

Use of ^1H NMR chemical shifts to determine the absolute configuration and enantiomeric purity for enantiomers of 3,3'-disubstituted-MeO-BIPHEP derivatives¹

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Abstract: The absolute configuration of a series of 3,3'-disubstituted-MeO-BIPHEP derivatives can be determined by the ^1H NMR chemical shift of the methoxyl group when the 3,3'-disubstituted-MeO-BIPHEP derivative is mixed with (–)-(2*R*,3*R*)-dibenzoyltartaric acid ((–)-DBTA) (1:2) and its NMR spectrum is run in CDCl_3 . The chemical shift of the methoxyl group in the S_{ax} enantiomer always occurred at higher field than the corresponding R_{ax} enantiomer. Integration of the corresponding methoxyl signals provides the enantiomeric purity of any mixtures.

Key words: assignment of absolute configuration, 2,2'-bis(diphenylphosphino)-1,1'-biaryls, MeO-BIPHEP derivatives, asymmetric Heck reaction, ^1H NMR chemical shifts.

Résumé : La configuration absolue d'une série de dérivés MeO-BIPHEP 3,3'-disubstitués peut être déterminée par RMN du ^1H , en utilisant le déplacement chimique du groupe méthoxyle et en procédant à la détermination des spectres RMN des dérivés MeO-BIPHEP 3,3'-disubstitués en présence d'acide (–)-(2*R*,3*R*)-dibenzoyltartrique (1 : 2) dans du CDCl_3 . Le déplacement chimique du groupe méthoxyle dans l'énantiomère S_{ax} se trouve toujours à un champ plus élevé que celui de l'énantiomère R_{ax} correspondant. L'intégration des signaux des groupes méthoxyles correspondants permet d'évaluer la pureté énantiomérique de tous les mélanges.

Mots clés : attribution d'une configuration absolue, 2,2'-bis(diphénylphosphino)-1,1'-biaryles, dérivés MeO-BIPHEP, réaction de Heck asymétrique, déplacements chimiques en RMN du ^1H .

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Introduction

Over the past few years, we have been interested in the development of synthetic routes towards the preparation of 3,3'-disubstituted-MeO-BIPHEP derivatives **4–11** for use as chiral ligands in a variety of transition-metal-catalyzed asymmetric transformations involving palladium and rhodium (1, 2).³ During the course of these studies it became necessary to not only resolve the resulting racemic mixtures of biaryl products **2** obtained from Ullmann couplings of the corresponding aryl halides **1** (Scheme 1), but also to assign the absolute configuration to each of the enantiomers. The standard method reported for the optical resolution of **3** is via the mixing of (\pm)-**3** and (–)-(2*R*,3*R*)-dibenzoyltartaric acid ((–)-DBTA) (1:1.5) in DCM-EtOAc , followed by the crystallization of the (*R*)-**3**:(–)-DBTA complex from the solution (**3**). We tried to resolve compounds **3–6**, **8**, and **10** us-

ing this resolution method; however, we were only successful with compounds **4**, **5**, and **8** using either (–)-DBTA or (–)-(2*R*,3*R*)-ditoluoyltartaric acid (DTTA). Two solutions to the resolution problem were developed. The first was to attach the chiral auxiliary ($R = \text{OSiMe}_2\text{-}(L)\text{-menthol}$) to **2** ($R^1 = \text{Me}$, $R^2 = \text{OH}$) to create diastereomers that could then be separated by silica gel chromatography (**1a**). Removal of the chiral auxiliary then gave enantiomers of **2** ($R^1 = \text{Me}$, $R^2 = \text{OH}$) that were then converted to **7**. The second solution was to replace the methyl moiety in **1** ($R^1 = \text{Me}$) with the chiral auxiliary ((*S*)- $\text{H}_3\text{CCH}(\text{OAc})\text{C}=\text{O}$) and then perform the Ullmann coupling to give a mixture of diastereomers **2** that were easily separated by silica gel chromatography (**1b**). The chiral auxiliary was then replaced by a methyl group, thereby providing biaryls **3–10**. However, the absolute configuration of the axis of chirality in biaryls **3–11** still had to be determined. This paper describes how the absolute con-

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This manuscript is dedicated to Dr. Arthur J. Carty for his contributions to the field of organometallic chemistry, his work for the chemistry community throughout Canada, and for being an inspiration in the classroom.

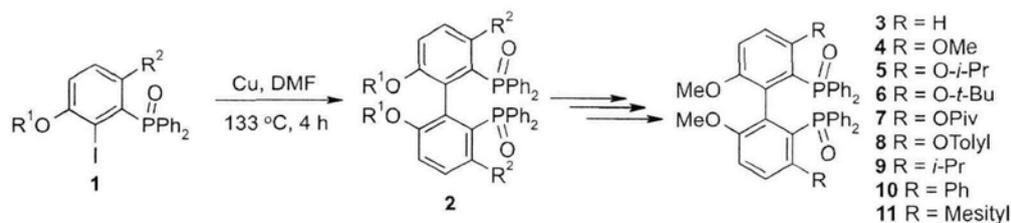
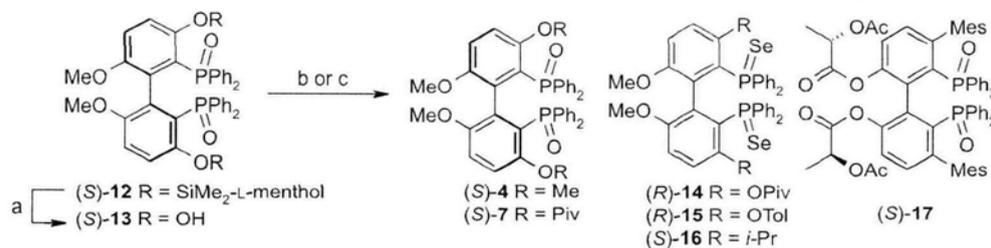
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Scheme 1.

Scheme 2. (a) HF-pyr, THF, $-70\text{ }^{\circ}\text{C}$ to rt, 1 h (89%); (b) MeI, DMF, K_2CO_3 , rt, 24 h (95%); (c) pivalyl chloride, Et_3N , DCM (94%).

figuration for biaryls **3–11** were assigned and how the absolute configuration of a series of 3,3'-disubstituted-MeO-BIPHEP derivatives can be determined by the ^1H NMR chemical shift of the methoxy group when the 3,3'-disubstituted-MeO-BIPHEP derivative is mixed with (–)-DBTA (1:2).

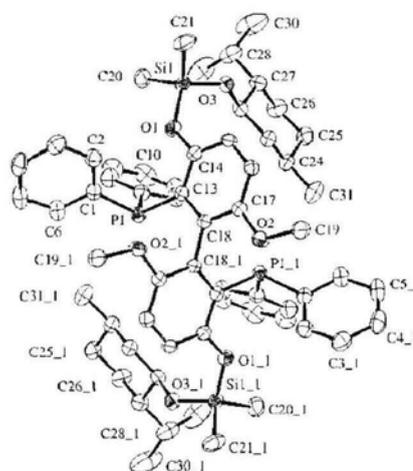
Results and discussion

Determining the absolute configuration of the axis of chirality in biaryls **3–11**

The absolute configurations of biaryls **3–11** were determined by obtaining the X-ray crystal structure of some derivatives of biaryls **3–5** and **7–11** that contain a chiral auxiliary, by using the Flack parameter (4) or using ^1H NMR chemical shifts of the methoxy group when the 3,3'-disubstituted-MeO-BIPHEP derivative is mixed with (–)-DBTA (1:2).⁴

The absolute configuration of synthesized MeO-BIPHEP **3** was assigned by comparing the sign of the optical rotation obtained from the synthesized sample with that reported by Schmid et al. (3). Biaryls (S)-**4** and (S)-**7** were prepared from the corresponding 3,3'-dihydroxybiaryl system (S)-**13** (Scheme 2). The absolute configuration of (S)-**13** was determined from the X-ray crystal structure of the SiMe_2 -(L)-menthol derivative **12** (Fig. 1). Figure 1 indicates that **12** has an axis of chirality of S. The absolute configuration of (S)-**5** was determined by obtaining an X-ray crystal structure of (S)-**5** when complexed with two molecules of (L)-DTTA (Fig. 2). The absolute configurations of (R)-**7**, (R)-**8**, and (S)-**9** were determined from the Flack parameter (4) of the X-ray crystal structure of their corresponding phosphine-selenides (R)-**14**, (R)-**15**, and (S)-**16** (Scheme 2 and Figs. 3–5). Finally the absolute configuration of (R)-**10** and (S)-**11**

Fig. 1. ORTEP diagram of (–)-(S)-**12** drawn with 30% probability ellipsoids. Hydrogen atoms are represented as spheres of arbitrary size.



were determined by the Flack parameter (4) of the X-ray crystal structure of the phosphine oxide (R)-**10** (Fig. 6) and the lactate derivative (S)-**17** (Scheme 2 and Fig. 7), respectively.

Use of ^1H NMR chemical shifts of the methoxy group to determine the absolute configuration of MeO-BIPHEP derivatives

As mentioned above, the reported (3) procedure for the resolution of MeO-BIPHEP **3** is by the mixing of (\pm)-**3** and (–)-DBTA (1:1.5) in DCM–EtOAc, followed by the crystallization of the complex (R)-**3**:(–)-DBTA from the solution. While we were successful with the resolution of **8** with (–)-DBTA, we found **4** and **5** were better resolved using

⁴ Supplementary data for this article are available on the journal Web site (<http://canjchem.nrc.ca>) or may be purchased from the Depository of Unpublished Data, Document Delivery, CISTI, National Research Council Canada, Ottawa, ON K1A 0R6, Canada. DUD 4079. For more information on obtaining material refer to http://cisti-icist.nrc-cnrc.gc.ca/irm/unpub_e.shtml. CCDC 239964, 285584, 285585, 285586, 285587, 285588, and 285589 contain the crystallographic data for this manuscript. These data can be obtained, free of charge, via www.ccdc.cam.ac.uk/conts/retrieving.html (Or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax +44 1223 336033; or deposit@ccdc.cam.ac.uk).

Fig. 2. ORTEP diagram of (-)-*S*-**5** complexed with two molecules of (*L*)-DTTA drawn with 30% probability ellipsoids. Hydrogen atoms are represented as spheres of arbitrary size.

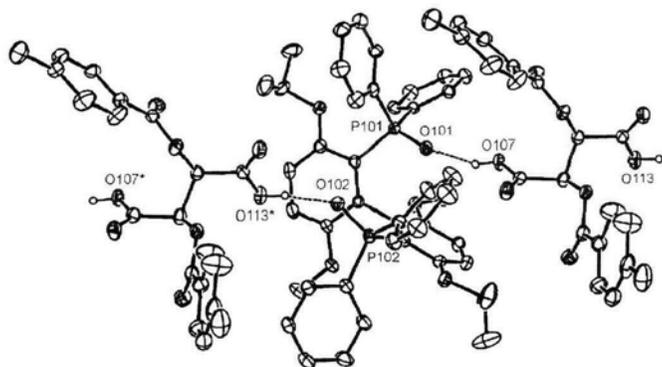
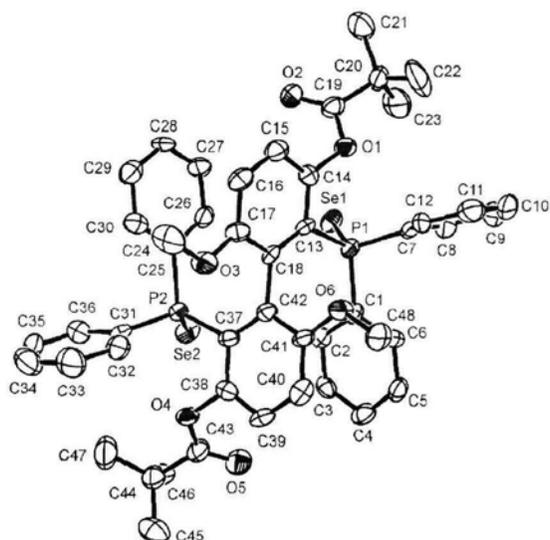


Fig. 3. ORTEP diagram of (+)-*R*-**14** drawn with 30% probability ellipsoids. Hydrogen atoms are represented as spheres of arbitrary size.



(+)-DTTA. Attempts to resolve compounds **3**, **6**, and **10** by this procedure failed even after trying modified resolution conditions. While trying to resolve the latter grouping of biaryls, we decided to examine the ^1H NMR spectrum of compounds (\pm)-**3-6**, **8**, and **10** in the presence of 2 equiv. of (-)-DBTA to determine if indeed diastereomeric complexes were formed. In all cases, a pair of singlets integrating for 3H each were observed between 2.8 and 3.6 ppm. The two signals corresponded to the methoxy groups⁵ for each of the diastereomeric complexes in solution. Although the diastereomeric complexes were formed in solution with compounds (\pm)-**6** and **10** and 2 equiv. of (-)-DBTA, the crystals obtained were always a mix of both diastereomers. Thus enantiomerically pure **3**, **6**, **7**, and **9-11** were prepared by alternative methods (1). Once compounds **3-11** were obtained, the enantiopurity of the compounds was determined by complexing them with 2 equiv. of (-)-DBTA and observing the region between 2.8 and 3.6 ppm in the ^1H NMR spectrum. Once resolved, only one methoxy signal was ob-

Fig. 4. ORTEP diagram of (+)-*R*-**15** drawn with 30% probability ellipsoids. Hydrogen atoms are represented as spheres of arbitrary size.

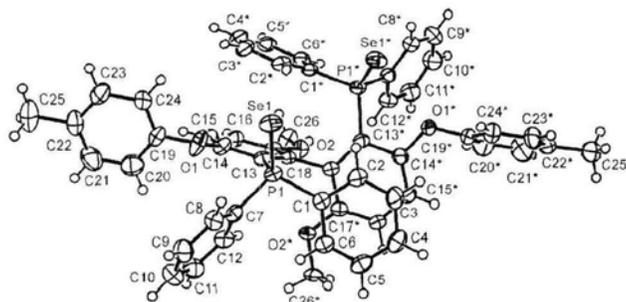


Fig. 5. ORTEP diagram of (+)-*S*-**16** drawn with 30% probability ellipsoids. Hydrogen atoms are represented as spheres of arbitrary size.

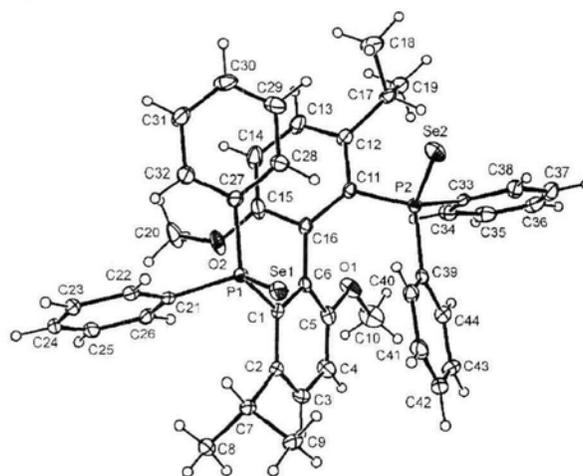
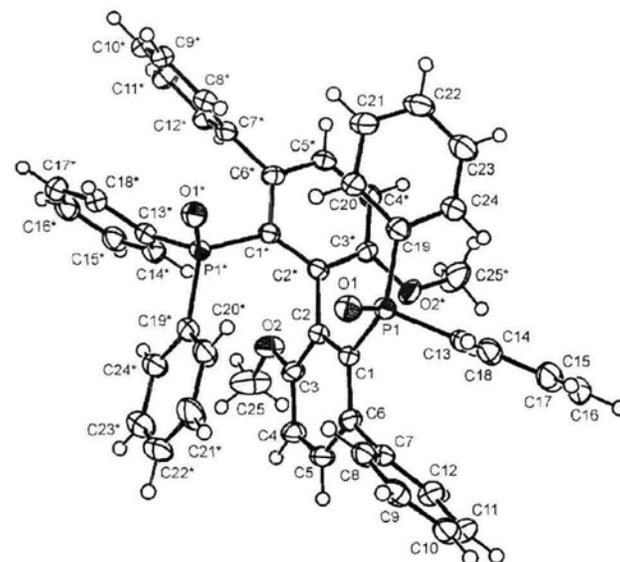


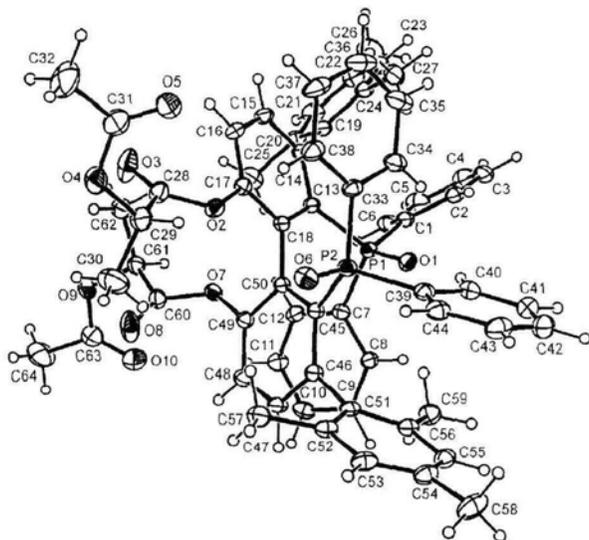
Fig. 6. ORTEP diagram of (+)-*R*-**10** drawn with 30% probability ellipsoids. Hydrogen atoms are represented as spheres of arbitrary size.



⁵Each methoxy signal arising from the two diastereomeric complexes corresponds to both the C6 and C6' methoxy groups within one complex. The C6 and C6' methoxy groups are homotopic by virtue of a C2 axis, even when complexed with (-)-DBTA.

Table 1. ^1H NMR shifts of the methoxy group for complexes of **3–11** with 2 equiv. of (–)-DBTA.

Compound	3,3'-Group	$[\alpha]_D^{20}$ (c solvent) for (<i>S</i>)-enantiomer	Chemical shift (ppm) (CDCl_3)	
			(<i>S</i>)-enantiomer	(<i>R</i>)-enantiomer
3	H	–130.4 (1.00, CHCl_3)	2.90	3.04
4	OMe	–130.1 (1.05, CHCl_3)	2.87	3.07
5	O- <i>i</i> -Pr	–80.1 (0.53, CHCl_3)	2.84	3.09
6	O- <i>t</i> -Bu	–44.1 (1.42, CHCl_3)	2.75	3.05
7	OPiv	–1.1 (2.70, CHCl_3)	2.98	3.11
8	OTolyl	–124.0 (1.40, CHCl_3)	2.82	3.13
9	<i>i</i> -Pr	+17.1 (0.76, CHCl_3)	3.02	3.30
10	Ph	+347.0 (1.04, CHCl_3)	3.54	3.58
11	Mesityl	+47.0 (0.82, CHCl_3)	3.30	3.35

Fig. 7. ORTEP diagram of (+)-(*S*)-**17** drawn with 30% probability ellipsoids. Hydrogen atoms are represented as spheres of arbitrary size.

served for each of compounds **3–11**, indicating the samples were enantiopure. What was interesting is that when we correlated the absolute configuration of the axis of chirality to the chemical shift of the methoxy signals complexed with 2 equiv. of (–)-DBTA, we found that the chemical shift of the methoxy group of the (*S*)-enantiomer was always upfield of the methoxy signal for the (*R*)-enantiomer (Table 1).

The only 3,3'-disubstituted compound in Table 1 whose absolute configuration was not determined by X-ray crystallography was biaryl **6** (3,3'-diO-*t*-Bu-MeO-BIPHEP). The absolute stereochemistry was assigned based on the ^1H NMR shifts of the methoxy groups when complexed with 2 equiv. of (–)-DBTA (Table 1). The individual enantiomers of **6** were separated as previously described (1*b*). Additional support for the hypothesis that the absolute configuration of compound **6** was *R* (based on the NMR shifts in Table 1) came when the corresponding bisphosphine, (+)-(*R*)-**26** (made by the reduction of bisphosphine oxide (+)-(*R*)-**6** (1)) was used in the Heck arylation of 2,3-dihydrofuran (Table 2) (5). With all the reactions recorded with compounds **23–25** and **27–30**, the biaryl enantiomer with the *R*-axis of chirality always gave (*R*)-**20** as the major product. This was also observed with (*R*)-BINAP (entry 9). The reaction with the enantiomer assigned as (*R*)-**26** from the ^1H NMR data

(Table 1) also provided (*R*)-**20** as the major product, thereby providing additional evidence (although not entirely conclusive) that the absolute configuration of **6** could be assigned by following the general trend shown in Table 1.

Conclusions

We have shown that the absolute stereochemistry of 3,3'-disubstituted-MeO-BIPHEP derivatives can be correlated to the chemical shift of the methoxy signal when the BIPHEP derivative is complexed with 2 equiv. of (–)-DBTA. In all cases the methoxy signal from the *S*-enantiomer:(–)-DBTA complex appeared at higher field than the *R*-enantiomer:(–)-DBTA complex. In addition, the enantiomeric purity of scalemic mixtures of MeO-BIPHEP derivatives can be obtained by integration of methoxy signals when the MeO-BIPHEP derivative is complexed with 2 equiv. of (–)-DBTA.

Experimental procedures

Compounds **3–11** were prepared as previously described (1). ^1H NMR spectra were obtained on a 300 MHz NMR spectrometer. All spectra were obtained in CDCl_3 , and the chemical shifts (ppm) are relative to the CHCl_3 peak as an internal reference (7.27 ppm for ^1H). X-ray crystal structures were determined by Dr. Masood Parvez at the University of Calgary, Calgary, Alberta.

General procedure for preparation of the 1:2 complexes of biaryls **3–11**:(–)-DBTA

To a solution of phosphine oxide **3–11** (~10 μmol) in CDCl_3 was added a solution of (–)-DBTA (~20 μmol) in CDCl_3 (0.4 mL). The clear solution was then analyzed by NMR.

General procedure for the Heck reaction with 2,3-dihydrofuran (**18**)

Under a nitrogen atmosphere, the chiral phosphine (0.03 equiv.) and $\text{Pd}(\text{OAc})_2$ (0.067 equiv.) were placed in a scintillation vial equipped with a magnetic stirring bar. The vial was sealed with a Teflon-faced silicone septum under nitrogen. The reagents were dissolved in dry benzene (1.65 mL/equiv. PhOTf) and stirred at room temperature for 10 min. Phenyl triflate (1 equiv.), DIPEA (3.39 equiv.), and 2,3-dihydrofuran (5.60 equiv.) were added sequentially, and the vial was placed in a preheated, thermostatically controlled 40 $^\circ\text{C}$ oil bath for 24 h. Hexanes (8.26 mL/equiv.

Table 2. Asymmetric Heck results with ligands 3–10.

Entry	Ligand	Conversion (%)	Ratio of products		
			(<i>R</i>)-20 (% ee)	21	(<i>S</i>)-22 (% ee)
1	(+)-(<i>R</i>)-23	65	83 (92)	7	10 (63)
2	(+)-(<i>R</i>)-24	6	100 (9)	0	0
3	(+)-(<i>R</i>)-25	37	93 (77)	0	7 (0)
4	(+)-(<i>R</i>)-26	100	96 (89)	0	4 (11) ^a
5	(+)-(<i>R</i>)-27	100	99 (90)	0	1 (10)
6	(+)-(<i>R</i>)-28	57	97 (20)	0	3 (85)
7	(-)-(<i>R</i>)-29	12	66 (51)	0	34 (25)
8	(-)-(<i>R</i>)-30	60	99 (>99)	0	1 (>99) ^{a,b}
9	(+)-(<i>R</i>)-BINAP	41	91 (81)	0	9 (61) ^c

^aThe major enantiomer of 22 had the *R*-configuration.^b10 mol% Pd(OAc)₂, 20 mol% (-)-(*R*)-9.^cResults reported by Hayashi and co-workers (5).

ligand) were then added, and the resulting slurry was filtered through a plug of silica gel. The filtrate was analyzed by chiral GC (Cyclodex B column, 80 °C start temperature, 2 min initial hold time, 1 °C/min ramp rate, 160 °C final temperature, helium carrier gas at 2.0 mL/min, FID detection), with the reaction components eluting in the following order: phenyl triflate (10.81 min), (*S*)-2-phenyl-2,3-dihydrofuran (26.57 min), (*R*)-2-phenyl-2,3-dihydrofuran (26.97 min), 2-phenyl-4,5-dihydrofuran (29.11 min), (*S*)-2-phenyl-2,5-dihydrofuran (31.51 min), (*R*)-2-phenyl-2,5-dihydrofuran (31.91 min).

X-ray crystal data for compound (*S*)-12

Monoclinic *C*2; *a* = 28.3813(7) Å, *b* = 9.6063(2) Å, *c* = 11.1778(4) Å, β = 105.3695(10)°, *V* = 2938.52(14) Å³; *Z* = 2; *R* = 0.042; *wR* = 0.083.

X-ray crystal data for compound (*S*)-5

Monoclinic *P*2₁; *a* = 13.0510(10) Å, *b* = 23.083(2) Å, *c* = 21.525(3) Å, β = 95.548(4)°, *V* = 6454.2(12) Å³; *Z* = 4, *R* = 0.054; *wR* = 0.147. The asymmetric unit is composed of two independent pairs of molecules of C₄₄H₄₄O₆P₂ and C₂₀H₁₈O₈, an ordered molecule of CH₃CN, and three disordered half molecules of CH₃CN. The non-hydrogen atoms of the complex molecules and ordered solvate were refined anisotropically; the C and N atoms of the disordered solvates were allowed isotropic displacement parameters. Phenyl rings were constrained as regular hexagons with C—C 1.39 Å and C—C—C 120°. Hydrogen atoms were included at geometrically idealized positions and were not refined; H-atoms of the disordered CH₃CN molecules were ignored.

X-ray crystal data for compound (*R*)-14

Orthorhombic *P*2₁2₁2₁; *a* = 18.334(2) Å, *b* = 18.530(2) Å, *c* = 33.367(6) Å, *V* = 11 336(3) Å³; *Z* = 8. The asymmetric unit is composed of two independent molecules of C₄₈H₄₈O₆P₂Se₂, an ordered molecule of C₃H₆O₃, and two

disordered half molecules of C₃H₆O₃. A *t*-Bu group and an O11,C91–C95 moiety in one of the C₄₈H₄₈O₆P₂Se₂ molecules are disordered. Most of the non-hydrogen atoms were refined anisotropically. Phenyl rings were constrained as regular hexagons with C—C = 1.39 Å and C—C—C = 120°. Hydrogen atoms were included at geometrically idealized positions and were not refined; H-atoms of the disordered C₃H₆O₃ half molecules were ignored. The final cycle of full-matrix least-squares refinement using SHELXL97 (6) converged with unweighted and weighted agreement factors, *R* = 0.074; *wR* = 0.212 (all data), respectively, and goodness of fit, *S* = 1.01. The absolute configuration was established by the Flack method (4). The Flack parameter for the inverted structure was 0.992(13). Therefore, the inverted structure was rejected as the one present in the crystal.

X-ray crystal data for compound (*R*)-15

Orthorhombic *C*222₁; *a* = 12.1890(10) Å, *b* = 17.261(2) Å, *c* = 22.239(4) Å, α = β = γ = 90°, *V* = 4679.0(11) Å³, *Z* = 4. The final cycle of full-matrix least-squares refinement using SHELXL97 (6) converged with unweighted and weighted agreement factors *R* = 0.033, *wR* = 0.072 (all data), respectively, and goodness of fit, *S* = 1.03. The absolute configuration was established by the Flack method (4). The Flack parameter for the inverted structure was 0.995(6). Therefore, the inverted structure was rejected as the one present in the crystal.

X-ray crystal data for compound (*S*)-16

Monoclinic *P*2₁; *a* = 13.577(2) Å, *b* = 18.990(4) Å, *c* = 17.459(3) Å, α = γ = 90°, β = 98.903(10)°, *V* = 4447.2(14) Å³; *Z* = 2. The asymmetric unit is composed of two molecules of the complex, a CH₃CN of solvation and a half molecule of C₆H₁₄ of solvation that was disordered over two sites with partial occupancy factors of 0.25 each. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included at geometrically idealized positions and were not

refined; H-atoms of the disordered C_6H_{14} were ignored. The final cycle of full-matrix least-squares refinement using SHELXL97 (6) converged with unweighted and weighted agreement factors $R = 0.038$, $wR = 0.095$ (all data), respectively, and goodness of fit, $S = 1.09$. The absolute configuration was established by the Flack method (4). The Flack parameter for the inverted structure was 0.976(5). Therefore, the inverted structure was rejected as the one present in the crystal.

X-ray crystal data for compound (R)-10

Monoclinic C_2 ; $a = 22.090(6)$ Å, $b = 9.557(3)$ Å, $c = 12.174(2)$ Å, $\alpha = \gamma = 90^\circ$, $\beta = 103.889(15)^\circ$, $V = 2495.0(11)$ Å³; $Z = 2$. The asymmetric unit is composed of a half molecule of the complex lying about a twofold axis, a CH_2Cl_2 of solvation on a general position, and a disordered half molecule of CH_2Cl_2 of solvation lying on a special position. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included at geometrically idealized positions and were not refined; H-atoms of the disordered CH_2Cl_2 were ignored. The final cycle of full-matrix least-squares refinement using SHELXL97 (6) converged with unweighted and weighted agreement factors, $R = 0.0548$, $wR = 0.113$ (all data), respectively, and goodness of fit, $S = 1.04$. The absolute configuration was established by the Flack method (4). The Flack parameter for the inverted structure was 0.95(8). Therefore, the inverted structure was rejected as the one present in the crystal.

X-ray crystal data for compound (S)-17

Monoclinic $P2_1$; $a = 11.8900(10)$ Å, $b = 21.565(4)$ Å, $c = 22.128(15)$ Å, $\alpha = \gamma = 90^\circ$, $\beta = 93.399(10)^\circ$, $V = 5663.8(15)$ Å³; $Z = 4$. The asymmetric unit contains two molecules of the complex and a water of solvation. In one of the molecules, C160-C164 and O18-O20 were disordered over two sites each. Most of the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included at geometrically idealized positions and were not refined. The final cycle of full-matrix least-squares refinement using SHELXL97

(6) converged with unweighted and weighted agreement factors $R = 0.05$, $wR = 0.125$ (all data), respectively, and goodness of fit, $S = 1.03$. The absolute configuration was established by the Flack method (4). The Flack parameter for the inverted structure was 0.97(6). Therefore, the inverted structure was rejected as the one present in the crystal.

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References

- (a) E. Gorobets, G.-R. Sun, B.M.M. Wheatley, M. Parvez, and B.A. Keay. *Tetrahedron Lett.* **45**, 3597 (2004); (b) E. Gorobets, B.M.M. Wheatley, J.M. Hopkins, R. McDonald, and B.A. Keay. *Tetrahedron Lett.* **46**, 3843 (2005).
- (a) N.G. Andersen, M. Parvez, R. McDonald, and B.A. Keay. *Can. J. Chem.* **82**, 145 (2004); (b) N.G. Andersen, R. McDonald, and B.A. Keay. *Tetrahedron: Asymmetry*, **12**, 263 (2001); (c) N.G. Andersen, M. Parvez, and B.A. Keay. *Org. Lett.* **2**, 2817 (2000); (d) D. Che, N.G. Andersen, S.Y.W. Lau, M. Parvez, and B.A. Keay. *Tetrahedron: Asymmetry*, **11**, 1919 (2000).
- (a) R. Schmid, M. Cereghetti, B. Heiser, P. Schonholzer, and H.-J. Hansen. *Helv. Chim. Acta.* **71**, 897 (1988); (b) R. Schmid, J. Foricher, M. Cereghetti, and P. Schönholzer. *Helv. Chim. Acta* **74**, 370 (1991).
- H.D. Flack. *Acta Crystallogr. Sect. A*, **A39**, 876 (1983).
- (a) F. Ozawa, A. Kubo, Y. Matsumoto, and T. Hayashi. *Organometallics*, **12**, 4188 (1993); (b) F. Ozawa, A. Kubo, and T. Hayashi. *J. Am. Chem. Soc.* **113**, 1417 (1991).
- G.M. Sheldrick. SHELXL97 [computer program]. University of Göttingen, Göttingen, Germany. 1997.