Enantioselective Synthesis and Enhanced Circularly Polarized Luminescence of S-Shaped Double Azahelicenes

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S *Supporting Information*

ABSTRACT: The enantioselective synthesis of azahelicenes and S-shaped double azahelicenes has been achieved via the Au-catalyzed sequential intramolecular hydroarylation of alkynes. The use of excess AgOTf toward a Au(I) complex is crucial for this transformation. Interestingly, the circularly polarized luminescence activity of the S-shaped double azahelicenes was significantly higher than that of the azahelicenes.

Scheme 1

H elicenes, possessing fascinating π-conjugated helical structures, have long attracted much attention because of their potential applications to functional organic materials.[1] Therefore, research on the structure−chiroptical property relationship[2] and asymmetric synthesis of helicenes[3] is highly important. With respect to the structure−chiroptical property relationship, several studies on electronic and steric effects by the introduction of substituents on helicenes have been reported recently,[2] while chiroptical properties of double helicenes have not been well investigated to date.[4,5] With respect to the asymmetric synthesis, several catalytic enantioselective syntheses of helicenes have been developed by applying the transition-metal-catalyzed aromatic ring construction.[6−10] As the most successful example, the transition-metal-catalyzed [2 + 2 + 2] cycloaddition[12] of alkynes has been applied to the catalytic enantioselective synthesis of helicenes and moderate to high enantioselectivities have been accomplished by using chiral Rh(I),[7] Ni(0),[8a−c] Co(I),[8d] and Ir(I)[9] complexes. However, the enantioselective synthesis of an azahelicene[11] and the double helicene[3] has not been accomplished to date.

Recently, the transition-metal-catalyzed intramolecular hydroarylation of alkynes has also been applied to the catalytic helicene synthesis,[12] while an enantioselective variant has not been developed. However, our research group reported the enantioselective intramolecular hydroarylation of alkynes to produce axially chiral 4-aryl-2-quinolinones with high ee values by using chiral Pd(II) or Au(I) catalysts (Scheme 1).[13] In this transformation, achiral alkyne **A** is efficiently converted to axially chiral biaryl **B** through the formation of a pyridone ring. We anticipated that the enantioselective sequential intramolecular hydroarylation of achiral diyne **C** would proceed to give helically
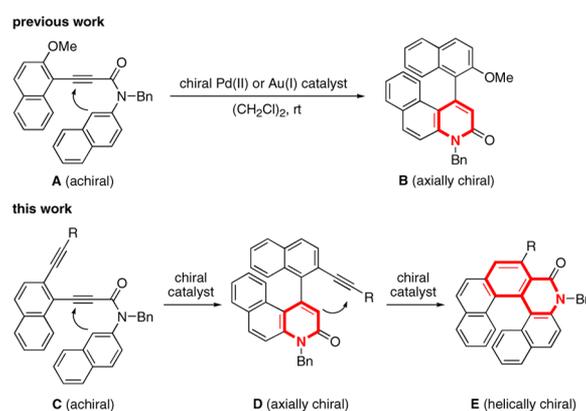
chiral azahelicene **E** through axially chiral biaryl **D** by using a single chiral transition-metal catalyst (Scheme 1).[14] In this paper, we disclose the Au-catalyzed enantioselective synthesis and enhanced circularly polarized luminescence of S-shaped double azahelicenes.

We first examined the reaction of diyne **1a**[15] with a cationic Pd(II) or Au(I)/(R)-BINAP [2,2′-bis(diphenylphosphino)-1,1′-binaphthyl] complex.[13] Although no reaction was observed using the Pd catalyst, the use of the Au catalyst afforded biaryl **2a** in good yield (Table 1, entry 1). Interestingly, the use of excess AgOTf toward the Au complex[16] promoted the desired sequential hydroarylation to give biaryl **2a** and azahelicene **3a** in the same yields (entry 2). Elevating the reaction temperature completed the sequential hydroarylation to give **3a** in excellent yield, while the ee value of **3a** significantly decreased (entry 3). Finally, increasing the amount of the Au catalyst afforded **3a** in excellent yield with a good ee value (entry 4).

The substituent effect of the enantioselective azahelicene synthesis was examined, which revealed that a 2-methoxyphenyl group at the alkyne terminus and two naphthyl groups are necessary to obtain high product yields and/or high ee values (Table 2). The reaction of phenyl-substituted diyne **1b**[15] proceeded to give aza[6]helicene **3b** with a lower yield and ee

Table 1. Screening of Catalysts for Enantioselective Sequential Intramolecular Hydroarylation of Diyne 1a to Azahelicene 3a[a]
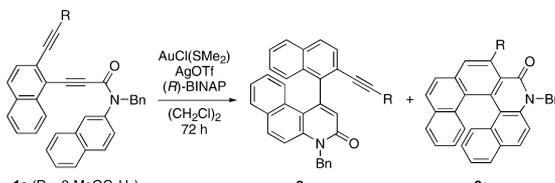
entry	AuCl(SMe$_2$) (mol %)	AgOTf (mol %)	(R)-BINAP (mol %)	temp (°C)	2a % yield[b] (ee, ±)	3a % yield[b] (ee, ±)
1	20	20	10	rt	76 (56, +)	0
2	20	30	10	rt	42 (61, +)	42 (79, −)
3	20	30	10	80	0	80 (56, −)
4	30	45	15	rt	0	96 (69, −)

[a]1a (0.050 mmol) and (CH$_2$Cl)$_2$ (2.0 mL) were used. Absolute configurations of 2a and 3a were not determined. [b]Isolated yield.

Table 2. Substituent Effect on Enantioselective Sequential Intramolecular Hydroarylation of Diynes 1 to Azahelicenes 3[a]
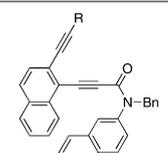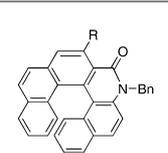
entry	diyne 1	azahelicene 3
1	1a (R = 2-MeOC$_6$H$_4$)	(−)-3a / 96% yield, 69% ee
2	1b (R = Ph)	(−)-3b / 56% yield, 39% ee
3[b]	1c (R = H)	(+)-3c / 44% yield, 30% ee
4	1d (R = 2-MeOC$_6$H$_4$)	(−)-3d / 83% yield, 48% ee
5	1e (R = 2-MeOC$_6$H$_4$)	(−)-3e / 97% yield, 36% ee
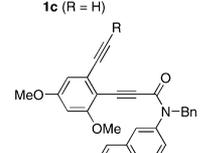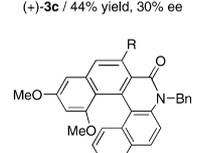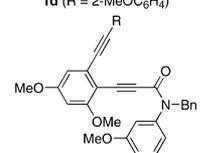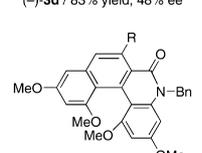
[a]Reactions were conducted using AuCl(SMe$_2$) (0.030 mmol), AgOTf (0.045 mmol), (R)-BINAP (0.015 mmol), 1a−e (0.10 mmol), and (CH$_2$Cl)$_2$ (2.0 mL) at rt for 72 h. The cited yields are of the isolated products. Absolute configurations of 3a−e were not determined. [b]A reaction was conducted using AuCl(SMe$_2$) (0.050 mmol), AgOTf (0.10 mmol), (S)-BINAP (0.025 mmol), 1c (0.10 mmol), and (CH$_2$Cl)$_2$ (2.0 mL) at rt for 7 days.

value than in the case of 3a (entry 1 vs 2). Furthermore, the reaction of terminal diyne 1c[15] was sluggish and the corresponding aza[6]helicene 3c was obtained with a low yield and ee value (entry 3). Diynes 1d,e,[15] possessing dimethoxyphenyl groups in place of naphthyl groups, were converted to the corresponding aza[5] and [4]helicenes 3d,e in high yields, while their ee values were low to moderate (entries 4 and 5). The

thermal stabilities of thus obtained azahelicenes 3a−e toward racemization were examined, which revealed that all azahelicenes retained their initial ee values after heating in (CH$_2$Cl)$_2$ at 80 °C for 24 h, even in the case of aza[4]helicene 3e.

Diyne 1f, possessing two naphthyl groups and a removable 4-methoxybenzyl group on the nitrogen, was prepared starting from known alkynoic acid 4[13] as shown in Scheme 2. The formation of carboxylic acid chloride from 4 with 1-chloro-N,N,2-trimethyl-1-propenylamine followed by amidation with aminonaphthalene 5 furnished the corresponding amide 6. Acid hydrolysis of the MOM protecting group furnished the corresponding naphthol 7. Triflation followed by the Pd-catalyzed Sonogashira cross-coupling with arylacetylene 8 afforded the desired diyne 1f. This diyne 1f was subjected to the Au-catalyzed enantioselective sequential intramolecular hydroarylation to give aza[6]helicene (−)-3f in high yield with a good ee value. Removal of the 4-methoxybenzyl group on the nitrogen followed by chlorination with phosphoryl chloride afforded aza[6]helicene (−)-9f, possessing a pyridine unit, without racemization.

The successful enantioselective synthesis of azahelicenes prompted our investigation into the diastereo- and enantioselective synthesis of S-shaped double azahelicenes via the Au-catalyzed double sequential intramolecular hydroarylation of achiral tetrayne 1g as shown in Scheme 3. Triflation of commercially available 2-hydroxy-1-naphthaldehyde (10) followed by the Pd-catalyzed Sonogashira cross-coupling with 8 furnished alkyne 11. The Corey−Fuchs reaction followed by methoxycarbonylation and alkaline hydrolysis furnished alkynoic acid 12. Etherification of 4-hydroxybenzonitrile (13) followed by reduction furnished amine 14. The copper(I)/DMPAO [2-(2,6-dimethylphenylamino)-2-oxoacetic acid]-catalyzed double C−N bond formation,[17] between 14 and 2,6-dibromonaphthalene, afforded diamine 15. Condensation of thus obtained acid 12 and diamine 15 afforded the desired tetrayne 1g. Although a high catalyst loading was required, the Au-catalyzed enantioselective double sequential intramolecular hydroarylation of 1g proceeded at room temperature.[18] Pleasingly, enantiopure S-shaped double azahelicene (+)-3g[19] and a mixture of racemic-3g and meso-3g were separately isolated through silica gel preparative TLC. This phenomenon can be explained by the fact that the excess enantiopure (+)-3g (R_f = 0.45) traveled slower than meso/rac-3g (R_f = 0.64) on the TLC plate due to the lower solubility of enantiopure 3g than meso/rac-3g in the mobile phase (hexane/EtOAc = 1:1).[20] Indeed, enantiopure (−)-3g was obtained using (R)-BINAP in place of (S)-BINAP. Removal of the 4-alkoxybenzyl group on the nitrogen followed by chlorination afforded S-shaped double azahelicene 9g,[19] possessing two pyridine units.

The photophysical properties of azahelicenes (3f and 9f) and S-shaped double azahelicenes (3g and 9g) are summarized in Table 3.[21] Double azahelicenes showed red shifts of absorption and emission maxima compared with azahelicenes. Double azahelicenes showed higher quantum yields in CHCl$_3$ solution than azahelicenes, and that of 3g (Φ_F = 0.190) was the highest among four azahelicenes.[22] The optical rotation values of double azahelicenes 3g and 9g were smaller than those of single azahelicenes 3f and 9f possibly due to the presence of two pseudo-axially chiral methoxyphenyl groups. Finally, we conducted circularly polarized luminescence (CPL) measurements (differential emission of right circularly polarized light versus left circularly polarized light in chiral molecular systems) of four azahelicenes in chloroform. Unfortunately, CPL

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dx.doi.org/10.1021/ja500841f | J. Am. Chem. Soc. 2014, 136, 5555−5558
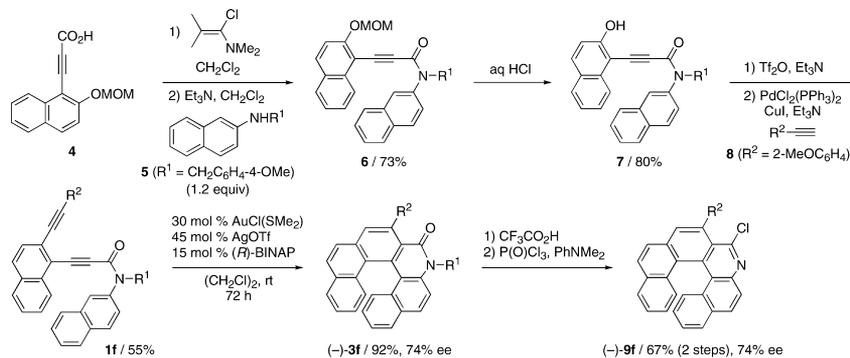
Scheme 2

Scheme 3
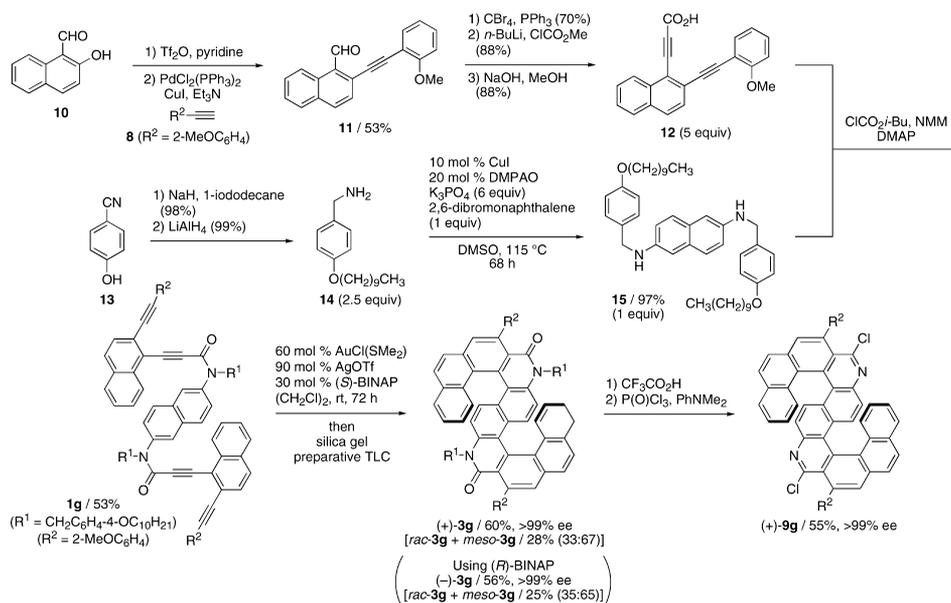
Table 3. Photophysical Properties of Azahelicenes and S-Shaped Double Azahelicenes[a]

compd	UV-absorption λ_{max}/nm	fluorescence λ_{max}/nm (excitation wavelength/nm)	ϕ_F (excitation wavelength/nm)	$[\alpha]_D^{25}$ [d]	$g_{lum} = 2(I_L - I_R)/(I_L + I_R)$[e] (excitation wavelength/nm)
(−)-**3f**	317, 381[b]	467 (317)[b]	0.051 (400)[b]	1355	<0.001 (375)
(−)-**8f**	325[b]	467 (317)[b]	0.021 (380)[b]	1273	<0.001 (375)
(+)-**3g**	284, 448[c]	471, 492 (284)[c]	0.190 (400)[c]	377	0.028 ± 0.002 (375)
(−)-**9g**	260, 329, 445[c]	454, 480 (329)[c]	0.094 (400)[c]	1086	0.011 ± 0.001 (375)

[a]Measured in CHCl$_3$ at 25 °C. [b]At 1.0×10^{-5} M. [c]At 1.0×10^{-6} M. [d]Values are calculated as 100% ee. [e]The ee values of the compounds are as follows: (−)-**3f** and (−)-**9f**, 74% ee; (+)-**3g** and (−)-**9g**, >99% ee.

intensities for azahelicenes **3f** and **9f** were below our measurable limit ($g_{lum} < 0.001$). However, surprisingly, double azahelicenes **3g** and **9g** exhibited CPL activities, as the CPL spectra of (+) and (−) helicenes are mirror images. The degree of CPL is given by the luminescence dissymmetry ratio, which is defined as $g_{lum} = 2(I_L - I_R)/(I_L + I_R)$, where I_L and I_R are the luminescence intensities of left and right circularly polarized light. The values were $g_{lum} = 0.028$ at 492 nm for (+)-**3g** and $g_{lum} = -0.011$ at 454 nm for (−)-**9g** in chloroform; those values are comparable to recently reported helically chiral small organic molecules showing high CPL activities.[23]

In conclusion, we have achieved the enantioselective synthesis of azahelicenes and S-shaped double azahelicenes via the Au-catalyzed sequential intramolecular hydroarylation of alkynes.

The use of excess AgOTf toward a Au(I) complex is crucial for this transformation. Interestingly, the circularly polarized luminescence activity of the S-shaped double azahelicenes was significantly higher than that of the azahelicenes. Future work will focus on the synthesis of novel helicenes, showing good chiroptical properties, via the catalytic enantioselective aromatic ring construction.

■ **ASSOCIATED CONTENT**

Ⓢ Supporting Information

Experimental procedures and compound characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

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(18) Enantioselective synthesis of a double biaryl, see the SI.

(19) The absolute configurations of (+)-**3g** and (+)-**9g** have not been determined. The relative configurations are shown in Scheme 3.

(20) Enantiopure **3g** is less soluble than *meso/rac*-**3g** in hexane.

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dx.doi.org/10.1021/ja500841f | *J. Am. Chem. Soc.* 2014, 136, 5555−5558