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New *P*-chirogenic *tert.*-butyl-xantphos ligands and their application in asymmetric hydrogenation and alkylation

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ABSTRACT

The synthesis of a broad library of new *P*-chirogenic Xantphos ligands is reported. A special feature is 2,7-di-*tert.*-butyl substituents in the backbone which requires the modification of the original synthetic approach. In comparison to related ligands reported formerly the substitution has a considerable influence on the results (yield and % e.e.) of metal catalyzed reactions, e.g. asymmetric rhodium catalyzed hydrogenation of isophorone and the palladium catalyzed alkylation, respectively.

1. Introduction

Efforts in the application of chiral phosphines employed as ligands in asymmetric reactions were particularly inspired by the conclusion of W. S. Knowles in his Nobel-Prize lecture in 2001: "We felt strongly if one wanted to get high ee values, the asymmetry would have to be directly on the phosphorus. That is where the action is." [1] An early highlight in this regard represents the preparation of *P*-chirogenic compounds by Horner et al. [2] which pathed the way for the synthesis and application of DiPAMP as ligand in the homogeneous rhodium catalyzed asymmetric hydrogenation of prochiral enamides[3]. However, in the following decades the focus in this area was mainly directed on the use of chelating phosphines with chirality in the backbone (e.g. with *C*-stereogenic centers, axes and planes) [4].

Around the turn of the millennium a renewed interest in *P*-chirogenic ligands became visible. Thus, meanwhile well-known diphosphines like BisP*[5], QuinoxP* [6], MiniPhos [7], and Tang-Phos [8] were developed showing excellent results in several asymmetric transformations (Fig. 1). Stimulated by this success the number of *P*-chirogenic ligands and its successful application in asymmetric reactions has grown enormously in the last years [9].

Recently, we have published a large family of diphosphines with two *P*-chirogenic triarylphosphines interlinked via an ether-bridge with xanthene, diphenyl ether, or dibenzofuran backbone, respectively [10].

Some of these meanwhile commercially available ligands showed excellent results in the rhodium catalyzed asymmetric hydrogenation of isophorone [10] and in the stereoselective copper catalyzed hydroallylation of disubstituted cyclopropenes [11]. Xantphos itself developed by van Leeuwen and co-workers and used in numerous transition metal catalyzed reaction, e.g. hydroformylation[12], is characterized by two *tert.*-butyl groups in 2,7-position of the xanthene backbone. Taking the effect of remote substituents in phosphorus ligands on the course of the catalytic reactions into account[13], now we tried to introduce two *P*-chirogenic groups in this particular backbone. This target required a modified synthesis. Moreover, in subsequent asymmetric catalytic

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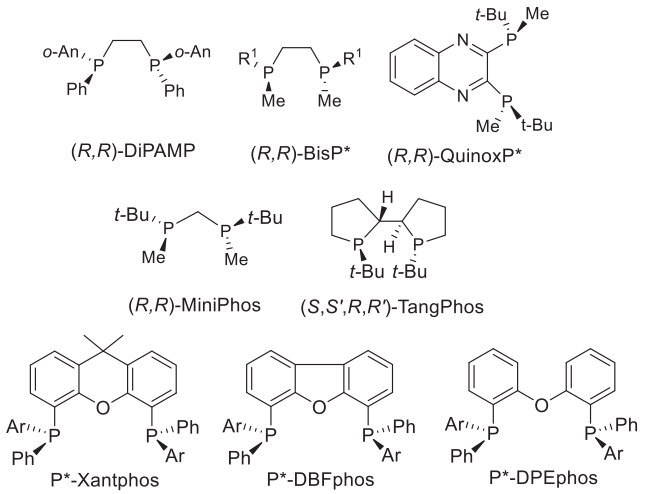


Fig. 1. Some prominent examples of *P*-chirogenic ligands.

reactions significant effects caused by the additional *tert.*-butyl substituents in comparison to the parent structures became obvious.

2. Results and discussion

2.1. Synthesis

In the first part of the synthesis of *P*-chirogenic 2,7-*tert.*-butyl-Xantphos derivatives **2a-t** we followed the established method of Jugé et al. for the preparation of borane-protected *P*-chirogenic methyl aryl(phenyl)phosphinites **1a-t** and their free derivatives **1′a-t** [9g,14]. Based on the experiences in the synthesis of other *P*-chirogenic Xantphos ligands (see reference 10) the borane-group in **1a-t** was removed first *in situ* and then the unprotected chiral methyl phosphinite **1′a-t** was added to dilithiated 2,7-di-*tert.*-butyl-xanthene (Scheme 1). In first trials, we started with the simple and commercially available 2,7-di-*tert.*-butyl-xanthene and followed the approach recently published for non-substituted Xantphos derivatives [10,15]. But the yields of **2** were unsatisfactorily. Therefore, we switched to the relevant 4,5-di-bromo compounds. With them in hand we noted significant better results [16]. By variation of the corresponding aryl groups in **1** twenty 2,7-di-*tert.*-butyl derivatives **2a-t** were obtained as enantiopure compounds after crystallization or purification by column chromatography, respectively, from the raw products.

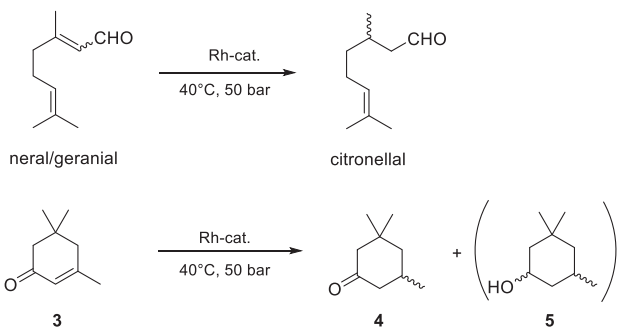
2.2. Rhodium catalyzed asymmetric hydrogenation

Our first intention was to apply the new diphosphines **2** as ligands in the rhodium catalyzed asymmetric hydrogenation of neral and geranial (parts of citral) for the stereoselective synthesis of citronellal as precursor for the technical menthol manufacture [17]. But the enantioselectivities noted were only poor (less than 30% e.e.). Therefore, some of these new diphosphines were tested in the asymmetric hydrogenation of isophorone **3** like already described for other similar *P*- chirogenic ligands (Scheme 2) [10].

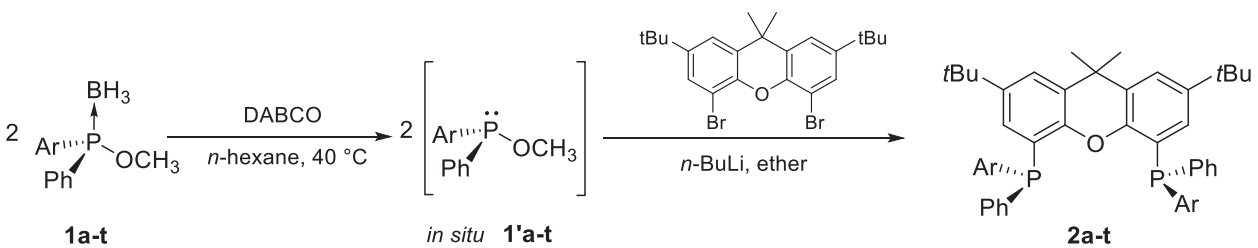
For the catalytic reaction we employed two metal sources Rh(acac)(cod) (**I**) and Rh(acac)$(CO)_2$ (**II**). These metal complexes allowed the asymmetric hydrogenation of both components of citral at ambient and enhanced pressure [17]. Like citral components (neral and geranial) also isophorone **3** represents structurally an α,β-unsaturated carbonyl compound but without the possibility of *E/Z*-isomerization. After prolongation of the reaction time the formation of the undesired alcohol **5** by reduction of carbonyl group was observed. For comparison the results of "nondecorated" *P**-chirogenic Xantphos **6** derivatives have been added to Table 1.

Our preliminary tests clearly showed that the application of Rh(cod)(acac) (**I**) led to significantly lower enantioselectivities in comparison to the use of Rh(acac)$(CO)_2$ (**II**) (Table 1, entries 1 and 2). Obviously, the catalytically active species in both reactions are different. We already noted this effect in the (non-asymmetric) hydrogenation of neral and geranial, respectively [17]. The relevant kinetic curves of the hydrogenation consumption were different. Up to now, the reason for this behavior is not clear.

Therefore, we have used in subsequent trials only Rh(acac)$(CO)_2$ (**II**) as metal source. Beside the *ortho*-aryloxyphenyl group (xanthene backbone) all chiral diphosphines of types **2** and **6** bear phenylphosphino moieties with a methyl, or an *o*-, *m*-*p*-substituted aryl as second substituent. In the asymmetric hydrogenation of isophorone under identic conditions the effect of the additional *tert.*-butyl groups in the xanthene backbone is significant in some



Scheme 2. Rhodium catalyzed asymmetric hydrogenation of isophorone **3.**



Ar: **a**: 2-MeO-Ph, **b**: 2-Me-Ph, **c**: 3-MeO-Ph, **d**: 3-Me-Ph, **e**: 4-MeO-Ph, **f**: 4-Me-Ph, **g**: 1-naphthyl, **h**: 2-naphthyl, **i**: 9-phenantryl, **j**: 3,5-MeO-Ph, **k**: 2-EtO-Ph, **l**: 2-Et-Ph, **m**: 3-EtO-Ph, **n**: 3-Et-Ph, **o**: 4-EtO-Ph, **p**: 2-*i*PrO-Ph, **q**: 2-*i*Pr-Ph, **r**: 3-*i*PrO-Ph, **s**: 3-*i*Pr-Ph, **t**: 4-dibenzofuranyl

Scheme 1. Synthetic approach to *P*-chirogenic 2,7-di-*tert.*-butyl-xantphos derivatives **2**.

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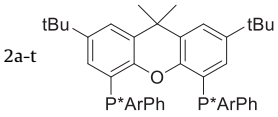
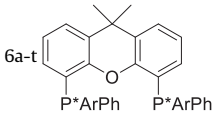
Table 1
Comparison of results in the asymmetric hydrogenation of isophorone with *P*-chirogenic diphosphines of type **2** and **6**[a]

ligand				 2a-t			 6a-t		
entry	ligand (Ar)	precatalyst[b]	solvent	time [h]	conversion[c] [%]	% e.e. (abs. conf.)[d]	time [h]	conversion[c] [%]	% e.e. (abs. conf.)[d]
1	**a** (2-MeO-Ph)	**I**	thf	4	100 (19)	20.6 (*S*)	4	100 (25)	8.8 (*R*)
		I	toluene	8	100 (14)	5.4 (*S*)	8	100 (30)	8.8 (*R*)
		II	thf	4	100 (2)	79.9 (*S*)	4	100 (3)	84.0 (*S*)
		II	toluene	20	100 (5)	77.4 (*S*)	20	100 (19)	84.0 (*S*)
2	**b** (2-Me-Ph)	**I**	thf	2	100 (10)	0.1 (*R*)	15	85 (3)	36.5 (*R*)
		I	toluene	15	99 (5)	0.1 (*S*)	15	70 (2)	50.1 (*R*)
		II	thf				4	100 (1)	96.5 (*S*)
		II	toluene	15	33 (0)	89.3 (*S*)	4	100 (1)	96.4 (*S*)
3	**c** (3-MeO-Ph)	**II**	thf	4	46 (1)	6.7 (*S*)	4	87 (1)	10.1 (*S*)
		II	toluene	8	41 (1)	9.0 (*S*)	8	74 (1)	12.5 (*S*)
4	**e** (4-MeO-Ph)	**II**	thf	8	88 (2)	0.7 (*R*)	8	94 (2)	0.5 (*S*)
		II	toluene	8	92 (2)	2.5 (*R*)	8	45 (4)	1.5 (*S*)
5	**f** (4-Me-Ph)	**II**	thf	4	21 (1)	1.3 (*R*)	4	20 (1)	0.3 (*R*)
		II	toluene	8	19 (1)	1.3 (*R*)	8	19 (1)	1.7 (*S*)
6	**g** (1-naphthyl)	**II**	thf	15	54 (1)	66.7 (*S*)	4	84 (2)	91.2 (*S*)
		II	toluene	15	12 (1)	82.6 (*S*)	4	87 (2)	91.9 (*S*)
7	**h** (2-naphthyl)	**II**	thf	8	56 (1)	17.4 (*S*)	20	57 (3)	19.7 (*S*)
		II	toluene	8	15 (1)	17.1 (*S*)	20	50 (1)	17.0 (*S*)
8	**i** (4-phenantryl)	**II**	thf				4	89 (1)	91.9 (*S*)
		II	toluene	15	17 (0)	81.0 (*S*)	4	89 (1)	91.9 (*S*)
9	**j** (3,5-MeO-Ph)	**II**	thf	4	50 (7)	16.0 (*S*)	4	50 (3)	24.6 (*S*)
		II	toluene	4	87 (2)	38.9 (*S*)	4	20 (0)	25.8 (*S*)
10	**k** (2-EtO-Ph)	**II**	thf	4	98 (7)	83.5 (*S*)	4	80 (6)	29.1 (*S*)
		II	toluene	8	100 (1)	85.1 (*S*)	4	15 (0)	36.2 (*S*)
11	**l** (2-Et-Ph)	**II**	thf	4	22 (0)	87.9 (*S*)	4	22 (0)	16.0 (*S*)
		II	toluene	4	10 (0)	85.1 (*S*)	4	15 (0)	19.0 (*S*)
12	**n** (3-Et-Ph)	**II**	thf	4	69 (1)	13.2 (*S*)			
		II	toluene	8	46 (5)	10.3 (*S*)			
13	**t** (4-DBF)	**II**	thf				4	81 (1)	18.1 (*S*)
		II	toluene				8	47 (0)	14.3 (*S*)

[a] Rh/**2**/isophorone = 1/1.2/200, 5 MPa H_2, 40 °C.
[b] Rh(acac)(cod) = **I**, Rh(acac)$(CO)_2$ = **II**.
[c] Estimated by ^{1}H NMR, in parenthesis the part of alcohol **5**.
[d] Enantioselectivity of **4** estimated by GC on chiral column.

cases. Differences in the yield of the saturated ketone by more than 60% have been noted (e.g. entry 2). It seems that the new ligands of type **2** suppress more the formation of the undesired alcohols **5** than ligands of type **6** especially when Rh(cod)(acac) (**I**) was used as rhodium source.

In general, structurally related ligands induced similar ee-values. Enantioselectivities ranges from almost zero, e.g. ligands of type **2f**/**6f** until 80 to >90% e.e. with ligands of type **2a**/**6a** or **2g**/**6g**. The latter are characterized either by *ortho*-methoxy groups or 1-naphthyl groups.

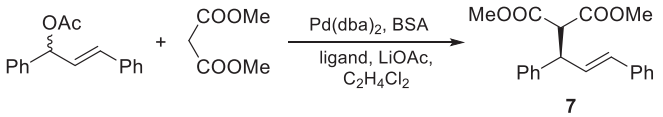
Aryl substituents away from the *ortho*-position in the third aryl group have only marginal (*meta*-position) or nearly no influence (*para*-substitution) on the stereoselective induction of the asymmetric hydrogenation (e.g. entries 2, 3 and 5 or entries 6, 7, 8). In the latter example the change from the 1-naphthyl group (phenyl ring owing benzannulated ring in 2,3-position) to the 2-naphthyl group (now 3,4-position) the enantioselectivity of product dropped. But with derivative **2i** having a phenantryl group as a combination of both benzannulated rings the stereoselectivity increased again.

Also, some surprising results has been noted. While for the 2-methoxy/2-methyl substituted derivatives **2a** and **2b** and also for the "undecorated" xanthene bridge ones **6a** and **6b** good enantioselectivities were concluded the enantioselectivity dropped down dramatically in case of the 2-ethoxy/2-ethyl derivatives (**2k** and **2l** *vs.* **6k** and **6l**). Interestingly, from point of view enantioselectivity the introduction of the additional *tert.*-butyl groups in the backbone of xanthene had an unfavorable effect.

2.3. Pd-mediated asymmetric alkylation

To test the asymmetric induction of *P*-chirogenic Xantphos ligands in stereoselective transformation, we employed them in allylation of dimethylmalonate by 1,3-diphenylallyl acetate using chiral palladium complexes (Scheme 3). This benchmark reaction was chosen because the only hitherto known *P*-chirogenic Xantphos ligand **2u** (owing a chiral PPhMe-moiety, Fig. 2) was applied in this reaction by the Hamada group in 1997 (up to 85% e.e.) [18].

For comparison we synthesized also the analogous Xantphos analogue **6u** without *tert.*-butyl substituents in 2,7-position by the same procedure applying (*S*)-methoxy(methyl)(phenyl)phosphine borane complex. In contrast to the ligand of type **2a-t** or **6a-t** diphosphines **2u** and **6u** possess two aryl groups and one methyl group (Fig. 2). Due to this substitution pattern the phosphine



Scheme 3. Pd-catalyzed asymmetric alkylation of 1,3-diphenylallyl acetate with dimethyl malonate.

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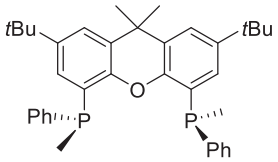
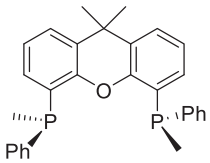


2u



6u

Fig. 2. Examples for *P*-chirogenic Xantphos derivatives with *P*-methyl groups.

groups become more electron donating.

As Table 2 illustrates superior enantioselectivities can also be find by application of ligands bearing additional *ortho*-substituents in the second aryl group (beside the *ortho*-substituted aryl group of xanthene).

Thus, ligands with 2-methoxy or 2-methyl groups (**2a,** and **6a,b**) yielded results in stereoselectivity superior than those noted by Hamada et al. applying diphosphine **2u** (entries 1 and 2 *vs.* entry 11). The similar compound **6u** (without 2,7-*tert.*-butyl groups, see Fig. 2) gives under our reaction conditions only 59% e.e. (entry 11). Also, ligands with 1-naphthyl and 4-phenantryl group owing annulated aryl rings in 2,3-position allow the formation of **7** with enantioselectivities up to 90% (entries 6 and 8). As already found for the hydrogenation reaction the shift to the 3- and 4-substituted derivatives leads to a significant lowering of enantioselectivity (entries 3, 4, 5, 7 and 9). Comparing the results of 3-MeO-phenyl derivatives with the double substituted 3,5-di-MeO-phenyl compound the downward trend can held back slightly (entries 3 and 9). Also, in this stereoselective reaction it seems that with increasing bulkiness of the *ortho*-substituent the stereoselectivity of reaction is negatively affected (entries 1 and 2 *vs.* 10). Reduction of the amount of the additive (LiOAc) did not significantly influence the results. Only in a few cases the conversion was diminished (entries 8 and 9).

3. Conclusion

The new *P*-chirogenic *P**-Xantphos ligands **2a-t** can serve as ligands in the asymmetric reaction of the rhodium catalyzed hydrogenation of isophorone and the palladium mediated alkylation of allyl acetate. In general, only ligands bearing *ortho*-aryl substituents induced satisfying enantioselectivities in both asymmetric transformations. The molecular structure of diphosphine **2j** corresponds well to that of the already published "nondecorated" *P*-chiral Xantphos ligands of type **6** [10]. Obviously the additional *tert.*-butyl groups in the backbone do not influence the geometric structure (P1—P2 distance 4.34 Å, (C1—O1—C13 angle 119.22(13)°, angle between planes (C1—C6) vs. (C8—C13) 3.86(9)°) of the ligand (Fig. 3). Differences in the catalytic performance must therefore be

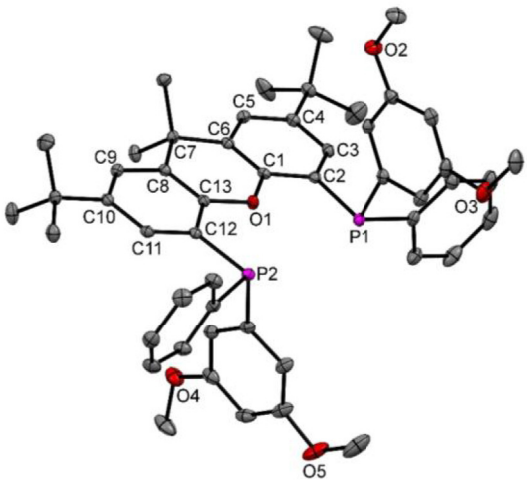
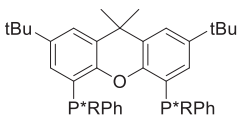
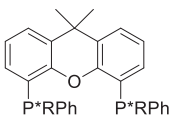


Fig. 3. Molecular structure of the *P*-chirogenic 3,5-dimethoxy-phenyl derivative **2j** in the crystal. Displacement ellipsoids correspond to 30% probability. Hydrogen atoms are omitted for clarity [19].

Table 2
Results in asymmetric Pd-catalyzed alkylation of 1,3-diphenylallyl acetate with *P*-chirogenic Xantphos derivatives **2** and **6**[a]

ligand						
entry	ligand (R)	LiOAc [eq.][b]	yield[c] [%]	% e.e. (abs. conf.)[d]	yield[c] [%]	% e.e. (abs. conf.)[d]
1	**a** (2-MeO-Ph)	1	92	88.6 (*R*)	92	93.3 (*R*)
2	**b** (2-Me-Ph)	1	90	80.0 (*R*)	82	90.4 (*R*)
3	**c** (3-MeO-Ph)	1	81	12.8 (*R*)	88	15.1 (*R*)
4	**e** (4-MeO-Ph)	1	86	9.4 (*S*)	91	7.0 (*S*)
5	**f** (4-Me-Ph)	1	90	8.2 (*S*)	90	4.7 (*S*)
6	**g** (1-naphthyl)	1	88	90.2 (*R*)	89	87.4 (*R*)
		0.5	96	88.7 (*R*)		
		0.2	91	88.8 (*R*)		
		0.1	90	88.8 (*R*)		
7	**h** (2-naphthyl)	1	83	1.8 (*S*)	92	13.4 (*R*)
8	**i** (4-phenantryl)	1	89	89.9 (*R*)	88	87.9 (*R*)
		0.2			91	88.5 (*R*)
9	**j** (3,5-MeO-Ph)	1	86	46.1 (*R*)	92	36.4 (*R*)
		0.5			90	36.4 (*R*)
		0.2			31	39.9 (*R*)
10	**q** (2-*i*Pr-Ph))	1	79	45.2 (*R*)		
11	**u** (Me)	1	96[e,f]	85 (*R*)[e,f]	48	58.5 (*S*)

[a] $Pd(dba)_2$/ligand/allyl acetate/DMM/BSA = 1/1/100/100/100, −20 °C to r.t.
[b] In relation to the amount of substrate.
[c] Isolated yield after chromatographic separation.
[d] Enantioselectivity of compound **7** estimated by HPLC on chiral column.
[e] Amount of LiOAc was not indicated in the literature.
[f] Published in reference 18.

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attributed to different polarities.

4. Experimental section

All solvents were dried and freshly distilled under argon before use. All reactions were performed under an argon atmosphere by using standard Schlenk techniques. Thin-layer chromatography was performed on precoated TLC plates (silica gel). Flash chromatography was carried out with silica gel 60 (particle size 0.040–0.063 mm) with a CombiFlash R_F system (Teledyne ISCO). NMR spectra were recorded generally at Bruker AV 400 spectrometer at the following frequencies: 400.13 MHz (1H), 100.61 MHz (^{13}C), 161.98 MHz (^{31}P) or at Bruker AV 300 (300.13 MHz (^{1}H), 75.47 MHz (^{13}C), 121.49 MHz (^{31}P)). Chemical shifts of ^{1}H and ^{13}C NMR spectra are reported in ppm downfield from used solvent $CDCl_3$ as internal standard (7.25 ppm/77.00 ppm). Chemical shifts of ^{31}P NMR spectra are referred to H_3PO_4 as external standard. Signals are quoted as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet) and br (broad). Mass spectra were recorded on a Thermo Electron MAT 95-XP or an Agilent 1200/6210 Time-of-flight LC-MS. For chiral HPLC-analysis a device Agilent 1100 Series was used. For GC-analysis a device Agilent 7890 was applied. The X-ray diffraction data were collected on a Bruker Kappa APEX II Duo diffractometer with Cu-Kα radiation. The structure was solved using SIR2004 [20] and refined by full-matrix least-squares techniques on F^2 (SHELXL-2014) [21]. Mercury was applied for graphical representation [22].

The various (*R*)-(aryl)(methoxy)(phenyl)phosphine *P*-borane complexes **1a-t** were prepared by the already described procedure [10].

The enantiomeric purity of diphosphines **2a-t** and **6a-u** were verified by NMR-measurement (resulting *meso*-compounds by epimerization show different nmr-shifts) and comparison of the optical rotation after the synthesis and storage for a longer time.

4.1. General procedure for the synthesis (1S,1′S)-(2,7-di-tert-butyl-9,9-dimethyl-9H-xanthene-4,5-diyl)bis((aryl)(phenyl)phosphine) (**2a-t**)

Methyl phosphinite *P*-borane complex **1a-t** (3.3 mmol) was dissolved in hexane (10 mL) and DABCO (6.6 mmol, 739 mg) was added. After stirring at 40 °C for 20 h the precipitate (DABCO*BH_3) was filtered off quantitatively. In a second Schlenk-tube 3.3 mmol of *n*-butyllithium (2.06 mL of 1.6 M solution in hexane) was added slowly to a solution of 4,5-dibromo-2,7-di-*tert*-butyl-9,9-dimethyl-9H-xanthene (1.5 mmol, 720 mg) in thf (10 mL) at a temperature of −78 °C for the dilithiation. The stirring was continued for 3–4 h and during this period the temperature was allowed to rise up to −20 °C. The above yielded filtrate was added slowly to the cooled solution (−45 °C) of the dilithiated xanthene. After further stirring for 20 h at ambient temperature the volume was reduced to 1/3 under vacuum and water (10 mL) was added. After extraction with DCM (2 × 25 mL) the combined organic phases were washed again and dried (Na_2SO_4). The solvent was evaporated, and the residue was purified by column chromatography or crystallization.

4.1.1. (1S,1′S)-(+)-(2,7-di-tert-butyl-9,9-dimethyl-9H-xanthene-4,5-diyl)bis((2-methoxyphenyl)(phenyl)phosphine) (**2a**)

Yield: 905 mg (80%) as white solid crystallized from EtOH; mp. = 104–106 °C; $[\alpha]_D^{20}$ +28.5 (c 1.0, $CHCl_3$); δ_H (300.1 MHz, CDC1$_3$) 7.36 (2H, d, *J* 2.4 Hz, arom. H), 7.22 (2H, m, arom. H), 7.19–7.09 (10H, m, arom. H), 6.80 (2H, m, arom. H), 6.69 (2H, dt, *J* 7.5, 0.9 Hz, arom. H), 6.54–6.48 (4H, m, arom. H), 3.68 (6H, s, 2xOCH_3), 1.65 (6H, s, 2xCH_3), 1.08 (18H, s, 6xCH_3); δ_C (75.5 MHz, $CDCl_3$) 161.2 (t, *J* 7.6 Hz, 2xC-OMe), 151.0 (t, *J* 9.9 Hz, 2xC-O), 144.9 (2xC-C), 137.5 (m, 2xC-P), 133.8 (m, 4xCH), 133.5 (2xCH), 129.5 (4xCH), 129.0 (2xC-C), 127.8 (2xCH), 127.6 (m, 4xCH), 126.6 (m, 2xC-P), 124.3 (m, 2xC-P), 122.2 (2xCH), 120.6 (2xCH), 110.0 (2xCH), 55.4 (2xOCH_3), 34.9 (m, C), 34.4 (2xC), 31.6 (2xCH_3), 31.3 (6xCH_3); δ_P (121.5 MHz, $CDCl_3$) −25.5; *m/z* (EI, 70 eV) 750 (100, $[M]^+$), 735 (5, $[M - CH_3]^+$), 673 (15, $[M\text{-}Ph]^+$), 521 (15, $[M\text{-}CH_3\text{-}PPh(2\text{-anisyl})+H]^+$); HRMS (EI, $[M]^+$) *m/z* calculated for $C_{49}H_{52}O_3P_2$ 750.33862, found: 750.33755.

4.1.2. (1S,1′S)-(+)-(2,7-di-tert-butyl-9,9-dimethyl-9H-xanthene-4,5-diyl)bis((2-methylphenyl)(phenyl)phosphine) (**2b**)

Yield: 805 mg (75%) as white solid from column chromatography (cyclohexane/AcOEt 98/2); mp. = 91–93 °C; $[\alpha]_D^{23}$ +7.9 (c 1.0, $CHCl_3$); δ_H (300.1 MHz, CDC1$_3$) 7.37 (2H, d, *J* 2.3 Hz, arom. H), 7.25–7.07 (14H, m, arom. H), 6.97 (2H, dt, *J* 7.4, 1.4 Hz, arom. H), 6.70 (2H, m, arom. H), 6.47 (2H, m, arom. H), 2.29 (6H, s, 2xCH_3), 1.66 (6H, s, 2xCH_3), 1.08 (18H, s, 6xCH_3); δ_C (100.6 MHz, $CDCl_3$) 150.7 (m, 2xC-O), 145.3 (2xC-C), 142.2 (m, 2xC-Me), 136.6 (m, 2xC-P), 136.3 (m, 2xC-P), 134.1 (m, 4xCH), 132.6 (2xCH), 129.7 (m, 2xCH), 129.5 (2xCH), 128.9 (2xC-C), 128.2 (2xCH), 128.1 (2xCH), 128.0 (m, 4xCH), 125.6 (2xCH), 123.6 (m, 2xC-P), 122.8 (2xCH), 34.9 (C), 34.4 (2xC), 32.0 (2xCH_3), 31.2 (6xCH_3), 21.3 (m, 2xCH_3); δ_P (121.5 MHz, $CDCl_3$) −22.7; *m/z* (EI, 70 eV) 718 (100, $[M]^+$), 703 (10, $[M - CH_3]^+$), 641 (5, $[M\text{-}Ph]^+$), 505 (13, $[M\text{-}CH_3\text{-}PPh(2\text{-tolyl})+H]^+$); HRMS (ESI, $[M+H]^+$) *m/z* calculated for $C_{49}H_{53}OP_2$ 719.35662, found: 719.35675.

4.1.3. (1S,1′S)-(−)-(2,7-di-tert-butyl-9,9-dimethyl-9H-xanthene-4,5-diyl)bis((3-methoxyphenyl)(phenyl)phosphine) (**2c**)

Yield: 905 mg (47%) as a white solid from column chromatography (cyclohexane/AcOEt 98/2); mp. = 84–85 °C; $[\alpha]_D^{23}$ − 7.3 (*c* 1.0, $CHCl_3$); δ_H (300.1 MHz, CDC1$_3$) 7.36 (2H, d, *J* 2.3 Hz, arom. H), 7.24–7.08 (12H, m, arom. H), 6.79–6.71 (6H, m, arom. H), 6.53 (2H, m, arom. H), 3.64 (6H, s, 2xOCH_3), 1.65 (6H, s, 2xCH_3), 1.08 (18H, s, 6xCH_3); δ_C (75.5 MHz, $CDCl_3$) 159.1 (m, 2xC-OMe), 150.5 (m, 2xC-O), 145.3 (2xC-C), 139.2 (m, 2xC-P), 137.4 (m, 2xC-P), 133.9 (m, 4xCH), 129.3 (2xCH), 128.9 (2xC-C), 128.9 (m, 2xCH), 128.1 (2xCH), 128.0 (m, 4xCH), 126.3 (m, 2xCH), 124.4 (m, 2xC-P), 123.0 (2xCH), 118.8 (m, 2xCH), 114.3 (2xCH), 55.0 (2xOCH_3), 34.8 (m, C), 34.5 (2xC), 32.1 (2xCH_3), 31.3 (6xCH_3); δ_P (121.5 MHz, $CDCl_3$) −15.2; *m/z* (EI, 70 eV) 750 (44, $[M]^+$), 735 (9, $[M - CH_3]^+$), 673 (1, $[M\text{-}Ph]^+$), 643 (1, $[M\text{-}(3\text{-anisyl})]^+$); HRMS (EI, $[M]^+$) *m/z* calculated for $C_{49}H_{52}O_3P_2$ 750.33862, found: 750.33735.

4.1.4. (1S,1′S)-(+)-(2,7-di-tert-butyl-9,9-dimethyl-9H-xanthene-4,5-diyl)bis((3-methylphenyl)(phenyl)phosphine) (**2d**)

Yield: 585 mg (54%) as white solid from column chromatography (cyclohexane/AcOEt 98/2); mp. = 71–73 °C; $[\alpha]_D^{24}$ +7.5 (*c* 1.0, $CHCl_3$); δ_H (300.1 MHz, CDC1$_3$) 7.37 (2H, d, *J* 2.3 Hz, arom. H), 7.25–7.16 (10H, m, arom. H), 7.14–7.01 (6H, m, arom. H), 6.94 (2H, m, arom. H), 6.55 (2H, m, arom. H), 2.23 (6H, s, 2xCH_3), 1.67 (6H, s, 2xCH_3), 1.10 (18H, s, 6xCH_3); δ_C (75.5 MHz, $CDCl_3$) 150.6 (m, 2xC-O), 145.2 (2xC-C), 137.8 (m, 2xC-P), 137.4 (m, 2xC-Me), 137.2 (m, 2xC-P), 134.7 (m, 2xCH), 133.9 (m, 4xCH), 130.8 (m, 2xCH), 129.4 (2xCH), 128.9 (2xCH), 128.9 (2xC-C), 127.9 (2xCH), 127.9 (m, 4xCH), 127.9 (2xCH), 124.7 (m, 2xC-P), 122.8 (2xCH), 34.8 (C), 34.5 (2xC), 31.9 (2xCH_3), 31.3 (6xCH_3), 21.4 (m, 2xCH_3); δ_P (121.5 MHz, $CDCl_3$) −16.2; *m/z* (EI, 70 eV) 718 (100, $[M]^+$), 703 (21, $[M - CH_3]^+$), 641 (2, $[M\text{-}Ph]^+$), 505 (4, $[M\text{-}CH_3\text{-}PPh(3\text{-tolyl})+H]^+$); HRMS (ESI, $[M+H]^+$) *m/z* calculated for $C_{49}H_{53}OP_2$ 719.35662, found: 719.35724.

4.1.5. (1S,1′S)-(−)-(2,7-di-tert-butyl-9,9-dimethyl-9H-xanthene-4,5-diyl)bis((4-methoxyphenyl)(phenyl)phosphine) (**2e**)

Yield: 585 mg (52%) as white solid from column chromatography (heptane/AcOEt 98/2); mp. = 160–164 °C; $[\alpha]_D^{21}$ − 38.7 (*c* 1.0,

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$CHCl_3$); δ_H (400.1 MHz, $CDC1_3$) 7.42 (2H, d, *J* 2.3 Hz, arom. H), 7.23–7.11 (14H, m, arom. H), 6.76 (4H, m, arom. H), 6.54 (2H, m, arom. H), 3.78 (6H, s, 2xOCH_3), 1.68 (6H, s, 2xCH_3), 1.18 (18H, s, 6xCH_3); δ_C (100.6 MHz, $CDCl_3$) 159.8 (2xC-OMe), 150.4 (t, *J* 9.3 Hz, 2xC-O), 145.1 (2xC-C), 138.5 (m, 2xC-P), 135.6 (m, 4xCH), 133.5 (m, 4xCH), 129.2 (2xCH), 128.8 (2xC-C), 128.2 (m, 2xC-P), 127.9 (m, 4xCH), 127.7 (2xCH), 125.1 (m, 2xC-P), 122.7 (2xCH), 113.7 (m, 4xCH), 55.1 (2xOCH_3), 34.8 (m, C), 34.4 (2xC), 32.1 (2xCH_3), 31.3 (6xCH_3); δ_P (162.0 MHz, $CDCl_3$) −17.5; *m/z* (EI, 70 eV) 750 (100, $[M]^+$), 735 (5, $[M - CH_3]^+$), 536 (30, [M-PPh(4-anisyl)+H]$^+$), 521 (30, [M-CH_3-PPh(4-anisyl)+H]$^+$); HRMS (EI, $[M]^+$) *m/z* calculated for $C_{49}H_{52}O_3P_2$ 750.33862, found: 750.34064.

4.1.6. (1S,1′S)-(−)-(2,7-di-tert-butyl-9,9-dimethyl-9H-xanthene-4,5-diyl)bis((4-methylphenyl)(phenyl)phosphine) (**2f**)

Yield: 875 mg (81%) as white solid from column chromatography (cyclohexane/AcOEt 98/2); mp. = 80–82 °C; $[\alpha]_D^{24}$ − 29.3 (*c* 1.0, $CHCl_3$); δ_H (300.1 MHz, $CDC1_3$) 7.36 (2H, d, *J* 2.3 Hz, arom. H), 7.25–7.15 (10H, m, arom. H), 7.13–7.06 (4H, m, arom. H), 7.03–6.98 (4H, m, arom. H), 6.58 (2H, m, arom. H), 2.31 (6H, s, 2xCH_3), 1.65 (6H, s, 2xCH_3), 1.10 (18H, s, 6xCH_3); δ_C (75.5 MHz, $CDCl_3$) 150.5 (m, 2xC-O), 145.1 (2xC-C), 138.0 (m, 2xC-Me), 137.6 (m, 2xC-P), 133.9 (m, 4xCH), 133.9 (4xCH), 133.4 (m, 2xC-P), 129.5 (m, 2xCH), 128.9 (m, 4xCH), 128.9 (2xC-C), 127.9 (m, 4xCH), 127.9 (2xCH), 124.4 (m, 2xC-P), 123.0 (2xCH), 34.8 (C), 34.5 (2xC), 32.1 (2xCH_3), 31.3 (6xCH_3), 21.3 (m, 2xCH_3); δ_P (121.5 MHz, $CDCl_3$) −16.8; *m/z* (EI, 70 eV) 718 (100, $[M]^+$), 703 (26, $[M - CH_3]^+$), 520 (21, [M-PPh(4-tolyl)+H]$^+$); 505 (46, [M-CH_3-PPh(4-tolyl)+H]$^+$); HRMS (ESI, $[M+H]^+$) *m/z* calc.: for $C_{49}H_{53}OP_2$ 719.35662, found: 719.35675; (ESI, $[M+Na]^+$) *m/z* calculated for $C_{49}H_{52}NaOP_2$ 741.33856, found: 741.33748.

4.1.7. (1S,1′S)-(−)-(2,7-di-tert-butyl-9,9-dimethyl-9H-xanthene-4,5-diyl)bis((1-naphthyl)(phenyl)phosphine) (**2g**)

Yield: 885 mg (74%) as white solid crystallized from column chromatography (cyclohexane/AcOEt 98/2); mp. = 110–112 °C; $[\alpha]_D^{21}$ − 24.2 (*c* 1.0, $CHCl_3$); δ_H (300.1 MHz, $CDC1_3$) 8.20 (2H, m, arom. H), 7.82 (2H, m, arom. H), 7.74 (2H, m, arom. H), 7.44 (2H, ddd, *J* 8.1, 7.0, 1.3 Hz, arom. H), 7.38 (2H, m, arom. H), 7.32 (2H, ddd, *J* 8.3, 6.8, 1.4 Hz, arom. H), 7.22 (2H, m, arom. H), 7.16–6.99 (10H, m, arom. H), 6.86 (2H, m, arom. H), 6.39 (2H, m, arom. H), 1.69 (6H, s, 2xCH_3), 0.99 (18H, s, 6xCH_3); δ_C (100.6 MHz, $CDCl_3$) 150.8 (m, 2xC-O), 145.3 (2xC-C), 136.4 (m, 2xC-P), 135.6 (m, 2xC-P), 135.0 (m, 2xC-C), 134.2 (m, 4xCH), 133.3 (m, 2xC-C), 131.5 (2xCH), 130.0 (2xCH), 129.2 (2xC-C), 128.9 (2xCH), 128.2 (2xCH), 128.2 (2xCH), 127.9 (m, 4xCH), 127.0 (m, 2xCH), 125.7 (2xCH), 125.5 (2xCH), 125.3 (2xCH), 123.6 (m, 2xC-P), 122.8 (2xCH), 35.0 (C), 34.4 (2xC), 31.7 (2xCH_3), 31.2 (6xCH_3); δ_P (121.5 MHz, $CDCl_3$) −23.6; *m/z* (EI, 70 eV) 790 (100, $[M]^+$), 775 (13, $[M - CH_3]^+$), 664 (21, [M-$C_{10}H_7$+H]$^+$); HRMS (ESI, $[M+H]^+$) *m/z* calculated for $C_{55}H_{53}OP_2$ 791.35662, found: 791.35706.

4.1.8. (1S,1′S)-(−)-(2,7-di-tert-butyl-9,9-dimethyl-9H-xanthene-4,5-diyl)bis((2-naphthyl)(phenyl)phosphine) (**2h**)

Yield: 710 mg (60%) as white solid from CH_2Cl_2/hexane; mp. = 152–154 °C; $[\alpha]_D^{21}$ − 101.8 (*c* 1.0, $CHCl_3$); δ_H (400.1 MHz, $CDC1_3$) 7.77 (2H, m, arom. H), 7.70–7.60 (6H, m, arom. H), 7.48–7.39 (6H, m, arom. H), 7.26 (2H, m, arom. H), 7.13–7.06 (4H, m, arom. H), 7.04–6.98 (6H, m, arom. H), 6.58 (2H, m, arom. H), 1.72 (6H, s, 2xCH_3), 1.07 (18H, s, 6xCH_3); δ_C (75.5 MHz, $CDCl_3$) 150.8 (m, 2xC-O), 145.4 (2xC-C), 137.3 (m, 2xC-P), 135.2 (m, 2xC-P), 133.9 (2xCH), 133.8 (m, 4xCH), 133.2 (m, 2xC-C), 133.2 (m, 2xC-C), 130.4 (m, 2xCH), 129.3 (2xCH), 129.2 (2xC-C), 128.1 (2xCH), 128.0 (2xCH), 127.8 (m, 4xCH), 127.6 (2xCH), 127.2 (m, 2xCH), 126.0 (2xCH), 125.7 (2xCH), 124.3 (m, 2xC-P), 122.8 (2xCH), 34.9 (m, C), 34.5 (2xC), 31.8 (2xCH_3), 31.3 (6xCH_3); δ_P (162.0 MHz, $CDCl_3$) −15.0; *m/z* (EI, 70 eV) 790 (100, $[M]^+$), 775 (15, $[M - CH_3]^+$), 664 (3, [M-$C_{10}H_7$+H]$^+$); HRMS (ESI, $[M+H]^+$) *m/z* calculated for $C_{55}H_{53}OP_2$ 791.35662, found: 791.35657, (ESI, $[M+Na]^+$) *m/z* calculated for $C_{55}H_{52}NaOP_2$ 813.33856, found: 813.33800.

4.1.9. (1S,1′S)-(−)-(2,7-di-tert-butyl-9,9-dimethyl-9H-xanthene-4,5-diyl)bis((9-phenantryl)(phenyl)phosphine) (**2i**)

Yield: 700 mg (52%) as white solid from CH_2Cl_2/hexane after chromatographical purification (cyclohexane/AcOEt 98/2); mp. = 170–173 °C; $[\alpha]_D^{22}$ − 22.3 (*c* 1.0, $CHCl_3$); δ_H (300.1 MHz, $CDC1_3$) 8.71–8.61 (4H, m, arom. H), 8.24 (2H, m, arom. H), 7.64–7.56 (4H, m, arom. H), 7.47–7.38 (8H, m, arom. H), 7.08 (2H, m, arom. H), 6.98–8.78 (10H, m, arom. H),6.46 (2H, m, arom. H), 1.75 (6H, s, 2xCH_3), 0.99 (18H, s, 6xCH_3); δ_C (75.5 MHz, $CDCl_3$) 151.1 (m, 2xC-O), 145.5 (2xC-C), 135.9 (m, 2xC-P), 134.0 (m, 4xCH), 131.6 (m, 2xC-C), 131.6 (m, 2xC-C), 132.9 (2xCH), 131.6 (m, 2xC-C), 130.8 (m, 2xC-C), 130.1 (m, 2xCH), 130.0 (m, 2xC-P), 129.5 (2xC-C), 128.7 (2xCH), 128.0 (2xCH), 128.0 (2xCH), 127.8 (m, 4xCH), 126.6 (2xCH), 126.3 (m, 2xCH), 126.1 (m, 2xCH), 126.0 (2xCH), 123.5 (m, 2xC-P), 122.6 (2xCH), 122.6 (2xCH), 122.4 (2xCH), 35.1 (m, C), 34.4 (2xC), 31.2 (2xCH_3), 31.2 (6xCH_3); δ_P (121.5 MHz, $CDCl_3$) −21.0; *m/z* (EI, 70 eV) 890 (100, $[M]^+$), 875 (22, $[M - CH_3]^+$), 591 (21, [M-CH_3-PPh(9-Phen)+H]$^+$), 178 (31, $[C_{14}H_{10}]^+$); HRMS (ESI, $[M+H]^+$) *m/z* calculated for $C_{63}H_{57}OP_2$ 890.38009, found: 891.388840, (ESI, $[M+Na]^+$) *m/z* calculated for $C_{63}H_{56}NaOP_2$ 913.36986, found: 913.36767.

4.1.10. (1S,1′S)-(−)-(2,7-di-tert-butyl-9,9-dimethyl-9H-xanthene-4,5-diyl)bis((3,5-dimethoxyphenyl)(phenyl)phosphine) (**2j**)

Yield: 775 mg (64%) as white solid from column chromatography (cyclohexane/AcOEt 98/2); mp. = 78–80 °C; $[\alpha]_D^{21}$ − 5.7 (*c* 1.0, $CHCl_3$); δ_H (300.1 MHz, $CDC1_3$) 7.37 (2H, d, *J* 2.3 Hz, arom. H), 7.24–7.16 (10H, m, arom. H), 6.56 (2H, m, arom. H), 6.39–6.33 (4H, m, arom. H), 6.31 (2H, m, arom. H), 3.64 (12H, s, 4xOCH_3), 1.66 (6H, s, 2xCH_3), 1.11 (18H, s, 6xCH_3); δ_C (75.5 MHz, $CDCl_3$) 160.2 (m, 4xC-OMe), 150.6 (m, 2xC-O), 145.3 (2xC-C), 140.1 (m, 2xC-P), 137.2 (m, 2xC-P), 133.9 (m, 4xCH), 129.3 (2xCH), 129.0 (2xC-C), 128.2 (2xCH), 127.9 (m, 4xCH), 124.2 (m, 2xC-P), 122.9 (2xCH), 111.3 (4xCH), 100.9 (2xCH), 55.1 (4xOCH_3), 34.8 (m, C), 34.4 (2xC), 31.9 (2xCH_3), 31.3 (6xCH_3); δ_P (121.5 MHz, $CDCl_3$) −13.7; *m/z* (EI, 70 eV) 810 (100, $[M]^+$), 795 (43, $[M - CH_3]^+$), 779 (11, $[M\text{-}OCH_3]^+$), 551 (16, [M-CH_3-PPh(3,5-MeO-Ph)+H]$^+$); HRMS (EI, $[M]^+$) *m/z* calculated for $C_{51}H_{56}O_5P_2$ 810.35975, found: 810.35888.

4.1.11. (1S,1′S)-(−)-(2,7-di-tert-butyl-9,9-dimethyl-9H-xanthene-4,5-diyl)bis((2-ethoxyphenyl)(phenyl)phosphine) (**2k**)

Yield: 740 mg (63%) as white solid from column chromatography (cyclohexane/AcOEt 98/2); mp. = 78–80 °C; $[\alpha]_D^{21}$ − 2.2 (*c* 1.0, $CHCl_3$); δ (300.1 MHz, $CDC1_3$) 7.36 (2H, d, *J* 2.4 Hz, arom. H), 7.26–7.09 (12H, m, arom. H), 6.76 (2H, m, arom. H), 6.69 (2H, dt, *J* 7.4, 1.0 Hz, arom. H), 6.64–6.55 (4H, m, arom. H), 3.88 (4H, m, 2xOCH_2), 1.66 (6H, s, 2xCH_3), 1.09 (18H, s, 6xCH_3), 0.98 (6H, t, *J* 7.0 Hz, 2xCH_3); δ_C (75.5 MHz, $CDCl_3$) 160.4 (m, 2xC-OEt), 150.8 (m, 2xC-O), 144.9 (2xC-C), 136.8 (m, 2xC-P), 134.0 (m, 4xCH), 133.4 (m, 2xCH), 129.6 (2xCH), 129.5 (2xCH), 128.8 (2xC-C), 128.0 (2xCH), 127.7 (m, 4xCH), 126.3 (m, 2xC-P), 123.7 (m, 2xC-P), 122.7 (2xCH), 120.6 (2xCH), 111.0 (2xCH), 63.8 (2xOCH_2), 34.9 (m, C), 34.4 (2xC), 32.0 (2xCH_3), 31.3 (6xCH_3), 14.4 (2xCH_3); δ_P (121.5 MHz, $CDCl_3$) −23.8; *m/z* (EI, 70 eV) 778 (100, $[M]^+$), 763 (6, $[M - CH_3]^+$), 701 (35, $[M\text{-}Ph]^+$), 673 (20, $[M\text{-}Ph\text{-}C_2H_4]^+$), 535 (17, [M-$CH_3$-PPh(2-EtO-Ph)+H]$^+$); HRMS (ESI, $[M+H]^+$) *m/z* calculated for $C_{51}H_{57}O_3P_2$ 779.37775, found: 779.37897, ($[M+Na]^+$) *m/z* calculated for $C_{51}H_{56}NaO_3P_2$ 801.35969, found: 801.35636.

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*4.1.12. (1S,1′S)-(+)-(2,7-di-tert-butyl-9,9-dimethyl-9H-xanthene-4,5-diyl)bis((2-ethylphenyl)(phenyl)phosphine) (**2l**)*

Yield: 615 mg (55%) as white solid crystallized from ethanol after chromatographical purification (cyclohexane/AcOEt 98/2); mp. = 139–140 °C; $[\alpha]_D^{24}$ +46.8 (*c* 1.0, $CHCl_3$); δ (400.1 MHz, $CDC1_3$) 7.34 (2H, d, *J* 2.4 Hz, arom. H), 7.25–7.13 (14H, m, arom. H), 6.97 (2H, m, arom. H), 6.72 (2H, m, arom. H), 6.45 (2H, m, arom. H), 2.78 (4H, m, $2xCH_2$), 1.66 (6H, s, $2xCH_3$), 1.07 (18H, s, $6xCH_3$), 1.06 (6H, t, *J* 7.5 Hz, $2xCH_3$); δ_C (100.6 MHz, $CDCl_3$) 150.4 (m, 2xC-O), 148.5 (m, 2xC-Et), 145.0 (2xC-C), 137.6 (m, 2xC-P), 136.1 (m, 2xC-P), 134.0 (m, 4xCH), 133.5 (2xCH), 129.6 (2xCH), 128.7 (2xC-C), 128.4 (2xCH), 127.9 (m, 4xCH), 127.8 (2xCH), 127.7 (2xCH), 125.6 (2xCH), 124.5 (m, 2xC-P), 122.6 (2xCH), 34.8 (m, C), 34.4 (2xC), 32.1 ($2xCH_3$), 31.3 ($6xCH_3$), 27.1 (m, $2xCH_2$), 15.1 ($2xCH_3$); δ_P (121.5 MHz, $CDCl_3$) −25.5; *m/z* (EI, 70 eV) 746 (100, $[M]^+$), 731 (5, $[M-CH_3]^+$), 669 (16, $[M\text{-}Ph]^+$), 641 (14, $[M\text{-}Ph\text{-}C_2H_4]^+$), 534 (10, [M-PPh(2-Et-Ph)+H]$^+$), 519 (14, [M-PPh(2-Et-Ph)+H]$^+$); HRMS (ESI, $[M+H]^+$) *m/z* calculated for $C_{51}H_{57}OP_2$ 747.38792, found: 747.38815.

*4.1.13. (1S,1′S)-(−)-(2,7-di-tert-butyl-9,9-dimethyl-9H-xanthene-4,5-diyl)bis((3-ethoxyphenyl)(phenyl)phosphine) (**2m**)*

Yield: 400 mg (34%) as a white solid from column chromatography (cyclohexane/AcOEt 99/1); mp. = 63–65 °C; $[\alpha]_D^{22}$ − 8.3 (*c* 1.0, $CHCl_3$); δ_H (300.1 MHz, $CDC1_3$) 7.36 (2H, d, *J* 2.3 Hz, arom. H), 7.24–7.15 (10H, m, arom. H), 7.10 (2H, m, arom. H), 6.79–6.71 (6H, m, arom. H), 6.57 (2H, m, arom. H), 3.85 (4H, m, $2xOCH_2$), 1.64 (6H, s, $2xCH_3$), 1.29 (6H, t, *J* 7.0 Hz, $2xCH_3$), 1.09 (18H, s, $6xCH_3$); δ_C (75.5 MHz, $CDCl_3$) 158.5 (m, 2xC-OEt), 150.5 (m, 2xC-O), 145.3 (2xC-C), 138.9 (m, 2xC-P), 137.3 (m, 2xC-P), 133.9 (m, 4xCH), 129.4 (2xCH), 128.9 (2xC-C), 128.9 (m, 2xCH), 128.2 (2xCH), 127.9 (m, 4xCH), 126.2 (m, 2xCH), 124.4 (m, 2xC-P), 123.0 (2xCH), 119.2 (m, 2xCH), 115.1 (2xCH), 63.1 ($2xOCH_2$), 34.9 (m, C), 34.5 (2xC), 32.0 ($2xCH_3$), 31.3 ($6xCH_3$), 14.7 ($2xCH_3$); δ_P (121.5 MHz, $CDCl_3$) −15.0; *m/z* (EI, 70 eV) 778 (4, $[M]^+$), 576 (12), 561 (27); HRMS (ESI, $[M+H]^+$) *m/z* calculated for $C_{51}H_{57}O_3P_2$ 779.37775, found: 779.37755, (ESI, $[M+Na]^+$) *m/z* calculated for $C_{51}H_{56}NaO_3P_2$ 801.35969, found: 801.35945.

*4.1.14. (1S,1′S)-(+)-(2,7-di-tert-butyl-9,9-dimethyl-9H-xanthene-4,5-diyl)bis((3-ethylphenyl)(phenyl)phosphine) (**2n**)*

Yield: 550 mg (49%) as white solid from column chromatography (cyclohexane/AcOEt 98/2); mp. = 66–68 °C; $[\alpha]_D^{24}$ +16.5 (*c* 1.0, $CHCl_3$); δ_H (400.1 MHz, $CDC1_3$) 7.37 (2H, d, *J* 2.2 Hz, arom. H), 7.25–7.17 (10H, m, arom. H), 7.15–7.04 (6H, m, arom. H), 6.94 (2H, m, arom. H), 6.53 (2H, m, arom. H), 2.53 (4H, q, *J* 7.6 Hz, $2xCH_2$), 1.66 (6H, s, $2xCH_3$), 1.12 (6H, t, *J* 7.6 Hz, $2xCH_3$), 1.10 (18H, s, $6xCH_3$); δ_C (100.6 MHz, $CDCl_3$) 150.6 (m, 2xC-O), 145.1 (2xC-C), 143.6 (m, 2xC-Et) 137.8 (m, 2xC-P), 137.5 (m, 2xC-P), 133.9 (m, 4xCH), 133.6 (m, 2xCH), 131.1 (m, 2xCH), 129.3 (2xCH), 128.9 (2xC-C), 128.0 (2xCH), 127.9 (2xCH), 127.8 (m, 4xCH), 127.7 (2xCH), 124.9 (m, 2xC-P), 122.7 (2xCH), 34.8 (C), 34.4 (2xC), 31.9 ($2xCH_3$), 31.3 ($6xCH_3$), 28.8 ($2xCH_2$), 15.6 (m, $2xCH_3$); δ_P (121.5 MHz, $CDCl_3$) −16.1; *m/z* (EI, 70 eV) 746 (100, $[M]^+$), 731 (22, $[M-CH_3]^+$), 519 (4, [M-CH_3-PPh(3-Et-Ph)+H]$^+$); HRMS (ESI, $[M+H]^+$) *m/z* calculated for $C_{51}H_{57}OP_2$ 747.38792, found: 747.38778.

*4.1.15. (1S,1′S)-(−)-(2,7-di-tert-butyl-9,9-dimethyl-9H-xanthene-4,5-diyl)bis((4-ethoxyphenyl)(phenyl)phosphine) (**2o**)*

Yield: 640 mg (55%) as white solid crystallized from ethanol after chromatographical purification (cyclohexane/AcOEt 98/2); mp. = 84–86 °C; $[\alpha]_D^{22}$ − 39.0 (*c* 1.0, $CHCl_3$); δ_H (300.1 MHz, $CDC1_3$) 7.37 (2H, d, *J* 2.4 Hz, arom. H), 7.24–7.10 (14H, m, arom. H), 6.76 (4H, m, arom. H), 6.57 (2H, m, arom. H), 4.01 (4H, q, *J* 7.0 Hz, $2xOCH_2$), 1.67 (6H, s, $2xCH_3$), 1.42 (6H, t, *J* 7.0 Hz, $2xCH_3$), 1.12 (18H, s, $6xCH_3$); δ_C (75.5 MHz, $CDCl_3$) 159.2 (2xC-OEt), 150.4 (m, 2xC-O), 145.1 (2xC-C), 138.5 (m, 2xC-P), 135.7 (m, 4xCH), 133.5 (m, 4xCH), 129.2 (2xCH), 128.8 (2xC-C), 128.2 (m, 2xC-P), 127.9 (m, 4xCH), 127.7 (2xCH), 125.1 (m, 2xC-P), 122.7 (2xCH), 114.3 (m, 4xCH), 63.1 ($2xOCH_2$), 34.8 (m, C), 34.4 (2xC), 32.1 ($2xCH_3$), 31.3 ($6xCH_3$), 14.8 ($2xCH_3$); δ_P (121.5 MHz, $CDCl_3$) −17.5; *m/z* (EI, 70 eV) 778 (100, $[M]^+$), 701 (17, $[M\text{-}Ph]^+$), 577 (20), 535 (9, [M-CH_3-PPh(4-EtO-Ph)+H]$^+$); HRMS (ESI, $[M+H]^+$) *m/z* calculated for $C_{51}H_{57}O_3P_2$ 779.37775, found: 779.37787.

*4.1.16. (1S,1′S)-(+)-(2,7-di-tert-butyl-9,9-dimethyl-9H-xanthene-4,5-diyl)bis((2-isopropoxyphenyl)(phenyl)phosphine) (**2p**)*

Yield: 835 mg (69%) as white solid from column chromatography (cyclohexane/AcOEt 99/1); mp. = 78–80 °C; $[\alpha]_D^{23}$ +17.5 (*c* 1.0, $CHCl_3$); δ (300.1 MHz, $CDC1_3$) 7.34 (2H, d, *J* 2.3 Hz, arom. H), 7.29–7.21 (4H, m, arom. H), 7.18–7.10 (8H, m, arom. H), 6.72 (2H, m, arom. H), 6.67–6.54 (6H, m, arom. H), 4.38 (2H, sept, *J* 6.1 Hz, 2xOCH), 1.65 (6H, s, $2xCH_3$), 1.09 (18H, s, $6xCH_3$), 1.01 (6H, t, *J* 6.1 Hz, $2xCH_3$), 0.96 (6H, t, *J* 6.1 Hz, $2xCH_3$); δ_C (75.5 MHz, $CDCl_3$) 159.2 (m, 2xC-OiPr), 150.9 (m, 2xC-O), 144.6 (2xC-C), 137.7 (m, 2xC-P), 134.2 (m, 4xCH), 133.7 (m, 2xCH), 129.7 (2xCH), 129.1 (2xCH), 128.7 (2xC-C), 127.9 (m, 2xC-P), 127.7 (2xCH), 127.6 (m, 4xCH), 124.5 (m, 2xC-P), 122.5 (2xCH), 120.1 (2xCH), 111.6 (2xCH), 69.9 (2xOCH), 34.8 (m, C), 34.4 (2xC), 32.1 ($2xCH_3$), 31.3 ($6xCH_3$), 22.0 ($2xCH_3$), 21.6 ($2xCH_3$); δ_P (121.5 MHz, $CDCl_3$) −24.6; *m/z* (EI, 70 eV) 806 (100, $[M]^+$), 729 (12, $[M\text{-}Ph]^+$), 687 (20, $[M\text{-}Ph\text{-}C_3H_6]^+$); HRMS (ESI, $[M+H]^+$) *m/z* calculated for $C_{53}H_{61}O_3P_2$ 807.40905, found: 807.40956, ($[M+Na]^+$) *m/z* calculated for $C_{53}H_{60}NaO_3P_2$ 829.39099, found: 829.39036.

*4.1.17. (1S,1′S)-(+)-(2,7-di-tert-butyl-9,9-dimethyl-9H-xanthene-4,5-diyl)bis((2-isopropylphenyl)(phenyl)phosphine) (**2q**)*

Yield: 550 mg (47%) as white solid crystallized from ethanol after chromatographical purification (cyclohexane/AcOEt 98/2); mp. = 157–159 °C; $[\alpha]_D^{22}$ +40.2 (*c* 1.0, $CHCl_3$); δ (400.1 MHz, $CDC1_3$) 7.35 (2H, d, *J* 2.3 Hz, arom. H), 7.32–7.16 (14H, m, arom. H), 6.95 (2H, dt, *J* 7.5, 1.4 Hz, arom. H), 6.73 (2H, m, arom. H), 6.45 (2H, m, arom. H), 3.66 (2H, m, 2xCH), 1.67 (6H, s, $2xCH_3$), 1.12 (6H, 6, *J* 6.8 Hz, $2xCH_3$), 1.09 (18H, s, $6xCH_3$), 1.08 (6H, 6, *J* 6.8 Hz, $2xCH_3$); δ_C (100.6 MHz, $CDCl_3$) 153.4 (m, 2xC-O), 150.1 (m, 2xC-*i*Pr), 145.0 (2xC-C), 138.0 (m, 2xC-P), 135.4 (m, 2xC-P), 134.2 (m, 4xCH), 133.5 (2xCH), 129.6 (2xCH), 128.7 (2xCH), 128.5 (2xC-C), 127.8 (m, 4xCH), 127.8 (2xCH), 125.6 (2xCH), 125.0 (2xCH), 124.9 (m, 2xC-P), 122.7 (2xCH), 34.8 (m, C), 34.4 (2xC), 32.3 ($2xCH_3$), 31.3 ($6xCH_3$), 30.8 (m, 2xCH), 24.4 (m, $2xCH_3$), 23.7 ($2xCH_3$); δ_P (121.5 MHz, $CDCl_3$) −26.4; *m/z* (EI, 70 eV) 774 (26, $[M]^+$), 697 (9, $[M\text{-}Ph]^+$), 655 (11, [M-2-*i*Pr-Ph]$^+$), 548 (69, [M-PPh(2-iPr-Ph)+H]$^+$), 548 (100, [M-CH_3-PPh(2-iPr-Ph)+H]$^+$); HRMS (ESI, $[M+H]^+$) *m/z* calculated for $C_{53}H_{61}OP_2$ 775.41922, found: 775.41890, ($[M+Na]^+$) *m/z* calculated for $C_{53}H_{60}NaOP_2$ 797.40116, found: 797.40179.

*4.1.18. (1S,1′S)-(−)-(2,7-di-tert-butyl-9,9-dimethyl-9H-xanthene-4,5-diyl)bis((3-isopropoxyphenyl)(phenyl)phosphine) (**2r**)*

Yield: 715 mg (59%) as a white solid from column chromatography (cyclohexane/AcOEt 99/1); mp. = 74–75 °C; $[\alpha]_D^{23}$ − 8.5 (*c* 1.0, $CHCl_3$); δ_H (300.1 MHz, $CDC1_3$) 7.35 (2H, d, *J* 2.3 Hz, arom. H), 7.24–7.16 (10H, m, arom. H), 7.11 (2H, m, arom. H), 6.80–6.69 (6H, m, arom. H), 6.54 (2H, m, arom. H), 4.32 (2H, sept, *J* 6.1 Hz, 2xOCH), 1.64 (6H, s, $2xCH_3$), 1.19 (6H,d, *J* 6.0 Hz, $2xCH_3$), 1.18 (6H,d, *J* 6.0 Hz, $2xCH_3$), 1.09 (18H, s, $6xCH_3$); δ_C (75.5 MHz, $CDCl_3$) 157.5 (m, 2xC-O*i*Pr), 150.5 (m, 2xC-O), 145.2 (2xC-C), 138.8 (m, 2xC-P), 137.4 (m, 2xC-P), 133.9 (m, 4xCH), 129.3 (2xCH), 129.0 (m, 2xCH), 128.9 (2xC-C), 128.2 (2xCH), 127.9 (m, 4xCH), 126.2 (m, 2xCH), 124.5 (m, 2xC-P), 122.9 (2xCH), 120.4 (m, 2xCH), 116.7 (2xCH), 69.7 (2xOCH), 34.8 (m, C), 34.5 (2xC), 32.0 ($2xCH_3$), 31.3 ($6xCH_3$), 22.0 ($2xCH_3$), 22.0 ($2xCH_3$); δ_P (121.5 MHz, $CDCl_3$) −15.3; *m/z* (EI, 70 eV) 806 (90, $[M]^+$), 791 (10, $[M-CH_3]^+$), 564 (89, [M-PPh(3-*i*PrO-Ph)+H]$^+$), 549

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(100, [M-PPh(3-*i*PrO-Ph)-CH_3+H]$^+$); HRMS (ESI, [M+H]$^+$) *m/z* calculated for $C_{53}H_{61}O_3P_2$ 807.40956, found: 807.40894, (ESI, [M+Na]$^+$) *m/z* calculated for $C_{53}H_{60}NaO_3P_2$ 829.39099, found: 829.39147.

*4.1.19. (1S,1′S)-(+)-(2,7-di-tert-butyl-9,9-dimethyl-9H-xanthene-4,5-diyl)bis((3-isopropylphenyl)(phenyl)phosphine) (**2s**)*

Yield: 675 mg (58%) as white solid from column chromatography (cyclohexane/AcOEt 99/1); mp. = 74–75 °C; $[\alpha]_D^{21}$ +26.7 (*c* 1.0, $CHCl_3$); δ_H (400.1 MHz, $CDC1_3$) 7.35 (2H, d, *J* 2.4 Hz, arom. H), 7.24–7.18 (10H, m, arom. H), 7.15–7.08 (6H, m, arom H), 6.91 (2H, m, arom. H), 6.50 (2H, m, arom. H), 2.78 (2H, sept, *J* 6.9 Hz, 2xCH), 1.64 (6H, s, 2xCH_3), 1.14 (6H, d, *J* 7.0 Hz, 2xCH_3), 1.13 (6H, t, *J* 6.9 Hz, 2xCH_3), 1.08 (18H, s, 6xCH_3); δ_C (100.6 MHz, $CDCl_3$) 150.5 (m, 2xC-O), 148.2 (m, 2xC-*i*Pr), 145.1 (2xC-C), 137.6 (m, 2xC-P), 137.3 (m, 2xC-P), 133.9 (m, 4xCH), 132.2 (m, 2xCH), 131.3 (m, 2xCH), 129.3 (2xCH), 128.9 (2xC-C), 128.0 (2xCH), 128.0 (2xCH), 127.9 (m, 4xCH), 126.3 (2xCH), 125.0 (m, 2xC-P), 122.7 (2xCH), 34.8 (m, C), 34.4 (2xC), 34.0 (2xCH), 31.9 (2xCH_3), 31.3 (6xCH_3), 24.0 (2xCH_3), 23.9 (m, 2xCH_3); δ_P (121.5 MHz, $CDCl_3$) −16.0; *m/z* (EI, 70 eV) 774 (100, [M]$^+$), 759 (14, [M − CH_3]$^+$), 698 (3, [M-Ph + H]$^+$), 656 (3, [M-(3-*i*Pr-Ph)+H]$^+$), 548 (69, [M-PPh(3-*i*Pr-Ph)+H]$^+$), 533 (1, [M-CH_3-PPh(3-*i*Pr-Ph)+H]$^+$); HRMS (ESI, [M+H]$^+$) *m/z* calculated for $C_{53}H_{61}OP_2$ 775.41922, found: 775.41913.

*4.1.20. (1S,1′S)-(−)-(2,7-di-tert.-butyl-9,9-dimethyl-9H-xanthen-4,5-diyl)bis((dibenzo[b,d]-furan-4-yl)(phenyl)phosphine) (**2t**)*

Yield: 630 mg (48%) as white solid from column chromatography (cyclohexane/AcOEt 99/1); mp. = 115–118 °C; $[\alpha]_D^{22}$ − 55.5 (*c* 1.0, $CHCl_3$); δ_H (300.1 MHz, $CDC1_3$) 7.92 (2H, m, arom. H), 7.80 (2H, dd, *J* 7.7, 1.3 Hz, arom. H), 7.45–7.27 (8H, m, arom. H), 7.13–6.98 (8H, m, arom. H), 6.93–6.85 (4H, m, arom. H), 6.76 (2H, m, arom. H), 6.53 (2H, m, arom. H), 1.70 (6H, s, 2xCH_3), 1.01 (18H, s, 6xCH_3); δ_C (100.6 MHz, $CDCl_3$) 158.1 (m, 2xC-O), 156.0 (2xC-O), 151.0 (m, 2xC-O), 145.4 (2xC-C) 135.7 (m, 2xC-P), 133.6 (m, 4xCH), 131.5 (2xCH), 129.4 (2xCH), 129.2 (2xC-C), 128.1 (2xCH), 127.6 (m, 4xCH), 126.8 (2xCH), 124.3 (2xC-C), 123.3 (2xC-C), 122.8 (2xCH), 122.7 (m, 2xC-P), 122.6 (2xCH), 122.3 (2xCH), 121.3 (m, 2xC-P), 120.7 (2xCH), 120.4 (2xCH), 112.1 (2xCH), 35.0 (m, C), 34.4 (2xC) 31.6 (2xCH_3), 31.2 (6xCH_3); δ_P (121.5 MHz, $CDCl_3$) −27.3; *m/z* (EI, 70 eV) 870 (100, [M]$^+$), 855 (34, [M − CH_3]$^+$), 581 (23, [M-PPh(4-DBF)-CH_3+H]$^+$), 168 (15, [DBF]$^+$; HRMS (ESI, [M+H]$^+$) *m/z* calculated for $C_{59}H_{53}O_3P_2$ 871.34644, found: 871.34658, (ESI, [M+Na]$^+$) *m/z* calculated for $C_{59}H_{62}NaO_3P_2$ 893.32839, found: 893.32840.

*4.1.21. (1R,1′R)-(+)-(9,9-dimethyl-9H-xanthene-4,5-diyl) bis(methyl-(phenyl)phosphine) (**6u**)*

(*S*)-Methoxy(methyl)(phenyl)phosphine borane complex [23] (4.4 mmol, 740 mg) was dissolved in hexane (15 mL) and DABCO (8.8 mmol, 987 mg) was added. After stirring at 40 °C for 20 h the precipitate (DABCO*BH_3) was filtered off quantitatively. In a second Schlenk-tube 4.4 mmol of *n*-butyllithium (2.75 mL of 1.6 M solution in hexane) was added slowly to a solution of 9,9-dimethyl-9*H*-xanthene (2.0 mmol, 421 mg) and TMEDA (4.4 mmol, 511 mg) in diethyl ether (15 mL) at −45 °C for the dilithiation. The stirring was continued for 18 h and during this period the temperature rises to ambient temperature. The above yielded filtrate was added slowly to the cooled solution (−45 °C) of the dilithiated xanthene. After further stirring for 20 h at ambient temperature the volume was reduced to 1/3 under vacuum and water (10 mL) was added. After extraction with DCM (2 × 25 mL) the combined organic phases were washed again and dried (Na_2SO_4). The solvent was evaporated, and the residue was purified by column chromatography (cyclohexane/AcOEt = 95/5). For further purification the yielded residue was recrystallized (dichloromethane/hexane).

Yield: 200 mg (22%) as white solid after crystallization (dichloromethane/hexane); mp. = 173–175 °C; $[\alpha]_D^{26}$ +8.4 (*c* 1.0, $CHCl_3$); δ_H (300.1 MHz, $CDC1_3$) 7.57–7.49 (4H, m, arom. H), 7.42–7.33 (8H, m, arom. H), 6.98 (2H, t, *J* 7.6 Hz, arom H), 6.76 (2H, m, arom. H), 1.64 (6H, s, 2xCH_3), 1.57 (6H, t, *J* 1.9 Hz, 2xCH_3); δ_C (75.5 MHz, $CDCl_3$) 151.9 (m, 2xC-O), 138.6 (m, 2xC-P), 132.9 (m, 4xCH), 129.8 (2xCH), 129.6 (2xC-C), 128.5 (m, 2xC-P), 128.4 (d, *J* 5.8 Hz, 2xCH), 128.4 (d, *J* 6.5 Hz, 2xCH), 126.1 (2xCH), 123.3 (2xCH), 34.3 (C), 32.2 (2xCH_3), 11.6 (m, 2xCH_3); δ_P (121.5 MHz, $CDCl_3$) −36.6; *m/z* (EI, 70 eV) 454 (100, [M]$^+$), 439 (28, [M − CH_3]$^+$), 332 (28, [M-PMePh + H]$^+$), 317 (90, [M-PMePh-Me + H]$^+$); HRMS (EI, [M]$^+$) *m/z* calculated for $C_{29}H_{28}OP_2$ 454.16099, found: 454.16077.

The absolute stereochemistry of **6u** was confirmed by X-ray analyses. CCDC 1985240 contains the supplementary crystallographic data.

4.2. General procedure for the asymmetric hydrogenation

All reactions were carried out using an automatic device [HPChemScan, Fa. HEL Ltd.] which allows the parallel hydrogenation in up to eight mini-autoclaves (16 mL). Every autoclave was equipped with a proper glass vial and loaded with 0.5 μmmol Rh-precursor and 0.6 μmol of ligand **2** or **6**. After assembling of autoclaves into the device isophorone (1 mmol, 3 mL of a 0.333 M stock solution) was added under argon atmosphere. The autoclaves were purged three times with argon (0.6 MPa) and then three times with hydrogen (1 MPa). The autoclaves were heated to 40 °C under ambient pressure. Then hydrogen pressure was adjusted to 5 MPa. When the reaction was finished the system was cooled down and after release of pressure the autoclaves were purged again with argon (5 cycles). The conversion and parts of product and undesired alcohol were estimated by NMR. The enantioselectivities were determined by gas chromatography.

4.3. General procedure for the asymmetric alkylation

A solution of dimethyl malonate (1 mmol, 132 mg), (±)-*trans*-1,3-diphenylallyl acetate (1 mmol, 252 mg) and lithium acetate (1 mmol, 66 mg) in 1,2-dichloroethane (5 mL) was cooled down to −20 °C in a Schlenk-tube. Then (*N,O*)-bis(trimethylsilyl) acetamide (BSA, 1 mmol, 203 mg) and $Pd(dba)_2$-complex (0.01 mmol, 5.75 mg) were added. The solution was stirred for 24 h and the temperature increased to room temperature. To work-up the solution was diluted with dichloromethane (20 mL) and washed once with water (10 mL). After phase separation the organic phase was dried (Na_2SO_4) and filtrated. The solvents were removed under vacuum on a rotavapor and the residue was purified by column chromatography (cyclohexane/AcOEt = 19:1) to yield the pure alkylation product **7**. The enantiomeric purity was estimated by chiral HPLC (Chiralpak IA (150 × 4.6 mm), hexane/*iso*-PrOH = 95/5, 1 mL/min, t_R = 6.1 min (*R*)-enantiomer and t_R = 7.3 min (*S*)-enantiomer).

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