# Synthesis of Allenes Bearing Phosphine Oxide Groups and **Investigation of Their Reactivity toward Gold Complexes**

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Dedicated to Prof. Steve Buchwald on the occasion of his 60<sup>th</sup> birthday.

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Abstract: A collection of phosphine oxide allenes has been prepared. Their coordination to gold(I) has been studied giving new coordination complexes when a pendant pyridine moiety was present. Alternatively, their gold(I)-catalyzed cycloisomerization has proven to be quite efficient. An almost complete axial-to-central chirality transfer in the cyclization process was observed, opening the potential access to valuable enantiopure phosphorus derivatives.

Keywords: allenes; gold carbenes; gold catalysis; phosphines

Allenes are fascinating molecular substrates. Their specific electronic configuration coupled to their extended tetrahedral spatial arrangement guarantee special and valuable properties.<sup>[1]</sup> When substituted by Lewis base substituents, the allene assembly can serve as a ligand,<sup>[2]</sup> possibly conveying axial chirality. Illustration of this principle was initially provided in 2008 by Krause, who reported the preparation of allenic bipyridines I and the corresponding silver and copper complexes.<sup>[3]</sup> In 2009, Ready developed chiral phosphine oxide allenes II as versatile organocatalysts for the asymmetric ring opening of *meso*-epoxides.<sup>[4]</sup> The same group then further adapted the parent structure II to append phosphine groups bearing CF<sub>3</sub> electronwithdrawing groups in place of the phosphine oxide ones. The resulting ligand could coordinate to Rh(I), featuring coordination to the allene moiety, and provide complex III, which proved to be a highly efficient catalyst for the enantioselective arylation of  $\alpha$ keto esters (Scheme 1).<sup>[5]</sup>

Because of our long-standing interest in gold catalvsis,<sup>[6]</sup> we wished to investigate the reactivity of new allene scaffolds bearing phosphine oxide groups as coordinating units. Coordination of gold(I) to allenes has indeed been theoretically studied in order to rationalize some reaction pathways.<sup>[7]</sup> In addition, some coordination complexes have also been isolated and characterized by X-ray crystallography. Fürstner isolated a complex between tetradimethylaminoallene



Fürstner 2008

Our objective



Scheme 1. Allene ligands and complexes.



<sup>[a]</sup> From the addition of PyZnBr on **2**.

Scheme 2. Preparation of allene ligands.

and  $Ph_3PAuSbF_6$  featuring  $\eta^1$  central coordination<sup>[8]</sup> while Widenhoefer has also reported an X-ray crystal structure of the  $\eta^2$  dimethylallene-Au<sup>+</sup>PPh<sub>3</sub> complex.<sup>[9]</sup>

Our objective was to use allenylphosphine oxides **IV** as probes for two types of applications. The first aim was the generation of new gold coordination complexes, possibly implying the phosphine oxide moiety.<sup>[10]</sup> These could be new precatalytic species or models of proposed intermediates. The second objective was to involve these substrates in cycloisomerization reactions when using appropriate R substituent on **IV** in order to deliver new phosphorus-containing chiral substrates.

Allenylphosphine oxide precursors were easily obtained in a few steps as shown in Scheme 2. Ketone **1** is smoothly alkylated by the lithium anion of methyldiphenylphosphine oxide. The resulting alcohol is then acylated (**2**), setting the stage for a copper-cata-



Scheme 3. Formation of gold chloride complexes 11a and 11b.

lyzed  $S_N 2'$  process which allows the introduction of various  $R^2$  groups and furnishes allenes 5–7.<sup>[1a,b,11]</sup> Alternatively, we also used the Pd(0) coupling reaction between a zinc reagent and propargyl acetate 2 to obtain 8 and 9, as well as pyridyl allenes 10a and 10b from acetates 4a and 4b.<sup>[3]</sup> It should be noted that 10a could also be prepared in slightly better yield (41%), based on the addition of PyZnBr to 2.

Our initial attempts to obtain new allene-gold complexes consisted in mixing 1 equiv. of allenes 5-7 with 1 equiv. of Me<sub>2</sub>SAuCl. However, we could not isolate any complex from these substrates. So we turned our attention to pyridyl-allenes 10a and 10b which incorporate an additional stronger Lewis base site of coordination. In the presence of Me<sub>2</sub>SAuCl, a quantitative reaction took place delivering gold complexes 11a and 11b for which the structures were secured by single-crystal X-ray diffraction (Scheme 3 and Figure 1).<sup>[12]</sup> Careful examination of the literature provided pieces of rationalization for the unforeseen formation of complexes 11a and 11b. Gevorgyan showed that similar allenylpyridine units could be activated by gold providing indolizines through nucleophilic addition of the pyridine nitrogen on the electrophilic allene gold complex.<sup>[13]</sup> Quite recently, Kumar and Waldmann described a synthesis of cyclic alkyl aminocarbene gold(I) complexes from the addition of Me<sub>2</sub>SAuCl to 1,7-envnes.<sup>[14]</sup>

Post-functionalization of vinylgold complexes has been documented in the literature.<sup>[13b,15]</sup> However,



Figure 1. Crystal structures of complexes 11a and 11b.



Figure 2. Summary of calculations for complex 11b: (A) Mayer bond order, (B) molecular orbital showing the delocalization between AuCl and carbene, (C) electrostatic potential (blue: positive; red: negative).

complexes **11a** and **11b** proved quite unreactive to treatment with triflic acid to promote protodeauration,<sup>[15d]</sup> addition of electrophilic halide sources (I<sub>2</sub>, NIS), and attempts of palladium couplings with aryl halides.<sup>[16]</sup> This excited our curiosity and led us to taking a closer look at the crystal structures of **11a** and **11b**. Interestingly, gold carbenes without a stabilizing heteroatom in the  $\alpha$  position have been isolated only recently.<sup>[17]</sup> The Au–C bond distances of 1.993(4) Å for **11a** and 1.984(2) Å for **11b** are in the low range of previously isolated gold carbenes,<sup>[18]</sup> similar to the shortest 1.984(4) Å Au–C bond so far observed by Miqueu, Amgoune and Bourissou for an *o*-carborane diphenylphosphine gold(I) diphenylcarbene complex.<sup>[17d]</sup>

To get more insight into the mesomeric structures 11a and 11b (vinylgold vs. gold carbene), we performed DFT calculations using the Turbomole program package (V6.4). B3LYP, supplemented by the D3 correction which was used as functional and the def2-SV(P) as basis set. Namely, structure 11b was optimized starting from X-ray crystallographic data. In order to better understand the electronic structure of this unusual gold-carbene complex, various theoretical analyses were conducted. First, using the Mayer bond order analysis (Figure 2A), it was possible to conclude that the main mesomeric form for complex 11b is the vinylgold one, as written in Scheme 3. The specific reactivity of this complex can be better understood by looking at one of the orbitals involving interactions between the AuCl fragment and the carbene part (Figure 2B).  $\pi$ -bonding between gold and chloride is also delocalized on the pyridinium moiety of the carbene, thus enhancing what is traditionally described as the back-donation. The fact that the carbene is a good electron acceptor is further confirmed by plotting the electrostatic potential (Figure 2C). While the Au-Cl fragment is found to be electronrich, the *in-situ* created carbene moiety has a positive electrostatic potential and is thus a good electron-ac-

**Table 1.** HOMO and LUMO energy (in eV) for various goldligands.

	PPh <sub>3</sub>	DIPP-NHC	SPhos	11b (no AuCl)
LUMO HOMO	$-0.77 \\ -5.55$	0.82 -5.75	$-0.52 \\ -4.85$	-1.11 -4.55

ceptor. To further substantiate these findings, comparisons were made with other classical gold ligands. Namely we compared the HOMO/LUMO energies of a typical phosphine (PPh<sub>3</sub>), a standard carbene (DIPP-NHC), a  $\pi$ -accepting phosphine (SPhos, Buchwald ligand<sup>[19]</sup>) and our new carbene. The data are summarized in Table 1.

It appears from Table 1 that the carbene derived from **11b** is more electrophilic than the usual carbene (DIPP-NHC) and in the same range as a phosphine, especially the SPhos or Buchwald phosphine.

We then wanted to test the generality of the formation of gold complexes such as **11a** and **11b**. We used a cationic gold precursor and exposed substrate **10b** to 0.7 equiv. of a 1:1 mixture of Ph<sub>3</sub>PAuCl and AgOTf (Scheme 4) in refluxing dichoroethane for 18 h. The corresponding complex **12b** was obtained in fair yield (63%) exhibiting characteristic spectral data by <sup>31</sup>P NMR as shown in Scheme 4 and also a <sup>13</sup>C NMR resonance at 203 ppm (doublet, <sup>2</sup> $J_{C,P}$ =114 Hz) diagnostic of a vinylgold species.<sup>[20]</sup> We also tried to further functionalize this complex. Protodeauration with triflic acid smoothly provided indolizinium salt **13**, whose structure was confirmed by X-ray crystallography,<sup>[12]</sup> while iodolysis gave vinyliodine derivative **14**.

Complexes 11a, 11b and 12b are chemical cul-desacs with no possible evolution in these reaction conditions. We hypothesized that the intervention of a nucleophile on the activated allene that liberates a proton would trigger a protodeauration and regenerate the gold catalyst. We therefore examined the reactivity of allenes 5 and 6 in the presence of a catalytic





Scheme 4. Ph<sub>3</sub>PAu–vinyl gold complex and reactivity.

quantity of gold catalyst. However, these reactions proved to be rather sluggish giving among a mixture of dienic products 15 and 16 as major components and single diastereomers. We deduced that the involved nucleophilic component was not electron-rich enough. Gratifyingly, allene 8 underwent the expected hydroarylation reaction in satisfactory yield providing indenylphosphine oxide 17. Our next attempt focused on the Au(I)-catalyzed rearrangement of vinylallene 9.<sup>[21]</sup> In that case, the expected cyclopentadiene product 19 was formed in 71% yield (Scheme 5). All these reactions must transit via gold intermediate 18 bearing a stereogenic center. We surmised that if chirality transfer<sup>[22]</sup> takes place in the cycloisomerization step, then access to novel enantiopure phosphines whose chirality relies on a quaternary center  $\beta$  to the phosphorus atom should be possible. To probe this point, we ran a preparative chiral HPLC on 8 and obtained both enantiomers with ees > 98%. We engaged (-, CD 254 nm)- $8^{[23]}$  in the same conditions as above and gratifyingly isolated (-, CD 254 nm)-17 with a 97% ee evidencing an almost total transfer of chirality. To the best of our knowledge, this is the first example of chirality transfer for a tetrasubstituted allene.

In conclusion, we herein report the reactivity of readily accessible phosphine oxides containing allenes with gold(I) salts. With a pendant pyridine moiety, some new examples of gold carbene complexes with no adjacent heteroatoms have been isolated and fully characterized, both analytically and theoretically. Alternatively, with a nucleophilic component bearing a labile proton, cycloisomerization takes place and delivers highly valuable scaffolds bearing a phosphine oxide moiety. The complete axial-to-central chirality transfer observed in one case augurs well for the preparation of enantiopure phosphines.

# **Experimental Section**

Scheme 5. Catalytic reactions.

### Synthesis of Ph<sub>3</sub>PAu–Vinyl Gold Complex 12b

A mixture of  $Ph_3PAuCl$  (140 mg, 0.28 mmol, 1 equiv.) and AgOTf (72 mg, 0.28 mmol, 1 equiv.) in DCE (4 mL) was stirred for 3.5 h at room temperature. The mixture was filtered to remove the AgCl and added to a solution of allene 10b (200 mg, 0.39 mmol, 1.4 equiv.) in DCE (10 mL) and heated at 50 °C for overnight. After 16 h, the reaction was monitored by <sup>31</sup>P NMR, the peak at ~45 ppm (Ph\_3PAuOTf) had disappeared. The mixture was concentrated under reduced pressure to afford **12b** as a brown solid; yield: 250 mg (63%).

#### Synthesis of Indolizinium Salt 13

To a solution of gold complex **12b** (140 mg, 0.13 mmol, 1 equiv.) in CH<sub>2</sub>Cl<sub>2</sub> (2 mL) was added dropwise TfOH (12  $\mu$ L, 0.14 mmol, 1.08 equiv.). After 6 h at room temperature, a black solid precipitated. The reaction was monitored by <sup>31</sup>P NMR until disappearance of the peaks of starting gold complex **12b**. The black solid was removed by filtration on Celite®. Water was added to the residue (10 mL) and the resultant mixture was diluted with CH<sub>2</sub>Cl<sub>2</sub> (5 mL). The aqueous phase was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3×10 mL) and the combined organic layers were washed with brine (10 mL), dried over anhydrous MgSO<sub>4</sub>, filtered and concentrated under reduced pressure. The residue was purified by precipitation in CH<sub>2</sub>Cl<sub>2</sub> and Et<sub>2</sub>O to afford **13** as a pale brown solid; yield: 84 mg (quant.).

#### Synthesis of (-)-17 from Allene (-)-8

To a solution of Ph<sub>3</sub>PAuCl (4 mg, 0.009 mmol, 0.05 equiv.) in dry and degassed CH<sub>2</sub>Cl<sub>2</sub> (1.8 mL) was added AgSbF<sub>6</sub> (3 mg, 0.009 mmol, 0.05 equiv.). After 5 min stirring at room temperature, the formation of AgCl was observed as a white solid. Then, a solution of allene (-)-**8** (98 mg, 98% *ee*, 0.18 mmol, 1 equiv.) in CH<sub>2</sub>Cl<sub>2</sub> (8.5 mL) was added. The reaction mixture was stirred at reflux temperature for 4 h and monitored by TLC. When the reaction was complete, the mixture was filtered through a short pad of Celite® and washed with Et<sub>2</sub>O and CH<sub>2</sub>Cl<sub>2</sub>. The solution was concentrated under reduced pressure. The residue was purified by silica gel chromatography with EtOAc/Pentane (gradient: from 3:7 until 1:1) as eluent to afford cyclic product (-)-**17** as a pale yellow solid; yield: 83 mg (97% *ee*, 85%).

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# References

- For a monograph, see: a) N. Krause, A. S. K. Hashmi, (Eds.), Modern Allene Chemistry, Wiley-VCH, Weinheim, 2004; b) for a review, see: S. Yu, S. Ma, Angew. Chem. 2012, 124, 3128–3167; Angew. Chem. Int. Ed. 2012, 51, 3074–3112; for some recent examples, see: c) M. Hasegawa, Y. Sone, S. Iwata, H. Matsuzawa, Y. Mazaki, Org. Lett. 2011, 13, 4688–4691.
- [2] For selected examples, see: a) S. Sentets, R. Serres, Y. Ortin, N. Lugan, G. Lavigne, Organometallics 2008, 27, 2078–2091; b) E. V. Banide, J. P. Grealis, H. Müller-Bunz, Y. Ortin, M. Casey, C. Mendicute-Fierro, M. C. Lagunas, M. J. McGlinchey, J. Organomet. Chem. 2008, 693, 1759–1770; c) S. Milosevic, E. V. Banide, H. Müller-Bunz, D. G. Gilheany, M. J. McGlinchey, Organometallics 2011, 30, 3804–3817.
- [3] S. Löhr, J. Averbeck, M. Schürmann, N. Krause, *Eur. J. Inorg. Chem.* **2008**, 552–556.

- [4] X. Pu, X. Qi, J. M. Ready, J. Am. Chem. Soc. 2009, 131, 10364–10365.
- [5] F. Cai, X. Pu, X. Qi, V. Lynch, A. Radha, J. M. Ready, J. Am. Chem. Soc. 2011, 133, 18066–18069.
- [6] a) L. Fensterbank, M. Malacria, Acc. Chem. Res. 2014, 47, 953-965; see also: b) A. Simonneau, F. Jaroschik, D. Lesage, M. Karanik, R. Guillot, M. Malacria, J.-C. Tabet, J.-P. Goddard, L. Fensterbank, V. Gandon, Y. Gimbert, Chem. Sci. 2011, 2, 2417-2422; c) F. Schröder, C. Tugny, E. Salanouve, H. Clavier, L. Giordano, D. Moraleda, Y. Gimbert, V. Mouriès-Mansuy, J.-P. Goddard, L. Fensterbank, Organometallics 2014, 33, 4051-4056; d) M. Guitet, P. Zhang, F. Marcelo, C. Tugny, J. Jimenez-Barbero, O. Buriez, C. Amatore, V. Mouriès-Mansuy, J.-P. Goddard, L. Fensterbank, Y. Zhang, S. Roland, M. Ménand, M. Sollogoub, Angew. Chem. 2013, 125, 7354-7359; Angew. Chem. Int. Ed. 2013, 52, 7213-7218; e) F. Nzulu, A. Bontemps, J. Robert, M. Barbazanges, L. Fensterbank, J.-P. Goddard, M. Malacria, C. Ollivier, M. Petit, J. Rieger, F. Stoffelbach, Macromolecules 2014, 47, 6652-6656.
- [7] a) M. Malacria, L. Fensterbank, V. Gandon, *Top. Curr. Chem.* 2011, 302, 157–182; b) E. Soriano, I. Fernandez, *Chem. Soc. Rev.* 2014, 43, 3041–3105; c) W. Yang, A. S. K. Hashmi, *Chem. Soc. Rev.* 2014, 43, 2941–2955.
- [8] A. Fürstner, M. Alcarazo, R. Goddard, C. W. Lehmann, Angew. Chem. 2008, 120, 3254–3258; Angew. Chem. Int. Ed. 2008, 47, 3210–3214.
- [9] T. J. Brown, A. Sugie, M. G. Dickens, R. A. Widenhoefer, *Organometallics* **2010**, *29*, 4207–4209.
- [10] For a review on poly-coordinate gold(I) salts, see:
  a) M. C. Gimeno, A. Laguna, *Chem. Rev.* **1997**, *97*, 511–522; for the extra-coordination by a P=O moiety, see: b) C. Hahn, L. Cruz, A. Villalobos, L. Garza, S. Adeosun, *Dalton Trans.* **2014**, *43*, 16300–16309.
- [11] S. Yu, S. Ma, Chem. Commun. 2011, 47, 5384–5418.
- [12] Crystallographic data for structures of compounds 11a, 11b and 13 were deposited at the Cambridge Crystallographic Data Centre with numbers CCDC 1055995 (11a), CCDC 1055996 (11b) and CCDC 1055997 (13). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif.
- [13] a) T. Schwier, A. W. Sromek, D. M. L. Yab, D. Chernyak, V. Gevorgyan, J. Am. Chem. Soc. 2007, 129, 9868–9878; for related species that are based on oxygen rather than nitrogen, see: b) L.-P. Liu, B. Xu, M. S. Mashuta, G. B. Hammond, J. Am. Chem. Soc. 2008, 130, 17642–17643; c) R. Döpp, C. Lothschütz, T. Wurms, M. Pernpointer, S. Keller, F. Rominger, A. S. K. Hashmi, Organometallics 2011, 30, 5894–5903.
- [14] F. Kolundzic, A. Murali, P. Perez-Galan, J. O. Bauer, C. Strohmann, K. Kumar, H. Waldmann, *Angew. Chem.* **2014**, *126*, 8260–8264; *Angew. Chem. Int. Ed.* **2014**, *53*, 8122–8126.
- [15] For reviews, see: a) L.-P. Liu, G. B. Hammond, *Chem. Soc. Rev.* 2012, *41*, 3129–3139; b) A. S. K. Hashmi, *Angew. Chem.* 2010, *122*, 5360–5369; *Angew. Chem. Int. Ed.* 2010, *49*, 5232–5241; see also: c) A. S. K. Hashmi, L. Schwarz, J.-H. Choi, T. M. Frost, *Angew. Chem.* 2000, *112*, 2382–2385; *Angew. Chem. Int. Ed.* 2000, *39*, 2285–2288; d) Y. Chen, D. Wang, J. L. Peter-

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sen, N. G. Akhmedov, X. Shi, Chem. Commun. 2010, 46, 6147–6149; e) D. Weber, M. A. Tarselli, M. R. Gagné, Angew. Chem. 2009, 121, 5843–5846; Angew. Chem. Int. Ed. 2009, 48, 5733–5736; f) A. S. K. Hashmi, T. D. Ramamurthi, F. Rominger, Adv. Synth. Catal. 2010, 352, 971–975; g) X. Zeng, R. Kinjo, B. Donnadieu, G. Bertrand, Angew. Chem. 2010, 122, 954–957; Angew. Chem. Int. Ed. 2010, 49, 942–945; h) A. S. K. Hashmi, T. D. Ramamurthi, M. H. Todd, A. S.-K. Tsang, K. Graf, Aust. J. Chem. 2010, 63, 1619–1626; i) A. S. K. Hashmi, T. D. Ramamurthi, F. Rominger, J. Organomet. Chem. 2009, 694, 592–597; j) T. Wang, S. Shi, M. Rudolph, A. S. K. Hashmi, Adv. Synth. Catal. 2014, 356, 2337–2342.

- [16] a) Y. Shi, S. D. Ramgren, S. A. Blum, Organometallics 2009, 28, 1275–1277; b) P. Garcia, M. Malacria, C. Aubert, V. Gandon, L. Fensterbank, ChemCatChem 2010, 2, 493–497; c) M. M. Hansmann, M. Pernpointner, R. Döpp, A. S. K. Hashmi, Chem. Eur. J. 2013, 19, 15290–15303.
- [17] For examples of gold carbenes with two C-substituents see: a) G. Seidel, A. Fürstner, Angew. Chem. 2014, 126, 4907–4910; Angew. Chem. Int. Ed. 2014, 53, 4807–4811;
  b) M. W. Hussong, F. Rominger, P. Krämer, B. F. Straub, Angew. Chem. 2014, 126, 9526–9529; Angew. Chem. Int. Ed. 2014, 53, 9372–9375; c) R. J. Harris, R. A. Widenhoefer, Angew. Chem. 2014, 126, 9523–9525; Angew. Chem. Int. Ed. 2014, 53, 9369–9371; d) M. Joost, L. Estevez, S. Mallet-Ladeira, K. Miqueu, A. Amgoune, D. Bourissou, Angew. Chem. 2014, 126, 14740–14744; Angew. Chem. Int. Ed. 2014, 53, 14512–14516.
- [18] For very interesting discussions, see: a) D. Benitez, N. D. Shapiro, E. Tkatchouk, Y. Wang, W. A. Goddard III, F. D. Toste, *Nat. Chem.* 2009, *1*, 482–486; b) Y. Wang, M. E. Muratore, A. M. Echavarren, *Chem. Eur. J.* 2015, *21*, 7332–7339; c) L. Nunes dos Santos Compri-

dos, J. E. M. N. Klein, G. Knizia, J. Kästner, A. S. K. Hashmi, *Angew. Chem.* **2015**, *127*, DOI: 10.1002/ange.201412401; *Angew. Chem. Int. Ed.* **2015**, *54*, DOI: 10.1002/anie.201412401.

- [19] D. S. Surry, S. L. Buchwald, Angew. Chem. 2008, 120, 6438–6461; Angew. Chem. Int. Ed. 2008, 47, 6338–6361.
- [20] For a similar <sup>13</sup>C NMR spectrum, see: ref.<sup>[13b]</sup>
- [21] a) H. Funami, H. Kusama, N. Iwasawa, Angew. Chem.
  2007, 119, 927–929; Angew. Chem. Int. Ed. 2007, 46, 909–911; b) J. H. Lee, F. D. Toste, Angew. Chem. 2007, 119, 930–932; Angew. Chem. Int. Ed. 2007, 46, 912–914; c) G. Lemière, V. Gandon, K. Cariou, T. Fukuyama, A.-L. Dhimane, L. Fensterbank, M. Malacria, Org. Lett. 2007, 9, 2207–2209; d) V. Gandon, G. Lemière, A. Hours, L. Fensterbank, M. Malacria, Angew. Chem. 2008, 120, 7644–7648; Angew. Chem. Int. Ed. 2008, 47, 7534–7538; e) G. Lemière, V. Gandon, K. Cariou, A. Hours, T. Fukuyama, A.-L. Dhimane, L. Fensterbank, M. Malacria, J. Am. Chem. Soc. 2009, 131, 2993–3006.
- [22] For a review on chirality transfers in gold catalysis, see:
  a) N. T. Patil, *Chem. Asian J.* 2012, *7*, 2186–2194; see also with allenes:
  b) Z. Liu, A. S. Wasmuth, S. G. Nelson, *J. Am. Chem. Soc.* 2006, *128*, 10352–10353;
  c) N. Morita, N. Krause, *Org. Lett.* 2004, *6*, 4121–4123;
  d) Z. Zhang, C. Liu, R. E. Kinder, X. Han, H. Qian, R. A. Widenhoefer, *J. Am. Chem. Soc.* 2006, *128*, 9066–9073;
  e) C.-Y. Yang, G.-Y. Lin, H.-Y. Liao, S. Datta, R. S. Liu, *J. Org. Chem.* 2008, *73*, 4907–4914; for a review on axial-to-central chirality transfer in cyclization processes, see:
  f) D. Campolo, S. Gastaldi, C. Roussel, M. P. Bertrand, M. Nechab, *Chem. Soc. Rev.* 2013, *42*, 8434–8466.
- [23] The sign has been determined by the circular dichroism detector at 254 nm in the mobile phase used for the chiral HPLC separation (see the Supporting Information).