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Asymmetric Dearomatization of 1-Aminonaphthalene Derivatives by Gold-Catalyzed Intramolecular Double C−C Bond Formation

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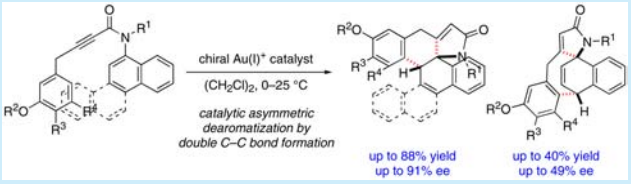
Supporting Information

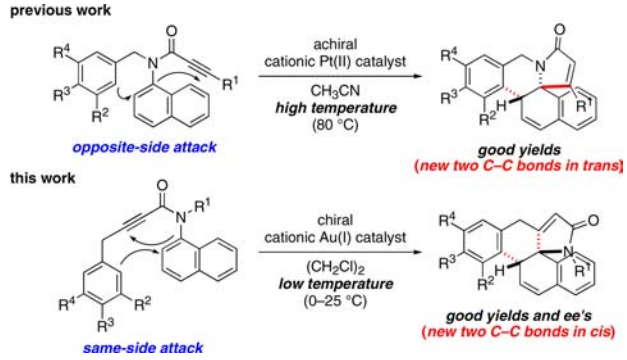
ABSTRACT: It has been established that a cationic gold(I)/axially chiral biaryl bisphosphine complex catalyzes asymmetric dearomatization of 1-aminonaphthalene derivatives by the intramolecular double C−C bond formation. Two different dearomatization products were obtained depending on the substituents on the benzyl groups at the alkyne termini.



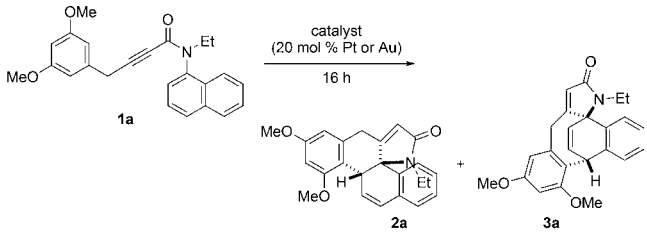
Catalytic asymmetric dearomatization of arenes through C−C bond formation is a useful method for the construction of chiral cyclic frameworks.[1] Previously reported catalytic asymmetric dearomatization reactions have been focused on the oxidative single C−C bond formation at the ortho or para position of the substituent to produce chiral cyclohexadiene derivatives.[2−5] For example, a number of the transition-metal-catalyzed asymmetric oxidative dearomatization reactions of phenol[2,3] or aniline[4] derivatives to produce chiral cyclohexadienone or iminocyclohexadiene derivatives through the oxidative single C−C bond formation have been reported. However, catalytic asymmetric dearomatization through redox-neutral double C−C bond formation at the ipso and ortho or para positions of the substituent to produce chiral cyclohexadiene derivatives has not been reported to date.[6−8] On the other hand, our research group recently reported the cationic platinum(II) complex-catalyzed dearomatization of *N*-benzyl-substituted propiolic acid 1-naphthylamides through the redox-neutral intramolecular double C−C bond formation (Scheme 1, top).[9] Although the reactions afforded racemic dearomatization products and required high temperature, this report is the first example of the catalytic dearomatization of arenes through the double C−C bond formation.[7] In this transformation, the double C−C bond formation proceeds in a *trans* fashion. In this paper, we disclose the first example of the catalytic asymmetric dearomatization of arenes through the double C−C bond formation at low temperature in a *cis* fashion using 3-benzyl-substituted propiolic acid 1-naphthylamides as substrates and a chiral cationic gold(I) complex as a catalyst (Scheme 1, bottom).[10−12]

We first examined the reaction of 3-benzyl-substituted propiolic acid 1-naphthylamide **1a** as shown in Scheme 2. Under the same reaction conditions as our previously reported dearomatization reactions of *N*-benzyl-substituted propiolic acid 1-naphthylamides using the cationic platinum(II) catalyst,[9]

Scheme 1



Scheme 2



$PtCl_2$/2AgOTf, CH_3CN, 80 °C	42%	0% (56% conv)
$PtCl_2$/(*R*)-BINAP/2AgOTf, CH_3CN, 80 °C	0%	0% (<10% conv)
$AuCl(SMe_2)$/$AgBF_4$, $(CH_2Cl)_2$, 80 °C	25%	0% (72% conv)
$AuCl(SMe_2)$/0.5(*R*)-BINAP/$AgBF_4$, $(CH_2Cl)_2$, 25 °C	54%, 54% ee	35%, 29% ee (100% conv)

the desired dearomatization reaction of **1a** proceeded to give the corresponding pentacyclic compound **2a**, while the reaction was sluggish and the product yield was moderate. The presence

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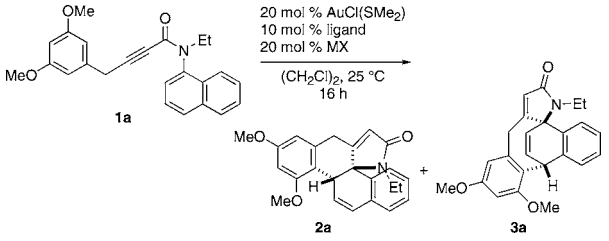
Table 1. Optimization of Reaction Conditions for Gold-Catalyzed Asymmetric Dearomatization of 1a[a]



entry	ligand	MX	conv (%)	**2a**/% yield[b] (% ee)	**3a**/% yield[b] (% ee)
1	(*R*)-BINAP	$AgBF_4$	100	54 (54)	35 (29)
2	(*R*)-H_8–BINAP	$AgBF_4$	100	61 (52)	21 (15)
3	(*R*)-Segphos	$AgBF_4$	100	44 (39)	40 (43)
4	(*S*,*S*)-Chiraphos	$AgBF_4$	50	30 (2)	19 (2)
5	(*R*,*R*)-Me-Duphos	$AgBF_4$	89	39 (3)	24 (9)
6	(*R*)-tol-BINAP	$AgBF_4$	100	54 (61)	35 (33)
7	(*R*)-xyl-BINAP	$AgBF_4$	100	74 (76)	26 (40)
8	(*R*)-dtbm-BINAP	$AgBF_4$	0	0	0
9	(*R*)-xyl-H_8–BINAP	$AgBF_4$	100	70 (67)	22 (20)
10	(*R*)-tol-Segphos	$AgBF_4$	100	58 (49)	37 (44)
11	(*R*)-xyl-Segphos	$AgBF_4$	100	68 (61)	25 (49)
12	(*R*)-xyl-BINAP	AgOTf	100	54 (82)	30 (39)
13	(*R*)-xyl-BINAP	$AgSbF_6$	100	66 (81)	27 (40)
14	(*R*)-xyl-BINAP	NaBARF	50	30 (73)	3 (32)
15[c]	(*R*)-xyl-BINAP	$AgSbF_6$	100	57 (91)	19 (43)
16[d]	(*R*)-xyl-BINAP	$AgSbF_6$	100	67 (87)	23 (44)

[a]$AuCl(SMe_2)$ (0.010 mmol), ligand (0.0050 mmol), MX (0.010 mmol), **1a** (0.050 mmol), and $(CH_2Cl)_2$ (2.0 mL) were used. [b]Isolated yield. [c]Reactions were conducted using $AuCl(SMe_2)$ (0.010 mmol), (*R*)-xyl-BINAP (0.0050 mmol), MX (0.010 mmol), **1a** (0.10 mmol), and $(CH_2Cl)_2$ (2.0 mL) at 0 °C for 72 h. [d]A reaction was conducted using (*R*)-xyl-BINAP-$(AuCl)_2$ (0.010 mmol), $AgSbF_6$ (0.020 mmol), **1a** (0.20 mmol), and $(CH_2Cl)_2$ (2.0 mL) at 0 °C for 72 h.

of a bisphosphine ligand, BINAP, significantly lowered the reaction rate. The use of a cationic gold(I) catalyst increased the conversion of **1a**, while the yield of **2a** was decreased. Pleasingly, the presence of (*R*)-BINAP significantly increased the reaction rate to give **2a** in 54% yield with 54% ee. Interestingly, the double C–C bond formation not only at the ipso and ortho positions but also at the ipso and para positions proceeded to give **3a** in 35% yield with 29% ee.

Thus, the optimization of reaction conditions for the gold(I)-catalyzed asymmetric dearomatization of **1a** was examined using 20 mol % of chiral gold(I) complexes at 25 °C as shown in Table 1. Various axially chiral biaryl bisphosphine ligands were screened (entries 1–3), which revealed that the use of H_8-BINAP, possessing a larger dihedral angle than binap,[13] increased the yield of **2a** and decreased the yield of **3a** (entry 2) (Figure 1). On the contrary, the use of Segphos, possessing a smaller dihedral angle than BINAP,[13] decreased the yield of **2a** and increased the yield of **3a** (entry 3). Nonbiaryl bisphosphine ligands were ineffective (entries 4 and 5). Axially chiral biaryl bisphosphine ligands bearing sterically demanding aryl groups on the phosphorus were also tested (entries 6–11). The use of xyl-BINAP increased the yield and ee value of **2a** (entry 7). Screening of silver salts (entries 7 and 12–14) revealed that the use of $AgSbF_6$ afforded **2a** in the highest ee value (entry 13). The reaction of **1a** was carried out at 0 °C using 10 mol % of the gold(I)-SbF_6 catalyst to give **2a** in the highest ee value, while the yield of **2a** was decreased (entry 15). Finally, the use of an isolated chiral gold(I) catalyst, (*R*)-xyl-BINAP-$(AuCl)_2$, improved the yield of **2a** with slight decrease of the ee value (entry 16).

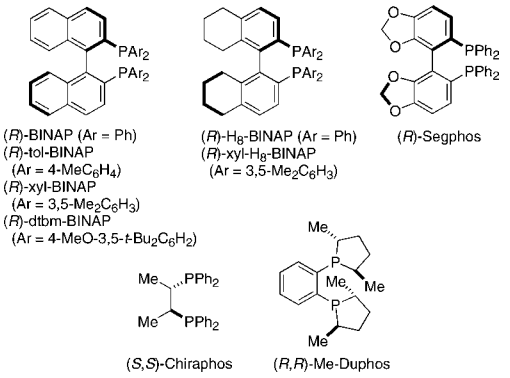


Figure 1. Structures of chiral bisphosphine ligands.

With the optimized conditions in hand, the scope of substrates was examined as shown in Table 2. The reactions of 1-naphthylamides **1a–d**, possessing a 3,5-dimethoxy benzyl group (entries 1–4), afforded the corresponding dearomatization products **2a–d** and **3a–d** in good yields, although the ee values of **2c,d**, possessing sterically more demanding isobutyl and benzyl groups on the nitrogen (entries 3 and 4), were lower than those of **2a,b**, possessing ethyl and methyl groups on the nitrogen (entries 1 and 2). Interestingly, although the reactions of 1-naphthylamides **1e–h** possessing various electron-rich benzyl groups (entries 5–8) afforded the corresponding dearomatization products **2e–h** in moderate to high yields, the corresponding eight-membered products **3a–d** were not generated at all. Not only 1-aminonaphthalene derivatives **1a–h** but also 6-aminochrysene derivative **1i**

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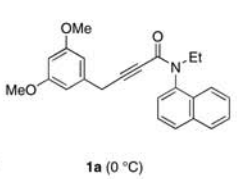
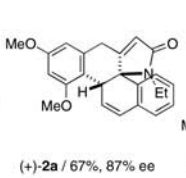
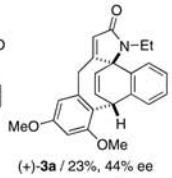
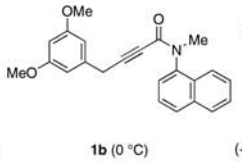
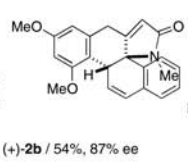
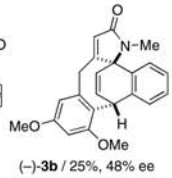
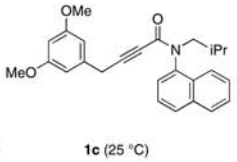
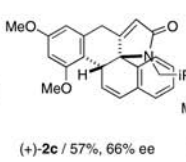
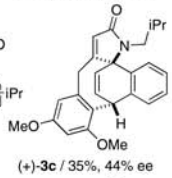
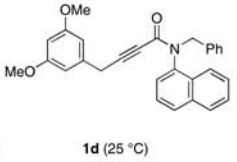
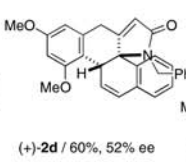
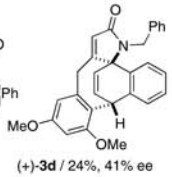
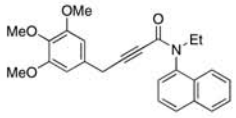
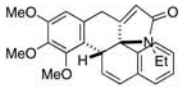
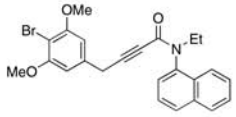
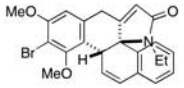
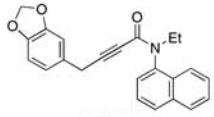
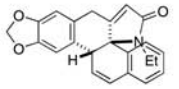
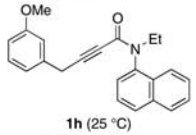
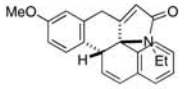
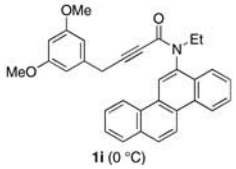
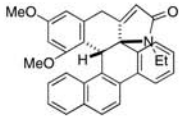
Table 2. Gold-Catalyzed Asymmetric Dearomatization of 1-Aminonaphthalene Derivatives 1a–i[a]

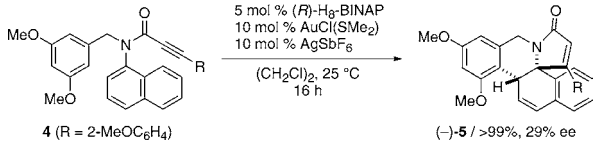
entry	1 (temp)	2, 3 / yield,[b] ee	
1	 **1a** (0 °C)	 (+)-**2a** / 67%, 87% ee	 (+)-**3a** / 23%, 44% ee
2	 **1b** (0 °C)	 (+)-**2b** / 54%, 87% ee	 (−)-**3b** / 25%, 48% ee
3	 **1c** (25 °C)	 (+)-**2c** / 57%, 66% ee	 (+)-**3c** / 35%, 44% ee
4	 **1d** (25 °C)	 (+)-**2d** / 60%, 52% ee	 (+)-**3d** / 24%, 41% ee
5	 **1e** (25 °C)	 (+)-**2e** / 88%, 62% ee	
6	 **1f** (25 °C)	 (4b*S*,12b*R*)-(+)-**2f** / 55%, 45% ee	
7	 **1g** (25 °C)	 (+)-**2g** / 73%, 51% ee	
8	 **1h** (25 °C)	 (+)-**2h** / 69%[c], 60% ee	
9	 **1i** (0 °C)	 (+)-**2i** / 56%, 40% ee	

[a]Reactions were conducted using (*R*)-xyl-BINAP-$(AuCl)_2$ (0.010 mmol), $AgSbF_6$ (0.020 mmol), **1** (0.20 mmol), and $(CH_2Cl)_2$ (2.0 mL) at 0–25 °C for 72 h. [b]Isolated yield. [c]The corresponding regioisomer was generated in ca. 5% yield, although it could not be isolated in a pure form.

produced the corresponding dearomatization product **2i** with moderate yield and ee value (entry 9).

The cationic gold(I)/biaryl bisphosphine catalyst was applied to the asymmetric dearomatization of *N*-benzyl-substituted propiolic acid 1-naphthylamide **4**. After ligand screening, H_8-BINAP was selected as the best ligand, while the ee value of the corresponding dearomatization product **5** was low (Scheme 3).

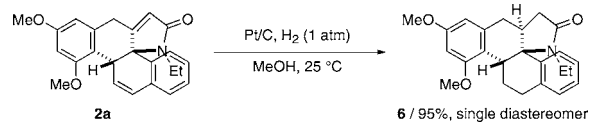
Scheme 3



Therefore, the present substrate design using not *N*-benzyl- but 3-benzyl-substituted propiolic acid 1-naphthylamide derivatives is advantageous to realize good enantioselectivity.

Finally, hydrogenation of dearomatized product **2a** was examined as shown in Scheme 4. The hydrogenation of two isolated double bonds proceeded by using Pt/C as a catalyst to give **6** in high yield as a single diastereomer.

Scheme 4



In conclusion, we have established that a cationic gold(I)/axially chiral biaryl bisphosphine complex catalyzes asymmetric dearomatization of 1-aminonaphthalene derivatives by intramolecular double C–C bond formation. Two different dearomatization products were obtained depending on substituents on benzyl groups at the alkyne termini. Future works will focus on expanding the reaction scope and elucidation of the reaction mechanism.

■ ASSOCIATED CONTENT

Supporting Information

Experimental procedures, compound characterization data, and X-ray crystallographic information files. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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