SHORT COMMUNICATION

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Asymmetric Synthesis of C_2-Symmetric Axially Chiral Biaryls through Rhodium-Catalyzed and Alkyne-Controlled Diastereoselective Double [2+2+2] Cycloaddition

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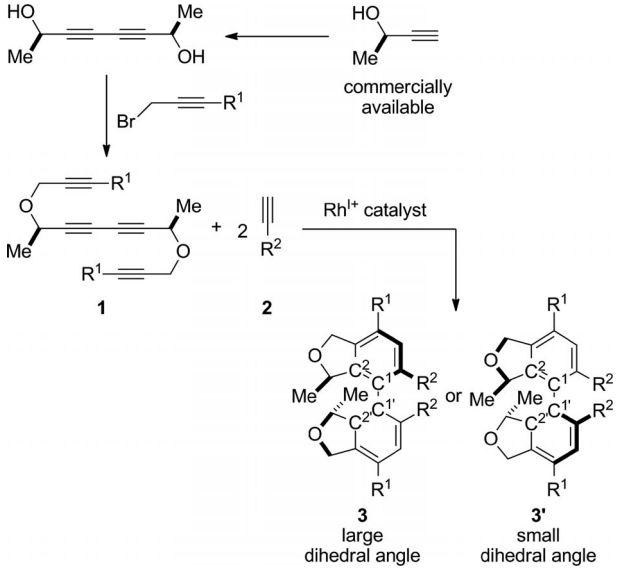
The asymmetric synthesis of C_2-symmetric axially chiral biaryls was achieved by the cationic rhodium(I)/1,3-bis(diphenylphosphino)propane (dppp) complex catalyzed diastereoselective double [2+2+2] cycloaddition of (*R*)-3-butyn-2-ol-derived tetraynes with functionalized monoynes. Interestingly, the use of propiolates afforded biaryls possessing large dihedral angles, and in contrast, the use of propargyl alcohol afforded biaryls possessing small dihedral angles.

Introduction

A number of asymmetric syntheses of axially chiral biaryls[1] by transition-metal-catalyzed enantioselective [2+2+2] cycloaddition[2] have been reported by using rhodium(I),[3] iridium(I),[4] and cobalt(I)[5] complexes as catalysts. These reactions clearly demonstrate the high synthetic utility of asymmetric annulation for the synthesis of axially chiral biaryls.[6] However, the asymmetric synthesis of axially chiral biaryls by transition-metal-catalyzed diastereoselective [2+2+2] cycloaddition by using chiral alkynes has not been well examined.[7,8] Hapke and co-workers reported recently the cobalt(I)-catalyzed diastereoselective [2+2+2] cycloaddition of chiral proline-derived diynes with nitriles, which led to axially chiral arylpyridines, but the diastereoselectivities were insufficient (up to 1.75:1 *dr*).[7]

Our research group reported the rhodium(I)-catalyzed enantioselective double [2+2+2] cycloaddition of a tetrayne with methyl propiolate leading to a C_2-symmetric axially chiral biaryldicarboxylic ester.[3c] However, the product yield and *ee* value were moderate (44% yield, 70%*ee*). Thus, we designed the rhodium(I)-catalyzed diastereoselective [2+2+2] cycloaddition of chiral tetrayne **1**, which can be readily prepared from commercially available chiral 3-butyn-2-ol, with functionalized monoyne **2** to afford functionalized C_2-symmetric axially chiral biaryl **3** or **3′** possessing a large or small dihedral angle (C^2–C^1–$C^{1'}$–$C^{2'}$), respectively (Scheme 1). A number of C_2-symmetric axially chiral biaryls possessing small dihedral angles are available,[9] but those possessing a dihedral angle larger than that in 2,2′-disubstituted 5,5′,6,6′,7,7′,8,8′-octahydro-1,1′-binaphthyl derivatives[10] are not readily accessible. Therefore, the selective synthesis of biaryl **3** would be more attractive.



Scheme 1. Rhodium(I)-catalyzed diastereoselective [2+2+2] cycloaddition of chiral tetrayne **1** with functionalized monoyne **2**.

Results and Discussion

We first investigated the reaction of (*R*)-3-butyn-2-ol (>99% *ee*)-derived internal tetrayne (*R*,*R*)-**1a** with methyl propiolate (**2a**, 4 equiv.) at room temperature in the presence of a cationic rhodium(I)/1,4-bis(diphenylphosphino)-butane (dppb) complex (20 mol-%). Pleasingly, the reaction

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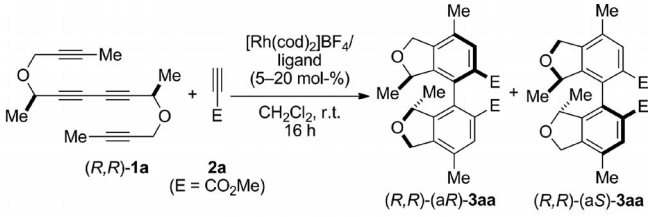
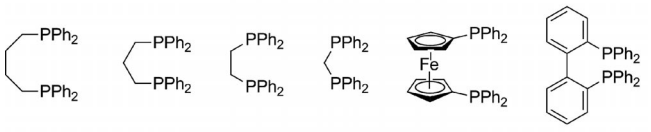
proceeded regio- and diastereoselectively to give corresponding biaryldicarboxylic ester[11] (a*R*)-**3aa** in moderate yield (Table 1, Entry 1). Interestingly, not biaryl (a*S*)-**3aa** possessing a small dihedral angle but biaryl (a*R*)-**3aa** possessing a large dihedral angle was obtained exclusively. Screening of bis(phosphine) ligands[12] revealed that the use of bis(phosphine) ligands with larger bite angles afforded (a*R*)-**3aa** with complete diastereoselectivity (Table 1, Entries 1, 2, 5, and 6), whereas poor diastereoselectivities were observed by using bis(phosphine) ligands with smaller bite angles (Table 1, Entries 3 and 4). In the cases of 1,3-bis(diphenylphosphino)propane (dppp), 1,2-bis(diphenylphosphino)ethane (dppe), and 1,1-bis(diphenylphosphino)methane (dppm), $[Rh(nbd)_2]BF_4$ (nbd = norbornadiene) was used in place of $[Rh(cod)_2]BF_4$ (cod = 1,5-cyclooctadiene) to avoid the formation of catalytically inactive 1:2 [Rh/bis(phosphine)] complexes. Biaryl (a*R*)-**3aa** was obtained in the highest yield by using dppp as the ligand (Table 1, Entry 2). Pleasingly, the catalyst loading and amount of **2a** could be reduced to 5 mol-% (Table 1, Entry 7) and 2.4 equiv. (Table 1, Entry 8), respectively.

With the optimized reaction conditions in hand, we tested the generality of the reaction with respect to both cycloaddition partners as shown in Table 2. Tetrayne (*R*,*R*)-**1a** reacted with both methyl and ethyl propiolates (**2a** and **2b**) to give corresponding biaryldicarboxylic esters (a*R*)-**3aa** and (a*R*)-**3ab** in good yields (Table 2, Entries 1 and 2). Not only (*R*,*R*)-**1a** but also terminal tetrayne (*R*,*R*)-**1b** (Table 2, Entry 3) and phenyl-substituted internal tetrayne (*R*,*R*)-**1c** (Table 2, Entry 4), prepared from (*R*)-3-butyn-2-ol (>99% *ee*), could be employed. Next, the reactions of tetraynes with propargyl alcohol (**2c**) were examined. Pleasingly, the reactions of tetraynes (*R*,*R*)-**1a** and (*R*,*R*)-**1c** with **2c** proceeded to give corresponding biaryldimethanols[11] (a*S*)-**3ac** and (a*S*)-**3cc** in moderate yields with complete diastereoselectivity in both cases, although high catalyst loadings were required (Table 2, Entries 5 and 6). Interestingly, biaryls **4** possessing small dihedral angles were obtained exclusively. Unfortunately, the reactions with methyl- and phenyl-substituted monoynes **2d** and **2e** were inefficient (Table 2, Entries 7 and 8). In Entries 4–8, longer reaction times and/or higher catalyst loadings were required to complete the second annulation to give the biaryls. Notably, complete diastereoselectivity was observed in all entries. Al-

Table 1. Screening of reaction conditions for rhodium-catalyzed double [2+2+2] cycloaddition of (*R*,*R*)-**1a** with **2a**.

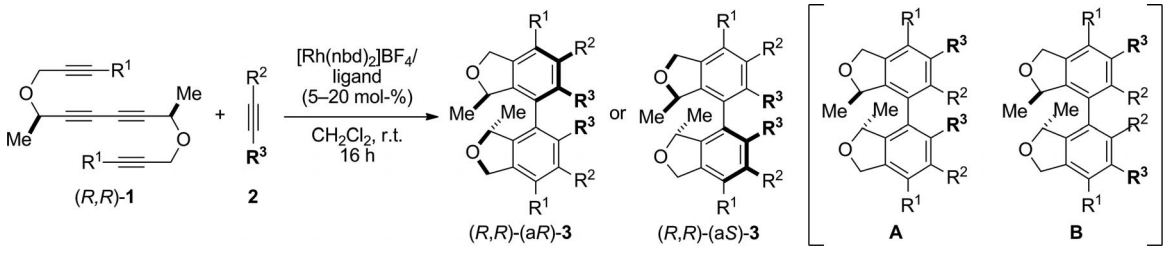




Entry	Ligand	Catalyst [mol-%]	**2a** [equiv.]	Yield[a] [%]	(a*R*)-**3aa**/ (a*S*)-**3aa**
1	dppb	20	4.0	57	100:0
2[b]	dppp	20	4.0	73	100:0
3[b]	dppe	20	4.0	70	59:41
4[b]	dppm	20	4.0	9	44:56
5	dppf	20	4.0	54	100:0
6	biphep	20	4.0	19	100:0
7	dppp	5	4.0	75	100:0
8	dppp	5	2.4	69	100:0

[a] Yield of isolated product. [b] $[Rh(nbd)_2]BF_4$ was used.

Table 2. Rhodium-catalyzed diastereoselective double [2+2+2] cycloaddition of tetraynes (*R*,*R*)-**1a**–**c** with monoynes **2a**–**e**.[a]

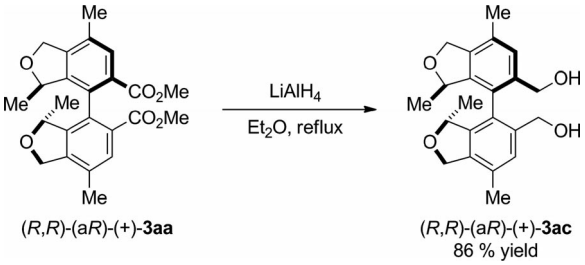


Entry	**1** (R^1)	**2** (R^2, R^3; equiv.)	Catalyst [mol-%]	Time [h]	**3**, yield[b] [%]	**A** or **B**, yield[c] [%]
1	(*R*,*R*)-**1a** (Me)	**2a** (H, CO_2Me; 2.4)	5	16	(a*R*)-(+)-**3aa**, 69	<10
2	(*R*,*R*)-**1a** (Me)	**2b** (H, CO_2Et; 2.4)	5	16	(a*R*)-(+)-**3ab**, 70	<10
3	(*R*,*R*)-**1b** (H)	**2a** (H, CO_2Me; 5)	5	16	(a*R*)-(+)-**3ba**, 44	**B**, ca. 30
4	(*R*,*R*)-**1c** (Ph)	**2a** (H, CO_2Me; 5)	10	16	(a*R*)-(+)-**3ca**, 50	<10
5	(*R*,*R*)-**1a** (Me)	**2c** (H, CH_2OH; 5)	10	16	(a*S*)-(–)-**3ac**, 41	**A**, ca. 45
6	(*R*,*R*)-**1c** (Ph)	**2c** (H, CH_2OH; 4)	20	16	(a*S*)-(–)-**3cc**, 41	**A**, ca. 20
7	(*R*,*R*)-**1a** (Me)	**2d** (Me, CO_2Et; 5)	20	72	(a*R*)-(+)-**3ad**, 31	**A**, ca. 20
8	(*R*,*R*)-**1a** (Me)	**2e** (Ph, CO_2Et; 2.4)	20	72	(a*R*)-(–)-**3ae**, 27	<10

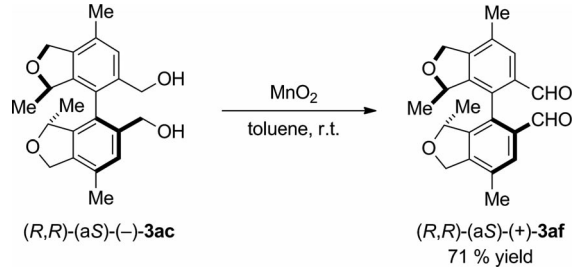
[a] Reactions were conducted with $[Rh(nbd)_2]BF_4$ (5–20 mol-%), dppp (5–20 mol-%), (*R*,*R*)-**1a**–**c** (1 equiv.), **2a**–**e** (2.4 or 5 equiv.), and CH_2Cl_2 at room temperature. [b] Yield of isolated product. [c] These undesired regioisomers were not isolated in pure form.

though the precise reason cannot be explained at the present stage, significant amounts of undesired regioisomers **A** or **B** were generated in some entries. Homo-[2+2+2] cycloaddition products from tetraynes **1a**–**c** were also generated other than these regioisomers.

Reduction and oxidation of the thus-obtained biaryls were briefly examined. Reduction of biarylcarboxylic ester (a*R*)-**3aa** with $LiAlH_4$[13] afforded biaryldimethanol (a*R*)-**3ac** (Scheme 2). Oxidation of biaryldimethanol (a*S*)-**3ac** with MnO_2[14] afforded biaryldicarbaldehyde (a*S*)-**3af** (Scheme 3).



Scheme 2. Reduction of biarylcarboxylic ester (*R*,*R*)-(a*R*)-**3aa**.



Scheme 3. Oxidation of biaryldimethanol (*R*,*R*)-(a*S*)-**3ac**.

The atropisomeric configurations of biaryls (a*R*)-(+)-**3aa**,[15] (a*R*)-(+)-**3ab**,[16] (a*R*)-(+)-**3ba**,[15] and (a*S*)-(–)-**3ac**[15] were confirmed by X-ray crystallographic analyses. Dihedral angles of biaryldicarboxylic esters (a*R*)-(+)-**3aa** and (a*R*)-(+)-**3ba** (114 and 100°; Figures 1 and 2, respectively) in the crystal are markedly larger than that of biaryldimethanol (a*S*)-(–)-**3ac** (84°; Figure 3). The atropisomeric configuration of (a*S*)-(–)-**3cc** was confirmed by a NOESY experiment.[17] The atropisomeric configurations of (a*R*)-(+)-**3ca**, (a*R*)-(+)-**3ad**, and (a*R*)-(–)-**3ae** were also confirmed by NOESY experiments of the corresponding biaryldimethanol.[17]

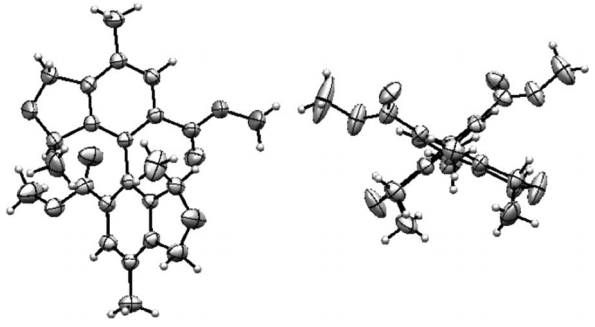


Figure 1. ORTEP diagram of (*R*,*R*)-(a*R*)-(+)-**3aa** with ellipsoids at 50% probability.

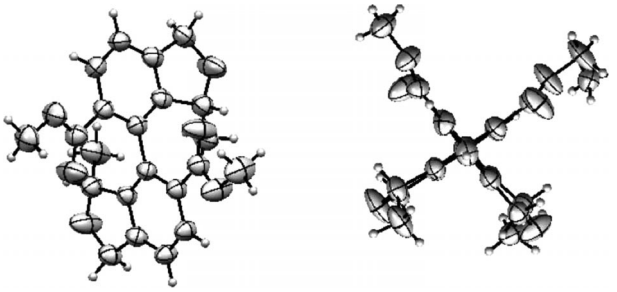


Figure 2. ORTEP diagram of (*R*,*R*)-(a*R*)-(+)-**3ba** with ellipsoids at 50% probability.

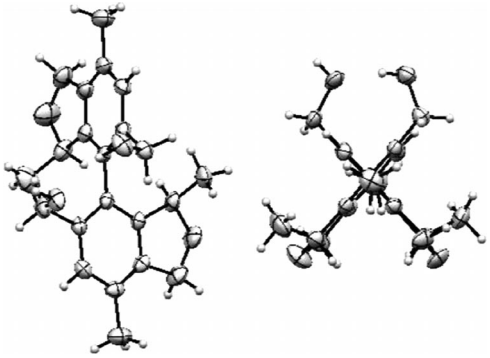
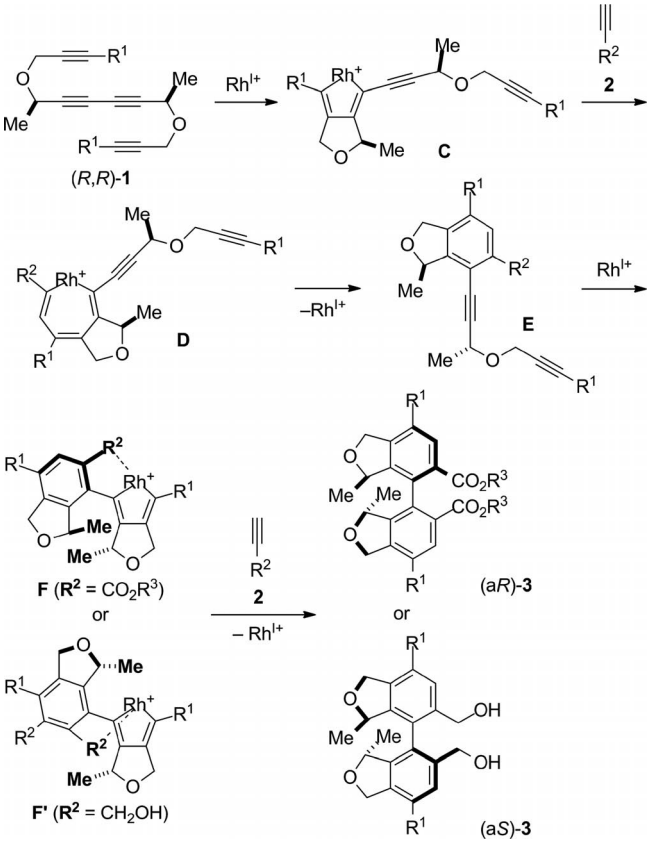
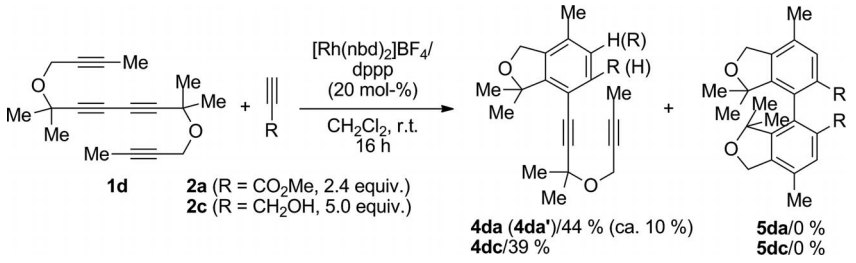


Figure 3. ORTEP diagram of (*R*,*R*)-(a*S*)-(–)-**3ac** with ellipsoids at 50% probability.

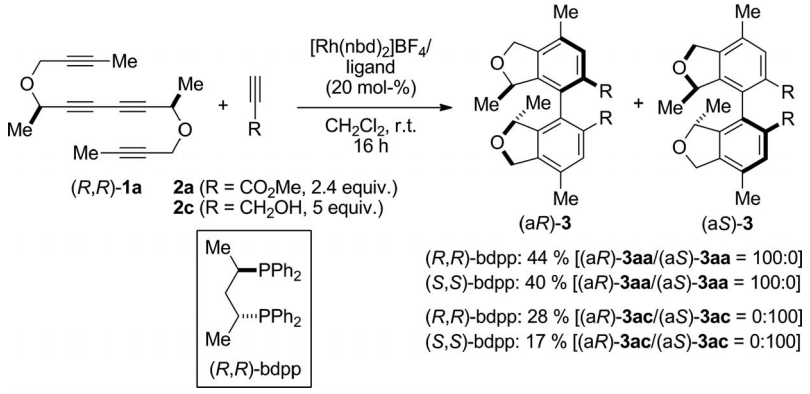
Scheme 4 depicts a possible mechanism for the observed diastereoselectivities, although this proposal is speculative



Scheme 4. Possible explanation for diastereoselectivities.



Scheme 5. Reactions of 2-methyl-3-butyn-2-ol-derived tetrayne **1d** with monoynes **2a** and **2c**.



Scheme 6. Reactions of (*R*,*R*)-**1a** with **2a** and **2c** by using a cationic rhodium(I)/(*R*,*R*)-bdpp or (*S*,*S*)-bdpp complex.

and a precise mechanism cannot be established at the present stage. The first [2+2+2] cycloaddition proceeds via rhodacycles **C** and **D** to give diyne **E**. Subsequent rhodacycle formation would afford intermediate **F** or **F′**. If the R^2 substituent is a larger alkoxycarbonyl group, intermediate **F** is preferred so that steric repulsion between the alkoxycarbonyl group and the methyl group of the rhodacycle can be avoided; this intermediate goes on to afford biaryl (a*R*)-**3**. In contrast, if the R^2 substituent is a smaller hydroxymethyl group, intermediate **F′** is preferred so that steric repulsion between the two methyl groups of the 1,3-dihydroisobenzofuran and the rhodacycle can be avoided; this intermediate goes on to afford biaryl (a*S*)-**3**.

We anticipated that the reactions of sterically demanding 2-methyl-3-butyn-2-ol-derived tetrayne **1d** with **2a** and **2c** would stop after single annulation owing to the large steric repulsion in both intermediates **F** and **F′**. Indeed, single annulation products **4da** (along with regioisomer **4da′**, which was not isolated in pure form) and **4dc** were obtained in moderate yields, whereas double annulation products **5da** and **5dc** were not obtained at all (Scheme 5).

Finally, we examined whether the ligand chirality could control the axial chirality. The reaction of (*R*,*R*)-**1a** with **2a** by using a cationic rhodium(I)/(*R*,*R*)-bdpp or (*S*,*S*)-bdpp complex afforded exclusively (a*R*)-**3aa** [Scheme 6, bdpp = 2,4-bis(diphenylphosphino)pentane]. In contrast, the reaction of (*R*,*R*)-**1a** with **2c** by using the cationic rhodium(I)/(*R*,*R*)-bdpp or (*S*,*S*)-bdpp complex afforded exclusively (a*S*)-**3ac** (Scheme 6). These results clearly indicated that the induction of axial chirality relies not on the ligand chirality but on the choice of the monoyne.

Conclusions

The asymmetric synthesis of C_2-symmetric axially chiral biaryls has been achieved by the cationic rhodium(I)/dppp complex catalyzed diastereoselective [2+2+2] cycloaddition of (*R*)-3-butyn-2-ol-derived tetraynes with functionalized monoynes. Interestingly, the use of propiolates afforded biaryls possessing large dihedral angles, and in contrast, the use of propargyl alcohol afforded biaryls possessing small dihedral angles. Future work will focus on the application of novel C_2-symmetric axially chiral biaryldicarboxylic acid and biaryldimethanol derivatives in organic synthesis.

Experimental Section

Typical Procedure: Under argon, $[Rh(nbd)_2]BF_4$ (3.7 mg, 0.010 mmol) and dppp (4.2 mg, 0.010 mmol) were dissolved in CH_2Cl_2 (2.0 mL), and the mixture was stirred at room temperature for 30 min. H_2 was introduced to the resulting solution in a Schlenk tube, and the mixture was warmed for 1 min. After stirring at room temperature for 1 h, the resulting solution was concentrated to dryness. To a CH_2Cl_2 (1.5 mL) solution of the residue was added a CH_2Cl_2 (0.5 mL) solution of (*R*,*R*)-**1a** (48.4 mg, 0.200 mmol) and **2a** (40.4 mg, 0.480 mmol) at room temperature. After stirring at room temperature for 16 h, the resulting solution was purified by preparative TLC (*n*-hexane/EtOAc, 3:1) to give (*R*,*R*)-(a*R*)-(+)-**3aa** (56.4 mg, 0.137 mmol, 69% yield; Table 2, Entry 1).

Supporting Information (see footnote on the first page of this article): Experimental procedures, characterization data, and copies of ^1H and ^{13}C NMR spectra.

Acknowledgments

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[16] The atropisomeric configuration of (*R*,*R*)-(+)-**3ab** may also be (a*R*), as determined by X-ray crystallographic analysis, although the quality of the crystal was not high enough.

[17] See the Supporting Information for more details.

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