Asymmetric Catalysis

DOI: 10.1002/anie.201300696

Enantioselective Synthesis of Planar-Chiral Carba-Paracyclophanes: Rhodium-Catalyzed [2+2+2] Cycloaddition of Cyclic Diynes with Terminal Monoynes**

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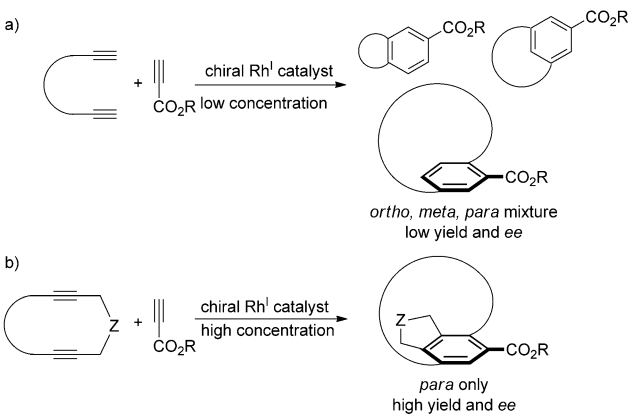
Planar-chiral [*n*]paracyclophanes are attractive chiral sources for chiral synthetic reagents and functional materials.[1] Therefore, their catalytic enantioselective synthesis is an important target in synthetic organic chemistry.[2,3] The first example was reported by our group in 2007.[4] We succeeded the enantioselective construction of the ansa chain by the rhodium- or palladium-catalyzed C–S bond formation, which affords dithia[9]–[12]paracyclophanes with moderate yields and enantioselectivities (up to 60% *ee*).[4] Subsequently in 2009, Shibata and co-workers reported the catalytic enantioselective synthesis of paracyclophanes by the enantioselective introduction of substituents on the benzene ring, which possesses the thermodynamically flexible ansa chain.[5,6] For example, the enantioselective synthesis of polyoxa[7,7] and [18]paracyclophanes by a palladium-catalyzed Sonogashira coupling (up to 79% *ee*),[5] and dioxa[10]–[17]paracyclophanes by the sparteine-mediated *ortho*-lithiation (up to 99% *ee*)[6] were reported. These examples achieved good to excellent enantioselectivities, but the obtainable products were limited to heteroatom-linked paracyclophanes.

In 2001, Kanomata and co-workers achieved the asymmetric synthesis of carba[10] and [11]paracyclophanes with thermodynamically flexible ansa chains by dynamic resolution of diastereomeric mixtures.[7] In 2009, Suzuki and co-workers achieved the selective synthesis of enantiomerically pure C_2-symmetric planar-chiral carba[10] and [12]paracyclophanes by the ring-closing alkene metathesis of chiral tetraenes and subsequent hydrogenation.[8,9] These examples are novel and useful, but the catalytic enantioselective synthesis was not accomplished. In contrast, our research group reported that achiral [7]–[21]cyclophanes, including paracyclophanes, can be synthesized in good yields by the rhodium-catalyzed [2+2+2] cycloaddition of α,ω-diynes with acetylenedicarboxylates.[10–13] Recently, we applied this methodology to the enantioselctive synthesis of planar chiral polyoxa[7]–[9]paracyclophanes using propiolates in place of acetylenedicarboxylates.[14–16] However, both product yields and enantioselectivities were insufficient (up to 20% yield and 75% *ee*), presumably because of the possible formation of mutiple rhodacycle intermediates (Scheme 1a).[14] Furthermore, this method is limited to the synthesis of polyoxa[*n*]-paracyclophanes, and requires low substrate concentrations (0.02 M) to suppress the undesired oligomerization reactions. To overcome these problems, we designed the [2+2+2] cycloaddition of a cyclic 1,6-diyne, possessing an all-carbon-long tether, with propiolates (Scheme 1b). This reaction design would afford the paracyclophane as the sole product and exclude the undesired formation of *ortho*- and *meta*-cyclophanes. Gleiter and co-workers reported the synthesis of structurally interesting cyclophanes (cyclobutadieno superphanes) by the cobalt-mediated [2+2] cycloaddition of cyclic diynes,[17,18] however, the paracyclophane synthesis by the [2+2+2] cycloaddition has not been accomplished. Herein, we disclose the high-yielding and highly enantioselective synthesis of planar-chiral carba[10]–[12]paracyclophanes by the cationic rhodium(I)/(*S*,*S*)-bdpp-catalyzed [2+2+2] cyclo-



Scheme 1. Enantioselective synthesis of planar-chiral paracyclophanes by rhodium-catalyzed [2+2+2] cycloadditions. a) Previous work. b) This work.

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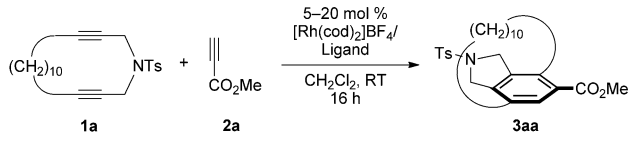
[**] This work was supported partly by a Grant-in-Aid for Scientific Research (No. 20675002) from MEXT and ACT-C from JST (Japan). We are grateful to Umicore for generous support in supplying rhodium complexes, and Takasago International Corporation for the gift of chiral propargyl alcohol (*R*)-**2j**.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201300696.

addition of cyclic 1,6-diynes with terminal monoynes under high substrate concentrations.[19]

We first investigated the [2+2+2] cycloaddition of the cyclic 1,6-diyne **1a** with methyl propiolate (**2a**; 5 equiv) in the presence of the cationic rhodium(I)/(*S*)-binap complex (20 mol%). Although the desired reaction proceeded at room temperature to give the desired carba[10]paracyclophane **3aa**, both the product yield and *ee* value were low (Table 1, entry 1). In this reaction, **2a** was consumed in the homo-[2+2+2] cycloaddition. In the previous reports, axially chiral biaryl bisphosphine ligands showed high catalytic activity and enantioselectivity for the rhodium-catalyzed [2+2+2] cycloaddition to produce cyclophanes.[10,14–16] However, interestingly, the use of a chiral nonbiaryl bisphosphine ligand [(*S*,*S*)-diop] significantly improved both product yield and *ee* value (entry 2). Screening of chiral nonbiaryl bisphosphine ligands (entries 2–10) revealed that the use of (*S*,*S*)-bdpp furnished **3aa** with the highest yield and *ee* value (entry 3). Pleasingly, the catalyst loading could be reduced to 5 mol% without erosion of the product yield and *ee* value (entry 11). Furthermore, the amount of **2a** could also be reduced to 1.2 equivalents (entry 12). Importantly, these optimized reaction conditions allowed a high substrate concentration of 0.1M (entry 12). The absolute configuration of (−)-**3aa** was unambiguously determined to *S* by the anomalous dispersion method (Figure 1).[20]

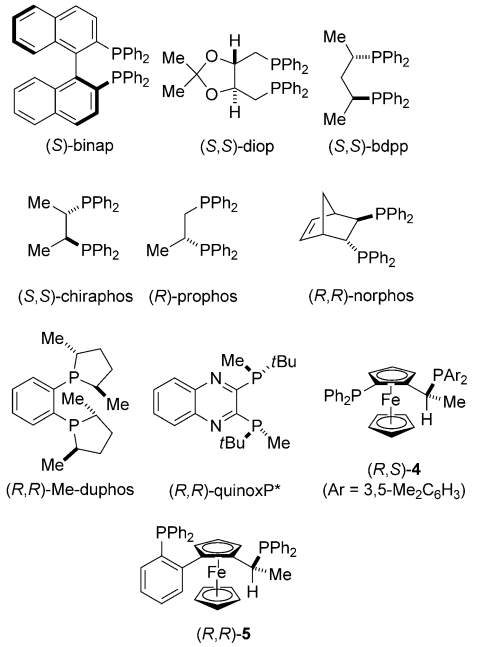
Table 1: Screening of chiral ligands for rhodium-catalyzed enantioselective [2+2+2] cycloaddition of **1a** with **2a**.[a]



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

Entry	Ligand	Catalyst (mol%)	**2a** (equiv)	Conv. of **1a** [%]	Yield [%][b]	*ee* [%]
1	(*S*)-binap	20	5.0	30	11	15 (*S*)
2	(*S*,*S*)-diop	20	5.0	100	82	81 (*R*)
3[c]	(*S*,*S*)-bdpp	20	5.0	100	91	91 (*S*)
4[c]	(*S*,*S*)-chiraphos	20	5.0	82	37	67 (*S*)
5[c]	(*R*)-prophos	20	5.0	100	44	37 (*R*)
6[c]	(*R*,*R*)-norphos	20	5.0	100	66	24 (*R*)
7[c]	(*R*,*R*)-Me-duphos	20	5.0	<5	<5	–
8[c]	(*R*,*R*)-quinoxP*	20	5.0	49	16	89 (*R*)
9	(*R*,*S*)-**4**	20	5.0	100	87	33 (*R*)
10	(*R*,*R*)-**5**	20	5.0	6	6	4 (*R*)
11[c,d]	(*S*,*S*)-bdpp	5	5.0	100	86	91 (*S*)
12[c,d]	(*S*,*S*)-bdpp	5	1.2	100	87	92 (*S*)

[a] $[Rh(cod)_2]BF_4$ (0.010 mmol), ligand (0.010 mmol), **1a** (0.050 mmol), **2a** (0.25 mmol), and CH_2Cl_2 (2.0 mL) were used. [b] Yield of isolated product. [c] $[Rh(nbd)_2]BF_4$ was used. [d] **1a** (0.20 mmol), and **2a** (0.24–1.00 mmol) were used. cod = cyclo-1,5-octadiene, nbd = 2,5-norbornadiene, Ts = 4-toluenesulfonyl.



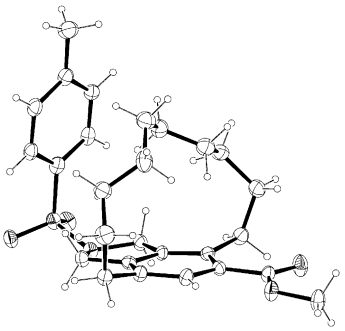
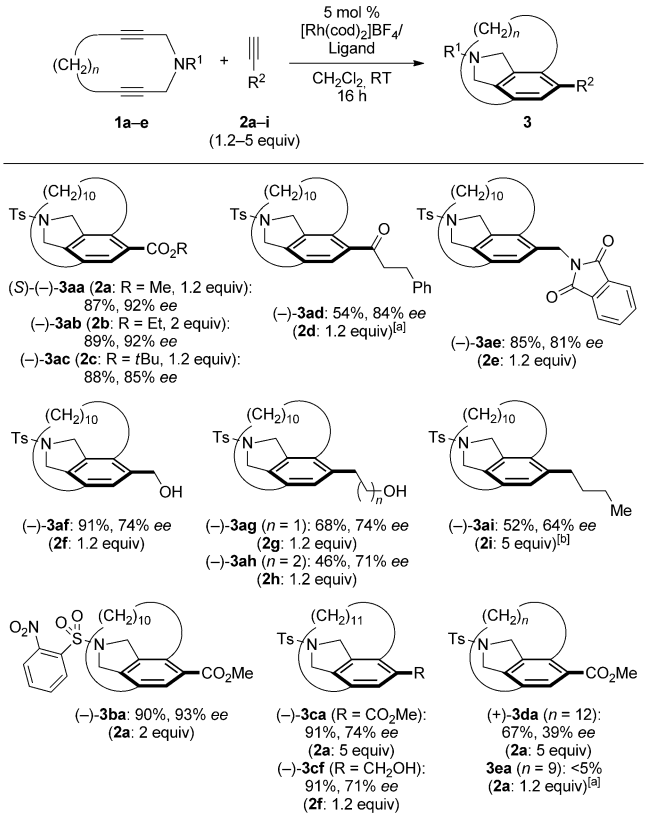


Figure 1. ORTEP diagram of (*S*)-(−)-**3aa**. Thermal ellipsoids shown at 20% probability.

With the optimized reaction conditions in hand, the scope of the carba[*n*]paracyclophane synthesis was examined (Scheme 2). With respect to monoynes, methyl, ethyl, and *tert*-butyl propiolates (**2a–c**) reacted with **1a** to give the carba[10]paracyclophanes **3aa–ac** with high yields and *ee* values. Not only esters **2a–c** but also the ketone **2d** reacted with **1a** to give the cyclophane **3ad** with a high *ee* value, however, the product yield was moderate and a high catalyst loading was required. The protected propargylamine **2e** and acetylenic alcohols **2f–h** could be employed, but the product yields are highly dependent upon the alkyl chain length (product yield: **2e,f** > **2g** > **2h**, alkyl chain length: **2e,f** < **2g** < **2h**). The unfunctionalized alkyne **2i** reacted with **1a** to give the cyclophane **3ai** with moderate yield and *ee* value, but a large excess of **2i** was necessary. With respect to cyclic 1,6-diynes, not only the tosylamide-linked diyne **1a** but the nosylamide-linked[21] diyne **1b** could also be employed. The effect of the diyne tether length was also examined. The carba[11]paracyclophanes **3ca** and **3cf** were obtained with good yields and *ee* values. However, the carba[12]paracyclophane **3da** was obtained with lower yield and *ee* value, and the carba[9]paracyclophane **3ea** was obtained in only a trace amount even when using a high catalyst loading.

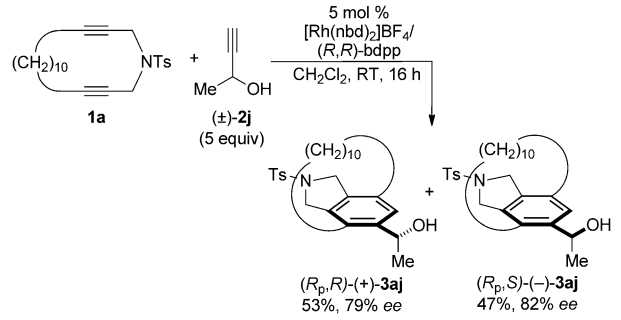
Planar-chiral compounds, possessing a chiral secondary alcohol moiety, are frequently employed as valuable intermediates for the chiral ligand synthesis, such as the chiral ferrocenyl phosphine ligands (*R*,*S*)-**4** and (*R*,*R*)-**5**.[22] Our research group previously reported the kinetic resolution of



Scheme 2. Scope of cyclic diynes and terminal monoynes. Reactions were conducted using $[Rh(nbd)_2]BF_4$ (0.010–0.040 mmol), (*S*,*S*)-bdpp (0.010–0.040 mmol), **1** (0.20 mmol), **2** (0.24–1.00 mmol), and CH_2Cl_2 (2.0 mL). The cited yields are of the isolated products.
[a] $[Rh(nbd)_2]BF_4$ (0.040 mmol) and (*S*,*S*)-bdpp (0.040 mmol) were used. [b] $[Rh(nbd)_2]BF_4$ (0.020 mmol) and (*S*,*S*)-bdpp (0.020 mmol) were used.

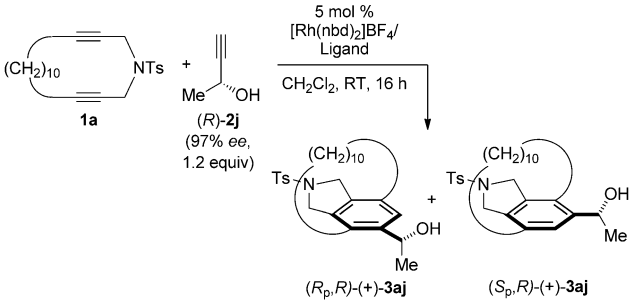
excess racemic tertiary propargyl alcohols (5 equiv) with 1,6-diynes (1 equiv) through a rhodium-catalyzed [2+2+2] cycloaddition.[23] Thus, the kinetic resolution of excess amounts of the racemic secondary propargyl alcohol (±)-**2j** (5 equiv) with **1a** (1 equiv) was attempted by using (*R*,*R*)-bdpp as a ligand. However, the corresponding diastereomeric pair of carba[10]paracyclophanes (R_p,*R*)-**3aj** and (R_p,*S*)-**3aj**, possessing an *R* configuration of planar chirality, were obtained in a ratio of approximately 1:1 with good *ee* values (Scheme 3).

Next, the reaction of the commercially available chiral secondary propargyl alcohol (*R*)-**2j** (97% *ee*) with **1a** using an achiral ligand (dppb = 1,4-bis(diphenyphosphino)butane) was examined, and (R_p,*R*)-**3aj** and (S_p,*R*)-**3aj** were obtained in a ratio of approximately 1:2 (Table 2, entry 1).[24] These results (Scheme 3 and Table 2, entry 1) indicated that the induction of planar chirality relies more on the ligand chirality than the alcohol chirality. Therefore, the reaction of (*R*)-**2j** with **1a** using the chiral ligand would afford the carba[10]-paracyclophane **3aj**, possessing the ligand-controlled planar chirality, as a major diastereomer. Indeed, (R_p,*R*)-**3aj** and (S_p,*R*)-**3aj** were obtained as major diastereomers with excellent *ee* values by using (*R*,*R*)-bdpp and (*S*,*S*)-bdpp, respectively, as a ligand (entries 2 and 3). On the contrary, the minor



Scheme 3. Rhodium-catalyzed [2+2+2] cycloaddition of **1a** with the racemic secondary propargyl alcohol **2j**.

Table 2: Rhodium-catalyzed [2+2+2] cycloaddition of cyclic diyne **1a** with chiral secondary propargyl alcohol (*R*)-**2j**.[a]



Entry	Ligand	(R_p,*R*)-(+)-**3aj**		(S_p,*R*)-(+)-**3aj**	
		Yield [%][b]	*ee* [%]	Yield [%][b]	*ee* [%]
1[c]	dppb	35	–	60	–
2	(*R*,*R*)-bdpp	87	>99	8	78
3	(*S*,*S*)-bdpp	11	83	77	99

[a] $[Rh(nbd)_2]BF_4$ (0.010 mmol), (*S*,*S*)-bdpp (0.010 mmol), **1a** (0.20 mmol), (*R*)-**2j** (97% *ee*, 0.24 mmol), and CH_2Cl_2 (2.0 mL) were used. [b] Yield of isolated product. [c] $[Rh(cod)_2]BF_4$ was used instead of $[Rh(nbd)_2]BF_4$.

diastereomers (S_p,*R*)-**3aj** (entry 2) and (R_p,*R*)-**3aj** (entry 3) were obtained with lower *ee* values than those of the major diastereomers. The relative configurations of two diastereomers were confirmed by the X-ray crystallographic analysis of (S_p,*R*)-(+)-**3aj** (Figure 2).[20]

Interestingly, the paracyclophane formation from internal monoyne **2k** was inefficient, even when employing a high catalyst loading and prolonged reaction time (Scheme 4).[25]

A possible mechanism for the enantioselective formation of the paracyclophane (*S*)-**3aa** is shown in Scheme 5. As the homo-[2+2+2] cycloaddition of cyclic diyne **1a** via a rhodacycle from **1a** was sluggish, the formation of (*S*)-**3aa** via **A** might be the major pathway. The formation of the intermediate **B**, which affords (*R*)-**3aa**, might be unfavorable as a result of steric repulsion between the tether of **1a** and the axial phenyl group of (*S*,*S*)-bdpp.[26] The formation of an intermediate of type **A** from **1a** and internal monoyne **2k** might be sluggish because of steric and/or electronic effects, which accounts for the low reactivity of **2k** toward **1a**.

In conclusion, we have achieved the high-yielding and highly enantioselective synthesis of carba[10]-[12]paracyclo-

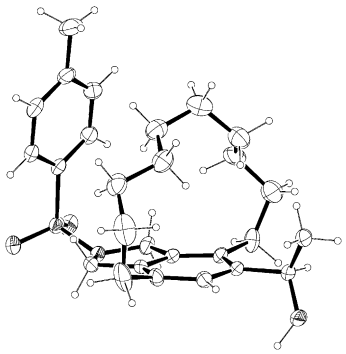
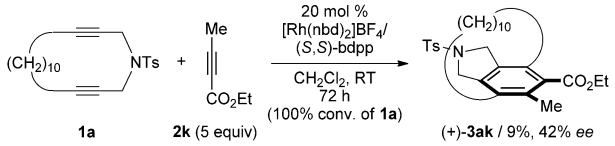
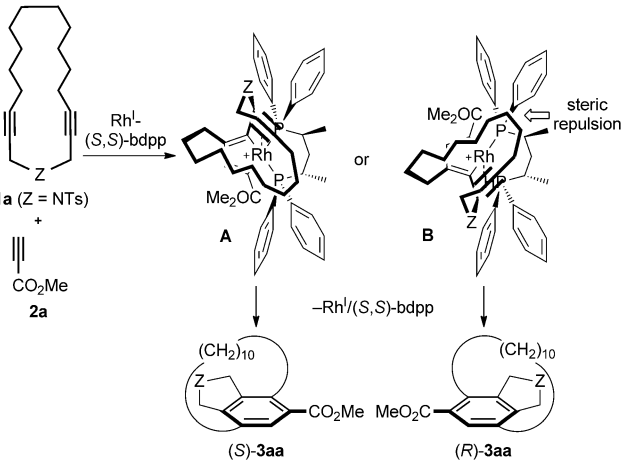


Figure 2. ORTEP diagram of (S_p,*R*)-(+)-**3aj**. Thermal ellipsoids shown at 20% probability.



Scheme 4. Rhodium-catalyzed [2+2+2] cycloaddition of **1a** with the internal monoyne **2k**.



Scheme 5. Possible reaction mechanism.

phanes with up to 91% yield and 93% *ee* by the cationic rhodium(I)/(*S*,*S*)-bdpp-catalyzed [2+2+2] cycloaddition of cyclic diynes with terminal monoynes under high substrate concentrations. Future work will focus on further utilization of cyclic diynes for the cyclophane synthesis and application of product paracyclophanes to chiral reagents.

Received: January 26, 2013
Published online: March 25, 2013

Keywords: alkynes · asymmetric catalysis · cycloadditions · cyclophanes · rhodium

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