

Enantioselective Synthesis of [6]Carbohelicenes

Elisa González-Fernández,[†] Leo D. M. Nicholls,[†] Lukas D. Schaaf,[†] Christophe Farès,[‡] Christian W. Lehmann,[‡] and Manuel Alcarazo^{*,†}

[†]Institut für Organische und Biomolekulare Chemie, Georg-August-Universität Göttingen, Tammannstraße 2, 37077 Göttingen, Germany

[‡]Max-Planck-Institut für Kohlenforschung, Kaiser Wilhelm Platz 1, 45470 Muelheim an der Ruhr, Germany

Supporting Information

ABSTRACT: The use of α -cationic phosphonites derived from TADDOL as ancillary ligands has allowed a highly regio- and enantioselective synthesis of substituted [6]-carbohelicenes by sequential Au-catalyzed intramolecular hydroarylation of diynes. Key for these results is the modular structure of these new ligands, and the enhanced reactivity that they impart to Au(I)-centers after coordination.

The asymmetric synthesis of ortho-annulated polycyclic skeletons, helicenes,¹ has received considerable attention during the past decade as a result of their unique chiroptical properties and their continually emerging applications in different areas of chemistry such as asymmetric organo-² or transition metal catalysis,³ molecular machines,⁴ or liquid crystal technology.⁵ Indeed, several diastereoselective approaches to helicenes and helicene derivatives have been reported;⁶ yet, syntheses built upon highly enantioselective catalytic processes are still scarce.⁷

Our research group has investigated during the past few years the synthesis and applications of α -cationic phosphines and their applications in catalysis.⁸ The use of these strong π -acceptor ligands has been proven to be highly beneficial in π -acid catalysis; specifically, tremendous enhancement of catalyst activity has been observed in the Au- and Pt-catalyzed intra- and intermolecular hydroarylation of alkynes, which allowed these transformations to be accomplished under comparatively mild conditions.⁹ Encouraged by the realization that alkyne hydroarylation has the potential to assemble aromatic rings into helicenes if applied on suitably designed substrates,¹⁰ we embarked on the design of an enantioselective route toward [6]carbohelicenes employing chiral cationic ancillary ligands. Herein, we summarize our progress in this direction.

The starting point for our approach was the synthesis of a library of chiral cationic phosphanes. Being aware of the difficulties inherent to asymmetric gold catalysis,¹¹ which stem from its linear coordination geometry and the outer-sphere nature of Au(I)-catalyzed processes, we reasoned that the new ligand structure had to be highly modular in order to tackle this challenge with any possibility of success. Cationic phosphonites of general formula 1 fulfill this requirement. The chiral information is provided by well-precedented TADDOL-derived moieties, which are cheap, easy to tune, and have already demonstrated their suitability in asymmetric gold catalysis.¹² In

addition, the imidazolium unit introduces a positive charge which eventually will be responsible for enhanced catalyst efficiency (Figure 1).

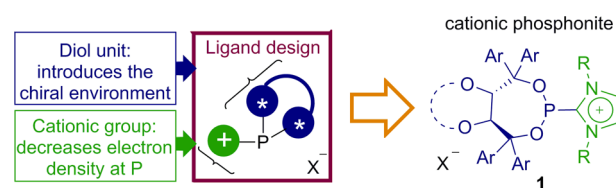


Figure 1. Structural design of cationic phosphonites.

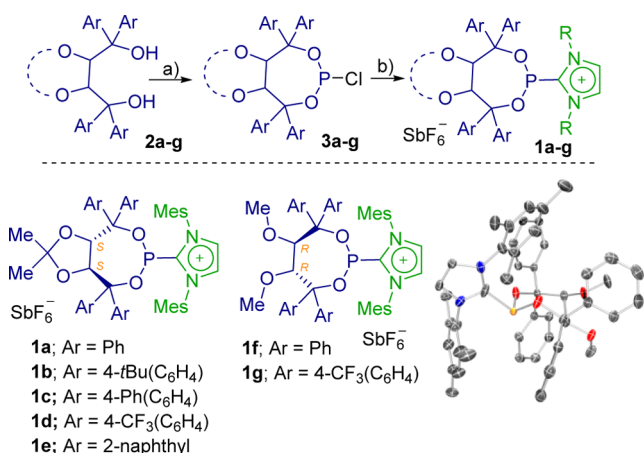
To bring our plan into practice, we first examined the synthesis of cationic phosphonites **1a–g**. Following known procedures, diols **2a–g** were prepared and subsequently condensed with PCl_3 to afford chlorophosphites **3a–g**.¹² Pyridine revealed to be the most suitable base for this step since it allows an efficient separation of **3a–g** from pyridinium hydrochloride by simple filtration. This is crucial for the next and final step, which involves the condensation of **3a–g** with free N-heterocyclic carbenes to afford **1a–g** (Scheme 1).¹³

The formation of cationic phosphonites **1a–g** was first suggested by the rise of a characteristic ^{31}P NMR signal ($\delta = 143\text{--}149$ ppm), and subsequently confirmed by single crystal X-ray diffraction of **1f**. This first structure of a cationic phosphonite is, in fact, quite suggestive. The geometry around the phosphorus atom is pyramidal (sum of angles 298.1°) and the electron pair located on this atom points toward the interior of the chiral cavity created by the aromatic substituents of both the TADDOL and imidazolium unit. Besides that, ligands **1a–g** are stable enough to resist chromatographic purification at low temperature, and can be handled for short times in air without apparent decomposition.

Mixing **1a–g** with $(\text{Me}_2\text{S})\text{AuCl}$ in dichloromethane led to the formation of the corresponding Au(I) complexes **4a–g** in good to excellent isolated yields. Coordination of the phosphonite to gold was evidenced by a pronounced upfield shift of their ^{31}P NMR signals ($\delta = 108\text{--}113$ ppm), to a range that perfectly overlaps with that of closely related Au(I)-phosphoramidite complexes. Unambiguous confirmation of the expected connectivity was once more obtained by X-ray diffraction of single crystals of **4e**, **4f** and **4g** (Scheme 2). The three structures depict

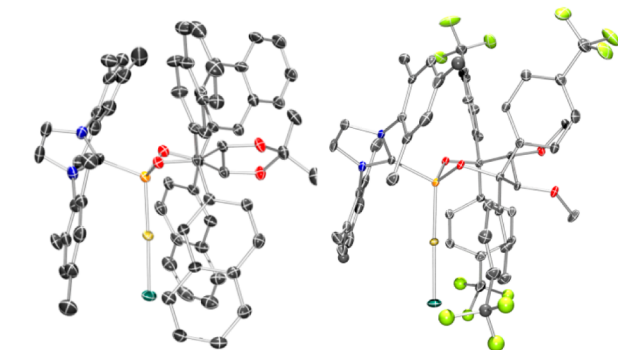
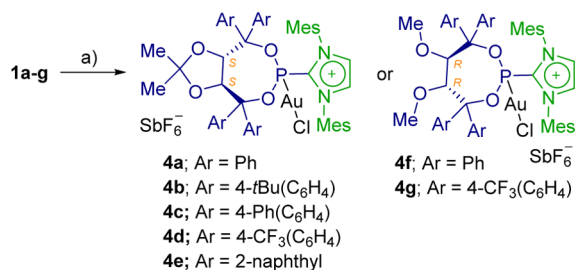
Received: December 6, 2016

Published: January 23, 2017

Scheme 1. Synthesis of Cationic Phosphonites and Structure of 1h in the Solid State^{14a}

^aReagents and conditions: (a) PCl₅, Pyridine, toluene, 0 → 60 °C; (b) IMes, Et₂O, -78 → 0 °C and then NaSbF₆. Yields (3 steps): **1a**, 69%; **1b**, 29%; **1c**, 48%; **1d**, 72%; **1e**, 64%; **1f**, 79%; **1g**, 65%. X-ray structure of **1f**; H atoms and anion removed for clarity.

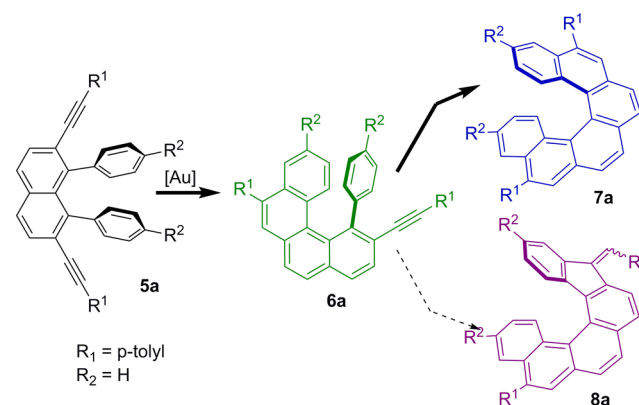
the Au atom immersed into a deep chiral pocket that will likely be key for the desired asymmetric transformation.

Scheme 2. Synthesis of Au-Complexes 4a–h and Structures of 4e and 4g^{14a}

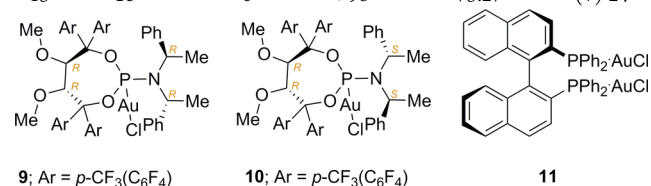
^aReagents and conditions: (a) (Me₂S)AuCl, CH₂Cl₂, -20 °C → rt. Yields: **4a**, 99%; **4b**, 98%; **4c**, 91%; **4d**, 91%; **4e**, 77%; **4f**, 94%; **4g**, 99%. H atoms and SbF₆⁻ anion removed for clarity.

Once this first set of Au-precatalysts was made available, they all were screened on the cyclization of diyne **5a** into helicene **7a**. Substrates of general formula **5** were chosen as adequate starting materials for the synthesis of [6]helicenes because they do not contain any interfering element of chirality, and can be assembled in gram scale through a robust and modular route (For the synthesis of **5a–k**, see the [Supporting Information](#)).

During our preliminary optimization of reaction conditions with precatalyst **4a**, we found that the desired helicene **7a** was formed with a very promising 86% ee employing 5 mol % of catalyst at 0 °C in CH₂Cl₂. Note, however, that the regioselectivity of the cyclization was not satisfactory and considerable amounts of **8a**, the product from the 5-*exo*-dig cyclization of one of the alkynes, was also obtained (Table 1,

Table 1. Screening of Chiral Au-Phosphonite and Related Complexes^a

Entry	Catalyst	Temp. (°C)	Yield (%) ^b	Ratio 7a:8a ^c	ee (%) 7a ^d
1	4a	0	98	70:30	(-)-86
2	4b	0	97	69:31	(-)-63
3	4c	0	84	88:12	(-)-36
4	4d	0	96	89:11	(-)-57
5	4e	0	96	98:2	(+)-14
6	4f	0	>98	80:20	(+)-77
7	4g	0	84	93:7	(+)-63
8	4a	-20	98	75:25	(-)-88
9	4f	-20	92	90:10	(+)-82
10	4g	-20	96 ^e	95:5	(+)-82
11 ^f	4g	-20	88	97:3	(+)-91
12	9	0	>98	81:19	(+)-40
13	10	0	>98	73:27	(+)-24



^aReaction conditions: 5 mol % of catalyst and 5 mol % of AgSbF₆ in CH₂Cl₂, 72 h. ^bCombined yields to **7a** and **8a**. Unless specified, the amount of intermediate **6a** in these mixtures was inferior to 2%. ^cDetermined by ¹H NMR and/or HPLC. ^dDetermined by chiral HPLC. ^eThe reaction mixture still contained 21% of **6a**. ^fC₆H₅F used as solvent, 10 mol% of **4g**/AgSbF₆, 96h.

Entry 1). Neither changing the steric nor electronic nature of the aryl substituents on the TADDOL moiety lead to any improvement in terms of ee of **7a** (Entries 2–5); yet, precatalyst **4d** decorated with 4-(trifluoromethyl)phenyl group on the TADDOL moiety substantially increased the regioselectivity of the process toward formation of the helicene without eroding irreversibly the enantioselectivity (**7a**:**8a**, 89:11; 57% ee; Entry 4). Hence, both the -Ph and *p*-CF₃(C₆H₄)- rings were kept for next optimization round consisting of the replacement of the acetamide backbone by a more flexible dimethyl ether motif.

The results obtained with precatalysts **4f** and **4g** were not conclusive. The enantioselectivities obtained were lower than the one provided by **4a**; however, the regioselectivity toward **7a** could be further improved to a respectable 93:7 ratio with the aid of complex **4g** (Entry 7). The effect of lowering the temperature to $-20\text{ }^{\circ}\text{C}$ was subsequently examined. Precatalyst **4a** proved not to be sensitive to this parameter (Entry 8); in contrast, under these conditions complex **4g** produced remarkable results in terms of regio- and enantioselectivity (Entry 10). Finally, a solvent screening identified fluorobenzene as the most appropriate one for this transformation.¹⁵ Helicene **7a** is thus obtained with excellent regioselectivity and a remarkable 91% ee. Note, however, that the catalyst loading had to be increased to 10% in order to obtain complete conversions. Under the same conditions, the structurally related phosphoramidite Au-complexes **9** and **10** do not display any catalytic activity, thus demonstrating the activating effect of the imidazolium moiety. Only at $0\text{ }^{\circ}\text{C}$ some reactivity was observed, but the regioselectivity and ee of the product obtained were inferior to those induced by **4g** (Entries 12 and 13). Au-complex **11**, based on a stronger σ -donor BINAP ligand does not show any activity at $0\text{ }^{\circ}\text{C}$ after activation with AgSbF_6 (1 equiv).¹⁶

With the optimal conditions in hand, the scope of the cyclization was evaluated using diynes **5b–k** which contain a diverse substitution pattern (See the Supporting Information for the X-ray structures of **5b** and **5k**). Gratifyingly, the high levels of regio- and enantioinduction imparted by **4g** were maintained through the series reaching up to 99% ee (**7e**). Only the methyl capped alkyne **5k** afforded significantly lower ee for reasons that are not completely understood at this moment (Chart 1).

Chart 1. Substrate Scope and Limitations^a

Diyne	Prod.	R ₁	R ₂	Yield	7:8	ee
5a	7a	<i>p</i> -tolyl	H	88%	97:3	91
5b	7b	Ph	H	77% ^b	95:5	92
5c	7c	<i>p</i> -F(C ₆ F ₄)	H	90% ^c	93:7	90
5d	7d	<i>p</i> -tolyl	Ph	84%	97:3	82
5e	7e	<i>p</i> -OBn(C ₆ H ₄)	H	98%	95:5	99 ^d
5f	7f	<i>p</i> -OMe(C ₆ H ₄)	H	90%	96:4	81
5g	7g	<i>p</i> -Cl(C ₆ H ₄)	OMe	92%	87:13	95
5h	7h	<i>p</i> -TMS(C ₆ H ₄)	H	76% ^e	87:13	87
5i	7i	<i>p</i> -TMS(C ₆ H ₄)	OMe	64%	73:27	94
5j	7j	<i>p</i> -(TIPSO-CH ₂)Ph	OMe	94%	80:20	82
5k	7k	Me	H	82%	99:1	63

^aReactions conditions: **5a–k** (0.02 mmol) with catalyst **4g**, 10 mol %, AgSbF_6 10 mol %, FC_6H_5 (0.05M), $-20\text{ }^{\circ}\text{C}$, 96 h. Yields are of the isolated 7:8 mixtures; de values were determined by ¹H NMR and HPLC; ee values were determined by chiral HPLC. ^b5% of unreacted **5b** and 14% of intermediate **6b** were still present in the reaction mixture. ^c8% of unreacted **5c** and 1% of intermediate **6c** were still present in the reaction mixture. ^dReaction carried out in dichloromethane. ^e3% of **6h** was still present in the reaction mixture.

All our attempts to obtain single crystals from the enantioenriched mixtures were unsuccessful, but racemates readily crystallized. This was enough to confirm the helical structure of the assembled products (Figure 2). To ascertain the absolute configuration of the helicenes prepared, the CD spectra of **7c**, **7e**, and **7g** were recorded (See the Supporting Information and Figure 2). The pattern and sign of these spectra correlate well with the one reported for (*P*)-[6]helicene, suggesting the same absolute configuration.¹⁷

Subsequently, a series of dynamic NMR studies was conducted to determine whether the first or the second hydroarylation is the

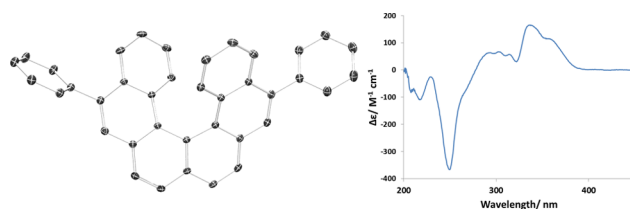
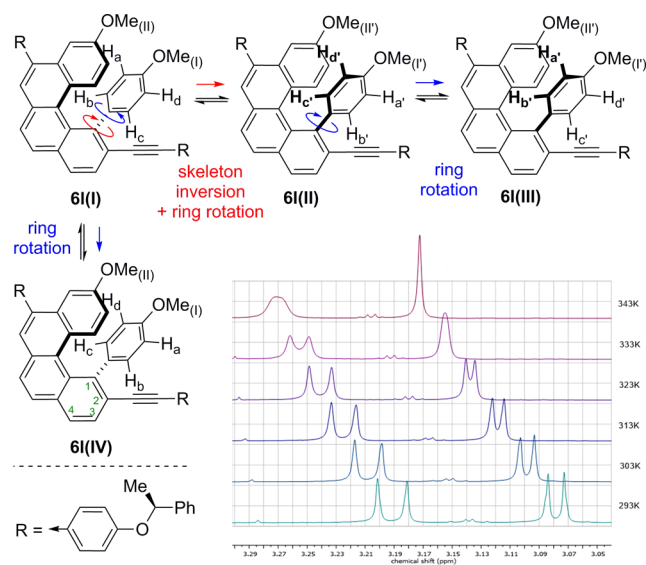


Figure 2. X-ray structure of *rac*-**7b** (left) and CD spectrum of **7e** (right). H atoms omitted for clarity. Ellipsoids shown at 50% probability. Only one of the two independent molecules present in the unit cell is shown.

enantio-determining step of the whole process. With this idea in mind, intermediate **6l** bearing chiral (*S*)-1-phenylethoxy substituents was prepared (See the Supporting Information). The presence of additional elements of asymmetry in this tetrahelicene renders isomers with different helicity diastereomers, making them observable by NMR spectroscopy. In the measured temperature series, two coalescence phenomena were observed. The first one with a coalescence temperature (T_C) of 313 K only involves exchange of *o*- and *m*-protons of the internal phenyl substituent, indicating simple rotation of this group (Scheme 3, blue arrows). The second, with a higher

Scheme 3. Dynamic Processes in Tetrahelicene Intermediates



coalescence temperature ($T_C = 338\text{ K}$), interconverts all diastereomeric pairs in **6l**; therefore, it implies stereoinversion of the helicene skeleton (Scheme 3, red arrows). NOESY/EXSY experiments also corroborate this view.

Spectra were recorded at the indicated temperatures in *d*₈-toluene on a 500 MHz spectrometer. Only the $-\text{OMe}$ region is shown.

At the coalescence temperature, the activation energy barriers ΔG^\ddagger were calculated to be 59.4 and 74.5 kJ/mol for the ring rotation and skeleton inversion, respectively. As expected, these values are slightly higher than those obtained for related tetrahelicenes with no substituent in position 2.¹⁸ From the Eyring plot of the exchange rates at different temperatures, the thermodynamic parameters were estimated for the skeletal inversion (See the Supporting Information, also for a similar analysis of the ring rotation process). The enthalpy of activation is relatively low, $\Delta H^\ddagger = 33.5\text{ kJ/mol}$, but there is a substantial negative contribution of entropy of activation ($\Delta S^\ddagger = -0.13\text{ kJ/}$

molK) to the ΔG^\ddagger , indicating that the entropy decreases to attain the transition state. This hints to a highly ordered transition state in which the phenyl substituent and the tetrahelicene unit are probably perpendicular. Finally, the half-life of the diastereomers of **6l** was estimated to be approximately 5 s at -20°C . Comparing this fast equilibration with our experimental reaction time (72–96 h), it can be concluded that a dynamic kinetic resolution process takes place during the second cyclization stemming from the preferred reaction of one enantiomer of **6** with the chiral catalyst.

In summary, a highly enantioselective synthesis of substituted [6]helicenes has been achieved via sequential Au-catalyzed hydroarylation of alkynes employing newly designed chiral cationic phosphinites as ancillary ligands. Ongoing work in our laboratory is focused on the further optimization of the phosphonite ligands for the enantioselective synthesis of heterohelicenes and higher order helicenes.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b12443.

Data for **1f** (CIF)

Data for **4e** (CIF)

Data for **4f** (CIF)

Data for **4g** (CIF)

Data for **5b** (CIF)

Data for **5k** (CIF)

Data for **7b** (CIF)

Data for **7k** (CIF)

Experimental details and NMR spectra (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*malcara@gwdg.de

ORCID

Manuel Alcarazo: 0000-0002-5491-5682

Author Contributions

E.G.F. and L.D.M.N. contributed equally.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

Financial support from the Deutsche Forschungsgemeinschaft (Al 1348/5-1) is gratefully acknowledged. We also thank A. Deege and H. Hinrichs (MPI-Kohlenforschung) for the ee determinations.

■ REFERENCES

- (1) (a) Shen, Y.; Chen, C. F. *Chem. Rev.* **2012**, *112*, 1463–1535. (b) Gingras, M. *Chem. Soc. Rev.* **2013**, *42*, 968–1006. (c) Gingras, M.; Félix, G.; Peresutti, R. *Chem. Soc. Rev.* **2013**, *42*, 1007–1050. (d) Gingras, M. *Chem. Soc. Rev.* **2013**, *42*, 1051–1095. (e) Urbano, A.; Carreño, M. C. *Org. Biomol. Chem.* **2013**, *11*, 699–708.
- (2) (a) Takenaka, N.; Chen, J.; Captain, B.; Sarangthem, R. S.; Chandrakumar, A. *J. Am. Chem. Soc.* **2010**, *132*, 4536–4537. (b) Lu, T.; Zhu, R.; An, Y.; Wheeler, S. E. *J. Am. Chem. Soc.* **2012**, *134*, 3095–3102. (c) Gicquel, M.; Zhang, Y.; Aillard, P.; Retailliau, P.; Voituriez, A.; Marinetti, A. *Angew. Chem., Int. Ed.* **2015**, *54*, 5470–5473.
- (3) Saleh, N.; Shen, C.; Crassous, J. *Chem. Sci.* **2014**, *5*, 3680–3694.
- (4) Chen, W. C.; Lee, Y. W.; Chen, C. T. *Org. Lett.* **2010**, *12*, 1472–1475.

(5) Saito, N.; Kanie, K.; Matsubara, M.; Muramatsu, A.; Yamaguchi, M. *J. Am. Chem. Soc.* **2015**, *137*, 6594–6601.

(6) For selected references, see: (a) Nakano, K.; Hidehira, Y.; Takahashi, K.; Hiyama, T.; Nozaki, K. *Angew. Chem., Int. Ed.* **2005**, *44*, 7136–7138. (b) Grandbois, A.; Collins, S. K. *Chem. - Eur. J.* **2008**, *14*, 9323–9329. (c) Carreño, M. C.; Enríquez, A.; García-Cerrada, S.; Sanz-Cuesta, M. J.; Urbano, A.; Maseras, F.; Nonell-Canals, A. *Chem. - Eur. J.* **2008**, *14*, 603–620. (d) Sehnal, P.; Krausová, Z.; Teplý, F.; Stará, I. G.; Starý, I.; Rulišek, L.; Šaman, D.; Císařová, I. *J. Org. Chem.* **2008**, *73*, 2074–2082. (e) Sehnal, P.; Stará, I. G.; Šaman, D.; Tichý, M.; Míšek, J.; Cvačka, L.; Rulišek, L.; Chocholoušová, J. V.; Vacek, J.; Goryl, G.; Szymonski, M.; Císařová, I.; Starý, I. *Proc. Natl. Acad. Sci. U. S. A.* **2009**, *106*, 13169–13174. (f) Jančařík, A.; Rybáček, J.; Cocq, K.; Chocholoušová, J. V.; Vacek, J.; Pohl, R.; Bednářová, L.; Fiedler, P.; Císařová, I.; Stará, I. G.; Starý, I. *Angew. Chem., Int. Ed.* **2013**, *52*, 9970–9975. (g) Kimura, Y.; Fukawa, N.; Miyauchi, Y.; Noguchi, K.; Tanaka, K. *Angew. Chem., Int. Ed.* **2014**, *53*, 8480–8483. (h) Šámal, M.; Chercheja, S.; Rybáček, J.; Chocholoušová, J. V.; Vacek, J.; Bednářová, L.; Šaman, D.; Stará, I. G.; Starý, I. *J. Am. Chem. Soc.* **2015**, *137*, 8469–8474.

(7) (a) Sawada, Y.; Furumi, S.; Takai, A.; Takeuchi, M.; Noguchi, K.; Tanaka, K. *J. Am. Chem. Soc.* **2012**, *134*, 4080–4083. (b) Shibata, T.; Uchiyama, T.; Yoshinami, Y.; Takayasu, S.; Tsuchikama, K.; Endo, K. *Chem. Commun.* **2012**, *48*, 1311–1313. (c) Jančařík, A.; Rybáček, J.; Cocq, K.; Chocholoušová, J. V.; Vacek, J.; Pohl, R.; Bednářová, L.; Fiedler, P.; Císařová, I.; Stará, I. G.; Starý, I. *Angew. Chem., Int. Ed.* **2013**, *52*, 9970–9975. (d) Nakamura, K.; Furumi, S.; Takeuchi, M.; Shibuya, T.; Tanaka, K. *J. Am. Chem. Soc.* **2014**, *136*, 5555–5558. (e) Kötzner, L.; Webber, M. J.; Martínez, A.; De Fusco, C.; List, B. *Angew. Chem., Int. Ed.* **2014**, *53*, 5202–5205. (f) Sako, M.; Takeuchi, Y.; Tsujihara, T.; Kodera, J.; Kawano, T.; Takizawa, S.; Sasai, H. *J. Am. Chem. Soc.* **2016**, *138*, 11481–11484.

(8) (a) Alcarazo, M. *Chem. - Eur. J.* **2014**, *20*, 7868–7877. (b) Alcarazo, M. *Acc. Chem. Res.* **2016**, *49*, 1797–1805.

(9) (a) Petušková, J.; Bruns, H.; Alcarazo, M. *Angew. Chem., Int. Ed.* **2011**, *50*, 3799–3802. (b) Carreras, J.; Patil, M.; Thiel, W.; Alcarazo, M. *J. Am. Chem. Soc.* **2012**, *134*, 16753–16758. (c) Carreras, J.; Gopakumar, G.; Gu, L.; Gimeno, A. M.; Linowski, P.; Petušková, J.; Thiel, W.; Alcarazo, M. *J. Am. Chem. Soc.* **2013**, *135*, 18815–18823. (d) Zozma, Á.; Deden, T.; Carreras, J.; Wille, C.; Petušková, J.; Rust, J.; Alcarazo, M. *Chem. - Eur. J.* **2014**, *20*, 2208–2214. (e) Tinnermann, H.; Wille, C.; Alcarazo, M. *Angew. Chem., Int. Ed.* **2014**, *53*, 8732–8736. (f) Haldón, E.; Kozma, Á.; Tinnermann, H.; Gu, L.; Goddard, R.; Alcarazo, M. *Dalton Trans.* **2016**, *45*, 1872–1876. (g) Dube, J.; Zheng, Y.; Thiel, W.; Alcarazo, M. *J. Am. Chem. Soc.* **2016**, *138*, 6869–6877.

(10) Mamane, V.; Hannen, P.; Fürstner, A. *Chem. - Eur. J.* **2004**, *10*, 4556–4575.

(11) (a) Widenhofer, R. *Chem. - Eur. J.* **2008**, *14*, 5382–5391. (b) Bongers, N.; Krause, N. *Angew. Chem., Int. Ed.* **2008**, *47*, 2178–2181. (c) Shapiro, N. D.; Toste, F. D. *Synlett* **2010**, 675–691. (d) Pradal, A.; Toule, P. Y.; Michelet, V. *Synthesis* **2011**, 1501–1514. (e) Zi, W.; Toste, F. D. *Chem. Soc. Rev.* **2016**, *45*, 4567–4589.

(12) For the use of TADDOL-derived phosphoramidites in asymmetric catalysis, see: (a) Lam, H. W. *Synthesis* **2011**, 2011–2043. (b) Teller, H.; Flügge, S.; Goddard, R.; Fürstner, A. *Angew. Chem., Int. Ed.* **2010**, *49*, 1949–1953. (c) Teller, H.; Corbet, M.; Mantilli, L.; Gopakumar, G.; Goddard, R.; Thiel, W.; Fürstner, A. *J. Am. Chem. Soc.* **2012**, *134*, 15331–15432.

(13) Maaliki, C.; Lepetit, C.; Canac, Y.; Bijani, C.; Duhayon, C.; Chauvin, R. *Chem. - Eur. J.* **2012**, *18*, 7705–7714.

(14) CCDC 1520358–1520365 contain the supplementary crystallographic data for this paper.

(15) Ilg, M. K.; Wolf, L. M.; Mantilli, L.; Farès, C.; Thiel, W.; Fürstner, A. *Chem. - Eur. J.* **2015**, *21*, 12279–12284.

(16) Precatalyst **4g** has also been preliminary tested in standard cycloisomerization reactions. See the Supporting Information.

(17) Nakai, Y.; Mori, T.; Inoue, Y. *J. Phys. Chem. A* **2012**, *116*, 7372–7385.

(18) Laarhoven, W. H.; Peters, W. H. M.; Tinnemans, A. H. A. *Tetrahedron* **1978**, *34*, 769–777.