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Ming-Phos/Gold(I)-Catalyzed Diastereo- and Enantioselective Synthesis of Indolyl-Substituted Cyclopenta[*c*]furans

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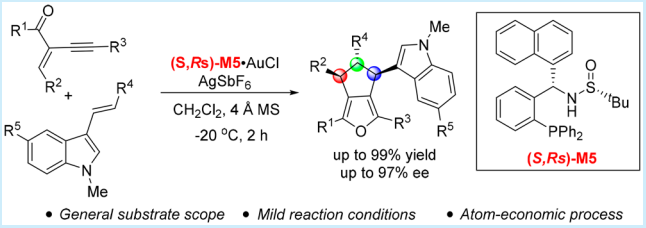
Supporting Information

ABSTRACT: A highly enantioselective gold(I)-catalyzed intermolecular tandem cyclization/[3 + 2] cycloaddition of 2-(1-alkynyl)-2-alken-1-ones with 3-stylindoles was achieved by using Ming-Phos as a chiral ligand. A variety of chiral highly substituted cyclopenta[*c*]furans were obtained in good yields (up to 99%) with excellent diastereoselectivities (>20:1) and enantioselectivities (up to 97% ee). The salient features of the present protocol include mild conditions, excellent yields, and high diastereo- and enantioselectivities, using readily available starting materials and a chiral ligand.



The synthesis of highly substituted furans has been an intense topic over past years, due to their pervasiveness in natural products and pharmaceuticals,[1] as well as their unique and useful building blocks in total synthesis.[2] Although many classical strategies[3] for their assembly have been developed, how to efficiently construct 3,4-fused bicyclic furans from readily accessible acyclic precursors is still a challenging task.[4] In this context, 2-(1-alkynyl)-2-alken-1-ones[5] have been extensively used for the synthesis of racemic 3,4-fused bicyclic furans derivatives via the metal-catalyzed intermolecular cycloaddition with nitrones,[6a] imines,[6b] 1,3-diphenyl-isobenzofuran,[6c] unactivated alkenes,[6e] and triazines.[6g] Recently, the Selander group explored an elegant indium(III)-mediated three-component reaction between 2-(1-alkynyl)-2-alken-1-ones with aldehydes and secondary amines, leading to cyclopenta[*c*]furans (Scheme 1a).[6f] Despite much progress that has been made for the synthesis of racemic 3,4-fused bicyclic furans via the intermolecular annulations of 2-(1-alkynyl)-2-alken-1-ones, the development of the asymmetric version still poses a considerable challenge, especially for the asymmetric gold catalysis, due to the linear binding mode of gold complexes causing the chiral ligand to be far away from the generated stereocenter.[7,8] To the best of our knowledge, only one example for the synthesis of optically active cyclopenta[*c*]furan has been developed by us to date (Scheme 1b).[8c] Therefore, novel protocols for rapidly assembling chiral cyclopenta[*c*]furan are in high demand.

In 2011, we reported a gold-catalyzed diastereoselective [3 + 2] cycloaddition of 2-(1-alkynyl)-2-alken-1-ones with 3-styrylindoles, providing an efficient and convenient synthetic route to highly substituted cyclopenta[*c*]furans.[6d] Unfortunately, the attempt to develop the asymmetric version of this cycloaddition failed after screening a series of different types of commercially available ligands. For example, the privileged chiral bisphosphine ligand (*R*)-**L1** derived gold complex[8a,10] led to very low enantioselectivity (16% ee) (Table 1, entry 1). Meanwhile, the enantioselectivity was also not satisfactory

Scheme 1. Synthesis of Cyclopenta[*c*]furans via the Annulations of 2-(1-Alkynyl)-2-alken-1-ones

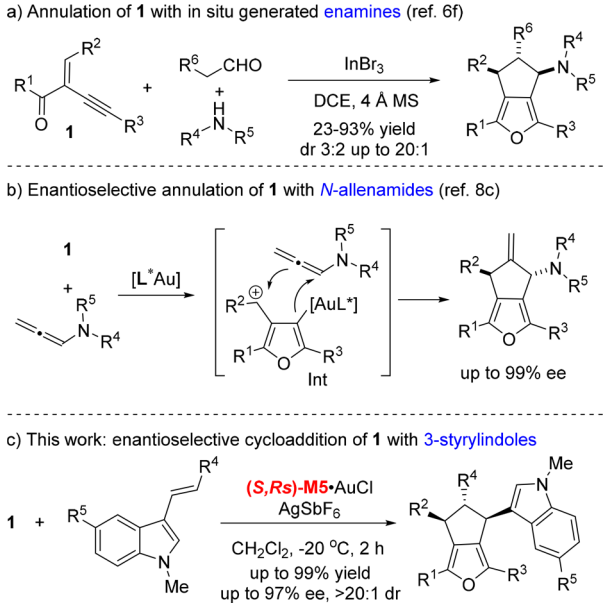


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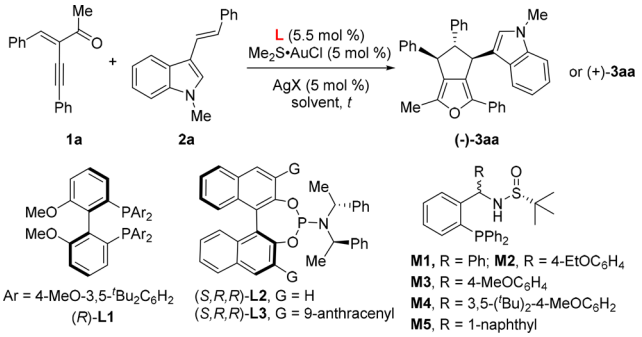
Table 1. Optimization of Reaction Conditions[a]



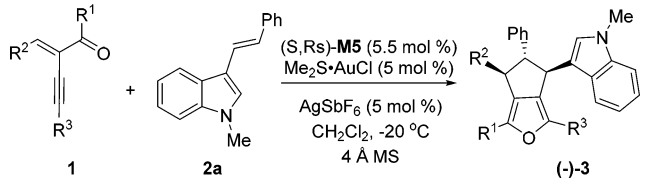
entry	ligand	AgX	solvent	t (°C)	ee (%)[b]
1	(*R*)-**L1**	AgOTf	DCE	25	(+)-**3aa**, 16
2	(*S,R,R*)-**L2**	AgOTf	DCE	25	(−)-**3aa**, 0
3	(*S,R,R*)-**L3**	AgOTf	DCE	25	(−)-**3aa**, 55
4	(*S,Rs*)-**M1**	AgOTf	DCE	25	(−)-**3aa**, 53
5	(*R,Rs*)-**M1**	AgOTf	DCE	25	(+)-**3aa**, 53
6	(*S,Rs*)-**M2**	AgOTf	DCE	25	(−)-**3aa**, 67
7	(*R,Rs*)-**M2**	AgOTf	DCE	25	(+)-**3aa**, 43
8	(*S,Rs*)-**M3**	AgOTf	DCE	25	(−)-**3aa**, 55
9	(*R,Rs*)-**M3**	AgOTf	DCE	25	(+)-**3aa**, 62
10	(*S,Rs*)-**M4**	AgOTf	DCE	25	(−)-**3aa**, 70
11	(*R,Rs*)-**M4**	AgOTf	DCE	25	(+)-**3aa**, 55
12	(*S,Rs*)-**M5**	AgOTf	DCE	25	(−)-**3aa**, 89
13	(*R,Rs*)-**M5**	AgOTf	DCE	25	(+)-**3aa**, 49
14	(*S,Rs*)-**M5**	AgOTf	Toluene	25	(−)-**3aa**, 77
15	(*S,Rs*)-**M5**	AgOTf	THF	25	(−)-**3aa**, 88
16	(*S,Rs*)-**M5**	AgOTf	CH_2Cl_2	25	(−)-**3aa**, 91
17	(*S,Rs*)-**M5**	AgOTf	DCE[c]	25	(−)-**3aa**, 93
18	(*S,Rs*)-**M5**	AgOTf	DCE[d]	25	(−)-**3aa**, 80
19	(*S,Rs*)-**M5**	$AgNTf_2$	DCE	25	(−)-**3aa**, 93
20	(*S,Rs*)-**M5**	$AgSbF_6$	DCE	25	(−)-**3aa**, 94
21	(*S,Rs*)-**M5**	$AgSbF_6$	CH_2Cl_2[c]	−20	(−)-**3aa**, 96
22	(*S,Rs*)-**M5**	$AgSbF_6$	CH_2Cl_2[c]	−40	(−)-**3aa**, 90

[a]Reaction conditions: Chiral gold complexes (5 mol %), AgX (5 mol %), **1a** (0.2 mmol), **2a** (0.24 mmol). Unless specified otherwise, conversions were determined by ^{1}H NMR analysis (99%, >20:1 dr). [b]Determined by HPLC on a chiral stationary phase. [c]100 mg of 4 Å MS were added. [d]Wet DCE, air atmosphere. DCE = 1,2-dichloroethane.

when using binol-derived phosphoramidites[11] (Table 1, entries 2−3). Recently, we designed and developed a new type of chiral ligand, called Ming-Phos,[9] which showed good performance in the gold-catalyzed asymmetric [3 + 3] cycloaddition of 2-(1-alkynyl)-2-alken-1-ones with nitrones.[8b] With the Ming-Phos ligand kit in hand, we next investigated a series of chiral Ming-Phoses. It was found that the modification of the aryl group and the relative configuration on carbon of the Ming-Phos have a large impact on the enantioselectivity (from 49% to 89% ee) (Table 1, entries 4−13). Among them, (*S,Rs*)-**M5** gave the highest ee (Table 1, entry 13). The solvent screening showed that toluene and THF led to a slight decrease in enantioselectivity (Table 1, entries 14 and 15). On the other hand, a slight increase in enantioselectivity was observed when DCE was replaced with dichloromethane as solvent (Table 1, entry 16). Notably, water exhibits a significantly negative impact on this reaction. For example, the ee value was increased to 93% by adding 4 Å MS and was decreased to 80% when the reaction was conducted in undried dichloromethane (Table 1, entries 17 and 18). A series of silver salts were then examined, and $AgSbF_6$ is the best choice (up to 94% ee) (Table 1, entries 12 and 19−20). Finally, running the reaction at −20 °C led to a slight improvement in enantioselectivity (96% ee), but the ee was decreased if the temperature was brought down to −40 °C (Table 1, entries 21−22).

With the optimal reaction conditions in hand, various 2-(1-alkynyl)-2-alken-1-ones **1** were explored to investigate the generality of this asymmetric cycloaddition, and the results are summarized in Table 2. The substrate scope is quite general,

Table 2. Scope with Respect to Various 2-(1-Alkynyl)-2-alken-1-ones 1[a]



entry	$R^1/R^2/R^3$	3	yield (%)[b]	ee[c] (%)
1	Me/Ph/Ph (**1a**)	**3aa**	97	96
2	Me/Ph/4-MeC_6H_4 (**1b**)	**3ba**	92	96
3[d]	Me/Ph/4-$MeOC_6H_4$ (**1c**)	**3ca**	95	93
4	Me/Ph/1-Naphthyl (**1d**)	**3da**	95	91
5	Me/Ph/4-$CF_3C_6H_4$ (**1e**)	**3ea**	83	93
6	Me/Ph/4-$NO_2C_6H_4$ (**1f**)	**3fa**	96	92
7	Me/4-ClC_6H_4/Ph (**1g**)	**3ga**	90	96
8	Me/4-BrC_6H_4/Ph (**1h**)	**3ha**	88	93
9[d]	Me/4-$MeOC_6H_4$/4-$MeOC_6H_4$ (**1i**)	**3ia**	73	92
10[e]	Ph/4-$MeOC_6H_4$/Ph (**1j**)	**3ja**	95	93

[a]All reactions were performed with **1** (0.3 mmol), **2a** (0.315 mmol), and catalyst (5 mol %) in CH_2Cl_2 at −20 °C for 2 h. [b]Yield of isolated products. dr >20:1. [c]Determined by HPLC on a chiral stationary phase. [d]At −5 °C, 18 h. [e]Dr = 18:1.

and all the reactions can deliver high yields with excellent enantioselectivities (89−96% ee). For example, the alkynyl moiety (R^3) with both an electron-rich and -deficient aryl group is compatible, furnishing the desired [3 + 2]-cycloadducts in 83−96% yields with excellent enantioselectivities (91−96% ee) (Table 2, entries 1−6). Moreover, good results were obtained for the reaction of **1g** and **1h** with 3-styrylindole **2a** (93−96% ee) (Table 2, entries 7−8). Notably, substituent R^1, which can be either an aliphatic or an aromatic group, has little impact on the yield and enantioselectivity (Table 2, entry 10). The absolute configuration of the cycloadduct (−)-**3ha** was unambiguously determined to be 4*S*,5*S*,6*R* by X-ray crystal structure analysis (Figure 1; CCDC 1838128).

We next examined the scope of the 3-styrylindole component (Table 3). A diverse array of 3-styrylindoles are well compatible, delivering the corresponding cycloadducts in 92−99% yields with excellent enantioselectivity (94−97% ee),

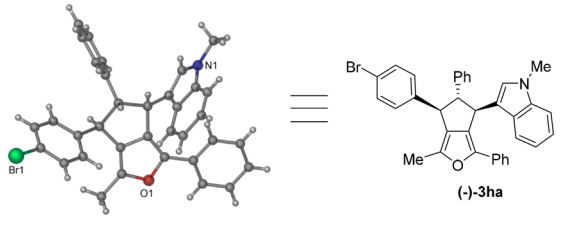


Figure 1. X-ray structure of (4*S*,5*S*,6*R*)-**3ha**.

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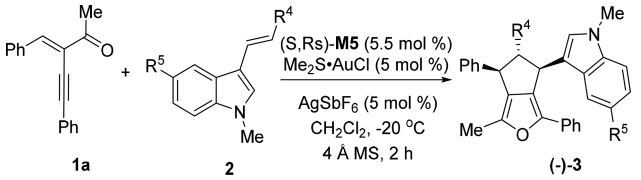
Table 3. Scope with Respect to Various 3-Styrylindole 2[a]



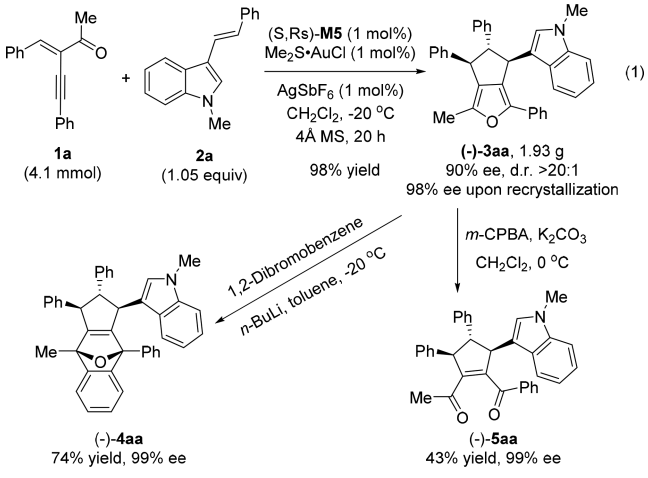
entry	R^4/R^5	3	yield (%)[b]	ee[c] (%)
1	4-MeC_6H_4/H (**2b**)	**3ab**	93	94
2	4-$MeOC_6H_4$/H (**2c**)	**3ac**	99	94
3	4-FC_6H_4/H (**2d**)	**3ad**	97	95
4	4-ClC_6H_4/H (**2e**)	**3ae**	93	96
5	4-BrC_6H_4/H (**2f**)	**3af**	99	96
6	4-$CF_3C_6H_4$/H (**2g**)	**3ag**	86	96
7	4-CNC_6H_4/H (**2h**)	**3ah**	92	97
8	4-$NO_2C_6H_4$/H (**2i**)	**3ai**	99	97
9	Ph/Me (**2j**)	**3aj**	98	90
10	Ph/MeO (**2k**)	**3ak**	98	92
11	Ph/Br (**2l**)	**3al**	73	87

[a]All reactions were performed with **1a** (0.3 mmol), **2** (0.315 mmol), and catalyst (5 mol %) in CH_2Cl_2 at −20 °C for 2 h. [b]Yield of isolated products. dr >20:1. [c]Determined by HPLC on a chiral stationary phase.

irrespective of the electronic property of the functionality at the styryl moieties (Table 3, entries 1−8). Moreover, different substituents, such as MeO, Me, and Br, could be introduced to the different positions of the indole moiety and the corresponding [3 + 2]-cycloadducts could be obtained in 73−98% yields with 87−92% ee (Table 3, entries 9−11).

It should be noted that this gold-catalyzed enantioselective [3 + 2] cycloaddition of 2-(1-alkynyl)-2-alken-1-ones with 3-styrylindoles is easy to scale-up. A gram-scale (4.1 mmol) reaction was investigated, delivering 1.93 g of (−)-**3aa** in 98% yield, with a slight loss of enantioselectivity (90% ee) with the use of a 1 mol % catalyst loading. After one recrystallization, the ee value was up to 98%. Furthermore, in order to reveal the synthetic utility of our method for generating useful and interesting chiral building blocks, we performed two synthetic transformations of the representative (−)-**3aa** (Scheme 2). For instance, (−)-**4aa** was obtained with 99% ee, via a Diels−Alder cycloaddition reaction of (−)-**3aa** with an in situ generated benzyne.[6e] Moreover, the furan ring could undergo ring opening under the oxidative conditions (*m*-CPBA), delivering functionalized compound (−)-**5aa**. Notably, the chiral 3-cyclopentyl indole skeleton is a crucial structure in the bioactive compounds.[12]

Scheme 2. Gram-Scale Synthesis and Further Transformation



In summary, the gold(I) complex attached with the novel Ming-Phos ligand is an effective catalyst system for the catalytic asymmetric intermolecular [3 + 2] cycloaddition of 2-(1-alkynyl)-2-alken-1-ones with 3-styrylindoles, furnishing the corresponding indolyl-substituted cyclopenta[*c*]furans in excellent yields (up to 99%) and high enantioselectivities (up to 97%). The salient features of the present protocol include mild conditions, excellent yields, and high diastereo- and enantioselectivities, using readily available starting materials and a chiral ligand.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.8b02701.

Experimental procedures, ^1H and ^{13}CNMR spectra and HPLC date for all products (PDF)

Accession Codes

CCDC 1838128 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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