst K_2PtCl_4 gave the product **3Aa** in the best yield. The yield could be improved either by lowering the reaction temperature to 40 °C or by adding activated, powdered molecular sieves (4 Å M.S.). The catalyst loading could be reduced from 5 to 1 mol% without affecting the yield of **3Aa**. However, a decrease in the yield of **3Aa** was observed when the amount of **2a** was reduced from 4 to 1.2 equivalents. The optimal reaction conditions were found to be 1 mol% of K_2PtCl_4 in the presence of molecular sieves (4 Å) with methanol as the solvent at 40 °C for 22 hours, and gave the product **3Aa** in 88% yield (Table 1, entry 1). Trifluoromethanesulfonic acid did not catalyze this reaction (Table S1, entry 28, in the Supporting Information).

[*] X.-Y. Liu, Prof. Dr. C.-M. Che
Department of Chemistry and Open Laboratory of Chemical Biology, Institute of Molecular Technology for Drug Discovery and Synthesis, The University of Hong Kong
Pokfulam Road, Hong Kong (P.R. China)
Fax: (+852) 2857-1586
E-mail: cmche@hku.hk

[**] This study was supported by The University of Hong Kong (University Development Fund), The Hong Kong Research Grants Council, and The University Grants Committee of the Hong Kong SAR of China (Area of Excellence Scheme, AoE/P-10/01).

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.200805383.

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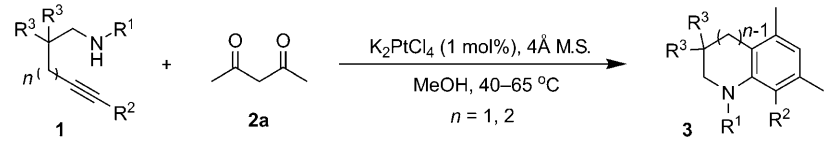
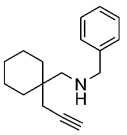
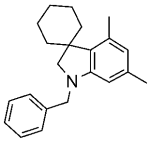
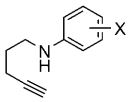
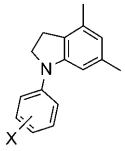
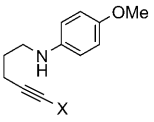
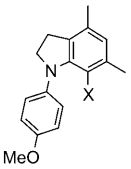
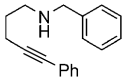
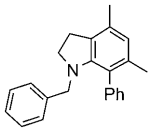
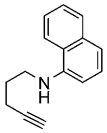
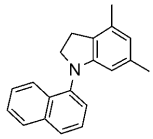
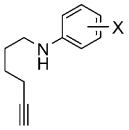
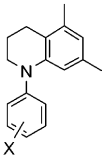
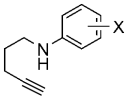
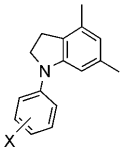
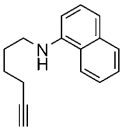
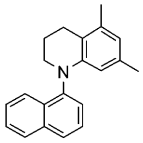
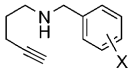
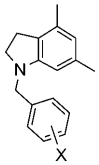
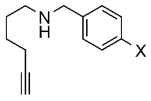
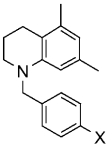
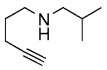
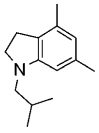
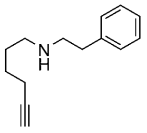
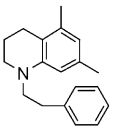
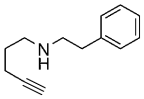
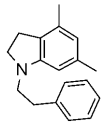
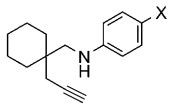
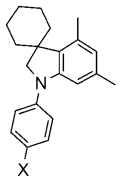
Table 1: Synthesis of indolines and tetrahydroquinolines from **2a** and various aminoalkynes **1A–W** through platinum(II)-catalyzed tandem reaction.[a]



1 **2a** **3**

Entry	X	Aminoalkyne		*t* [h]	Product		Yield [%][b]	Entry	X	Aminoalkyne		*t* [h]	Product		Yield [%][b]
1	4-OMe		**1A**	22		**3Aa**	88	14			**1N**	23		**3Na**	89
2	2-OMe		**1B**	22		**3Ba**	96	15[d]	Ph		**1O**	72		**3Oa**	51
3	4-OPh		**1C**	22		**3Ca**	91[c]	16[d]	Me		**1P**	24		**3Pa**	65[e]
4	4-Me		**1D**	32		**3Da**	76	17[d]			**1Q**	72		**3Qa**	76
5			**1E**	22		**3Ea**	95	18	4-OMe		**1R**	18		**3Ra**	77
6[d]	2-F		**1F**	24		**3Fa**	83	19[d]	2-OMe		**1S**	58		**3Sa**	79
7[d]	4-Cl		**1G**	36		**3Ga**	79	20[d]			**1T**	58		**3Ta**	78
8	4-Cl		**1H**	18		**3Ha**	99	21	H		**1U**	32		**3Ua**	88
9	H		**1I**	18		**3Ia**	99	22	Cl		**1V**	32		**3Va**	91
10			**1J**	22		**3Ja**	95	23			**1W**	30		**3Wa**	84
11			**1K**	20		**3Ka**	94								
12	OMe		**1L**	20		**3La**	95								
13	OPh		**1M**	20		**3Ma**	99								

[a] Reaction conditions: **1** (0.2 mmol), 2,4-pentanedione (0.8 mmol), K_2PtCl_4 (1 mol%), 4 Å M.S. (20 mg), MeOH (1 mL), 40 °C. [b] Yield of isolated product based on **1**. [c] Determined by ^1H NMR spectroscopy. [d] Reaction conditions: **1** (0.2 mmol), 2,4-pentanedione (0.8 mmol), K_2PtCl_4 (5 mol%), 4 Å M.S. (20 mg), MeOH (1 mL), 65 °C. [e] The reaction also afforded **3Ra** in 24% yield.

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Under the optimized reaction conditions, we treated **2a** with a variety of 1,4-aminoalkynes (Table 1) bearing aryl groups (with electron-donating substituents: **1A–D**; Table 1, entries 1–4 or with electron-withdrawing substituents: **1F–G**; Table 1, entries 6 and 7), a naphthalene group (**1E**; Table 1, entry 5), benzyl groups (**1H–I**; Table 1, entries 8 and 9), and alkyl groups (**1J–K**; Table 1, entries 10 and 11), and we isolated the indoline derivatives **3Aa–Ka** in 76–99% yield. For the aryl groups with electron-withdrawing substituents, a higher catalyst loading (5 mol%) and temperature (65°C) were required (Table 1, entries 6 and 7). Notably, the 1,4-aminoalkynes with R^3 as a cyclohexyl group underwent the platinum(II)-catalyzed tandem cyclization and furnished spirocyclic indolines **3La–Na** in 89–99% yield (Table 1, entries 12–14). The 1,4-aminoalkynes having an internal alkyne group are also applicable to this tandem cyclization reaction, and the reaction afforded highly substituted indolines **3Oa–Qa** in 51–76% yield, although a longer reaction time (for **1O**,**Q**), a higher temperature, and an increased catalyst loading (5 mol%) were required for complete substrate conversion (Table 1, entries 15–17).

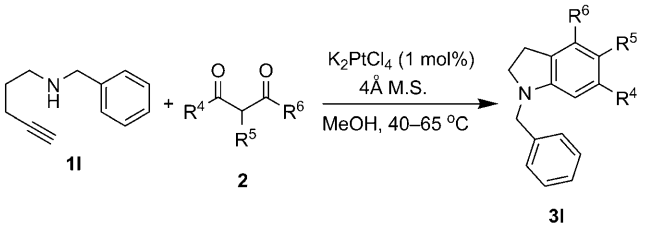
We then extended the reaction to 1,5-aminoalkynes. Under the optimized reaction conditions, treatment of **2a** with **1R–W** containing aryl and alkyl substituents gave 1,2,3,4-tetrahydroquinolines **3Ra–Wa** in 77–91% yield (Table 1, entries 18–23). 1,2,3,4-Tetrahydroquinolines are of importance in medicinal chemistry.[11]

Besides **2a**, a series of symmetric 1,3-diketones with alkyl and phenyl substituents were similarly treated with **1I**, and the corresponding indolines **3Ib–Id** were obtained in 92–98% yield (Table 2, entries 1–3). For hexafluoroacetylacetone (**2e**), the indoline **3Ie** was obtained in a lower yield (61%; Table 2, entry 4)—the low yield could be attributed to the electronic effect of the trifluoromethyl groups. Interestingly, unsymmetrical 1,3-diketones could also undergo the platinum(II)-catalyzed tandem cyclization to afford highly substituted indolines with high regioselectivity. The regioselectivity depends on both steric and electronic properties of the substituents on the 1,3-diketone substrates. For example, reactions of **2f–i** bearing an electron-withdrawing group (CF_3) gave **3If–Ii**[12] in 94–99% yield with high regioselectivity (Table 2, entries 5–8). Compounds **2j** and **2k** also underwent the tandem cyclization reaction, and gave **3Ij**[12] and **3Ik**[12] in 93% and 90% yield, respectively—albeit with diminished regioselectivity (Table 2, entries 9 and 10).

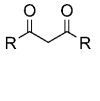
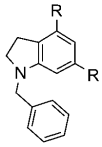
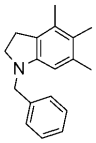
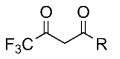
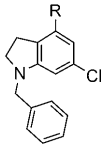
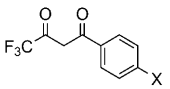
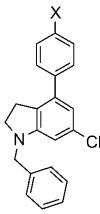
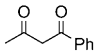
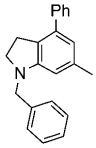
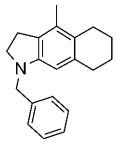
A proposed mechanism for this tandem cyclization reaction is depicted in Scheme 2, which involves platinum-catalyzed intramolecular hydroamination[3b,13] of aminoalkynes **1** to generate enamine **II**, and subsequent nucleophilic attack of the enol form (**2′**)[14] of **2** via 1,4- or 1,2-addition,[15] with subsequent cyclization to give intermediate **III**, which eliminates two water molecules to give **3**. The enamine **II** could also be formed through intramolecular cyclization of an aminoketone intermediate **I**, which might be generated by the platinum-catalyzed hydration of **1**.[16] In the literature, a similar cyclization reaction of enamines with 1,3-diketones has been reported[6]—however, the substrates were confined to push–pull enamines (which bear an additional electron-acceptor group at the β-position and a methyl group at the α-position) and hexafluoroacetylacetone or 1,1,1-trifluoroacetylacetone (both with a highly electrophilic carbonyl group)—but the reaction occurred under harsh conditions and gave a mixture of products in low yields and with poor selectivities.[6]

Electrospray ionization mass spectroscopic analysis of a solution of **1A** and K_2PtCl_4 (20 mol%) in MeOH that was

Table 2: Synthesis of highly substituted indolines from **1I** and 1,3-diketones **2b–k**.[a]



1I + **2** → **3I**

Entry	R or X	1,3-Diketone		*t* [h]	Product		Yield [%][b] (selectivity)[c]
1	Et		**2b**	24		**3Ib**	98
2	Ph		**2c**	22		**3Ic**	95
3			**2d**	24		**3Id**	92
4[d]	CF_3		**2e**	72		**3Ie**	61
5[e]	Me		**2f**	5		**3If**	98 (>20:1)
6[e]	H		**2g**	12		**3Ig**	99 (15:1)
7[e]	Me		**2h**	18		**3Ih**	97 (15:1)
8[e]	Cl		**2i**	18		**3Ii**	94 (13:1)
9			**2j**	20		**3Ij**	93 (5:1)
10			**2k**	24		**3Ik**	90 (6.3:1)

[a] Reaction conditions: **1I** (0.2 mmol), 1,3-diketone (0.8 mmol), K_2PtCl_4 (1 mol%), 4 Å M.S. (20 mg), MeOH (1 mL), 40°C. [b] Yield of isolated product based on **1I**. [c] Selectivity determined by ^1H NMR spectroscopy. [d] Reaction conditions: **1I** (0.2 mmol), **2e** (0.8 mmol), K_2PtCl_4 (5 mol%), 4 Å M.S. (20 mg), MeOH (1 mL), 65°C. [e] Reaction conditions: **1I** (0.2 mmol), **2f–i** (0.4 mmol), K_2PtCl_4 (1 mol%), 4 Å M.S. (20 mg), MeOH (1 mL), 40°C.

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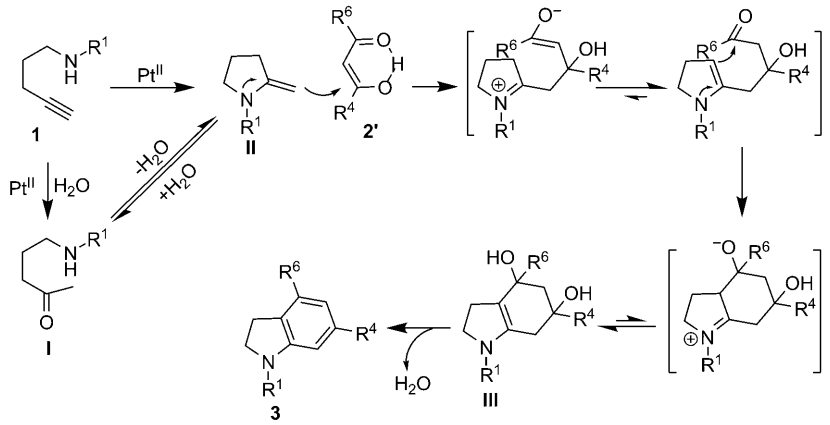
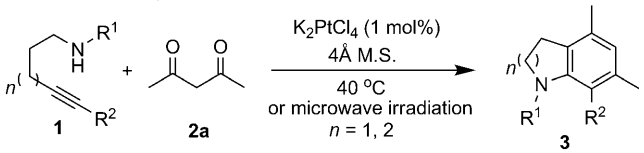


Scheme 2. A proposed mechanism.

Table 3: Synthesis of indolines and tetrahydroquinolines from **2a** and various aminoalkynes under different reaction conditions.



Entry	Aminoalkyne	*t* [h]	Product	Yield [%][a]
1[b]	**1I**	19	**3Ia**	97[c]
2[d]	**1A**	22	**3Aa**	74
3[d]	**1H**	18	**3Ha**	67
4[d]	**1I**	18	**3Ia**	61
5[e]	**1F**	2	**3Fa**	86
6[e]	**1G**	2.2	**3Ga**	90
7[e]	**1O**	2.5	**3Oa**	57
8[e]	**1T**	2.5	**3Ta**	76
9[e]	**1U**	1.3	**3Ua**	99

[a] Determined by ^{1}H NMR spectroscopy. [b] Reaction conditions: **1I** (10 mmol), 2,4-pentanedione (15 mmol), K_2PtCl_4 (1 mol%), 4 Å M.S. (2 g), MeOH (20 mL), 40°C. [c] Yield of isolated product based on **1I**. [d] Reaction conditions: **1** (0.2 mmol), **2a** (0.8 mmol), K_2PtCl_4 (1 mol%), H_2O (1 mL), 40°C. [e] Reactions were conducted with substrate (0.1 mmol), K_2PtCl_4 (1–5 mol%) in MeOH (1 mL) at 110°C under microwave irradiation.

stirred for 2 hours at 40°C revealed a peak at *m*/*z* 190, which is attributable to the protonated molecular ion of enamine **II** ($R^1 = p$-$MeOC_6H_5$). The K_2PtCl_4-catalyzed reaction of **1A** at 40°C for 2 hours and subsequent treatment with water gave *N*-(4-methoxyphenyl)-5-aminopentan-2-one in 95% yield [Eq. (1) of Scheme S1 in the Supporting Information]. Treatment of the aminoketone with **2a** for 20 hours with or without the catalyst gave **3Aa** in similar yields [Eq. (2) Scheme S1 in the Supporting Information]. This outcome suggests that the Pt species may not provide significant activation for the last stage of the cyclization cascade, but only activate the formation of the enamine intermediate.

A one-pot reaction of **1I** (10 mmol) with **2a** (15 mmol) on a gram scale in the presence of K_2PtCl_4 (1 mol%) for 19 hours afforded **3Ia** (2.66 g) in 97% yield (Table 3, entry 1). Notably, these cyclization reactions could also be conducted in water with satisfactory product yields (Table 3, entries 2–4). When the reaction was subjected to microwave irradiation, the reaction time was shortened from 24–72 hours to 1.3–2.5 hours and the corresponding products were obtained in up to 99% yield (Table 3, entries 5–9).

In summary, we have described a new, efficient platinum(II)-catalyzed tandem cyclization reaction from simple, readily available starting materials to furnish multiply substituted indolines in excellent yields with high regioselectivity under mild reaction conditions. The procedure is easy to perform and allows for a straightforward, diversity-oriented and regioselective synthesis of indoline derivatives with a broad substrate scope, thus rendering the method a valuable addition to alternative indoline syntheses.

Received: November 4, 2008
Published online: February 11, 2009

Keywords: 1,3-diketones · aminoalkynes · cyclization · platinum · synthetic methods

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