Asymmetric Catalysis

Deutsche Ausgabe: DOI: 10.1002/ange.201500299
Internationale Ausgabe: DOI: 10.1002/anie.201500299

Phosphahelicenes in Asymmetric Organocatalysis: [3+2] Cyclizations of γ-Substituted Allenes and Electron-Poor Olefins**

Maxime Gicquel, Yang Zhang, Paul Aillard, Pascal Retailleau, Arnaud Voituriez, and Angela Marinetti**

Abstract: *The first use of phosphahelicene in enantioselective organocatalysis is reported. New chiral phosphahelicenes have been prepared and enable highly enantioselective [3+2] cyclization reactions between arylidene- or alkylidenemalononitriles and γ-substituted allenoates or cyanoallenes. These reactions afford cyclopentene derivatives in both high yields and diastereoselectivities, with enantiomeric excesses of up to 97%.*

Although phosphine organocatalysis has been long known, it is only during the last fifteen years or so that it has turned into a versatile, highly useful synthetic method.[1] Especially endless efforts have been devoted to the development of enantioselective variants of these reactions.[2] Notably, recent studies have focused on the stereochemical control of the organocatalytic [3+2] cyclizations of allenes with alkenes, widely known as the Lu's reaction.[3] In this field remarkable advances have been achieved by taking advantage of either chiral cyclic phosphines or bifunctional (polyfunctional) acyclic phosphines, which display axial,[4] planar,[5] or central chirality.[6] We disclose here the first examples of highly enantioselective [3+2] cyclizations achieved by means of helically chiral phosphorus derivatives, namely the phosphahelicenes **3** (Figure 1).[7]

Our group has recently disclosed a new series of phosphahelicenes with phosphole units embedded at the end of a helical sequence of aromatic rings.[8] In this series, the chiral phospha[6]helicene **1** (*P*-Men*-HelPhos; Figure 1; Men* = L-menthyl) and its phosphathiahelicene analogue **2** (*P*-Men*-HelPhos-S), demonstrated good potential as ligands in gold catalysis, thus giving *ee* values of up to 96% in 1,6-enyne cycloisomerization reactions.[9] Next, in looking for more extensive uses of these helical phosphines in catalytic processes, including organocatalysis, we expanded our investigations to new compounds in which the L-menthyl group on phosphorus was replaced by an isopinocampheyl group

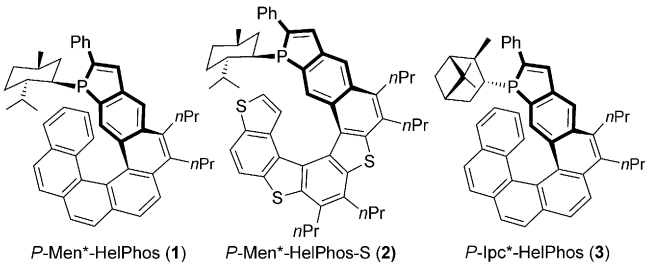
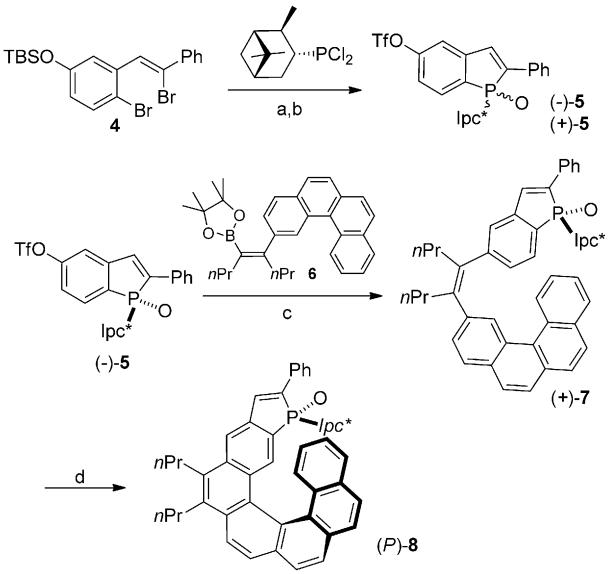


Figure 1. *P*-menthyl-phosphahelicenes from previous work and *P*-Ipc*-phosphahelicenes from this work.

[Ipc* = (1*R*,2*R*,3*R*,5*S*)-2,6,6-trimethyl-bicyclo[3.1.1]-heptan-3-yl], as typified by **3** in Figure 1. The rigid bicyclic structure of the chiral Ipc* auxiliary was anticipated to possibly induce high stereochemical control, especially in reactions such as organocatalytic processes which involve the phosphorus center itself.

Our strategy for the synthesis of the new *P*-Ipc*-substituted phosphahelicene oxide **8** (Scheme 1) relies on the oxidative photochemical cyclization of the diarylolefin **7** as



Scheme 1. Synthesis of the phosphahelicene oxide (*P*)-**8**. a) 1. *t*BuLi, −78°C, Et_2O; 2. H_2O_2, CH_2Cl_2; 3. TBAF, CH_2Cl_2, 76%; b) Cs_2CO_3, $PhNTf_2$, DMF, RT, 4h, 79%, 1:1 epimers ratio; c) $[Pd(SPhos)_2Cl_2]$, Cs_2CO_3, THF/H_2O (10:1), 80°C, 5h, 88%; d) *hν*, I_2, propylene oxide, cyclohexane/THF (70:1), 1h, 80%. DMF = *N*,*N*-dimethylformamide, TBAF = tetra-*n*-butylammonium fluoride, TBS = *tert*-butyldimethylsilyl, Tf = trifluoromethanesulfonyl, THF = tetrahydrofuran.

[*] M. Gicquel, Y. Zhang, P. Aillard, Dr. P. Retailleau, Dr. A. Voituriez, Dr. A. Marinetti
Institut de Chimie des Substances Naturelles
CNRS UPR 2301, Université Paris-Sud
91198 Gif-sur-Yvette (France)
E-mail: arnaud.voituriez@cnrs.fr
angela.marinetti@cnrs.fr

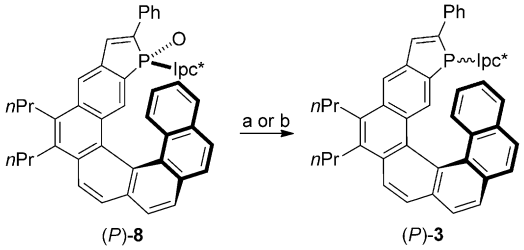
[**] Research reported in this paper has been supported by the CNRS. The authors thank the Institut de Chimie des Substances Naturelles, the China Scholarship Council, and the University of Paris Sud for grants to M.G., Y.Z. and P.A.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201500299.

the key step. It is based on the use of the *P*-Ipc*-substituted phosphindole oxide **5** as the key building block. The phosphindole oxide **5** is available as a mixture of two epimers, starting from (isopinocampheyl)dichlorophosphine[10] and the dibromoolefin **4**, by the dilithiation/cyclization sequence shown in Scheme 1.[9a] The two epimers of **5** were separated by column chromatography and the subsequent reactions have been carried out then on single epimers. Thus, the Suzuki coupling of (−)-**5** [$[\alpha]_D^{25}=-92$ ($c=1.6$, $CHCl_3$), ^{31}P NMR: $\delta=55$ ppm] with the olefinic boronate **6**[8a] led to the enantiomerically pure tetrasubstituted olefin (+)-**7** [$[\alpha]_D^{25}=+112$ ($c=1.5$, $CHCl_3$), ^{31}P NMR: $\delta=57$ ppm].

The final photocyclization step in Scheme 1 proved to be remarkably efficient and diastereoselective: starting from (+)-**7** it gave a single epimer of the desired phosphahelicene oxide **8** in 80% yield. The positive $[\alpha]_D$ value of **8**, $[\alpha]_D=+2375$ ($c=0.5$, $CHCl_3$), indicates that its helical scaffold has a *P*-configuration. The analogous photocyclization of (−)-**7** gives the phosphahelicene (*M*)-**8** in 70% yield upon isolation [$[\alpha]_D=-2430$ ($c=1$, $CHCl_3$); see Supporting Information for details]. In both cases, the photochemical cyclization step takes place with much higher yield than the analogous photocyclizations of *P*-L-menthyl-substituted olefins.[8a,9]

Reduction of the phosphine oxide (*P*)-**8** (^{31}P NMR: $\delta=59$ ppm) was carried out at 100 °C with phenylsilane and catalytic amounts of bis(4-nitrophenyl)phosphate (Scheme 2).[11] Under these reaction conditions, the trivalent



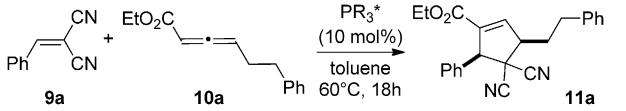
(*P*)-**8** (*P*)-**3**

Scheme 2. Reduction of the phosphahelicene oxide (*P*)-**8**. a) $PhSiH_3$, $(4\text{-}NO_2C_6H_4O)_2P(O)OH$, toluene, 100 °C, 4 h, 2:3 epimers ratio; b) $HSiCl_3$, toluene, −20 °C, 1 h, >10:1 epimers ratio at −20 °C.

P-Ipc*-HelPhos [(*P*)-**3**] was obtained as a mixture of two epimers in a 2:3 ratio (^{31}P NMR: $\delta=11$ and 6 ppm). Alternatively, reduction of (*P*)-**8** was carried out at low temperature with $HSiCl_3$ in toluene. The reaction mixture was monitored by ^{31}P NMR spectroscopy and showed that the reduction occurs at −20 °C, thus giving the two epimers in a greater than 10:1 ratio (major epimer: ^{31}P NMR $\delta=11$ ppm). Epimerization at phosphorus took place slowly at 0 °C (1:1 ratio after 1 h), and the thermodynamic ratio of 2:3 was attained after 0.5 hours of heating at 60 °C. The use of a $HSiCl_3/NEt_3$ mixture as the reducing agent gave the same results. These experiments show that the stereogenic center of these benzofused phospholes is configurationally unstable even at 0 °C, and thus fully supports previous literature studies.[12]

The reduction procedure (Scheme 2) was applied also to the synthesis of the epimeric phosphahelicene (*M*)-**3**. Both the *P*-Ipc*-substituted phosphahelicenes (*P*)-**3** and (*M*)-**3**, and the previously known *P*-menthyl-substituted HelPhos (*P*)-**1**[13] were engaged as catalysts in the [3+2] cyclization between benzylidenemalononitrile (**9a**) and ethyl 6-phenylhexa-2,3-dienoate (**10a**).[14,15] We were pleased to see that, despite the stereochemical lability of the phosphorus center, these phosphines display high regio-, diastereo-, and enantioselectivity in this organocatalytic reaction (Table 1). Both

Table 1: Screening of the HelPhos catalysts in an organocatalytic [3+2] cyclization reaction.



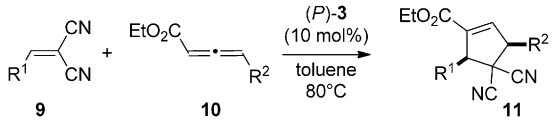
Entry	PR_3*	d.r. [%]	Yield [%]	*ee* [%]
1	*P*-Men*-HelPhos (*P*)-**1**	>95:5	30	89 (+)
2	*P*-Ipc*-HelPhos (*P*)-**3**	>95:5	37	95 (+)
3[a][b]	*P*-Ipc*-HelPhos (*P*)-**3**	>95:5	91	96 (+)
4	*P*-Ipc*-HelPhos (*M*)-**3**	85:15	83	68 (−)
5	(−)-**5′**[c]	90:10	35	8 (+)

[a] Reaction temperature = 80 °C. [b] As an additional experiment, reaction in entry 3 has been carried out at a 5 mol% catalyst loading: total conversion was attained after 48 h at 80 °C, thus giving **11a** in 96% *ee*. [c] The phosphindole oxide (−)-**5** was reduced to (−)-**5′** with $PhSiH_3$, $(4\text{-}NO_2C_6H_4O)_2P(O)OH$ and used then as the catalyst.

phosphahelicenes (*P*)-**1** and (*P*)-**3** afforded the cyclopentene **11a** as the unique [3+2] cyclization product, which results from the α-addition of the allenoate to the olefin (Michael-type addition of the allenoate through its α-carbon atom).[16] The *syn*-isomer was formed preferentially with greater than 95:5 diastereomeric ratio. The use of (*P*)-**1** as the catalyst provided **11a** in a moderate 30% yield with a high *ee* value (entry 1). Gratifyingly, the same product **11a** could be obtained in much higher enantiomeric excess (95% *ee*) and 37% yield, by using the newly synthesized (*P*)-**3** as the catalyst (entry 2). The yield could be further increased to 91%, while retaining the same 96% enantiomeric excess, by carrying out the reaction at 80 °C (entry 3). In analogous experiments, the opposite epimer, (*M*)-**3**, afforded the expected product **11a** in 68% *ee* only (entry 4). This result demonstrates that the relative configurations of the isopinocampheyl group and the helical scaffolds are suitably matched to attain good enantioselectivity levels. For comparison purposes, (−)-**5** (Scheme 1) was reduced into the corresponding trivalent phosphine (−)-**5′** and tested as a catalyst for the same reaction (entry 5). It provided a very low *ee* value, thus showing that helical chirality plays a major role in the stereochemical control of these cyclizations.

The scope of these enantioselective cyclizations was then investigated by using (*P*)-**3** as the catalyst. A wide range of substrates proved to be suitable for these reactions (Table 2). At first, we reacted ethyl 6-phenylhexa-2,3-dienoate with various arylidenemalononitrile derivatives (entries 1–10). When the R^1 substituent of the malononitrile derivative was either phenyl (entries 1 and 2) or a mono- or disubstituted

Table 2: Scope and limitations of the reaction.[a]



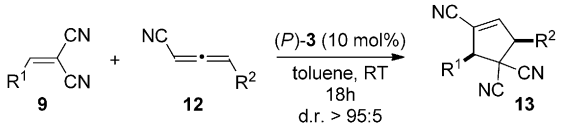
Entry	R^1	R^2	d.r. [%]	Yield [%]	*ee* [%]
1	Ph	$(CH_2)_2Ph$	>95:5	91 (**11a**)	96
2[b]	Ph	$(CH_2)_2Ph$	>95:5	92 (**11b**)	96
3	4-ClC_6H_4	$(CH_2)_2Ph$	95:5	84 (**11c**)	94
4	4-BrC_6H_4	$(CH_2)_2Ph$	90:10	83 (**11d**)	94
5	4-$OMeC_6H_4$	$(CH_2)_2Ph$	>95:5	84 (**11e**)	94
6	4-MeC_6H_4	$(CH_2)_2Ph$	>95:5	91 (**11f**)	95
7	3-BrC_6H_4	$(CH_2)_2Ph$	95:5	78 (**11g**)	92
8	2-BrC_6H_4	$(CH_2)_2Ph$	>95:5	94 (**11h**)	87
9	3,4-$Cl_2C_6H_3$	$(CH_2)_2Ph$	90:10	80 (**11i**)	88
10	1-naphthyl	$(CH_2)_2Ph$	95:5	79 (**11j**)	85
11	2-furyl	$(CH_2)_2Ph$	90:10	90 (**11k**)	95
12[c]	*N*-Me-2-indolyl	$(CH_2)_2Ph$	95:5	56 (**11l**)	89
13	2-thienyl	$(CH_2)_2Ph$	90:10	80 (**11m**)	95
14	cyclohexyl	$(CH_2)_2Ph$	>95:5	60 (**11n**)	82
15	Ph	CH_2-C_5H_9	>95:5	86 (**11o**)	95
16	Ph	$(CH_2)_2CO_2Me$	>95:5	89 (**11p**)	96
17	Ph	$(CH_2)_3Cl$	>95:5	70 (**11q**)	93
18	4-BrC_6H_4	CH_3	>95:5	71 (**11r**)	89
19	Ph	CH_3	95:5	73 (**11s**)	94
20	Ph	Ph	>95:5	74 (**11t**)	97

[a] Reactions were performed under Ar on a 0.10 mmol scale, in degased toluene (1.0 mL), at 80°C; **9**/**10** ratio = 1:2. Regio- and diastereoselectivities were evaluated by ^{1}H NMR spectroscopy on the crude reaction mixtures. The *ee* values were determined by HPLC using a chiral stationary phase. Racemic samples of **11a–t** were obtained with 5-phenyl-dibenzophosphole as the catalyst. [b] Benzyl 6-phenylhexa-2,3-dienoate was used instead of the corresponding ethyl ester. [c] In dichloroethane at 80°C.

aryl ring (entries 3–9), the expected adducts **11** could be isolated in high yields, regio- and diastereoselectivities and uniformly high enantiomeric excesses (87–96% *ee*). The olefins **9** in which the aryl substituent R^1 displays chloro, bromo, methyl, and methoxy substituents in various positions, including the sterically relevant *ortho*-position (entry 8), could be used without any decrease in terms of activity or selectivity. The reaction tolerates 2-heteroarylidenemalononitrile derivatives (entries 11–13). Noteworthy is that the reaction also proceeds with challenging substrates such as alkyl-substituted dicyanoolefins, albeit with some decrease in enantioselectivity (82% *ee* for R^1 = cyclohexyl, entry 14). Several γ-substituted allenes could be used, thus giving excellent yields and enantioselectivities, with up to 97% *ee* obtained with the phenyl-substituted allene (entries 15–20).

It is worth noting that the only reported examples of enantioselective [3+2] cyclizations between dicyanoolefins and γ-substituted allenoates relate to substrates in entries 18 and 19 of Table 2.[6d] These reactions were performed by using a chiral aminophosphine as the catalyst and gave the corresponding cyclopentenes in good yields but in moderate enantioselectivity. Moreover, they produced the *anti*-isomers as the major compounds, instead of the *syn* derivatives. Thus, our catalyst largely improves the previously known processes and complements the known catalyst.

Finally, to illustrate the versatility of the new catalyst (*P*)-**3**, we employed it in [3+2] cyclizations between 2-arylidenemalononitriles and γ-substituted buta-2,3-dienenitriles. To the best of our knowledge, cyanoallenes have been used only once in enantioselective phosphine-catalyzed cyclizations. These reactions involved imines as the cyclization partners and led to 2,5-dihydro-*1H*-pyrroles in up to 60% *ee*.[17] In our work, the enantioselective [3+2] cyclizations between **9** and the buta-2,3-dienenitriles **12** have been carried out in the presence of 10 mol% of (*P*)-**3** at room temperature (Scheme 3). The corresponding cyclopentenes **13a–c** were



13a, R^1 = Ph, R^2 = CH_2CH_2Ph 96%, 88% *ee*
13b, R^1 = 4-BrC_6H_4, R^2 = CH_2CH_2Ph 63%, 86% *ee*
13c, R^1 = Ph, R^2 = Ph 50%, 83% *ee*

Scheme 3. [3+2] cyclizations on γ-substituted buta-2,3-dienenitriles.

obtained in high yields, with total regioselectivity (α-adducts), and total diastereoselectivity (*syn* isomers).[18] The enantiomeric excesses were in the range of 83–88%. Thus, reactions in Scheme 3 represent the first examples of highly enantioselective phosphine-catalyzed cyclizations on cyanoallenes.

In summary, we have developed stereoselective access to a new series of chiral phosphahelicenes displaying an isopinocampheyl group on phosphorus. We have demonstrated the high potential of these phosphahelicenes in enantioselective nucleophilic organocatalysis by the development of [3+2] cyclization reactions between activated olefins and γ-substituted allenes giving *ee* values of up to 97%. Our results afford the first evidence for efficient stereochemical control of organocatalytic processes induced by helically chiral phosphines. From a synthetic point of view, these catalytic reactions provide an unprecedented and versatile approach to a series of enantioenriched, highly-substituted cyclopentenes derivatives.

Keywords: allenoates · cyclizations · enantioselectivity · organocatalysis · phosphahelicene

How to cite: *Angew. Chem. Int. Ed.* **2015**, *54*, 5470–5473
Angew. Chem. **2015**, *127*, 5560–5563

[1] For selected reviews, see: a) J. L. Methot, W. R. Roush, *Adv. Synth. Catal.* **2004**, *346*, 1035–1050; b) L.-W. Ye, J. Zhou, Y. Tang, *Chem. Soc. Rev.* **2008**, *37*, 1140–1152; c) C. Gomez, J.-F. Betzer, A. Voituriez, A. Marinetti, *ChemCatChem* **2013**, *5*, 1055–1065.

[2] a) A. Marinetti, A. Voituriez, *Synlett* **2010**, 174–194; b) Y. Lu, S.-X. Wang, X. Han, Y. Wang, *Synlett* **2011**, 2766–2778; c) Q.-Y. Zhao, Z. Lian, Y. Wei, M. Shi, *Chem. Commun.* **2012**, *48*, 1724–1732; d) Y. Xiao, Z. Sun, H. Guo, O. Kwon, *Beilstein J. Org. Chem.* **2014**, *10*, 2089–2121; e) Y. Wei, M. Shi, *Chem. Asian J.* **2014**, *9*, 2720–2734.

[3] C. Zhang, X. Lu, *J. Org. Chem.* **1995**, *60*, 2906–2908.

[4] a) J. E. Wilson, G. C. Fu, *Angew. Chem. Int. Ed.* **2006**, *45*, 1426 – 1429; *Angew. Chem.* **2006**, *118*, 1454 – 1457; b) A. Voituriez, N. Pinto, M. Neel, P. Retailleau, A. Marinetti, *Chem. Eur. J.* **2010**, *16*, 12541 – 12544; c) Y. Fujiwara, G. C. Fu, *J. Am. Chem. Soc.* **2011**, *133*, 12293 – 12297; d) M. Steurer, K. L. Jensen, D. Worgull, K. A. Jørgensen, *Chem. Eur. J.* **2012**, *18*, 76 – 79; e) D. Wang, Y. Wei, M. Shi, *Chem. Commun.* **2012**, *48*, 2764 – 2766; f) J. Marco-Martínez, V. Marcos, S. Reboredo, S. Filippone, N. Martin, *Angew. Chem. Int. Ed.* **2013**, *52*, 5115 – 5119; *Angew. Chem.* **2013**, *125*, 5219 – 5223.

[5] a) A. Voituriez, A. Panossian, N. Fleury-Brégeot, P. Retailleau, A. Marinetti, *J. Am. Chem. Soc.* **2008**, *130*, 14030 – 14031; b) N. Pinto, M. Neel, A. Panossian, P. Retailleau, G. Frison, A. Voituriez, A. Marinetti, *Chem. Eur. J.* **2010**, *16*, 1033 – 1045; c) N. Pinto, P. Retailleau, A. Voituriez, A. Marinetti, *Chem. Commun.* **2011**, *47*, 1015 – 1017; d) D. Duvvuru, N. Pinto, C. Gomez, J.-F. Betzer, P. Retailleau, A. Voituriez, A. Marinetti, *Adv. Synth. Catal.* **2012**, *354*, 408 – 414.

[6] a) G. Zhu, Z. Chen, Q. Jiang, D. Xiao, P. Cao, X. Zhang, *J. Am. Chem. Soc.* **1997**, *119*, 3836 – 3837; b) B. J. Cowen, S. J. Miller, *J. Am. Chem. Soc.* **2007**, *129*, 10988 – 10989; c) M. Sampath, T.-P. Loh, *Chem. Commun.* **2009**, 1568 – 1570; d) H. Xiao, Z. Chai, C.-W. Zheng, Y.-Q. Yang, W. Liu, J.-K. Zhang, G. Zhao, *Angew. Chem. Int. Ed.* **2010**, *49*, 4467 – 4470; *Angew. Chem.* **2010**, *122*, 4569 – 4572; e) X. Han, Y. Wang, F. Zhong, Y. Lu, *J. Am. Chem. Soc.* **2011**, *133*, 1726 – 1729; f) Q. Zhao, X. Han, Y. Wei, M. Shi, Y. Lu, *Chem. Commun.* **2012**, *48*, 970 – 972.

[7] Helical phosphine oxides have been used as catalysts in a few organocatalytic processes, thus giving low enantiomeric excesses only ($ee < 23\%$): S. Cauteruccio, D. Dova, M. Benaglia, A. Genoni, M. Orlandi, E. Licandro, *Eur. J. Org. Chem.* **2014**, 2694 – 2702.

[8] a) K. Yavari, S. Moussa, B. Ben Hassine, P. Retailleau, A. Voituriez, A. Marinetti, *Angew. Chem. Int. Ed.* **2012**, *51*, 6748 – 6752; *Angew. Chem.* **2012**, *124*, 6852 – 6856; b) K. Yavari, P. Retailleau, A. Voituriez, A. Marinetti, *Chem. Eur. J.* **2013**, *19*, 9939 – 9947; c) P. Aillard, P. Retailleau, A. Voituriez, A. Marinetti, *Chem. Commun.* **2014**, *50*, 2199 – 2201. For the synthesis of other phosphahelicenes, see: d) N. Fukawa, T. Osaka, K. Noguchi, K. Tanaka, *Org. Lett.* **2010**, *12*, 1324 – 1327; e) Y. Sawada, S. Furumi, A. Takai, M. Takeuchi, K. Noguchi, K. Tanaka, *J. Am. Chem. Soc.* **2012**, *134*, 4080 – 4083; f) K. Nakano, H. Oyama, Y. Nishimura, S. Nakasako, K. Nozaki, *Angew. Chem. Int. Ed.* **2012**, *51*, 695 – 699; *Angew. Chem.* **2012**, *124*, 719 – 723.

[9] a) K. Yavari, P. Aillard, Y. Zhang, F. Nuter, P. Retailleau, A. Voituriez, A. Marinetti, *Angew. Chem. Int. Ed.* **2014**, *53*, 861 – 865; *Angew. Chem.* **2014**, *126*, 880 – 884; b) P. Aillard, A. Voituriez, D. Dova, S. Cauteruccio, E. Licandro, A. Marinetti, *Chem. Eur. J.* **2014**, *20*, 12373 – 12376.

[10] A. Marinetti, F.-X. Buzin, L. Ricard, *J. Org. Chem.* **1997**, *62*, 297 – 301.

[11] Y. Li, L.-Q. Lu, S. Das, S. Pisiewicz, K. Junge, M. Beller, *J. Am. Chem. Soc.* **2012**, *134*, 18325 – 18329.

[12] W. Egan, R. Tang, G. Zon, K. Mislow, *J. Am. Chem. Soc.* **1971**, *93*, 6205 – 6216.

[13] The P-(L-menthyl)phosphahelicene **1** was obtained as a mixture of epimers in 55:45 ratio, after reduction of the corresponding phosphine oxide.

[14] For representative examples of the use of dicyanoolefins in phosphine-catalyzed cyclization reactions, see: a) X. Lu, Z. Lu, X. Zhang, *Tetrahedron* **2006**, *62*, 457 – 460; b) J. Feng, X. Lu, A. Kong, X. Han, *Tetrahedron* **2007**, *63*, 6035 – 6041; c) Y. S. Tran, O. Kwon, *J. Am. Chem. Soc.* **2007**, *129*, 12632 – 12633; d) H.-P. Deng, Y. Wei, M. Shi, *Org. Lett.* **2011**, *13*, 3348 – 3351; e) F. Zhong, X. Han, Y. Wang, Y. Lu, *Angew. Chem. Int. Ed.* **2011**, *50*, 7837 – 7841; *Angew. Chem.* **2011**, *123*, 7983 – 7987; f) F. Zhong, X. Han, Y. Wang, Y. Lu, *Chem. Sci.* **2012**, *3*, 1231 – 1234; g) F.-L. Hu, Y. Wei, M. Shi, *Adv. Synth. Catal.* **2014**, *356*, 736 – 742.

[15] For examples of enantioselective cyclizations on dicyanoolefins, see Ref. [6d] and M. Schuler, A. Voituriez, A. Marinetti, *Tetrahedron: Asymmetry* **2010**, *21*, 1569 – 1573.

[16] The α-addition mode is expected for γ-substituted allenoates: a) S. G. Pyne, K. Schafer, B. W. Skelton, A. H. White, *Chem. Commun.* **1997**, 2267 – 2268; b) M. Sampath, T.-P. Loh, *Chem. Sci.* **2010**, *1*, 739 – 742; c) C. Gomez, M. Gicquel, J.-C. Carry, L. Schio, P. Retailleau, A. Voituriez, A. Marinetti, *J. Org. Chem.* **2013**, *78*, 1488 – 1496; d) Ref. [6b].

[17] S. S. Kinderman, J. H. van Maarseveen, H. Hiemstra, *Synlett* **2011**, 1693 – 1696.

[18] Cyclopentenes **13c**, as well as **11b** and **11l**, have been characterized by X-ray diffraction studies.

Received: January 13, 2015
Published online: March 5, 2015

