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TADDOL-Derived Cationic Phosphonites: Toward an Effective Enantioselective Synthesis of [6]Helicenes via Au-Catalyzed Alkyne Hydroarylation

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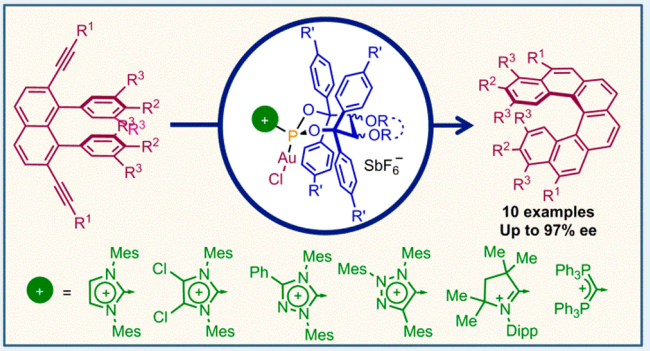
Supporting Information

ABSTRACT: A series of cationic phosphonites, all sharing a TADDOL skeleton but decorated with different positively charged substituents at phosphorus, were synthesized and tested as chiral ancillary ligands on the Au-catalyzed intramolecular hydroarylation of appropriate diynes toward carbo[6]helicenes with different substitution patterns. Our studies showed that the Au complexes derived from phosphonites bearing 1,3-dimesityl-1,2,3-triazolium and 1,4-dimesityl-1,2,4-triazolium substituents are the best precatalysts for the desired cyclization in terms of regio- and enantioselectivity of the products obtained. In contrast, all of our attempts to prepare Au complexes from cationic phosphonites derived from CAACs failed, and only ligand decomposition products could be isolated.



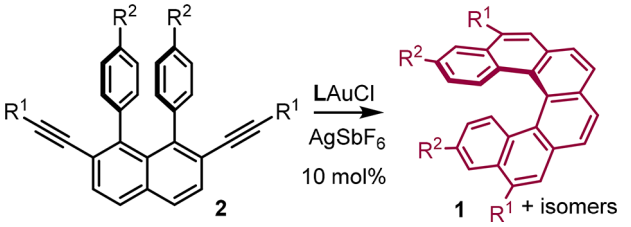
KEYWORDS: *asymmetric hydroarylation, Au catalysis, ligand design, helicenes, α-cationic ligands*

INTRODUCTION

The enantioselective synthesis of helicenes has received considerable attention during the last few years due to their continuously increasing number of applications, which range from ligand design to molecular machines.[1] Several diastereo- and enantioselective methods to obtain helicene type molecules have been reported;[2] however, most of these protocols are only valid to prepare heterohelicenes:[3] that is, structures showing a helical architecture but in which one or several carbon atoms from the parent skeleton have been formally replaced by a heteroatom. Highly enantioselective syntheses of purely carbon based helicenes (carbohelicenes) are scarce and, when available, their scope is still limited. To the best of our knowledge, the first highly enantioselective synthesis of such ortho-annulated polybenzenoid systems was reported by Starý employing a Ni-catalyzed [2 + 2 + 2] cycloaddition of appropriate triynes to afford dibenzo[6]helicenes.[4] Subsequent modifications of this original method by either the Starý group or others have allowed its extension to the preparation of structurally differentiated [6]-, [7]-, or even higher order carbohelicenes.[5]

Very recently, our group reported a new route to [6]carbohelicenes **1** via the sequential Au-catalyzed hydroarylation of suitably shaped diynes **2** (Scheme 1). In order to promote the necessary reactivity at the metal center and efficiently control the enantioselectivity of the cyclization process, monodentate cationic phosphonites of general formula

Scheme 1. Au-Catalyzed Enantioselective Synthesis of Helicenes



3 were designed and subsequently used as ancillary ligands.[6] In **3** the chiral information is provided by a well-precedented TADDOL-derived moiety, whose modular synthesis allows an easy modification of their structures upon convenience.[7] In addition, the positively charged imidazolium group directly attached to phosphorus is responsible for the enhancement of Lewis acidity at the metal center in comparison with traditional catalysts; this was later translated into higher catalyst efficiency.[8]

In our preliminary screening, the optimization of the TADDOL fragment of **3** was carried out, with ligands **3a,b,f**

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being those identified as most adequate in terms of translating enantioselectivity to the final helicene (Figure 1a). For

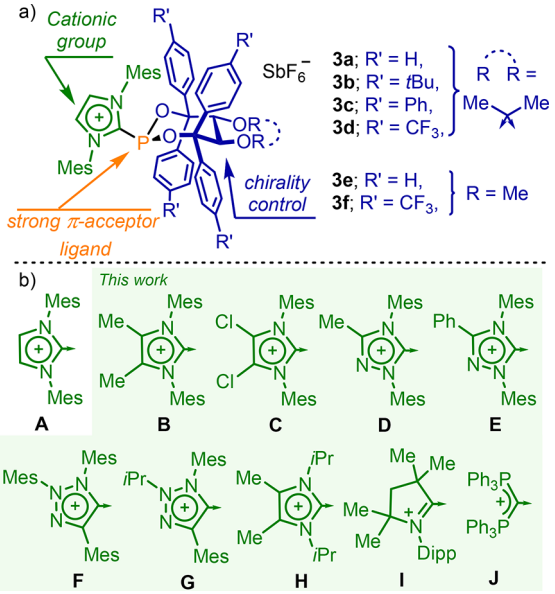

Figure 1. Structural design of cationic phosphonites: influence of the cationic group.

synthetic convenience the cationic part, a 1,3-dimesitylimidazolium group, was kept fixed at that time. We anticipated, however, that a more fine adjustment of the donor endowment in cationic phosphonites could also be crucial to further control the reactivity and/or the enantioselectivity of the final catalysts. Changing the nature of the group bearing the positive charge makes this tuning possible.[9] That conviction let us embark on the synthesis of a second generation of α-cationic phosphonites bearing a broad series of cationic substituents and the study of their influence in the model hydroarylation reaction. Specifically, imidazolium groups **B** and **C** and 1,2,4- and 1,2,3-triazolium groups **D**−**G** were selected because from their structures a minimal alteration of the original chiral pocket in phosphonites **3** could be inferred. Hence, the influence of the donor capacity of the ligands bound to gold on the enantioselectivity of the process might be accurately assessed without suffering from any significant disturbing effect derived from steric factors. Substituents **H**−**J** were included in our study in a deliberate attempt to further explore new structures not previously considered (Figure 1b).

RESULTS AND DISCUSSION

Synthesis and Characterization of Cationic Phosphonites. In our previous study, TADDOL units from ligand **3a** with Ph substituents and an acetonide backbone, **3b** sharing the same backbone but with 4-(*tert*-butyl)phenyl groups, and **3f** bearing 4-(trifluoromethyl)phenyl substituents and a noncyclic backbone were revealed to be the most suitable species to induce high enantioselectivities in the benchmark helicene synthesis. Hence, these motifs were chosen as starting points for this survey. The necessary chlorophosphites **4** were prepared on a gram scale following a modification of known procedures.[6,7] Subsequent reaction with the desired free carbenes or carbodiphosphorane afforded phosphonites **5a**−**m** in moderate to good yields after anion exchange with $NaSbF_6$ (see Figure 2 and the Supporting Information). With

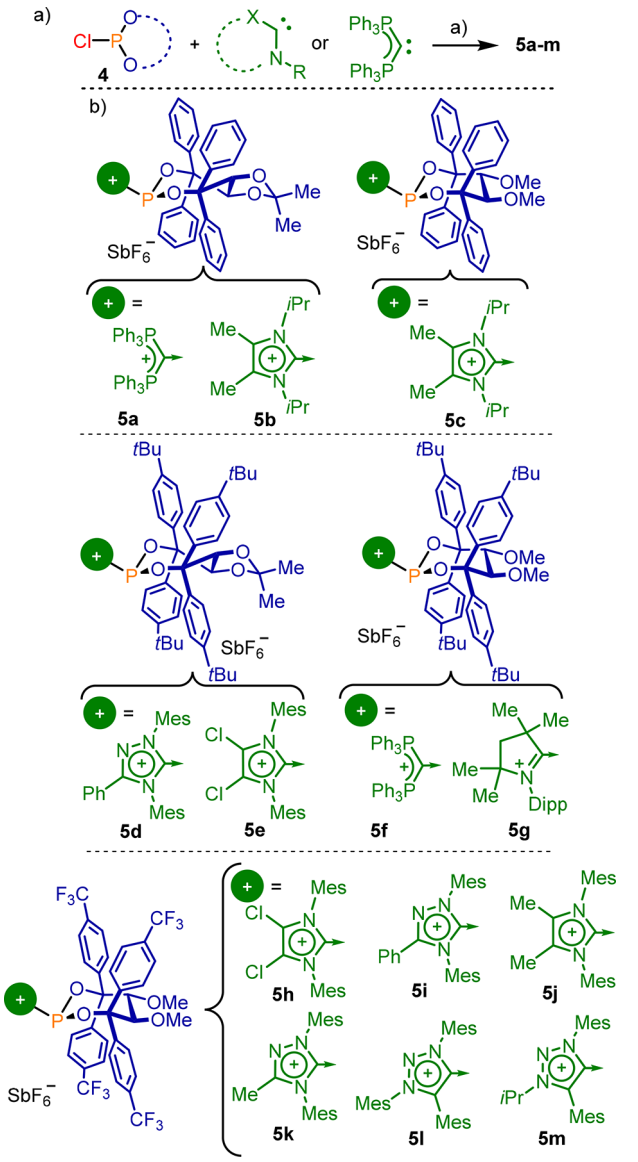

Figure 2. Cationic phosphonites prepared. Reagents and conditions: (a) chlorophosphite (1.0 equiv), carbene (1.0 equiv) or carbodiphosphorane (1.0−1.8 equiv), Et_2O or THF, and then $NaSbF_6$ (3.0 equiv). Yields: **5a**, 57%; **5b**, 51%; **5c**, 66%; **5d**, 44%; **5e**, 31%; **5f**, 32%; **5g**, 34%; **5h**, 30%; **5i**, 12%; **5j**, 68%; **5k**−**m**, not isolated (directly transformed to the corresponding Au complexes).

the exception of 1,4-dimesityl-3-methyl-1,2,4-triazol-5-ylidene, whose preparation and X-ray structure are described in the Supporting Information, all other carbenes used for the condensation with chlorophosphites were prepared by following previously described methods.[10]

The formation of the expected cationic phosphonites was monitored by ^{31}P NMR, where the distinct signal of chlorophosphites slowly disappeared and a new signal at δ 138−180 ppm concomitantly arose. Coupling with the other two phosphorus atoms makes this signal appear as a triplet in **5a**,**f** with J_{P-P} = 91.8 and 100.7 Hz, respectively. The solid-state structures of ligands **5c**,**l**,**m** were also determined by X-ray diffraction analysis (Figure 3 and the Supporting Information).[11] As expected, the phosphorus atom is pyramidal in the three ligands (sum of angles 291.8° for **5b**, 292.8° for **5l**, and 292.4° for **5m**) and its electron pair points toward the inner

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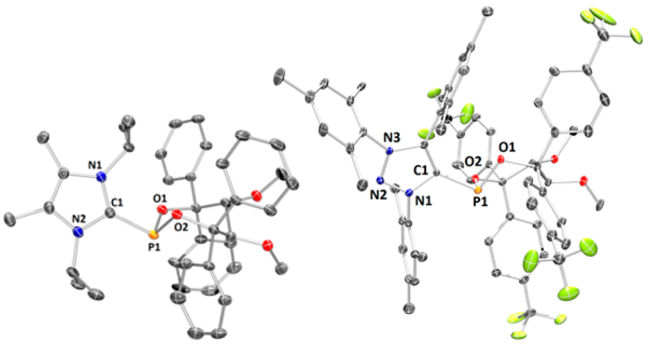
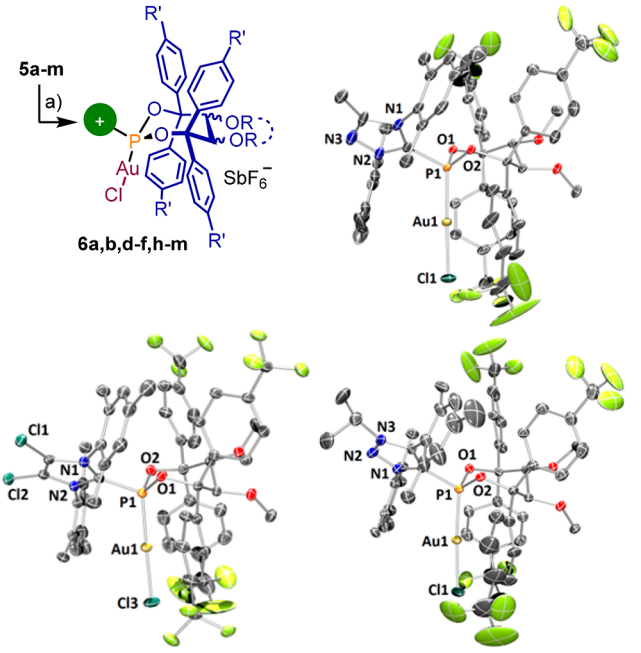


Figure 3. X-ray structures of **5c,l**. H atoms and SbF_6 anions are removed for clarity.[11]

part of the chiral cavity created by the TADDOL moiety. Of note, most cationic phosphonites resist column chromatographic purification on silica gel provided that this is done at low temperature (−10 °C).

Mixing the corresponding cationic phosphonites **5a−m** with $(Me_2S)AuCl$ led to the formation of Au complexes **6a,b,d−f,h−m**, which were obtained as white or light yellow solids in good to excellent yields (Scheme 2). Coordination of Au to the phosphorus center causes a pronounced upfield shift of the ^{31}P NMR signal in these compounds to a range of δ 110−114 ppm for **6b,d,e,g−m** and 129−131 ppm for **6a,f**. Single crystals suitable for X-ray structure determination of complexes **6h,j,k,m** were obtained by slow diffusion of pentane or toluene into saturated solutions of the title compounds in CH_2Cl_2; their structural diagrams, which confirmed the expected connectivities are also shown in Scheme 2 (**6h,k,m**) and the Supporting Information (**6j**).

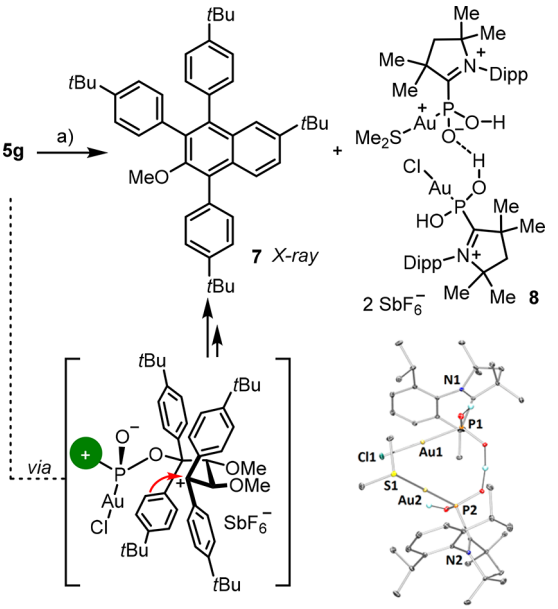
Scheme 2. Synthesis of Au Complexes 6a−f,h−m and Structures of 6h (Bottom Left), 6k (Top Right), and 6m (Bottom Right)[a]



[a]Reagents and conditions: (a) $(Me_2S)AuCl$ (1.0 equiv), CH_2Cl_2. Yields: **6a**, 99%; **6b**, 99%; **6d**, 85%; **6e**, 50%; **6f**, 99%; **6h**, 93%; **6i**, 25% (from **4i**); **6j**, 92%; **6k**, 17% (from **4k**); **6l**, 22%, two steps; **6m**, 20%, two steps. In the crystal structures, H atoms and SbF_6 anions are removed for clarity.[11]

It is of note that ligands **5c,g** did not afford the desired Au complexes; however, while many unidentified products are formed by decomposition of **5c**, the reaction between **5g** and $(Me_2S)AuCl$ is clean and the two new compounds that formed could be isolated. Triaryl-substituted naphthalene **7** contains, although modified, the carbon skeleton of the original TADDOL unit, while dimeric Au complex **8**, whose structure could only be ascertained after X-ray analysis (Scheme 3), is composed of a CAAC-substituted phosphonous acid coordinated to gold. The phosphorus atom in **5g** is the most electron poor atom along the series of ligands prepared due to the strong electron-withdrawing effect of the iminium group. Coordination of AuCl to this atom depletes even more electron density and makes the cationic phosphonite unit of **5g** an excellent leaving group. This triggers the initial formation of a carbocation, which starts a cascade consisting of Friedel−Crafts cyclization, elimination of the phosphonous acid derivative, acid-promoted elimination of methanol, and finally [1,2]-sigmatropic migration of an aryl group to the newly generated carbocation, leading to naphthalene **7** and Au complex **8** as a side product (see the Supporting Information for a detailed mechanistic proposal). TADDOL itself and some of its derivatives bearing electron-rich substituents are sensitive to Brønsted acids, and a similar naphthalene structure has been previously reported as their decomposition product.[12] Hence, it is not surprising to observe a related transformation promoted by coordination of the phosphonite ligand to a Lewis acid. None of the other Au complexes prepared seem to be affected by this undesired process.

Scheme 3. Decomposition Products from 5g and Structures of 7 and 8[a]



[a]Reagents and conditions: (a) $(Me_2S)AuCl$ (1.0 equiv), CH_2Cl_2. H atoms and SbF_6 anions are removed for clarity.[11]

Optimization of Diyne Precursor Synthesis. A previous synthetic route for the preparation of diynes of general formula **2** has been reported by our group by starting from 2,7-dimethylnaphthalene.[6] That method, although reproducible

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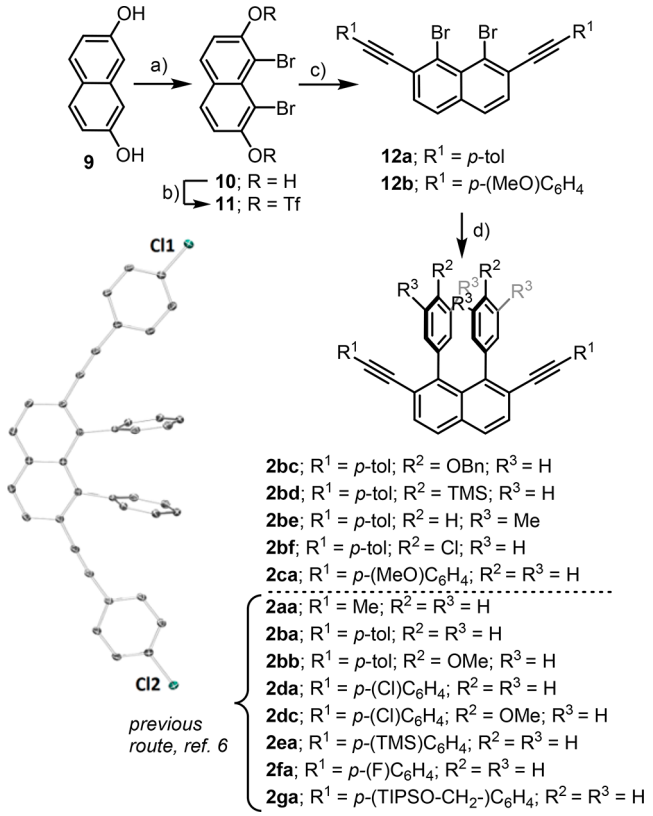
and scalable, is quite time consuming, since it requires a relatively long nine-step sequence to deliver the desired diynes. For these reasons we envisioned a more efficient protocol, which starts with the regioselective dibromination of naphthalene-2,7-diol (**9**) using *N*-bromosuccinimide to obtain **10**. Subsequent treatment of naphthalene **10** with Tf_2O affords bis-triflate **11**. This tetrafunctionalized compound reacts with aryl-substituted alkynes under typical Sonogashira conditions to cleanly produce the 2,7-bis-alkynylated products **12a,b** in good to excellent isolated yields.[13] Finally, at the last step of the sequence alkynes **12a,b** were transformed via Suzuki coupling with appropriate boronic acids into the desired diynes **2**. Employing this improved pathway, we have been able to shorten the original synthesis of the diyne precursors to only four steps and substantially increase the overall yields of the desired products (Scheme 4).

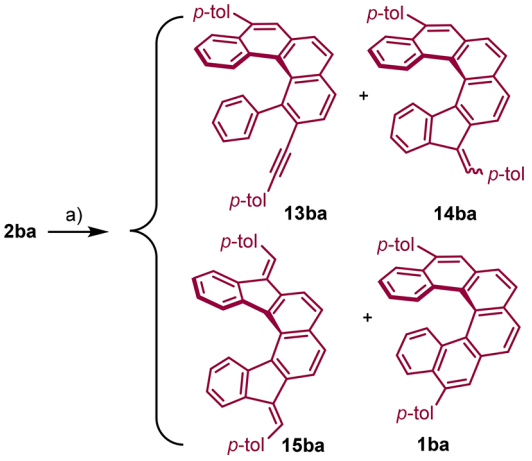
Scheme 4. Synthesis of Diyne Precursors and X-ray Structure of 2da[a]



[a]Reagents and conditions: (a) NBS (2.0 equiv), CH_3CN; (b) Tf_2O, (2.5 equiv); pyridine (3.0 equiv), 27%, two steps; (c) alkyne (7 equiv), $PdCl_2$(dppf) (5 mol %), CuI (10 mol %), **12a** 81%, **12b** 86%; (d) boronic acid (4.0 equiv), Cs_2CO_3 (3.0 equiv), $Pd_2(dba)_3$ (4 mol %), SPhos (8 mol %), **2bc** 46%, **2bd** 37%, **2be** 24%, **2bf** 22%, **2ca** 43%. H atoms are removed in the crystal structure for clarity.[11]

Catalysis. Once the substrate syntheses were optimized, we initially examined the performance of the new catalysts on the cycloisomerization of **2ba** toward helicene **1ba** (Table 1). Special emphasis was placed on comparing the originally optimized imidazolium-based ligand **3f** against those which have virtually identical sterical properties but contain either substituted imidazolium or triazolium groups. Whereas **3f** affords helicene **1ab** with 91% ee, its triazolium-derived cousins

Table 1. Screening of Chiral Au-Phosphonite Complexes[a]



entry	ligand	substrate	temp (°C)	13:14:15:1[b]	ee (%) 1ba[c]
1	**3f**	**2ba**	−20	0:3:0:97	(+)-91
2	**5a**	**2ba**	0	only **15ba**[d]	
3	**5b**	**2ba**	−20	45:5:0:50[e]	(−)-60
4	**5h**	**2ba**	−20	0:4:0:96	(+)-84
5	**5i**	**2ba**	−20	0:2:0:98	(+)-87
6	**5j**	**2ba**	−20	0:13:0:87	(+)-82
7	**5k**	**2ba**	−20	0:4:0:96	(+)-84
8	**5l**	**2ba**	−20	0:2:0:98	(+)-85
9	**5m**	**2ba**	−20	0:2:0:98	(+)-82

[a]Starting material was completely consumed after 96 h using 10 mol % of catalyst and 10 mol % of $AgSbF_6$ in C_6H_5F. [b]Determined by ^1H NMR and/or HPLC. [c]Determined by chiral HPLC. [d]5 mol % of catalyst and 5 mol % of $AgSbF_6$ were used as the catalyst mixture and CH_2Cl_2 as solvent. Product **15ba** was obtained in 43% isolated yield after crystallization. [e]Reaction time 72 h.

5i−m resulted in a reaction with a slightly lower enantioselectivity. Note, however, that both **5i** and **5l** improve the regioselectivity of the cyclization. This outcome is noteworthy from a practical point of view, since separation of helicenes **1** from fulvenes **14** has proven to be a difficult task and usually requires preparative HPLC.

Of note, ligand **5a** bearing a very bulky phosphonium-phosphorane group induces the selective formation of the product of double 5-*exo*-dig cyclization **15ba**, a bis-fulvene that has been only detected under these conditions (for the X-ray analysis of **15ba** see the Supporting Information). We postulate that the enormous steric demand of ligand **5a** favors the preferential coordination of Au to the external and less sterically demanding carbon from the alkyne moieties in **2ba**. This leads to the formation of five- instead of six-membered rings after the hydroarylation event.

The scope of the most promising catalysts, **5i,l**, was further evaluated using other diyne substrates which contain a reasonably diverse pattern of substitution (Table 2). Gratifyingly, in comparison with **3f**, triazolium-derived ligands substantially improved the regioselectivity of the cyclization toward the helicene products in all cases screened (compare, for example, entries 3 and 4 or entries 19 and 20 in Table 2). The enantioselectivity of the transformation also follows the same trend for most of the substrates. Ligands **5i,l** overtake the performance of the imidazolium-based ligand **3f** for products **1aa,bb,bc,be,ea,ga** (ee values 85−94%); however, for **1da,dc**, ligand **3f** is still able to afford the desired helicenes with slightly

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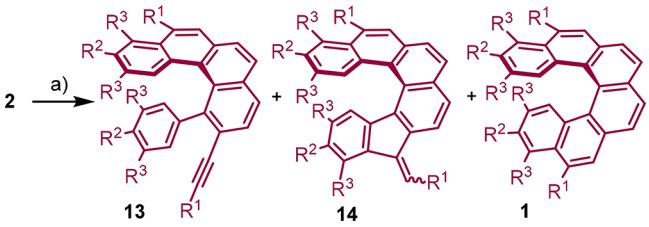
Table 2. Substrate Scope[a]



entry	ligand	substrate	product	yield of **1** (%)	**13**:**14**:**1**[c]	ee (%) **1**[d]
1	**3f**	**2bb**	**1bb**	99[b]	0:12:88	(+)-78
2	**5i**	**2bb**	**1bb**	83	0:4:96	(+)-86
3	**3f**	**2bc**	**1bc**	86[b]	0:13:87	(+)-75
4	**5i**	**2bc**	**1bc**	92	0:3:97	(+)-87
5	**3f**	**2be**	**1be**	84	0:12:88	(+)-75
6	**5i**	**2be**	**1be**	90	0:3:97	(+)-86
7	**3f**	**2bf**	**1bf**	trace		
8	**5i**	**2bf**	**1bf**	76[b]	7:7:86	(+)-92
9	**3f**	**2da**	**1da**	99[b]	16:3:81	(+)-97
10	**5i**	**2da**	**1da**	33	9:2:89	(+)-92
11	**5l**	**2da**	**1da**	48	0:1:99	(+)-88
12	**3f**	**2dc**	**1dc**	92[b]	0:13:87	(+)-95
13	**5i**	**2dc**	**1dc**	93	0:5:95	(+)-85
14	**3f**	**2aa**	**1aa**	82	0:1:99	(+)-63
15	**5e**	**2aa**	**1aa**	94	0:0:100	(−)-66
16	**5d**	**2aa**	**1aa**	95	0:0:100	(−)-70
17	**3f**	**2ea**	**1ea**	76[b]	3:14:83	(+)-87
18	**5l**	**2ea**	**1ea**	98	0:1:99	(+)-94
19	**3f**	**2ga**	**1ga**	94[b]	0:13:87	(+)-86
20	**5l**	**2ga**	**1ga**	95	0:1:99	(+)-89

[a]Starting material was completely consumed after 96 h at −20 °C, except for entries 9 (30%), 10 (50%), and 11 (52%) using 10 mol % of catalyst and 10 mol % of $AgSbF_6$ in C_6H_5F. [b]Calculated for inseparable mixtures of **13**, **14** and **1**. [c]Determined by ^1H NMR and/or HPLC. [d]Determined by chiral HPLC.

superior ee values. Au catalysts derived from triazolium-phosphonites are in general more active than their imidazolium cousins. This is beautifully illustrated by the cyclization of the deactivated substrate **2bf** (Table 2, entries 7 and 8). While only traces of the helicene are obtained employing precatalyst **3f**, Au complex **5i** afforded the desired product **2bf** with a remarkable 76% isolated yield (mixture of 3 isomers) and an ee value of 92%.

The CD spectra of **1aa,bb,bc,bf,be** have been recorded (Figure 4). The shape and sign of these spectra correlate quite well with that of *P*-[6]helicene, suggesting the same absolute configuration.[14] The photophysical properties of these five helicenes (absorption and fluorescence spectra) are summarized in the Supporting Information.

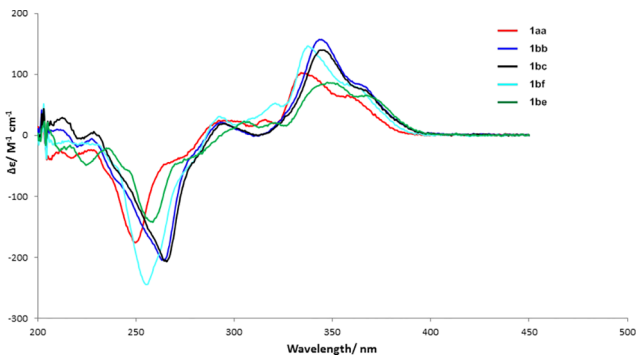


Figure 4. ECD spectra of **1aa,bb,bc,bf,be**.

CONCLUSIONS

A highly enantioselective synthesis of [6]helicenes of different substitution pattern via the Au(I)-catalyzed intramolecular hydroarylation of diynes is reported. In order to achieve the necessary levels of reactivity and enantioselectivity, chiral cationic phosphonite ligands containing imidazolium, 1,2,3-triazolium, and 1,2,4-triazolium rests were designed and tested as ancillary ligands. From the results obtained it can be concluded that Au complexes derived from these ancillary ligands are currently the most efficient catalysts for this kind of enantioselective transformation. The modularity of the synthetic route used to prepare ligands **3a−f** and **5a−m**, combined with their surprisingly high stability, makes us strongly believe they might find application in other asymmetric Au-catalyzed processes. Studies to evaluate this hypothesis are in progress in our laboratory.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.8b01374.

Crystallographic data (CIF)
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Preparation of ligands, catalysts, and substrates, supporting crystallographic information, and chiral HPLC analyses to determine the enantioselectivities of the products (PDF)

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Notes

The authors declare no competing financial interest.

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ABBREVIATIONS

CAAC, cyclic alkyl amino carbene
Dipp, diisopropylphenyl

REFERENCES

(1) (a) Shen, Y.; Chen, C. F. Helicenes: Synthesis and Applications. *Chem. Rev.* **2012**, *112*, 1463−1535. (b) Gingras, M. One hundred years of helicene chemistry. Part 1: non-stereoselective syntheses of carbohelicenes. *Chem. Soc. Rev.* **2013**, *42*, 968−1006. (c) Gingras, M.; Félix, G.; Peresutti, R. One hundred years of helicene chemistry. Part 2: stereoselective syntheses and chiral separations of carbohelicenes. *Chem. Soc. Rev.* **2013**, *42*, 1007−1050. (d) Gingras, M. One hundred years of helicene chemistry. Part 3: applications and properties of carbohelicenes. *Chem. Soc. Rev.* **2013**, *42*, 1051−1095. (e) Urbano, A.; Carreño, M. C. Enantioselective synthesis of helicenequinones and −bisquinones. *Org. Biomol. Chem.* **2013**, *11*, 699−708.

(2) For selected reports on diastereoselective syntheses see: (a) Carreño, M. C.; García-Cerrada, S.; Urbano, A. Enantiopure Dihydro-[5]-helicenequinones via Diels−Alder Reactions of Vinyl Dihydrophenanthrenes and (SS)-2-(p-Tolylsulfinyl)-1,4-benzoquinone. *J. Am. Chem. Soc.* **2001**, *123*, 7929−7930. (b) Nakano, K.; Hidehira, Y.; Takahashi, K.; Hiyama, T.; Nozaki, K. Stereospecific Synthesis of Hetero[7]helicenes by Pd-Catalyzed Double N-Arylation and Intramolecular O-Arylation. *Angew. Chem., Int. Ed.* **2005**, *44*, 7136−7138. (c) Carreño, M. C.; Enríquez, A.; García-Cerrada, S.; Sanz-Cuesta, M. J.; Urbano, A.; Maseras, F.; Nonell-Canals, A. Towards Configurationally Stable [4]Helicenes: Enantioselective Synthesis of 12-Substituted 7,8-Dihydro[4]helicene Quinones. *Chem. - Eur. J.* **2008**, *14*, 603−620. (d) Sehnal, P.; Krausová, Z.; Teplý, F.; Stará, I. G.; Starý, I.; Rulíšek, L.; Šaman, D.; Císařová, I. On the Origin of Diastereoselectivity in [2 + 2 + 2] Cycloisomerization of Chiral Triynes: Controlling Helicity of Helicene-like Compounds by Thermodynamic Factors. *J. Org. Chem.* **2008**, *73*, 2074−2082. (e) Sehnal, P.; Stará, I. G.; Šaman, D.; Tichý, M.; Míšek, J.; Cvačka, L.; Rulíšek, L.; Chocholoušová, J. V.; Vacek, J.; Goryl, G.; Szymonski, M.; Císařová, I.; Starý, I. An organometallic route to long helicenes. *Proc. Natl. Acad. Sci. U. S. A.* **2009**, *106*, 13169−13174. (f) Šámal, M.; Chercheja, S.; Rybáček, J.; Chocholoušová, J. V.; Vacek, J.; Bednárová, L.; Šaman, D.; Stará, I. G.; Starý, I. An Ultimate Stereocontrol in Asymmetric Synthesis of Optically Pure Fully Aromatic Helicenes. *J. Am. Chem. Soc.* **2015**, *137*, 8469−8474.

(3) Selected references for the enantioselective synthesis of heterohelicenes: (a) Shibata, T.; Uchiyama, T.; Yoshinami, Y.; Takayasu, S.; Tsuchikama, K.; Endo, K. Highly enantioselective synthesis of silahelicenes using Ir-catalyzed [2 + 2+2] cycloaddition. *Chem. Commun.* **2012**, *48*, 1311−1313. (b) Nakamura, K.; Furumi, S.; Takeuchi, M.; Shibuya, T.; Tanaka, K. Enantioselective Synthesis and Enhanced Circularly Polarized Luminescence of S-Shaped Double Azahelicenes. *J. Am. Chem. Soc.* **2014**, *136*, 5555−5558. (c) Kötzner, L.; Webber, M. J.; Martínez, A.; De Fusco, C.; List, B. Asymmetric catalysis on the nanoscale: the organocatalytic approach to helicenes. *Angew. Chem., Int. Ed.* **2014**, *53*, 5202−5205. (d) Kimura, Y.; Fukawa, N.; Miyauchi, Y.; Noguchi, K.; Tanaka, K. Enantioselective Synthesis of [9]- and [11]Helicene-like Molecules: Double Intramolecular [2 + 2+2] Cycloaddition. *Angew. Chem., Int. Ed.* **2014**, *53*, 8480−8483. (e) Sako, M.; Takeuchi, Y.; Tsujihara, T.; Kodera, J.; Kawano, T.; Takizawa, S.; Sasai, H. Efficient Enantioselective Synthesis of Oxahelicenes Using Redox/Acid Cooperative Catalysts. *J. Am. Chem. Soc.* **2016**, *138*, 11481−11484. (f) Klívar, J.; Jančařik, A.; Šaman, D.; Pohl, R.; Fiedler, P.; Bednárová, L.; Starý, I.; Stará, I. G. [2 + 2+2] Cycloisomerisation of Aromatic Cyanodiynes in the Synthesis of Pyridohelicenes and Their Analogues. *Chem. - Eur. J.* **2016**, *22*, 14401−14405. (g) Yamano, R.; Hara, J.; Murayama, K.; Sugiyama, H.; Teraoka, K.; Uehusa, H.; Kawauchi, S.; Shibata, Y.; Tanaka, K. Rh-Mediated Enantioselective Synthesis, Crystal Structures, and Photophysical/Chiroptical Properties of Phenanthrenol-Based [9]Helicene-like Molecules. *Org. Lett.* **2017**, *19*, 42−45.

(4) (a) Jančařik, A.; Rybáček, J.; Cocq, K.; Chocholoušová, J. V.; Vacek, J.; Pohl, R.; Bednárová, L.; Fiedler, P.; Císařová, I.; Stará, I. G.; Starý, I. Rapid Access to Dibenzohelicenes and their Functionalized Derivatives. *Angew. Chem., Int. Ed.* **2013**, *52*, 9970−9975. For a nonbezenoid system, but still carbon-based, see: (b) Sawada, Y.; Furumi, S.; Takai, A.; Takeuchi, M.; Noguchi, K.; Tanaka, K. Rhodium-Catalyzed Enantioselective Synthesis, Crystal Structures, and Photophysical Properties of Helically Chiral 1,1′-Bitriphenylenes. *J. Am. Chem. Soc.* **2012**, *134*, 4080−4083. For former enantioselective syntheses leading to moderate ee values, see: (c) Caeiro, J.; Pena, D.; Cobas, A.; Pérez, D.; Guitián, E. Asymmetric Catalysis in the [2 + 2+2] Cycloaddition of Arynes and Alkynes: Enantioselective Synthesis of a Pentahelicene. *Adv. Synth. Catal.* **2006**, *348*, 2466−2474. (d) Grandbois, A.; Collins, S. K. Enantioselective Synthesis of [7]Helicene: Dramatic Effects of Olefin Additives and Aromatic Solvents in Asymmetric Olefin Metathesis. *Chem. - Eur. J.* **2008**, *14*, 9323−9329.

(5) (a) Buchta, M.; Rybáček, J.; Jančařik, A.; Kudale, A. A.; Buděšinský, M.; Chocholoušová, J. V.; Vacek, J.; Bednárová, L.; Císarová, I.; Bodwell, C. J.; Starý, I.; Stará, I. G. Chimerical Pyrene-Based [7]Helicenes as Twisted Polycondensed Aromatics. *Chem. - Eur. J.* **2015**, *21*, 8910−8917. (b) Sánchez, I. G.; Šámal, M.; Nejedlý, J.; Karras, M.; Klívar, J.; Rybáček, J.; Buděšinský, M.; Bednárová, L.; Siedlerová, L.; Seidlerová, B.; Stará, I. G.; Starý, I. Oxahelicene NHC ligands in the asymmetric synthesis of nonracemic helicenes. *Chem. Commun.* **2017**, *53*, 4370−4373. (c) Murayama, K.; Shibata, Y.; Sugiyama, H.; Uekusa, H.; Tanaka, K. Synthesis, Structure, and Photophysical/Chiroptical Properties of Benzopicene-Based π-Conjugated Molecules. *J. Org. Chem.* **2017**, *82*, 1136−1144.

(6) González-Fernández, E.; Nicholls, L. D. M.; Schaaf, L. D.; Farès, C.; Lehmann, C. W.; Alcarazo, M. Enantioselective Synthesis of [6]Carbohelicenes. *J. Am. Chem. Soc.* **2017**, *139*, 1428−1431.

(7) For the use of TADDOL-derived phosphoramidites in asymmetric catalysis, see: (a) Lam, H. W. TADDOL-Derived Phosphonites, Phosphites, and Phosphoramidites in Asymmetric Catalysis. *Synthesis* **2011**, *2011*, 2011−2043. (b) Teller, H.; Flügge, S.; Goddard, R.; Fürstner, A. Enantioselective Gold Catalysis: Opportunities Provided by Monodentate Phosphoramidite Ligands with an Acyclic TADDOL Backbone. *Angew. Chem., Int. Ed.* **2010**, *49*, 1949−1953. (c) Teller, H.; Corbet, M.; Mantilli, L.; Gopakumar, G.; Goddard, R.; Thiel, W.; Fürstner, A. One-Point Binding Ligands for Asymmetric Gold Catalysis: Phosphoramidites with a TADDOL-Related but Acyclic Backbone. *J. Am. Chem. Soc.* **2012**, *134*, 15331−15432.

(8) Petuškova, J.; Bruns, H.; Alcarazo, M. Cyclopropenylylidene-Stabilized Diaryl and Dialkyl Phosphenium Cations: Applications in Homogeneous Gold Catalysis. *Angew. Chem., Int. Ed.* **2011**, *50*, 3799−3802. (b) Carreras, J.; Patil, M.; Thiel, W.; Alcarazo, M. Exploiting the π-Acceptor Properties of Carbene-Stabilized Phosphorus Centered Trications $[L3P]^{3+}$: Applications in Pt(II) Catalysis. *J. Am. Chem. Soc.* **2012**, *134*, 16753−16758. (c) Carreras, J.; Gopakumar, G.; Gu, L.; Gimeno, A. M.; Linowski, P.; Petuškova, J.; Thiel, W.; Alcarazo, M. Polycationic Ligands in Gold Catalysis: Synthesis and Applications of Extremely π-Acidic Catalysts. *J. Am. Chem. Soc.* **2013**, *135*, 18815−18823. (d) Kozma, Á.; Deden, T.; Carreras, J.; Wille, C.; Petuškova, J.; Rust, J.; Alcarazo, M. Coordination Chemistry of Cyclopropenylidene-Stabilized Phosphenium Cations: Synthesis and Reactivity of Pd and Pt Complexes. *Chem. - Eur. J.* **2014**, *20*, 2208−2214. (e) Tinnermann, H.; Wille, C.; Alcarazo, M. Synthesis, Structure, and Applications of Pyridiniophosphines. *Angew. Chem., Int. Ed.* **2014**, *53*, 8732−8736. (f) Haldón, E.; Kozma, Á.; Tinnermann, H.; Gu, L.; Goddard, R.; Alcarazo, M. Synthesis and reactivity of α-cationic phosphines: the effect of imidazolinium and amidinium substituents. *Dalton Trans.* **2016**, *45*, 1872−1876. (g) Dube, J. W.; Zheng, Y.; Thiel, W.; Alcarazo, M. α-Cationic Arsines: Synthesis, Structure, Reactivity, and Applications. *J. Am. Chem. Soc.* **2016**, *138*, 6869−6877. (h) Mehler, G.; Linowski, P.; Carreras, J.; Zanardi, A.; Dube, J. W.; Alcarazo, M. Bis(cyclopropenium)phosphines: Synthesis, Reactivity, and Applications. *Chem. - Eur. J.* **2016**, *22*, 15320−15327. (i) Gu, L.; Wolf, L. M.;

DOI: 10.1021/acscatal.8b01374
ACS Catal. 2018, 8, 6079−6085

Zieliński, A.; Thiel, W.; Alcarazo, M. α-Dicationic Chelating Phosphines: Synthesis and Application to the Hydroarylation of Dienes. *J. Am. Chem. Soc.* **2017**, *139*, 4948−4953.
(9) (a) Alcarazo, M. α-Cationic Phosphines: Synthesis and Applications. *Chem. - Eur. J.* **2014**, *20*, 7868−7877. (b) Alcarazo, M. Synthesis, Structure, and Applications of α-Cationic Phosphines. *Acc. Chem. Res.* **2016**, *49*, 1797−1805.
(10) (a) Ramírez, F.; Desai, N. B.; Hansen, B.; McKelvie, N. Hexaphenylcarbodiphosphorane, $(C6H_5)_3PCP(C_6H_5)_3$. *J. Am. Chem. Soc.* **1961**, *83*, 3539−3540. (b) Zybill, C.; Mueller, G. Mononuclear complexes of copper(I) and silver(I) featuring the metals exclusively bound to carbon. Synthesis and structure of (η^5-pentamethylcyclopentadienyl)[(triphenylphosphonio)(triphenylphosphoranylidene)methyl]copper(I). *Organometallics* **1987**, *6*, 2489−2494. (c) Kuhn, N.; Kratz, T. Synthesis of Imidazol-2-ylidenes by Reduction of Imidazole-2(3H)-thiones. *Synthesis* **1993**, *1993*, 561−562. (d) Arduengo, A. J., III; Davidson, F.; Dias, H. V. R.; Goerlich, J. R.; Khasnis, D.; Marshall, W. J.; Prakasha, T. K. An Air Stable Carbene and Mixed Carbene "Dimers. *J. Am. Chem. Soc.* **1997**, *119*, 12742−12749. (e) Lavallo, V.; Canac, Y.; Präsang, C.; Donnadieu, B.; Bertrand, G. Stable Cyclic (Alkyl)(Amino)Carbenes as Rigid or Flexible, Bulky, Electron-Rich Ligands for Transition-Metal Catalysts: A Quaternary Carbon Atom Makes the Difference. *Angew. Chem., Int. Ed.* **2005**, *44*, 5705−5709. (f) Bouffard, J.; Keitz, B. K.; Tonner, R.; Guisado-Barrios, G.; Frenking, G.; Grubbs, R. H.; Bertrand, G. Synthesis of Highly Stable 1,3-Diaryl-1H-1,2,3-triazol-5-ylidenes and Their Applications in Ruthenium-Catalyzed Olefin Metathesis. *Organometallics* **2011**, *30*, 2617−2627. (g) Kinuta, H.; Tobisu, M.; Chatani, N. Rhodium-Catalyzed Borylation of Aryl 2-Pyridyl Ethers through Cleavage of the Carbon−Oxygen Bond: Borylative Removal of the Directing Group. *J. Am. Chem. Soc.* **2015**, *137*, 1593−1600. (h) Yatham, V. R.; Harnying, W.; Kootz, D.; Neudörfl, J.-M.; Schlörer, N. E.; Berkessel, A. 1,4-Bis-Dipp/Mes-1,2,4-Triazolylidenes: Carbene Catalysts That Efficiently Overcome Steric Hindrance in the Redox Esterification of α- and β-Substituted α,β-Enals. *J. Am. Chem. Soc.* **2016**, *138*, 2670−2677.
(11) CCDC 1833537−1833542, 1835041, 1835043, 1835051, 1835052, 1835089, and 1835451−1835454 contain supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
(12) Seebach, D.; Rheiner, P. B.; Beck, A. K.; Kühnle, F. N. M.; Jaun, B. Preparation and Cationic Rearrangements of ortho- and para-Methoxy-TADDOLs. *Polish J. Chem.* **1994**, *68*, 2397−2413.
(13) Pozo, I.; Cobas, A.; Pena, D.; Guitián, E.; Pérez, D. 1,7-Naphthodiyne: a new platform for the synthesis of novel, sterically congested PAHs. *Chem. Commun.* **2016**, *52*, 5534−5537.
(14) Nakai, Y.; Mori, T.; Inoue, Y. Circular Dichroism of (Di)methyl- and Diaza[6]helicenes. A Combined Theoretical and Experimental Study. *J. Phys. Chem. A* **2013**, *117*, 83−93.

DOI: 10.1021/acscatal.8b01374
ACS Catal. 2018, 8, 6079−6085