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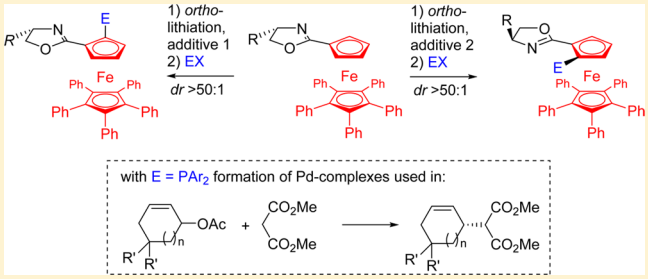
Sterically Demanding Planar Chiral P,N Ligands by Diastereoselective Ortho Lithiation of Pentaphenylferrocenyloxazolines and Their Application to Palladium-Catalyzed Substitutions with Cyclic Allylic Acetates

Marta Ayerbe Garcia, Wolfgang Frey, and René Peters*

Institut für Organische Chemie, Universität Stuttgart, Pfaffenwaldring 55, D-70569 Stuttgart, Germany

Supporting Information

ABSTRACT: Functionalized 1′,2′,3′,4′,5′-pentaphenylferrocenes are known as valuable ligands and catalysts. Planar chiral derivatives—e.g. Fu's pentaphenylferrocene fused pyridines or palladacycles developed in our group—have previously been described to be very efficient asymmetric catalysts for a number of applications. Nevertheless, protocols for diastereoselective ortho lithiations of 1′,2′,3′,4′,5′-pentaphenylferrocenes are still unknown. Such protocols could significantly increase the arsenal of accessible planar chiral pentaphenylferrocenes. In this full paper, we describe such diastereoselective ortho lithiations of pentaphenylferrocenyloxazolines. Both possible diastereomers can be produced in almost diastereomerically pure form depending on the choice of a Lewis base additive, which is required in the lithiation step for a sufficient reactivity. This development was utilized to prepare a set of planar chiral pentaphenylferrocene-based phosphino-oxazoline ligands. The latter were investigated in Pd-catalyzed allylic substitution reactions with cyclic allylic acetates to allow for a first comparison with related planar chiral ligands and provided good enantioselectivity with this challenging substrate class.



INTRODUCTION

Planar chiral ferrocenyl ligands have proven to be one of the most efficient ligand classes for asymmetric catalysis and are also extensively utilized on an industrial scale.[1,2] A key step in the preparation of planar chiral ferrocene ligands is usually a diastereoselective ortho lithiation to introduce and control the element of planar chirality.[1] A number of complementary ortho-lithiation approaches have been developed, which make use of a variety of ortho-directing groups such as amines,[3] oxazolines,[4] sulfoxides,[5] acetals,[6] hydrazones,[7] imidazolines,[8] oxazaphospholidineoxides[9] and amides.[10] To increase the steric demand of the ferrocene core, 1′,2′,3′,4′,5′-pentamethylferrocenes have also been studied in diastereoselective ortho metalations.[11] In contrast, diastereoselective ortho lithiations of 1′,2′,3′,4′,5′-pentaphenylferrocenes have not been reported yet. Previous attempts toward lithiations of chiral pentaphenylferrocenes have been unsuccessful due to insufficient reactivity.[12,11d,f] As a consequence, the corresponding planar chiral P,N ligands have thus far not been accessible for catalytic applications. Given the peculiar efficiency of pentaphenylferrocene-derived asymmetric catalysts in a diverse range of applications,[13] the diastereoselective ortho lithiation of chiral pentaphenylferrocenes could be an attractive tool to access new catalyst structures.

Herein, we now report two protocols for the highly diastereoselective ortho lithiation of pentaphenylferrocenyloxazolines. Depending on the protocol used, either the S_p-configured or the epimeric R_p-configured product is obtained with excellent diastereoselectivity starting from the same oxazoline substrate. The diastereoselective lithiations have served to prepare planar chiral phosphino-oxazoline hybrid ligands. The latter were used to synthesize Pd(II)-P,N complexes. To allow for a first comparison with the corresponding pentamethylferrocene oxazoline ligands,[11c] they have been investigated in allylic substitution reactions of cyclic allylic acetates.[14,15]

RESULTS AND DISCUSSION

Development of a Diastereoselective Ortho Metalation of Pentaphenylferrocenyloxazolines. Pentaphenylferrocenyloxazolines derived from valinol and *tert*-leucinol were prepared according to a published procedure.[11f] A number of ortho-lithiation conditions were then studied to allow for suitable reactivity and are summarized in Table 1. No reactivity was observed with *n*-, *s*-, or *t*-BuLi in ethereal solvents at −78 °C (entries 1−4). At 0 °C the ortho-methylated product **2a** was formed in low yield and with low diastereoselectivity using *n*-BuLi as base, after trapping of the generated carbanion with methyl iodide (entry 5). Essential for a satisfactory reactivity was the use of *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) as activating Lewis basic additive. With 1.5 equiv

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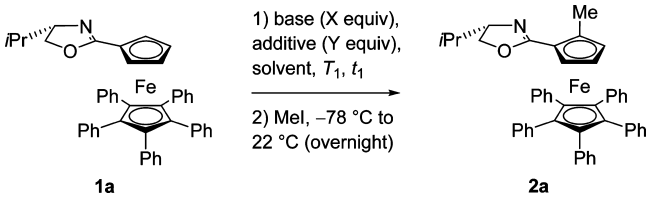
Table 1. Development of the Diastereoselective Ortho Lithiation of 1a



entry	base (X equiv)	additive (Y equiv)	solvent	T_1 (°C)	t_1 (h)	yield (%)[a]	dr[b]
1	*n*-BuLi (2.0)		THF	−78	3	0	
2	*s*-BuLi (2.0)		THF	−78	3	0	
3	*t*-BuLi (2.0)		THF	−78	3	0	
4	*n*-BuLi (2.0)		Et_2O	−78	3	0	
5	*n*-BuLi (2.0)		Et_2O	0	3	33	3:1
6	*n*-BuLi (1.5)	TMEDA (1.5)	Et_2O	−78	4	61	>50:1
7	*n*-BuLi (1.5)	TMEDA (3)	Et_2O	−78	4	70	>50:1

[a]Yield of isolated product after column chromatography. [b]Determined by ^{1}H NMR of the crude product.

of *n*-BuLi in combination with 1.5 equiv of TMEDA, the ortho lithiation could be performed at −78 °C to provide diastereomerically pure **2a** (entry 6). With double the amount of TMEDA the yield of **2a** could be further increased (entry 7).

The major isomer of product **2a** has been formed with an R_p,*S* configuration (for the determination of the absolute configuration, see below),[16] which is in harmony with a stereochemical model presented by Richards for ortho lithiations of ferrocenyl oxazolines.[4a] This model claims that the substituent at the stereocenter next to the oxazoline nitrogen atom should point toward the endo position (i.e., toward the metallocene) in order to minimize steric interactions with the N-coordinated alkyllithium base, since the latter adopts a position exo to the iron atom. Although a C_5Ph_5 ligand should add much to the steric hindrance of a metallocene backbone, thus resulting in an increased repulsion with the oxazoline substituent, the R_p,*S*-configured product is almost exclusively produced.

The optimized lithiation conditions (Table 1, entry 7) were then applied to the formation of different types of ortho-functionalized products (Table 2). Next to the ortho methylation of **1a** (entry 1), the ortho silylation (entry 4), and various ortho phosphinylations (entries 5 and 7−9) also provided the desired diastereomerically pure planar chiral products in useful yields under the same conditions. For good conversion it was necessary that the reaction of the generated organolithium species with the corresponding electrophile be allowed to proceed at room temperature overnight. For the ortho iodination both iodine and diiodoethane gave no desired product under the standard conditions. However, sufficient reactivity was achieved by the addition of $LiClO_4$ as an additive to activate diiodoethane as an electrophile (entry 3).

The oxazoline **1b** derived from *tert*-leucinol was investigated in the ortho methylation (Table 2, entry 2) and phosphinylation (with Ph_2PCl, entry 6) and also provided diastereomerically pure products, even though the repulsive interaction between the *tert*-butyl residue R and the C_5Ph_5 ligand should be further increased.

Epimeric products with the opposite sense of the element of planar chirality may be prepared with high diastereoselectivity, if the lithiation additive TMEDA is replaced by bis(2-*tert*-butoxyethyl) ether (Scheme 1). This methodology has recently been developed for the diastereoselective ortho lithiation of ferrocenyloxazolines bearing an unsubstituted Cp spectator

Scheme 1. Formation of an Epimeric 1,2-Disubstituted Pentaphenylferrocene

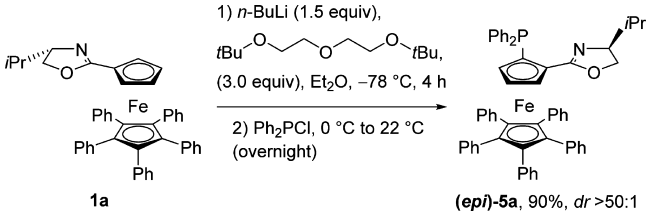
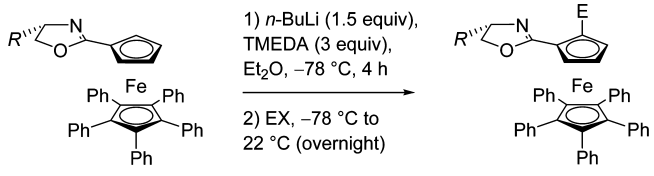


Table 2. Diastereoselective Ortho Functionalization of Pentaphenylferrocene Oxazolines 1



entry	product	R	EX	E	yield (%)[a]	dr[b]
1	**2a**	*i*Pr	MeI	Me	70	>50:1
2	**2b**	*t*Bu	MeI	Me	50	>50:1
3	**3a**	*i*Pr	$(ICH_2)_2/LiClO_4$	I	75	>50:1
4	**4a**	*i*Pr	Me_3SiOTf	Me_3Si	85	>50:1
5	**5a**	*i*Pr	Ph_2PCl	Ph_2P	80	>50:1
6	**5b**	*t*Bu	Ph_2PCl	Ph_2P	88	>50:1
7	**6a**	*i*Pr	$(4\text{-}MeOC_6H_4)_2PCl$	$(4\text{-}MeOC_6H_4)_2P$	68	>50:1
8	**7a**	*i*Pr	$(4\text{-}F_3CC_6H_4)_2PCl$	$(4\text{-}F_3CC_6H_4)_2P$	91	>50:1
9	**8a**	*i*Pr	$(3,5\text{-}(F_3C)_2C_6H_3)_2PCl$	$(3,5\text{-}(F_3C)_2C_6H_3)_2P$	39	>50:1

[a]Yield of isolated product after column chromatography. [b]Determined by ^{1}H NMR of the crude product.

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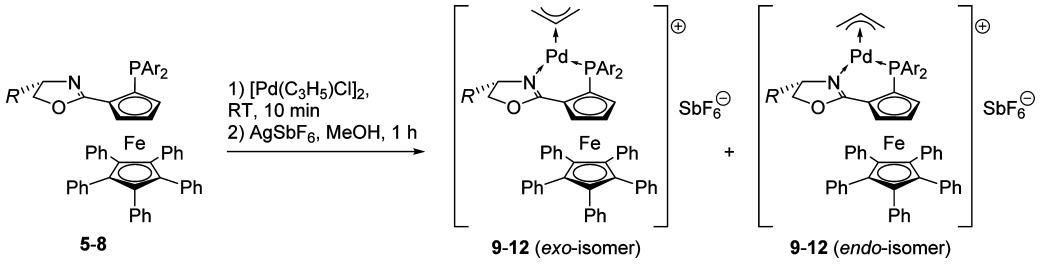
Table 3. Formation of Pd−Allyl Complexes 9−12

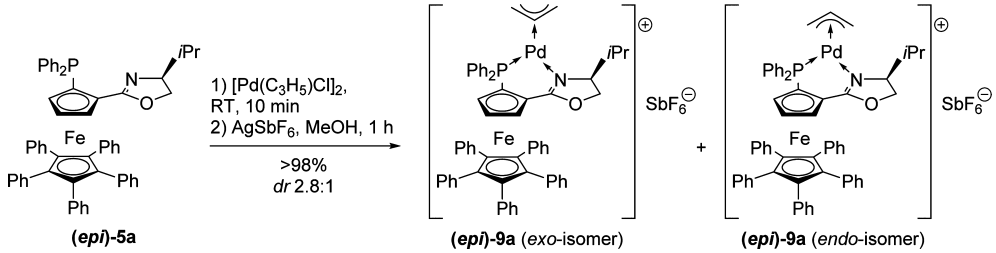


5-8 | 9-12 (*exo*-isomer) | 9-12 (*endo*-isomer)

entry	product	R	Ar	yield (%)[a]	dr[b]
1	**9a**	*i*Pr	Ph	>99	1.3:1
2	**9b**	*t*Bu	Ph	>99	>50:1
3	**10a**	*i*Pr	4-MeOC$_6$H$_4$	>99	1.3:1
4	**11a**	*i*Pr	4-F$_3$CC$_6$H$_4$	>99	1.5:1
5	**12a**	*i*Pr	3,5-(F$_3$C)$_2$C$_6$H$_3$	>99	1.4:1

[a]Yield of isolated product. [b]Determined by ^{1}H NMR.

Scheme 2. Complexation of *epi*-5a to the Pd−Allyl Fragment



(*epi*)-5a | (*epi*)-9a (*exo*-isomer) | (*epi*)-9a (*endo*-isomer)

ligand and is also applicable to pentaphenylferrocenes as showcased for the synthesis of the P,N ligand (*epi*)-5a.[17]

Formation and Structural Elucidation of η^3-Allyl Pd−P,N Complexes. To investigate the coordination behavior, we employed the P,N ligands **5**−**8** to prepare cationic Pd-allyl complexes **9**−**12** in a two-step, one-pot procedure via successive treatment with [Pd(C$_3$H$_5$)Cl]$_2$ and AgSbF$_6$ (Table 3).[11c] All of these complexations proceeded with quantitative yields. Whereas **5a** equipped with a PPh$_2$ donor group and bearing an *i*Pr residue at the oxazoline 4-position gave a ca. 1:1 mixture of isomers (entry 1, exo and endo allyl isomers; vide infra), the related **5b**, in which the *i*Pr is formally replaced by a *t*Bu group, provided exclusively the exo isomer (entry 2), which might be more favorable for steric reasons in that case. In addition, the coordination of the other *i*Pr-substituted oxazoline derivatives **6a**−**8a** resulted in almost equal amounts of both isomers (entries 3−5).

Complexation of the P,N ligand ***epi*-5a** with the opposite sense of planar chirality was achieved in a similar manner in nearly quantitative yield (Scheme 2). In that case a 2.8:1 mixture of isomers was formed.

The constitution and the S_p configuration of complexes **9a,b** have been determined by X-ray crystal structure analysis (Figure 1).[18] In the case of **9a**, the crystal contained a 55:45 mixture of an exo and an endo isomer. Only the exo isomer is depicted in Figure 1 (top). In contrast, the crystal of **9b** contained only the exo isomer (Figure 1, bottom). Both solid-state structures reveal a just slightly distorted square planar coordination geometry around the palladium centers. The Pd−ligand bond lengths and angles are similar to those found in related pentamethylferrocene-based Pd(II) complexes by Helmchen containing oxazoline and phosphine donors[11c] and [(η^3-allyl)(PHOX)Pd] complexes.[19] As expected, both Pd−C bond lengths are significantly different, with the carbon atom trans to phosphorus having the longer distance (**9a**, Pd−C = 2.211(5) Å; **9b**, Pd−C = 2.251(3) Å) in comparison to that trans to nitrogen (**9a**, Pd−C = 2.116(5) Å; **9b**, Pd−C = 2.120(3) Å), indicating the higher trans influence of the phosphino moiety.[20] The interplanar tilt angles between the allyl fragments and the P−Pd−N coordination planes are 56.5(7) and 68.4(8)° (**9a**, exo and endo, respectively) and 55.3(3)° (**9b**). The center distance of the Cp rings in one ferrocene fragment is 3.35 Å, which is similar to the case for other pentaphenylferrocenes.[10f,13j] The interplanar angles between the Cp ring and the attached phenyl moieties are in an interval of 37.0(2)−69.3(2)° (**9a**) and of 44.8(1)−68.3(1)° (**9b**), which is an expected behavior. The endo phenyl rings on the P atom and the isopropyl or *tert*-butyl residues connected to the oxazoline rings are both in close contact with phenyl substituents of the C$_5$Ph$_5$ ligand. To optimize these contact distances, both Cp rings of a ferrocene unit are significantly tilted toward each other (angle between ring planes 9.8(3)° (**9a**) and 9.2(2)° (**9b**)) to increase the distances between the C$_5$Ph$_5$ ligand and the *i*Pr/*t*Bu and P-Ph residues.[21] For the same reason the Cp-C atoms connected to the P moieties are considerably pyramidalized (sum of bond angles at the Cp-C atom for **9a**, 355.2(4)°; sum of bond angles at the Cp-P atom for **9b**, 355.4(2)°). Overall this results in a situation in which the Pd center is located 0.98(1) Å (**9a**) and 0.986(6) Å (**9b**) above the upper Cp plane. To minimize contacts, the Cp rings are also screwed out of the face-to-face orientation characterized by an average torsion angle (Cp1−Cp2) of −16.1° (**9a**) and −16.6° (**9b**).

The cyclohexenylium complex **13** is accessible in quantitative yield in a way similar to that for **9**−**12** (Scheme 3). Both in

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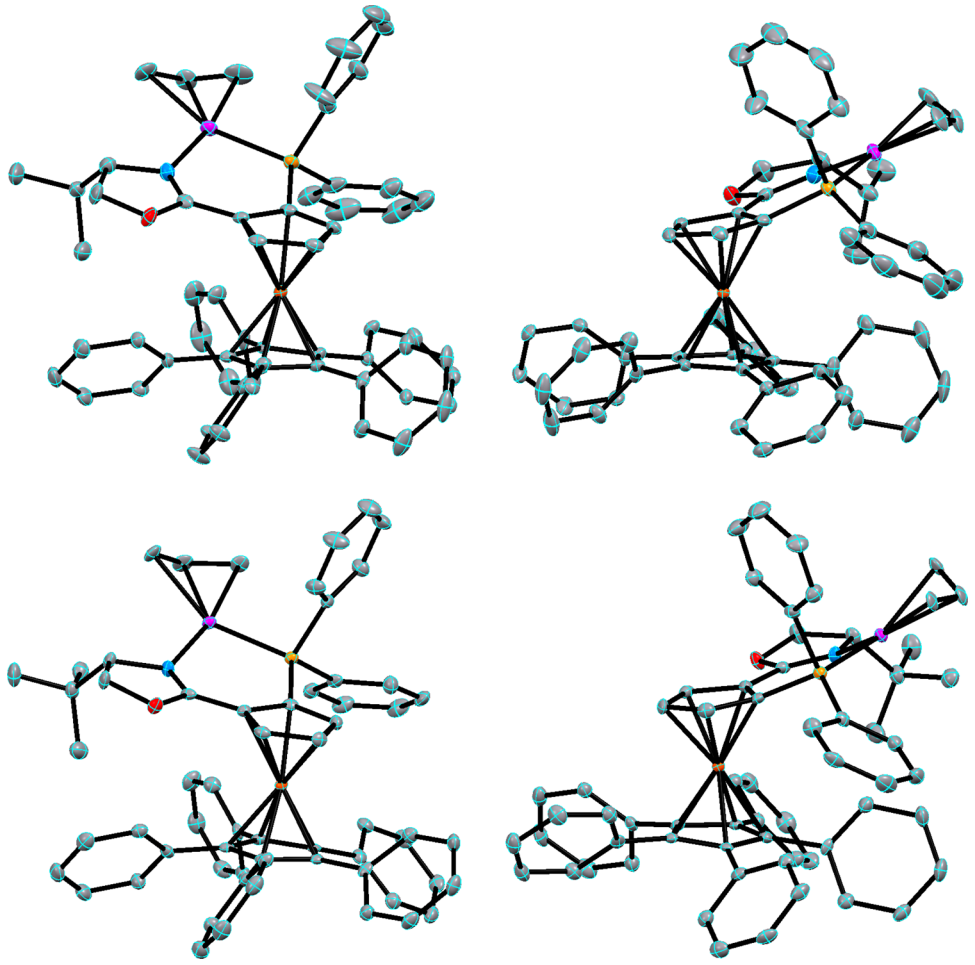
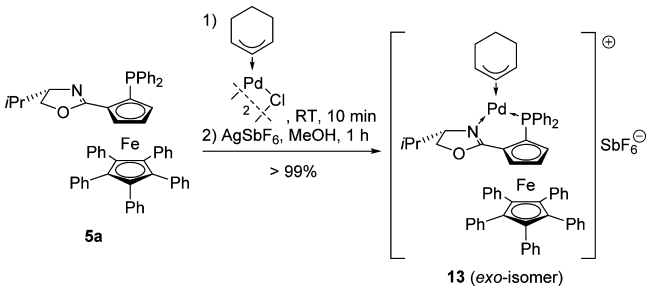


Figure 1. (top) X-ray single-crystal structure analysis of **9a**. Color code: C (gray); N (blue); O (red); P (yellow-orange); Fe (orange); Pd (magenta). Hydrogen atoms, the SbF_6 counterion, and dichloromethane (two per unit cell) are omitted for clarity in the ORTEP plot (ellipsoids at the 50% probability level). Two different views are shown for the exo isomer (the endo isomer is not depicted). Selected bond lengths (Å) and angles (deg): N–Pd, 2.086(4); P–Pd, 2.2608(13); C(trans to P)–Pd, 2.211(5); C(cis to P)–Pd, 2.116(5); N–Pd–P, 95.07(11); C(trans to P)–Pd–N, 101.76(19); C(trans to P)–Pd–C(cis to P), 67.8(2); C(cis to P)–Pd–P, 94.94(19); N–Pd–C(cis to P), 169.3(2); P–Pd–C(trans to P), 160.64(16). (bottom) X-ray single-crystal structure analysis of **9b**. Color code: C (gray); N (blue); O (red); P (yellow-orange); Fe (orange); Pd (magenta). Hydrogen atoms, the SbF_6 counterion, and diethyl ether (one per unit cell) are omitted for clarity in the ORTEP plot (ellipsoids at the 50% probability level). Two different views are shown. Selected bond lengths (Å) and angles (deg): N–Pd, 2.104(3); P–Pd, 2.2626(8); C(trans to P)–Pd, 2.251 (3); C(cis to P)–Pd, 2.120(3); N–Pd–P, 95.92(7); C(trans to P)–Pd–N, 102.15(11); C(trans to P)–Pd–C(cis to P), 66.61(11); C(cis to P)–Pd–P, 93.65(9); N–Pd–C(cis to P), 168.39(11); P–Pd–C(trans to P), 152.71(9).

solution and in the solid state a single isomer has been detected.

The X-ray crystal structure analysis of **13** revealed an exo configuration (Figure 2), which should be strongly favored to minimize repulsion of the cyclic allylic ligand with the pentaphenylferrocene core. The structure is otherwise quite similar to that of **9a** with a slightly distorted square planar coordination sphere of the palladium centers. Both Pd–C bond lengths are again significantly different, with the carbon atom trans to phosphorus having the longer distance (Pd–C = 2.2682(17) Å) in comparison to that trans to nitrogen (Pd–C = 2.1286(15) Å), in agreement with the greater trans influence of the phosphino moiety.[20] The interplanar tilt angle between the allyl fragment and the P–Pd–N coordination plane is 70.6(1)°, and the center distance of the Cp rings in one ferrocene fragment is 3.34 Å. In addition, in that case both Cp rings of one ferrocene unit are tilted toward each other with an angle between ring planes of 10.0(1)°. The Cp-C atom connected to the P atom is considerably pyramidalized (sum of bond angles at the Cp-C atom 355.3(1)°), resulting in a structure in which the Pd center is located 0.722(3) Å above the upper Cp plane.[22]

Scheme 3. Formation of the Pd–Allyl Complexes 13



Pd-Catalyzed Allylic Substitutions Using Cyclic Substrates. Complexes **9**–**12** were investigated in Pd-catalyzed asymmetric allylic substitutions with cycloalkenyl acetate

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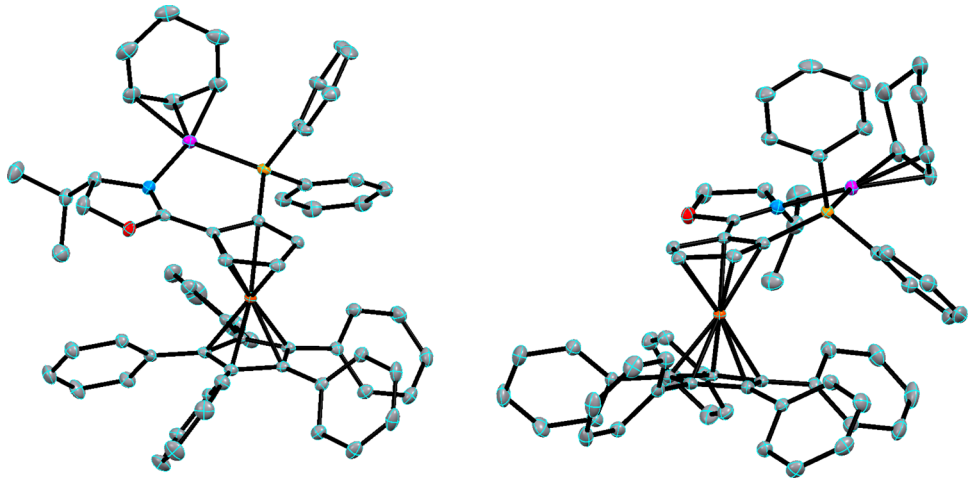
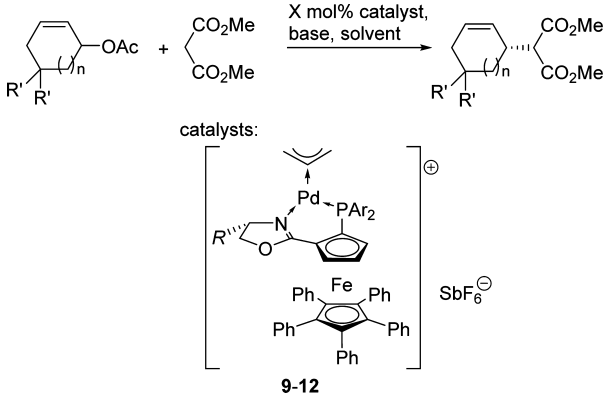


Figure 2. X-ray single crystal structure analysis of **13**. Color code: C (gray); N (blue); O (red); P (yellow-orange); Fe (orange); Pd (magenta). Hydrogen atoms, the SbF_6 counterion, and diethyl ether (one per unit cell) are omitted for clarity in the ORTEP plot (ellipsoids at the 50% probability level). Two different views are shown. Selected bond lengths (Å) and angles (deg): N–Pd, 2.1100(12); P–Pd, 2.2794(5); C(trans to P)–Pd, 2.2682(17); C(cis to P)–Pd, 2.1286(15); N–Pd–P, 94.31(4); C(trans to P)–Pd–N, 103.80(5); C(trans to P)–Pd–C(cis to P), 65.36(7); C(cis to P)–Pd–P, 96.13(5); N–Pd–C(cis to P), 167.41(6); P–Pd–C(trans to P), 161.37(4).

Table 4. Catalytic Asymmetric Allylic Alkylation of Cycloalkenyl Acetate Substrates



entry	*n*	R′	catalyst	R	Ar	X	base	solvent	*T* (°C)	*t* (h)	yield (%)[a]	ee (%)[b]
1	1	H	**9a**	*i*Pr	Ph	4	NaH	THF	22	1	>99	71
2	1	H	**9a**	*i*Pr	Ph	1	BSA/KOAc	CH_2Cl_2	22	1	>99	78
3	1	H	**9a**	*i*Pr	Ph	1	BSA/KOAc	CH_2Cl_2	−20	12	19	77
4	1	H	**9b**	*t*Bu	Ph	4	BSA/KOAc	CH_2Cl_2	22	15	15	51
5	1	H	**9a**	*i*Pr	Ph	1	BSA/NaOAc	CH_2Cl_2	22	1	>99	82
6	1	H	**9a**	*i*Pr	Ph	1	BSA/NaOAc	THF	22	1	>99	84
7	1	H	(*epi*)-**9a**	*i*Pr	Ph	1	BSA/NaOAc	THF	22	12	61	78
8[c]	1	H	**10a**	*i*Pr	4-$MeOC_6H_4$	1	BSA/NaOAc	THF	22	1	67	87
9	1	H	**11a**	*i*Pr	4-$F_3CC_6H_4$	1	BSA/NaOAc	THF	22	1	20	83
10	1	H	**12a**	*i*Pr	3,5-$(F_3C)_2C_6H_3$	1	BSA/NaOAc	THF	22	1	0	
11	1	Me	**9a**	*i*Pr	Ph	1	BSA/NaOAc	THF	22	12	>99	74
12	0	H	**9a**	*i*Pr	Ph	1	BSA/NaOAc	THF	22	1	>99	91[d]
13	0	H	**10a**	*i*Pr	4-$MeOC_6H_4$	1	BSA/NaOAc	THF	22	12	>99	91[d]
14	2	H	**9a**	*i*Pr	Ph	1	BSA/NaOAc	THF	22	12	80	90

[a]Yield of isolated product. [b]Determined by GC. [c]The catalyst was preformed prior to use. [d]Determined by ^{1}H NMR using $Eu(hfc)_3$ as chiral shift reagent.

substrates and dimethyl malonate (Table 4).[14,15] This reaction type was chosen to allow for a direct comparison with the structurally similar pentamethylferrocene-derived phosphino-oxazoline hybrid ligands described by Helmchen et al.[11c] They had demonstrated that the large steric demand of a 1′,2′,3′,4′,5′-pentamethylferrocene backbone allowed for high levels of enantioselection with these challenging substrates, whereas previously investigated Pd(II) complexes of planar chiral phosphino-oxazoline ligands required a stereogenic phosphino donor for high asymmetric induction.[15a] In general, enantioselectivity using cyclic allylic substrates is still difficult to control. This has been explained by the lower steric demand of their syn substituents in comparison to that for acyclic substrates, because the syn substituents are assumed to play a

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key role in the stereodifferentiation in the η^3-allyl Pd intermediates.[14]

If not mentioned otherwise, in our catalytic investigations the Pd complexes were prepared in situ from $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ and the corresponding ligand (1.1 equiv per Pd). Initial attempts were performed with cyclohexenyl acetate in THF using NaH as a base and 4 mol % of catalyst **9a**. The yield was quantitative after 1 h at 22 °C, but the enantioselectivity was only moderate (Table 4, entry 1). Switching from NaH in THF to KOAc/*N*,*O*-bis(trimethylsilyl)acetamide (BSA) in CH_2Cl_2 slightly improved the enantioselectivity, and the product was formed in quantitative yield after 1 h at 22 °C with a reduced catalyst loading of 1 mol % of **9a** (entry 2). Despite this high rate at 22 °C, at −20 °C the reaction was too slow for preparatively useful yields (entry 3). Moreover, the enantioselectivity was not improved by a lower temperature. With catalyst **9b** carrying the *tert*-butyl residue R, the reactivity was poor even at 22 °C (entry 4). Using **9a** again with NaOAc for KOAc (entry 5) and THF for CH_2Cl_2 (entry 6) further improved the enantioselectivity.

Under the optimized conditions the other Pd complexes prepared in this study have also been investigated. In contrast to our initial expectations, the use of diarylphosphine moieties with increased π acidity did not result in higher reactivity and enantioselectivity. Increased π acidity should result in a higher electrophilicity of the allylic C atom in the trans position.[14] However, with *p*-CF_3 substituents the product was formed in low yield and the enantioselectivity was even somewhat reduced (Table 4, entry 9).

With CF_3 substituents at positions 3 and 5 on the P-aryl moieties, there was no product formation at all (Table 4, entry 10). In contrast, with a *p*-OMe donor substituent the best enantioselectivity was attained, but the reactivity was lower than that with **9a** (entry 8). (***epi***)-**9a** is also notably less active than **9a** and is also inferior in terms of enantioselection (entry 7).

Since catalyst **9a** is thus the most active catalyst in this study, it was utilized for three additional cycloalkenyl acetates. A cyclohexenyl acetate with a tetrasubstituted C atom at the 5-position was significantly less reactive, but a quantitative yield could be obtained with a prolonged reaction time of 12 h (Table 4, entry 11). The increased steric bulk of the substrate has also a negative impact on the enantioselectivity. High reactivity and enantioselectivity was observed with cyclopentenyl acetate using catalysts **9a** and **10a** (entries 12 and 13). The corresponding cycloheptenyl substrate was less reactive, but good yield and enantioselectivity were attained after a reaction time of 12 h (entry 14).

A comparison with the results by Helmchen reveals that the reactivity and selectivity data are similar for pentamethyl- and pentaphenylferrocenes. An advantage of the latter systems is the greater stability of the pentaphenylferrocene core toward oxidative decomposition, since acceptor substituents increase the oxidation potential of ferrocenes, whereas donor substituents lead to a greater sensitivity toward oxidation.[23]

The stereochemical outcome of the reactions can be easily explained by the preferred exo configuration of the cycloalkenylium complexes and the expected regioselective nucleophilic attack of the malonate trans to the P donor as a result of the trans effect.[14] The screening of electronically different phosphines showed that higher π acidity of the phosphines did not lead to higher enantioselectivity and reactivity, as was initially expected. Moreover, an electron-rich phosphine even gave the highest enantioselectivity, yet at the cost of lower reactivity. A possible explanation for these observations might be that with less electron-rich phosphines in combination with the large steric demand of the pentaphenylferrocene core the complexes are more prone to undergo a Pd decomplexation, thus resulting in lower reactivity and reduced enantioselectivity. In contrast, the complexes of more electron rich phosphines might be more stable in terms of loss of Pd. In addition, with these complexes the regioselectivity for malonate attack is still high, but the reactivity is decreased in comparison to **9a** due to a less electrophilic allylic system. Interesting and unexpected is the fact that the use of (***epi***)-**9a** provided the same major enantiomer as the use of **9a**. This might suggest either that with (***epi***)-**9a** the P,N-chelate complex is not the catalytically most relevant species or that planar chirality has a smaller effect and that the oxazoline substituent dictates also in the present system the exo/endo configuration of the allyl complexes.

CONCLUSION

In conclusion, we have described the first diastereoselective ortho lithiations of chiral enantiopure 1′,2′,3′,4′,5′-pentaphenylferrocenes. Oxazoline moieties were used as efficient ortho-directing groups. By the choice of the lithiation conditions, both possible diastereomers with regard to the element of planar chirality can be accessed as single diastereomers. Trapping of the planar chiral organolithium species was achieved with a number of electrophiles. Using diarylphosphino chlorides, a small set of P,N ligands was prepared and then employed to form the corresponding Pd-allyl complexes. The latter were investigated in the allylic substitution of cyclic allylic acetates, and some of them allowed for good enantioselection with this challenging substrate class.

EXPERIMENTAL SECTION

General Considerations. All reactions were performed in oven-dried glassware under a positive pressure of nitrogen. All glassware used was washed with demineralized water to remove any traces of chloride. THF was dried under N_2 over molecular sieves in a solvent purification system. The solvents dichloromethane, chloroform, methanol, and ethyl acetate were used as purchased from commercial suppliers. Solvents were usually removed at 30−40 °C by rotary evaporation at 600−10 mbar pressure, and nonvolatile compounds were dried in vacuo at 0.1 mbar. **1a** and the starting material for **1b** were prepared according to the literature.[11f] Yields refer to isolated, pure compounds and are calculated in mole percent of the used starting material. NMR spectra were recorded at 21 °C operating at 300 or 500 MHz (^{1}H), 125 MHz (^{13}C), and 235 MHz (^{19}F). Chemical shifts are referred in terms of ppm, and *J* coupling constants are given in Hz. Abbreviations for multiplicities are as follows: s (singlet), d (doublet), t (triplet), m (multiplet), b (broad signal). IR spectra were recorded on an ATR unit, and the signals are given in wavenumbers (cm^{-1}). Optical rotation was measured at the sodium D line in a cell with 100 mm path length. Melting points were measured in open glass capillaries and are uncorrected. Mass spectra were measured on an ESI spectrometer. Single-crystal X-ray analysis was performed by Dr. Wolfgang Frey (Universität Stuttgart).

(*S*)-*N*-(1-Hydroxy-3-dimethylbutan-2-yl)-pentaphenylferrocenylamide.[11f] To a suspension of pentaphenylferrocenecarboxylic acid (391 mg, 0.6 mmol, 1 equiv) in DCM (10 mL) and DMF (ca. 5 μL, ca. 0.1 equiv) at room temperature was added oxalyl chloride (80 μL, 0.9 mmol, 1.5 equiv) in two portions within 5 min. Warning: significant amounts of CO and corrosive HCl are released, with pressure exchange via balloon. When all of the solid had dissolved, stirring was continued for 30 min, and then all volatiles were removed under reduced pressure. The resulting dark red solid residue was dissolved in DCM (8 mL) and triethylamine (101 mg, 130 μL, 1 mmol, 2 equiv), the solution was cooled to 0 °C, and a solution

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of (*L*)-leucinol (80 μL, 0.6 mmol, 1 equiv) in DCM (2 mL) was added in one portion. Stirring was continued at room temperature overnight, and then all volatiles were removed under reduced pressure and the red-orange residue was purified by column chromatography (pentane/EtOAc 3/1 → pure EtOAc) to yield the title product as an orange solid (391 mg, 0.55 mmol, 86%).

$C_{47}H_{43}FeNO_2$, mol wt: 709.69. Mp: 166.5−167.7 °C. $[\alpha]_D^{23}$ = −40.0° (*c* = 0.836 g dL^{-1}, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$, 21 °C): δ 7.17−7.05 (m, 25 H, H_{Ph}), 5.70 (d, *J* = 6.0, 1 H, N*H*), 4.82 (b, 1 H, H_{Fc}CCO), 4.48 (b, 1 H, H_{Fc}CCO), 4.40 (t, *J* = 3.0, 2 H, H_{Fc}), 3.66 (b, 2 H, CH_2OH), 3.37 (q, *J* = 6.0, 1 H, HNC*H*C), 1.74 (b, 1 H, O*H*), 0.92 (s, 9 H, C(CH_3)$_3$). ^{13}C NMR (125 MHz, $CDCl_3$, 21 °C): δ 168.8, 148.7, 142.4, 142.0, 134.9, 132.2, 129.4, 127.2, 127.0, 126.5, 126.1, 91.7, 88.1, 81.4, 78.1, 75.3, 72.0, 62.9, 60.5, 33.5, 27.1, 21.4. IR (solid): ν 3056, 3028, 2976, 2932, 2871, 2359, 2249, 1722, 1612, 1502, 1468, 1444, 1425, 1379, 1361, 1333, 1279, 1170, 1132, 1078, 1029, 972, 938, 909, 876, 813, 784, 767, 728, 698, 658, 577. HRMS (MALDI): *m*/*z* calcd for [M]$^+$ $C_{47}H_{43}FeNO_2$, 732.2536; found, 732.2526. A sufficient microanalysis could not be obtained due to solvent inclusion.

(*S*)-4-Isopropyl-2-pentaphenylferrocenyl-4,5-dihydrooxazole (1b). (*S*)-*N*-(1-Hydroxy-3-dimethylbutan-2-yl)-pentaphenylferrocenylamide (393 mg, 0.55 mmol, 1 equiv) was dissolved in DCM (3 mL) and triethylamine (230 μL, 1.6 mmol, 3 equiv). DMAP (ca. 7 mg, 0.05 mmol, 0.1 equiv) and *p*-tosyl chloride (131 mg, 0.7 mmol, 1.25 equiv) were added and the mixture was stirred at room temperature overnight. All volatiles were subsequently removed under reduced pressure, and the residue was purified by column chromatography (pentane/EtOAc 4/1) to yield the title product **1b** as a bright orange solid (334 mg, 0.48 mmol, 87% yield).

$C_{47}H_{41}FeNO$, mol wt: 691.68. Mp: 157.7−158.9 °C. $[\alpha]_D^{23}$ = −27.5° (*c* = 0.6 g dL^{-1}, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$, 21 °C): δ 7.12−7.01 (m, 25 H, H_{Ph}), 4.80 (m, 1 H, H_{Fc}), 4.71 (m, 1 H, H_{Fc}), 4.32 (m, 1 H, H_{Fc}), 4.29 (m, 1 H, H_{Fc}), 3.80 (m, 2 H, OCH_2), 3.45 (t, *J* = 12.0, 1 H, NC*H*), 0.76 (s, 9 H, C(CH_3)$_3$). ^{13}C NMR (125 MHz, $CDCl_3$, 21 °C): δ 162.8, 135.2, 132.4, 127.0, 126.1, 88.1, 74.7, 74.1, 67.7, 33.3, 26.0. IR (solid): ν 3109, 3086, 3056, 3030, 2951, 2901, 2865, 2244, 1652, 1600, 1576, 1502, 1482, 1443, 1411, 1393, 1378, 1363, 1327, 1302, 1266, 1209, 1179, 1156, 1117, 1074, 968, 908, 869, 848, 825, 800, 783, 766, 731, 699, 648, 621, 575, 558. HRMS (MALDI): *m*/*z* calcd for [M]$^+$ $C_{47}H_{41}FeNO$, 692.2611; found, 692.2594. A sufficient microanalysis could not be obtained due to solvent inclusion.

General Procedure for the Diastereoselective Ortho Functionalization of 1 (GP1). A solution of the corresponding oxazoline **1** (1 equiv) and TMEDA (3 equiv) in Et_2O (1 mL per 30 mg of **1**) was cooled to −78 °C and was then treated dropwise with *n*-BuLi (1.5 equiv). The resulting solution was stirred for 4 h at −78 °C and then warmed to 0 °C and treated with the corresponding electrophile (3 equiv). The reaction mixture was then warmed to room temperature, and stirring was continued overnight. The mixture was subsequently filtered over Celite and the solvent removed in vacuo. The crude product was purified by column chromatography (silica, PE/EtOAc, 95/5).

*1-[(4S)-Isopropyl-2-oxazolin-2-yl]-2-(R_p)-(methyl)-1′,2′,3′,4′,5′-pentaphenylferrocene (**2a**).* Following GP1 a red solid was obtained and isolated in a yield of 70% (dr > 50:1).

$C_{47}H_{41}FeNO$, mol wt: 691.68. Mp: 99.4−100.5 °C. $[\alpha]_D^{23}$ = −17.6° (*c* = 0.475 g dL^{-1}, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$, 21 °C): δ 7.16−7.04 (m, 25 H, H_{Ph}), 4.69 (m, 1 H, H_{Fc}), 4.20 (m, 2 H, H_{Fc}), 3.87−3.75 (m, 2 H, OCH_2), 3.62−3.59 (m, 1 H, NC*H*), 2.07 (s, 3 H, $CH_3C_5H_3R$), 1.36−1.25 (m, 1 H, CH_3CHCH_3), 0.99−0.97 (d, *J* = 6.5, 3 H, CH_3CHCH_3), 0.75 (d, *J* = 6.6 Hz, 3 H, CH_3CHCH_3). ^{13}C NMR (125 MHz, $CDCl_3$, 21 °C): δ 163.9, 135.4, 135.2, 132.6, 132.4, 127.1, 126.1, 88.0, 87.7, 77.9, 75.9, 74.9, 74.4, 73.2, 69.1, 32.9, 27.0, 20.6, 19.9, 18.7, 12.8. IR (solid): ν 3086, 3056, 3028, 2956, 2923, 2870, 2851, 2851, 2361, 1986, 1967, 1739, 1648, 1600, 1502, 1466, 1443, 1364, 1260, 1179, 1155, 1074, 1027, 973, 953, 910, 825, 800, 783, 742, 699, 661, 621, 573. HRMS (MALDI): *m*/*z* calcd for [MH]$^+$ $C_{47}H_{42}FeNO$, 692.2611; found, 692.2598. Anal. Calcd for ($C_{47}H_{41}FeNO{\cdot}6H_2O$): C, 75.70; H, 6.35; N, 1.88. Found: C, 76.02; H, 6.09; N, 1.98.

*1-[(4S)-tert-Butyl-2-oxazolin-2-yl]-2-(R_p)-(methyl)-1′,2′,3′,4′,5′-pentaphenylferrocene (**2b**).* Following GP1 a red solid was obtained and isolated in a yield of 50% (dr > 50:1).

$C_{48}H_{43}FeNO$, mol wt: 705.71. Mp: 146.8−147.2 °C. $[\alpha]_D^{23}$ = +112.9° (*c* = 0.106 g dL^{-1}, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$, 21 °C): δ 7.15−6.99 (m, 25 H, H_{Ph}), 4.72 (m, 1 H, H_{Fc}), 4.19 (m, 2 H, H_{Fc}), 3.83 (t, *J* = 8.4, 1 H, OCH_2), 3.70 (t, *J* = 8.2, 1 H, OCH_2), 3.53 (t, *J* = 9.2, 1 H, NC*H*), 2.02 (s, 3 H, $CH_3C_5H_3R$), 0.78 (s, 9 H, C(CH_3)$_3$). ^{13}C NMR (125 MHz, $CDCl_3$, 21 °C): δ 134.1, 131.5, 125.9, 125.1, 86.6, 76.7, 75.2, 74.8, 73.8, 66.6, 32.3, 29.9, 28.6, 25.6, 25.0, 11.5, 1.2. IR (solid): ν 3086, 3057, 3028, 2958, 2925, 2852, 2245, 1727, 1646, 1600, 1502, 1478, 1443, 1409, 1362, 1301, 1260, 1195, 1178, 1155, 1077, 1028, 1012, 970, 954, 906, 846, 799, 727, 698, 647, 620, 572, 557. HRMS (ESI): *m*/*z* calcd for [M]$^+$ $C_{48}H_{43}FeNO$, 706.2768; found, 706.2758. A sufficient microanalysis could not be obtained due to solvent inclusion.

*1-[(4S)-Isopropyl-2-oxazolin-2-yl]-2-(S_p)-(iodo)-1′,2′,3′,4′,5′-pentaphenylferrocene (**3a**).* Following GP1, **1a** (24 mg, 0.034 mmol) and TMEDA (0.015 mL, 0.1 mmol) were treated with *n*-butyllithium (15% in hexane, 0.030 mL, 0.053 mmol) at −78 °C. The solution was stirred for 4 h before warming to 0 °C. Then $LiClO_4$ (11 mg, 0.1 mmol) and ICH_2CH_2I (30 mg, 0.1 mmol) were added. The reaction was then warmed to room temperature and stirred overnight. Compound **3a** (206 mg, 0.025 mmol, 75%, dr > 50:1) was isolated as a red-yellow solid.

$C_{46}H_{38}FeINO$, mol wt: 803.55. Mp: 102.3−103.9 °C. $[\alpha]_D^{23}$ = −61.9° (*c* = 0.46 g dL^{-1}, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$, 21 °C): δ 7.17−7.03 (m, 25 H, H_{Ph}), 4.81 (m, 1 H, H_{Fc}), 4.51 (m, 1 H, H_{Fc}), 4.37 (t, *J* = 7.8, 1 H, H_{Fc}), 3.87−3.79 (m, 1 H, NC*H*), 3.70−3.65 (m, 2 H, OCH_2), 1.42 (m, 1 H, CH_3CHCH_3), 0.97 (d, *J* = 6.7, 3 H, CH_3CHCH_3), 0.77 (d, *J* = 6.8, 3 H, CH_3CHCH_3). ^{13}C NMR (75 MHz, $CDCl_3$, 21 °C): δ 134.0, 132.5, 127.1, 126.4, 88.8, 83.2, 78.4, 74.9, 72.8, 69.3, 48.7, 32.5, 29.7, 19.5, 18.2, 2.2. IR (solid): ν 2955, 2924, 2869, 2852, 2359, 1658, 1640, 1600, 1502, 1443, 1409, 1374, 1346, 1248, 1158, 1137, 1074, 1028, 978, 935, 908, 865, 844, 823, 800, 783, 742, 699. HRMS (ESI): *m*/*z* calcd for [M]$^+$ $C_{46}H_{38}FeINO$, 804.1421; found, 804.1405. A sufficient microanalysis could not be obtained due to the instability of the molecule.

*1-[(4S)-Isopropyl-2-oxazolin-2-yl]-2-(S_p)-(trimethylsilyl)-1′,2′,3′,4′,5′-pentaphenylferrocene (**4a**).* Following GP1 a reddish solid was obtained and isolated in a yield of 85% (dr > 50:1).

$C_{49}H_{47}FeNOSi$, mol wt: 749.83 g mol^{-1}. Mp: 125.9−126.6 °C. $[\alpha]_D^{23}$ = +1291.9° (*c* = 0.12 g dL^{-1}, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$, 21 °C): δ 7.16−7.03 (m, 25 H, H_{Ph}), 5.01 (m, 1 H, H_{Fc}), 4.48 (t, *J* = 3.0, 1 H, H_{Fc}), 4.40 (m, 1 H, H_{Fc}), 4.04 (dd, *J* = 6.0, *J* = 3.0, 1 H, OCH_2), 3.78 (t, *J* = 9.0, 1 H, NC*H*), 3.56 (m, 1 H, OCH_2), 1.64 (m, 1 H, CH_3CHCH_3), 1.02 (d, *J* = 6.0, 3 H, CH_3CHCH_3), 0.82 (d, *J* = 9.0, 3 H, CH_3CHCH_3), 0.04 (s, 9 H, (CH_3)$_3$Si). ^{13}C NMR (75 MHz, $CDCl_3$, 21 °C): δ 164.3, 135.4, 132.8, 132.5, 127.1, 126.3, 88.2, 83.6, 80.0, 79.3, 78.1, 73.0, 69.4, 33.0, 20.0,18.3, 0.8. IR (solid): ν 3087, 3056, 3029, 2955, 2924, 2894, 2870, 2850, 2245, 1946, 1881, 1806, 1648, 1600, 1576, 1502, 1468, 1443, 1410, 1383, 1366, 1314, 1288, 1243, 1179, 1155, 1139, 1122, 1063, 1027, 986, 906, 881, 833, 800,783, 727, 697, 648, 620, 571, 556. HRMS (ESI): *m*/*z* calcd for [M]$^+$ $C_{49}H_{47}FeNOSi$, 750.2850; found, 750.2844. Anal. Calcd for $C_{49}H_{47}FeNOSi$: C, 78.49; H, 6.32; N, 1.87. Found: C, 78.63; H, 6.28; N, 1.98.

*1-[(4S)-Isopropyl-2-oxazolin-2-yl]-2-(S_p)-(diphenylphosphino)-1′,2′,3′,4′,5′-pentaphenylferrocene (**5a**).* Following GP1 an orange-red solid was obtained and isolated in a yield of 80% (dr > 50:1).

$C_{58}H_{48}FeNOP$, mol wt: 861.83. Mp: 143.5−144.5 °C. $[\alpha]_D^{23}$ = +87.7° (*c* = 1 g dL^{-1}, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$, 21 °C): δ 7.40−6.93 (m, 35 H, H_{Ph}), 4.96 (m, 1 H, H_{Fc}), 4.44 (m, 1 H, H_{Fc}), 4.17 (m, 1 H, H_{Fc}), 3.56−3.30 (m, 2 H, OCH_2), 3.14−3.02 (t, *J* = 7.9, 1 H, NC*H*), 1.19 (m, 1 H, CH_3CHCH_3), 0.67 (d, *J* = 6.7, 3 H, CH_3CHCH_3), 0.35 (d, *J* = 6.6, 3 H, CH_3CHCH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 136.7, 136.3, 134.6, 132.8, 132.5, 132.3, 128.4, 127.1, 126.2, 88.0, 72.3, 26.9, 22.8, 19.4, 17.5. ^{31}P NMR (121.5 MHz, $CDCl_3$,

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21 °C): δ −27.7 (s). IR (solid): ν 3086, 3054, 3028, 2956, 2928, 2869, 2244, 1948, 1808, 1640, 1600, 1502, 1476, 1445, 1432, 1410, 1382, 1344, 1311, 1274, 1254, 1181, 1127, 1093, 1074, 1027, 982, 950, 907, 875, 848, 829, 800, 783, 739, 697, 647, 621, 572. HRMS (ESI): *m/z* calcd for $[MH]^+$ $C_{58}H_{49}FeNOP$, 862.2897; found, 862.2877. Anal. Calcd for $C_{58}H_{48}FeNO_2P\cdot(n\text{-pentane})\cdot CH_2Cl_2$: C, 74.28; H, 6.04; N, 1.35. Found: C, 74.48; H, 5.84; N, 1.63.

*1-[(4R)-Isopropyl-2-oxazolin-2-yl]-2-(R_p)-(diphenylphosphino)-1′,2′,3′,4′,5′- pentaphenylferrocene (epi-**5a**).* Following GP1 but using diethylene glycol dibutyl ether instead of TMEDA, **1a** (22 mg, 0.033 mmol) and diethylene glycol dibutyl ether (0.024 mL, 0.1 mmol) were treated with *n*-butyllithium (15% in hexane, 0.03 mL, 0.05 mmol) at −78 °C. The solution was stirred for 4 h before warming to 0 °C. Then $ClPPh_2$ (0.02 mL, 0.1 mmol) was added. The reaction mixture was warmed to room temperature and stirred overnight. The mixture was subsequently filtered over Celite and the solvent removed in vacuo. The crude product was purified by column chromatography (silica, PE/EtOAc, 95/5) to yield the product as an orange-red solid (249 mg, 0.029 mmol, 90%, dr > 50:1).

$C_{58}H_{48}FeNOP$, mol wt: 861.83. Mp: 139.8−140.9 °C. $[\alpha]_D^{23}$ = +37.7° (*c* = 0.15 g dL^{-1}, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$, 21 °C): δ 7.16−6.89 (m, 35 H, H_{Ph}), 5.24 (m, 1 H, H_{Fc}), 4.53 (t, *J* = 2.2, 1 H, H_{Fc}), 4.40 (m, 1 H, H_{Fc}), 3.70 (m, 1 H, NC*H*), 3.11 (dd, *J* = 3.0, *J* = 9.0, 1 H, OCH_2), 2.65 (dd, *J* = 6.0, *J* = 12, 1 H, OCH_2), 1.81 (m, 1 H, CH_3CHCH_3), 0.75 (d, *J* = 6.0, 3 H, CH_3CHCH_3), 0.61 (d, *J* = 6.0, 3 H, CH_3CHCH_3). ^{13}C NMR (75 MHz, $CDCl_3$, 21 °C): δ 134.4, 133.3, 132.5, 132.3, 128.8, 128.3, 127.4, 127.1, 127.0, 126.6, 126.4, 89.3, 88.8, 88.1, 71.2, 70.6, 70.1, 55.8, 53.4, 31.7, 27.2, 26.9, 19.2, 13.9. ^{31}P NMR (121.5 MHz, $CDCl_3$, 21 °C): δ −31.4 (s). IR (solid): ν 3053, 2958, 2928, 2870, 1893, 1731, 1646, 1600, 1501, 1444, 1433, 1409, 1373, 1324, 1254, 1181, 1156, 1095, 1073, 1027, 982, 920, 848, 829, 800, 783, 740, 696, 620, 571, 556. HRMS (ESI): *m/z* calcd for $[MH]^+$ $C_{58}H_{49}FeNOP$, 862.2897; found, 862.2911. A sufficient microanalysis could not be obtained due to solvent inclusion.

*1-[(4S)-tert-Butyl-2-oxazolin-2-yl]-2-(S_p)-(diphenylphosphino)-1′,2′,3′,4′,5′-pentaphenylferrocene (**5b**).* Following GP1 an orange-red solid was obtained and isolated in a yield of 88% (dr > 50:1).

$C_{59}H_{50}FeNOP$, mol wt: 875.85. Mp: 176.5−177.7 °C. $[\alpha]_D^{23}$ = +47.2° (*c* = 0.216 g dL^{-1}, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$, 21 °C): δ 7.35−6.98 (m, 35 H, H_{Ph}), 5.00 (m, 1 H, H_{Fc}), 4.47 (m, 1 H, H_{Fc}), 4.22 (m, 1 H, H_{Fc}), 3.42−3.24 (m, 3 H, OCH_2CHCN), 0.48 (s, 9 H, $(CH_3)_3C$). ^{13}C NMR (125 MHz, $CDCl_3$, 21 °C): δ 163.2, 136.8, 136.6, 134.8, 132.8, 132.2, 129.4, 128.4, 128.35, 128.30, 128.2, 127.7, 127.0, 126.2, 88.2, 83.4, 79.9, 78.3, 77.9, 67.9, 33.0, 25.9. ^{31}P NMR (121.5 MHz, $CDCl_3$, 21 °C): δ −28.3 (s). IR (solid): ν 3086, 3055, 3029, 2957, 2920, 2851, 2244, 1742, 1646, 1600, 1502, 1477, 1444, 1433, 1411, 1364, 1331, 1303, 1260, 1206, 1179, 1131, 1073, 1027, 983, 908, 828, 800, 783,731, 698, 647, 620, 572. HRMS (ESI): *m/z* calcd for $[MH]^+$ $C_{59}H_{51}FeNOP$, 876.3054; found, 876.3027. A sufficient microanalysis could not be obtained due to solvent inclusion.

*1-[(4S)-Isopropyl-2-oxazolin-2-yl]-2-(S_p)-(bis(4-methoxyphenyl)-phosphino)-1′,2′,3′,4′,5′-pentaphenylferrocene (**6a**).* Following GP1 an orange-red solid was obtained and isolated in a yield of 68% (dr > 50:1).

$C_{60}H_{52}FeNO_3P$, mol wt: 921.88. Mp: 160.9−161.3 °C. $[\alpha]_D^{23}$ = +86.2° (*c* = 0.291 g dL^{-1}, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$, 21 °C): δ 7.33−6.90 (m, 29 H, H_{Ph}), 6.80 (d, 2 H, *J* = 8.5, H_{Ph}CCOMe), 6.68 (d, 2 H, *J* = 8.4, H_{Ph}CCOMe), 4.92 (m, 1 H, H_{Fc}), 4.42 (m, 1 H, H_{Fc}), 4.16 (m, 1 H, H_{Fc}), 3.79 (s, 3 H, $COCH_3$), 3.67 (s, 3 H, $COCH_3$), 3.50 (m, 1 H, OCH_2), 3.33 (m, 1 H, NC*H*), 3.15 (t, *J* = 8.1, 1 H, OCH_2), 1.23 (m, 1 H, CH_3CHCH_3), 0.67 (d, *J* = 6.4, 3 H, CH_3CHCH_3), 0.36 (d, *J* = 6.7, 3 H, CH_3CHCH_3). ^{13}C NMR (75 MHz, $CDCl_3$, 21 °C): δ 137.7, 137.5, 134.7, 132.7, 126.8, 126.0, 113.9, 87.9, 55.0., 26.9, 19.1, 17.2. ^{31}P NMR (121.5 MHz, $CDCl_3$, 21 °C): δ −32.03 (s). IR (solid): ν 3054, 2955, 2869, 2834, 1641, 1592, 1567, 1497, 1441, 1401, 1345, 1281, 1246, 1125, 1091, 1074, 1028, 981, 949, 919, 875, 826, 797, 7416, 698. HRMS (ESI): *m/z* calcd for $[MH]^+$ $C_{60}H_{53}FeNO_3P$, 922.3109; found, 922.3119. A sufficient microanalysis could not be obtained due to solvent inclusion.

*1-[(4S)-Isopropyl-2-oxazolin-2-yl]-2-(S_p)-(bis[4-(trifluoromethyl)-phenyl]phosphino)-1′,2′,3′,4′,5′-pentaphenylferrocene (**7a**).* Following GP1 an orange-red solid was obtained and isolated in a yield of 91% (dr > 50:1).

$C_{60}H_{46}F_6FeNOP$, mol wt: 997.82. Mp: 140.2−141.1 °C. $[\alpha]_D^{23}$ = +123.1° (*c* = 0.5 g dL^{-1}, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$, 21 °C): δ 7.54−6.94 (m, 33 H, H_{Ph}), 5.01 (m, 1 H, H_{Fc}), 4.56 (m, 1 H, H_{Fc}), 4.14 (m, 1 H, H_{Fc}), 3.43 (m, 2 H, OCH_2), 3.15 (t, *J* = 7.5, 1 H, NC*H*), 1.14 (m, 1 H, CH_3CHCH_3), 0.64 (d, *J* = 6.7, 3 H, CH_3CHCH_3), 0.33 (d, *J* = 6.8, 3 H, CH_3CHCH_3). ^{13}C NMR (125 MHz, $CDCl_3$, 21 °C): δ 136.8, 136.6, 134.3, 132.6, 132.5, 132.3, 127.0, 126.4, 125.1, 88.3, 78.8, 78.0, 72.2, 68.9, 31.7, 18.9, 17.1. ^{31}P NMR (121.5 MHz, $CDCl_3$, 21 °C): δ −28.5 (s). ^{19}F NMR (235 MHz, $CDCl_3$, 21 °C): δ −62.84 (s), −62.89 (s). IR (solid): ν 3087, 3058, 3029, 2959, 2870, 2245, 1723, 1641, 1603, 1502, 1477, 1444, 1395, 1321, 1275, 1166, 1125, 1105, 1058, 1030, 1015, 980, 951, 906, 875, 826, 800, 783, 727, 696, 648, 621, 602, 572, 557. HRMS (ESI): *m/z* calcd for $[MH]^+$ $C_{60}H_{47}F_6FeNOP$, 998.2624; found, 998.2622. A sufficient microanalysis could not be obtained due to solvent inclusion.

*1-[(4S)-Isopropyl-2-oxazolin-2-yl]-2-(S_p)-(bis[3,5-(trifluoromethyl)phenyl]phosphino)-1′,2′,3′,4′,5′-pentaphenylferrocene (**8a**).* Following GP1 an orange-red solid was obtained and isolated in a yield of 39% (dr > 50:1).

$C_{62}H_{44}F_{12}FeNOP$, mol wt: 1133.82. Mp: 121.9−122.6 °C. $[\alpha]_D^{23}$ = −53.3° (*c* = 0.24 g dL^{-1}, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$, 21 °C): δ 7.89 (s, 1 H, F_3CCH_{Ph}), 7.73 (d, *J* = 7.0, 2 H, F_3CCH_{Ph}), 7.66 (s, 1 H, $F_3CCH_{Ph}CF_3$), 7.52 (d, *J* = 7.0, 2 H, F_3CCH_{Ph}), 7.14−6.97 (m, 25 H, H_{Ph}), 5.06 (m, 1 H, H_{Fc}), 4.64 (t, *J* = 2.7, 1 H, H_{Fc}), 4.15 (m, 1 H, H_{Fc}), 3.61 (t, *J* = 8.3, 1 H, NC*H*), 3.33 (m, 1 H, OC*H*), 3.15 (m, 1 H, OC*H*), 1.58 (m, 1 H, CH_3CHCH_3), 0.70 (d, *J* = 6.5, 3 H, CH_3CHCH_3), 0.41 (d, *J* = 6.5, 3 H, CH_3CHCH_3). ^{13}C NMR (125 MHz, $CDCl_3$, 21 °C): δ 161.8, 144.0, 143.8, 136.1, 134.0, 132.4, 132.0, 131.8, 127.1, 126.6, 124.1, 121.9, 88.5, 79.2, 79.1, 78.8, 73.0, 69.4, 32.1, 19.1, 17.8. ^{31}P NMR (121.5 MHz, $CDCl_3$, 21 °C): δ −26.8. ^{19}F NMR (235 MHz, $CDCl_3$, 21 °C): δ −62.6 (s), −62.8 (b), −63.0 (s). IR (solid): ν 3058, 2961, 1656, 1601, 1502, 1444, 1352, 1275, 1173, 1119, 1092, 1028, 980, 945, 896, 843, 800, 783, 741, 699, 680, 619, 573, 557, 535, 522. HRMS (ESI): *m/z* calcd for $[M]^+$ $C_{62}H_{44}F_{12}FeNOP$, 1134.2393. A sufficient microanalysis could not be obtained due to solvent inclusion.

General Procedure for the Synthesis of the Pd−Allyl Complexes 9−12 (GP2). A mixture of $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ (0.05 mmol), the corresponding ligand (0.1 mmol, 2.0 equiv), and dry CH_2Cl_2 (2 mL per 0.1 mmol of ligand) was stirred for 10 min at room temperature. Then a solution of $AgSbF_6$ (2.0 equiv) in dry methanol (0.5 mL per 0.1 mmol of $AgSbF_6$) was added, and the reaction mixture was stirred for an additional 1 h. Filtration through Celite and evaporation of the solvent gave the pure product.

*(η^3-Allyl)[1-[(4S)-isopropyl-2-oxazolin-2-yl]-2-(S_p)-(diphenylphosphino)-1′,2′,3′,4′,5′-pentaphenylferrocene]palladium Hexafluoroantimonate (**9a**).* Following GP2 a red crystalline solid was isolated in quantitative yield (dr = 1.3:1).

$C_{61}H_{53}F_6FeNOPPdSb$, mol wt: 1245.07. Mp: 131.8−132.0 °C dec. $[\alpha]_D^{23}$ = −657.0° (*c* = 0.206 g dL^{-1}, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$, 21 °C): mixture of two isomers in a ratio of 1.3:1 (called a and b), δ 7.63−6.96 (m, 50 H, H_{Ph}), 6.82 (b, 10 H, PCCH_{Ph}, isomer b), 6.75 (b, 10 H, PCCH_{Ph}, isomer a), 5.89 (m, 1 H, H_{allyl}, isomer a), 5.52 (m, 1 H, H_{Fc}, isomer a), 5.49 (m, 1 H, H_{Fc}, isomer b), 5.40 (m, 1 H, H_{allyl}, isomer b), 5.04 (m, 1 H, H_{Fc}, isomer b), 5.00 (m, 1 H, H_{Fc}, isomer a), 4.91 (m, 1 H, H_{Fc}, isomer a), 4.90 (m, 1 H, H_{allyl}, isomer a), 4.72 (m, 1 H, H_{allyl}, isomer b), 4.47 (t, *J* = 9.0, 1 H, NC*H*, isomer a), 4.41 (t, *J* = 9.0, 1 H, NC*H*, isomer b), 4.25 (m, 2 H, OCH_2, isomer a), 4.05 (q, *J* = 7.0, 1 H, H_{allyl}, isomer a), 4.00 (m, 1 H, H_{allyl}, isomer b), 3.77 (m, 2 H, OCH_2, isomer b), 3.43 (d, *J* = 7.0, 1 H, H_{allyl}, isomer a), 3.37 (d, *J* = 4.5, 1 H, H_{allyl}, isomer b), 2.69 (d, *J* = 13.8, 1 H, H_{allyl}, isomer b), 2.32 (d, *J* = 12.0, 1 H, H_{allyl}, isomer a), 1.93 (m, 1 H, CH_3CHCH_3), 1.41 (m, 1 H, CH_3CHCH_3), 0.93 (d, *J* = 7.0, 3 H, CH_3CHCH_3, isomer a), 0.88 (d, *J* = 7.0, 3 H, CH_3CHCH_3, isomer b), 0.34 (d, *J* = 7.0, 3 H, CH_3CHCH_3, isomer a), 0.26 (d, *J* = 7.0, 3 H, CH_3CHCH_3, isomer b). ^{13}C NMR (125 MHz, $CDCl_3$, 21 °C): δ

169.7, 136.0, 135.9, 135.6, 135.5, 133.4, 133.3, 132.1, 131.1, 131.0, 130.9, 130.8, 129.6, 129.5, 129.4, 129.3, 129.2, 127.8, 127.7, 127.4, 127.4, 89.8, 89.7, 69.7, 68.9, 32.0, 31.0, 30.9, 30.2, 29.8, 20.3, 19.8, 16.5, 15.2, 14.2, 14.1, 1.0. ^{31}P NMR (121.5 MHz, $CDCl_3$, 21 °C): δ 16.2 (s), 15.2 (s). IR (solid): ν 3057, 2924, 2854, 1724, 1600, 1503, 1480, 1441, 1410, 1383, 1267, 1246, 1172, 1100, 1076, 1028, 998, 834, 802, 784, 740, 699, 657, 622, 569, 622, 569, 546. HRMS (ESI): m/z calcd for $[M - SbF_6]^+$ = $C_{61}H_{53}FeNOPPd$, 1008.2266; found, 1008.2257. Anal. Calcd for $C_{61}H_{53}F_6FeNOPPdSb{\cdot}6H_2O$: C, 54.14; H, 4.84; N, 1.04. Found: C, 54.05; H, 4.65; N, 0.86.

*(η^3-Allyl)[1-[(4R)-isopropyl-2-oxazolin-2-yl]-2-(R_p)-(diphenylphosphino)-1′,2′,3′,4′,5′-pentaphenylferrocene]palladium Hexafluoroantimonate (**epi-9a**).* Following GP2 a red crystalline solid was isolated in quantitative yield (dr = 2.8:1).

$C_{61}H_{53}F_6FeNOPPdSb$, mol wt: 1245.07. Mp: > 190 °C dec. $[\alpha]_D^{23}$ = 186.5° (c = 0.73 g dL^{-1}, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$, 21 °C): mixture of two isomers in a ratio of 2.8:1 (called a and b), δ 7.28−7.17 (m, 11 H, H_{Ph}), 6.97 (m, 16 H, H_{Ph}), 6.83−6.78 (m, 17 H, H_{Ph}), 6.70−6.63 (m, 2 H, H_{Ph}), 5.79 (m, 1 H, H_{allyl}, isomer a), 5.60 (m, 1 H, H_{allyl}, isomer b), 5.25 (m, 2 H, H_{Fc}, isomer b), 4.92 (m, 2 H, H_{Fc}, isomer a), 4.73 (m, 1 H, H_{allyl}), 4.71 (m, 1 H, H_{allyl}), 4.44 (t, J = 9.9, 1 H, NC*H*, isomer a), 4.25 (d, J = 4.0, 1 H, H_{allyl}, isomer a), 4.22 (d, J = 4.5, 1 H, H_{allyl}, isomer b), 4.05 (m, 1 H, H_{Fc}, isomer a), 4.01 (m, 1 H, H_{Fc}, isomer b), 3.82 (dd, J = 10.4, J = 3.8, 2 H, OCH_2, isomer a), 3.66 (d, J = 5.2, 1 H, H_{allyl}, isomer a), 3.58 (t, J = 6.2, 1 H, NC*H*, isomer b), 3.50 (d, J = 8.0, 1 H, H_{allyl}, isomer b), 3.26 (dd, J = 5.6, J = 2.0, 2 H, OCH_2, isomer b), 3.02 (d, J = 12.2, 1 H, H_{allyl}, isomer b), 2.90 (d, J = 12.9, 1 H, H_{allyl}, isomer a), 1.88 (m, 1 H, CH_3CHCH_3), 1.66 (m, 1 H, CH_3CHCH_3), 0.84 (d, J = 6.0, 3 H, CH_3CHCH_3, isomer b), 0.76 (d, J = 7.8, 3 H, CH_3CHCH_3, isomer a), 0.14 (d, J = 6.0, 3 H, CH_3CHCH_3, isomer b), −0.14 (d, J = 6.9, 3 H, CH_3CHCH_3, isomer a). ^{13}C NMR (125 MHz, $CDCl_3$, 21 °C): δ 168.6, 135.0, 134.9, 134.3, 133.4, 133.2, 132.7, 132.3, 132.1, 132.0, 131.9, 131.8, 129.7, 129.6, 129.4, 129.3, 127.8, 127.7, 127.6, 89.7, 83.1, 82.5, 80.4, 79.0, 76.1, 75.1, 75.0, 72.7, 72.4, 68.0, 55.2, 48.2 31.9, 31.5, 29.9, 18.5, 18.1, 13.3, 12.8, 9.4. ^{31}P NMR (121.5 MHz, $CDCl_3$, 21 °C): δ 15.6 (s), 14.8 (s). IR (solid): ν 3057, 2961, 2925, 2852, 1600, 1578, 1544, 1502, 1480, 1463, 1439, 1410, 1384, 1312, 1279, 1261, 1244, 1172, 1101, 1075, 1027, 998, 908, 801, 783, 727, 697, 657, 571, 547. HRMS (ESI): m/z calcd for $[M - SbF_6]^+$ = $C_{61}H_{53}FeNOPPd$, 1008.2266; found, 1008.2266. A sufficient microanalysis could not be obtained due to solvent inclusion.

*(η^3-Allyl)[1-[(4S)-tert-butyl-2-oxazolin-2-yl]-2-(S_p)-(diphenylphosphino)-1′,2′,3′,4′,5′-pentaphenylferrocene]palladium Hexafluoroantimonate (**9b**).* Following GP2 a red crystalline solid was isolated in quantitative yield (dr > 50:1).

$C_{62}H_{55}F_6FeNOPPdSb$, mol wt: 1259.10. Mp: > 170 °C dec. $[\alpha]_D^{23}$ = −225.5° (c = 0.21 g dL^{-1}, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$, 21 °C): δ 7.78−6.68 (m, 35 H, H_{Ph}), 5.74 (m, 1 H, H_{allyl}), 5.63 (m, 1 H, H_{Fc}), 5.28 (m, 1 H, H_{allyl}), 5.01 (m, 1 H, H_{allyl}), 4.92 (m, 1 H, H_{allyl}), 4.88 (m, 1 H, H_{Fc}), 4.61 (m, 1 H, NC*H*), 4.21 (m, 2 H, OCH_2), 3.97 (m, 1 H, H_{allyl}), 3.22 (m, 1 H, H_{allyl}), 0.60 (s, 9 H, C(CH_3)$_3$). ^{13}C NMR (125 MHz, $CDCl_3$, 21 °C): δ 133.2, 132.3, 131.0, 130.9, 129.3, 129.3, 127.6, 127.4, 90.2, 29.7, 26.1, 1.0. ^{31}P NMR (121.5 MHz, $CDCl_3$, 21 °C): δ 18.5 (s). IR (solid): ν 3056, 2985, 1723, 1600, 1502, 1482, 1438, 1383, 1365, 1290, 1243, 1172, 1102, 1075, 1027, 988, 952, 908, 830, 802, 785, 735, 696, 654, 560, 542. HRMS (ESI): m/z calcd for $[M - SbF_6]^+$ = $C_{62}H_{55}FeNOPPd$, 1022.2423; found, 1022.2418. A sufficient microanalysis could not be obtained due to solvent inclusion.

*(η^3-Allyl)[1-[(4S)-isopropyl-2-oxazolin-2-yl]-2-(S_p)-(bis(4-methoxyphenyl)phosphino)-1′,2′,3′,4′,5′-pentaphenylferrocene]-palladium Hexafluoroantimonate (**10a**).* Following GP2 a red crystalline solid was isolated in quantitative yield (dr = 1.3:1).

$C_{63}H_{57}F_6FeNO_3PPdSb$, mol wt: 1305.12. Mp: 160.6−161.6 °C dec. $[\alpha]_D^{23}$ = −379.8° (c = 0.193 g dL^{-1}, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$, 21 °C): mixture of two isomers 1.34:1 (called a and b), δ 7.20−7.15 (m, 9 H, H_{Ph}), 7.02−6.95 (m, 20 H, H_{Ph}), 6.84−6.75 (m, 26 H, H_{Ph}), 6.59−6.49 (m, 4 H, H_{Ph}), 5.88 (m, 1 H, $H_{allyl,}$ isomer a), 5.50 (m, 1 H, $H_{allyl,}$ isomer b), 5.48 (m, 1 H, $H_{Fc,}$ isomer a), 5.44 (m, 1 H, $H_{Fc,}$ isomer b), 5.03 (m, 1 H, $H_{Fc,}$ isomer b), 4.98 (m, 1 H, $H_{Fc,}$ isomer a), 4.88 (t, J= 6.0, 1 H, NCH, isomer a), 4.86 (m, 1 H, H_{Fc}, isomer a), 4.85 (m, 1 H, H_{Fc}, isomer b), 4.73 (t, J = 7.8, 1 H, NC*H*, isomer b), 4.49 (t, J = 9.4, 1 H, OC*H*, isomer a), 4.41 (t, J = 9.6, 1 H, OC*H*, isomer a), 4.25 (t, J = 8.2, 1 H, OC*H*, isomer b), 4.21 (t, J = 8.6, 1 H, OC*H*, isomer b), 4.10 (d, J = 7.3, 2 H, H_{allyl}, isomer a), 3.89 (s, 3 H, OCH_3, isomer a), 3.88 (s, 3 H, OCH_3, isomer b), 3.77 (s, 3 H, OCH_3, isomer a), 3.76 (s, 3 H, OCH_3, isomer b), 3.46 (d, J = 4.5, 1 H, H_{allyl}, isomer a), 3.38 (d, J = 5.5, H_{allyl}, isomer b), 3.04 (d, J = 11.9, H_{allyl}, isomer b), 2.02 (m, 1 H, CH_3CHCH_3, isomer b), 1.52 (m, 1 H, CH_3CHCH_3, isomer a), 0.93 (d, J = 6.9, 3 H, CH_3CHCH_3, isomer a), 0.88 (d, J = 6.9, 3 H, CH_3CHCH_3, isomer b), 0.33 (d, J = 6.2, 3 H, CH_3CHCH_3, isomer a), 0.24 (d, J = 6.9, 3 H, CH_3CHCH_3, isomer b). ^{13}C NMR (63 MHz, $CDCl_3$, 21 °C): δ169.8, 162.8, 161.4, 137.5, 137.4, 137.0, 136.9, 133.5, 133.4, 132.9, 132.8, 132.7, 132.5, 132.1, 127.7, 127.6, 127.3, 124.3, 123.8, 120.6, 120.5, 119.8, 119.7, 119.3, 119.1, 115.4, 115.3, 115.2, 115.1, 115.0, 114.9, 111.3, 89.8, 89.6, 83.5, 83.5, 83.3, 81.8, 81.4, 80.9, 90.6, 78.0, 75.8, 69.5, 68.8, 63.1, 58.3, 57.0, 55.8, 55.6, 53.5, 50.9, 30.7, 30.1, 29.8, 20.3, 19.7, 16.3, 15.0. ^{31}P NMR (121.5 MHz, $CDCl_3$, 21 °C): δ 13.5, 12.2. IR (solid): ν 2957, 2918, 2849, 1592, 1566, 1538, 1500, 1462, 1441, 1408, 1381, 1286, 1256, 1179, 1095, 1074, 1022, 955, 917, 829, 801, 741, 698, 655, 571, 548. HRMS (ESI): m/z calcd for $[M - SbF_6]^+$ = $C_{63}H_{57}FeNO_3PPd$, 1068.2478; found, 1068.2466. A sufficient microanalysis could not be obtained due to instability.

*(η^3-Allyl)[1-[(4S)-isopropyl-2-oxazolin-2-yl]-2-(S_p)-(bis[4-(trifluoromethyl)phenylphosphino)-1′,2′,3′,4′,5′-pentaphenylferrocene]palladium Hexafluoroantimonate (**11a**).* Following GP2 a red crystalline solid was isolated in quantitative yield (dr = 1.5:1).

$C_{63}H_{51}F_{12}FeNOPPdSb$, mol wt: 1381.06. Mp: >190 °C dec. $[\alpha]_D^{23}$ = −451.7° (c = 0.176 g dL^{-1}, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$, 21 °C): mixture of two isomers 1.5:1 (called a and b), δ 7.59 (m, 4 H, $H_{Ph}CCCF_3CH_{Ph}$, isomer a), 7.596(m, 4 H, $H_{Ph}CCCF_3CH_{Ph}$, isomer b), 7.17 (t, J = 3.8, 10 H, H_{Ph}), 6.99 (q, J = 6.9, 20 H, H_{Ph}), 6.88 (d, J = 8.1, 10 H, H_{Ph}, isomer b), 6.76 (d, J = 7.5, 10 H, H_{Ph}, isomer a), 5.88 (m, 1 H, H_{allyl}, isomer a), 5.60 (m, 1 H, H_{Fc}, isomer a), 5.55 (m, 1 H, H_{Fc}, isomer b), 5.48 (m, 1 H, H_{allyl}, isomer b), 5.11 (m, 1 H, H_{Fc}, isomer b), 5.04 (m, 1 H, H_{Fc}, isomer a), 4.98 (m, 1 H, H_{Fc}, isomer a), 4.97 (m, 1 H, H_{allyl}, isomer a), 4.96 (m, 1 H, H_{Fc}, isomer b), 4.82 (m, 1 H, H_{allyl}, isomer b), 4.52 (t, J = 8.5, 1 H, NC*H*, isomer a), 4.43 (t, J = 9.0, 1 H, NC*H*, isomer b), 4.27 (q, J = 8.5, 2 H, OCH_2, isomer a), 4.09 (m, 1 H, H_{allyl}, isomer a), 4.08 (m, 1 H, H_{allyl}, isomer b), 3.88 (q, J = 12.0, 2 H, OCH_2, isomer b), 3.38 (m, 2 H, H_{allyl}), 3.37 (m, 1 H, H_{allyl}), 2.66 (d, J = 12.0, 1 H, H_{allyl}, isomer b), 2.37 (d, J = 12.0, 1 H, H_{allyl}, isomer a), 1.91 (m, 1 H, CH_3CHCH_3, isomer a), 1.90 (m, 1 H, CH_3CHCH_3, isomer b), 0.94 (d, J = 6.0, 3 H, CH_3CHCH_3, isomer a), 0.89 (d, J = 6.0, 3 H, CH_3CHCH_3, isomer b), 0.35 (d, J = 7.0, 3 H, CH_3CHCH_3, isomer a), 0.26 (d, J = 7.0, 3 H, CH_3CHCH_3, isomer b). ^{13}C NMR (125 MHz, $CDCl_3$, 21 °C): δ 169.8, 136.2, 133.2, 133.1, 132.0, 131.7, 131.6, 131.59, 131.5, 127.79, 127.72, 127.6, 127.5, 90.2, 90.0, 78.2, 78.0, 77.6, 76.6, 75.9, 69.9, 69.0, 31.1, 30.3, 29.8, 20.4, 19.8, 16.6, 15.1. ^{31}P NMR (202.5 MHz, $CDCl_3$, 21 °C): δ 16.9 (s), 15.7 (s). ^{19}F NMR (235 MHz, $CDCl_3$, 21 °C): δ −62.85 (b), −62.90 (b), −63.01 (s), −63.07 (s), −63.25 (b), −63.26 (b). IR (solid): ν 3058, 2958, 2923, 2851, 1727, 1600, 1502, 1465, 1014, 955, 919, 875, 832, 801, 740, 698, 656, 621, 600, 571, 559. HRMS (ESI): m/z calcd for $[M - SbF_6]^+$ = $C_{63}H_{51}F_6FeNOPPd$, 1144.2014; found, 1144.2019. A sufficient microanalysis could not be obtained due to instability.

*(η^3-Allyl)[1-[(4S)-isopropyl-2-oxazolin-2-yl]-2-(S_p)-(bis[3,5-trifluoromethyl)phenylphosphino)-1′,2′,3′,4′,5′-pentaphenylferrocene]palladium Hexafluoroantimonate (**12a**).* Following GP2 a red crystalline solid was isolated in quantitative yield (dr = 1.4:1).

$C_{65}H_{49}F_{18}FeNOPPdSb$, mol wt: 1517.06. Mp: 197.7−198.0 °C dec. $[\alpha]_D^{23}$ = −425.6° (c = 0.265 g dL^{-1}, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$, 21 °C): mixture of two isomers in a ratio of 1.4:1 (called a and b), δ 8.17 (m, 3 H, $H_{Ph}CCCF_3$), 7.89 (m, 1 H, $H_{Ph}CCCF_3$, isomer a), 7.87 (m, 1 H, $H_{Ph}CCCF_3$, isomer b), 7.67 (d, J = 11.5, 1 H, $H_{Ph}CCCF_3$, isomer a), 7.56 (d, J = 11.5, 1 H, $H_{Ph}CCCF_3$, isomer b), 7.19−6.68 (m, 50 H, H_{Ph}), 5.92 (m, 1 H, H_{allyl}, isomer a), 5.72 (m, 1 H, H_{Fc}, isomer a), 5.67 (m, 1 H, H_{Fc}, isomer b), 5.60 (m, 1 H, H_{allyl},

isomer a), 5.15 (m, 1 H, H_{Fc}, isomer a), 5.14 (m, 1 H, H_{Fc}, isomer b), 5.08 (t, J = 6.3, 1 H, H_{allyl}, isomer a), 4.98 (t, J = 8.0, 1 H, H_{allyl}, isomer b), 4.92 (m, 1 H, H_{Fc}, isomer b), 4.86 (m, 1 H, H_{Fc}, isomer a), 4.53 (m, 1 H, H_{allyl}, isomer a), 4.45 (m, 1 H, H_{allyl}, isomer b), 4.31−4.28 (m, 3 H, OCH_2, NC*H*, isomer a), 4.15 (m, 2 H, OCH_2, isomer b), 3.89 (t, J = 11.5, 1 H, NC*H*, isomer b), 3.40 (m, 1 H, H_{allyl}, isomer b), 3.39 (d, J = 7.7, 1 H, H_{allyl}, isomer a), 2.74 (d, J = 12.4, 1 H, H_{allyl}, isomer b), 2.57 (d, J = 12.2, 1 H, H_{allyl}, isomer a), 1.56 (m, 2 H, CH_3CHCH_3), 0.87 (d, J = 7.8, 3 H, CH_3CHCH_3, isomer b), 0.86 (d, J = 6.9, 3 H, CH_3CHCH_3, isomer a), 0.31 (d, J = 7.8, 3 H, CH_3CHCH_3, isomer a), 0.23 (d, J = 6.9, 3 H, CH_3CHCH_3, isomer b). ^{13}C NMR (125 MHz, $CDCl_3$, 21 °C): δ 169.6, 136.4, 136.0, 132.78, 132.70, 131.9, 127.9, 127.88, 127.85, 127.7, 125.3, 121.4, 121.1, 120.8, 90.7, 90.4, 88.1, 82.9, 70.5, 70.1, 66.1, 58.1, 34.2, 31.1, 30.6, 29.8, 22.5, 20.5, 20.0, 17.1, 15.9, 15.4, 14.1. ^{31}P NMR (121.5 MHz, $CDCl_3$, 21 °C): δ 20.3 (s), 19.1 (s). ^{19}F NMR (235 MHz, $CDCl_3$, 21 °C): δ −62.5 (s), −63.0 (b), −63.3 (s). IR (solid): ν 2959, 2923, 2851, 1711, 1600, 1503, 1465, 1443, 1355, 1278, 1187, 1122, 1095, 1028, 906, 844, 801, 741, 699, 681, 655, 621. HRMS (ESI): m/z calcd for $[M - SbF_6]^+ = C_{65}H_{49}F_{12}FeNOPPd$, 1280.1763; found, 1280.1777. A sufficient microanalysis could not be obtained due to instability.

[η^3-2-Cyclohexen-1-yl][[(4*S*)-isopropyl-2-oxazolin-2-yl]-2-(S_p)-(diphenylphosphino)-1′,2′,3′,4′,5′-pentaphenylferrocene]-palladium Hexafluoroantimonate (13). A mixture of $[Pd(\eta^3\text{-}C_6H_9)Cl]_2$ (8.8 mg, 0.02 mmol, 1 equiv),[24] **7a** (34 mg, 0.04 mmol, 2 equiv), and dry CH_2Cl_2 (1 mL) was stirred for 10 min at room temperature. Then a solution of $AgSbF_6$ (14 mg, 0.04 mmol, 2 equiv) in dry methanol (0.25 mL) was added and the mixture was stirred for an additional 1 h. Filtration through Celite and evaporation of the solvent gave the product as a red crystalline solid (51.4 mg, 0.04 mmol, >99%, dr > 50:1).

$C_{64}H_{57}F_6FeNOPPdSb$, mol wt: 1285.13. Mp: >162.8 °C dec. $[\alpha]_D^{23}$ = −614.8° (c = 0.185 g dL^{-1}, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$, 21 °C): δ 7.66−6.58 (m, 33 H, H_{Ph}), 5.9 (m, 1 H, H_{allyl}), 5.80 (t, J = 7.8, 1 H, H_{allyl}), 5.54 (m, 1 H, H_{Fc}), 4.94 (m, 1 H, H_{Fc}), 4.48 (m, 1 H, H_{Fc}), 4.56 (t, J = 9.0, 1 H, OCH_2), 4.31(m, 1 H, H_{allyl}), 4.26 (t, J = 8.5, 1 H, CNC*H*), 4.08 (m, 1 H, OCH_2), 2.01 (m, 1 H, CH_2), 1.26 (m, 1 H, CH_3CHCH_3), 1.02 (m, 1 H, CH_2), 0.96 (d, J = 6.5, 3 H, CH_3CHCH_3), 0.86 (m, 3 H, CH_2), 0.62 (m, 1 H, CH_2), 0.32 (d, J = 6.0, 3 H, CH_3CHCH_3). ^{13}C NMR (125 MHz, $CDCl_3$, 21 °C): δ169.9, 136.3, 136.2, 133.3, 133.1, 132.2, 132.1, 131.0, 130.9, 130.3, 129.7, 129.6, 129.0, 128.9, 127.79, 127.72, 127.4, 127.3, 109.7, 109.6, 98.8, 98.6, 89.6, 82.2, 80.7, 80.6, 78.4, 76.5, 75.2, 72.5, 72.4, 69.2, 30.8, 29.8, 28.19, 28.15, 27.4, 26.8, 24.7, 22.8, 21.7, 20.2, 19.7, 18.4, 16.1,1.2 . ^{31}P NMR (121.5 MHz, $CDCl_3$, 21 °C): δ 17.5 (s), 12.1 (s). IR (solid): ν 3088, 3057, 3029, 2961, 2925, 2852, 2365, 1721, 1599, 1502, 1481, 1441, 1410, 1383, 1313, 1283, 1246, 1169, 1101, 1075, 1044, 1028, 998, 954, 908, 848, 801, 728, 697, 658, 620. HRMS (ESI): m/z calcd for $[M - SbF_6]^+ = C_{64}H_{57}FeNOPPd$, 1048.2580; found, 1048.2573. Anal. Calcd for $C_{64}H_{57}F_6FeNOPPdSb$: C, 59.81; H, 4.47; N, 1.09. Found: C, 59.83; H, 4.74; N, 1.07.

General Procedure for the Allylic Alkylation of Cyclic Allylic Acetates (GP3). A mixture of $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ (0.5 mol %) and the corresponding ligand **5**−**8** (1.1 mol %) in dry THF (1 mL per mmol of substrate) was stirred for 15 min at room temperature. The corresponding allylic acetate was added, and the resulting mixture was stirred for 10 min at room temperature. Then dimethyl malonate (1 equiv) and BSA (1 equiv) were added. The reaction was started by the addition of NaOAc (0.03 equiv). After it was stirred for 1 h at 22 °C, the reaction mixture was filtered over Celite and the solvent removed in vacuo. The residue was subjected to column chromatography (silica, PE/Et_2O, 9/1).

(R)-Dimethyl 3-cyclohexenylmalonate: yield >99%, colorless oil; 87% ee (R)[25] as determined by GC (HRCG MEGA 2 serie HT system with a Bondex-UN-alpha+beta column; length of the column 20 m, i.d. 0.30 mm; film thickness 0.25 μm; carrier gas 0.4 bar of H_2; method 50 °C 1 min, ramp @ 10 °C min^{-1} until 80 °C, isotherm hold 1 min): R_t = 103.9 min (S) and 106.4 min (R).

$C_{11}H_{16}O_4$, mol wt: 212.24. $[\alpha]_D^{23}$ = +32.1 (c 1.0 g dL^{-1}, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$, 21 °C): δ 5.76−5.72 (m, 1 H, HCCH), 5.49−5.47 (m, 1 H, HCC*H*), 3.71 (s, 3 H, OCH_3), 3.70 (s, 3 H, OCH_3), 3.25 (d, J = 9.5, 1 H, OC*H*CCO), 2.90−3.84 (m, 1 H, H_2CHCH), 1.98−1.91 (m, 2 H, CH_2), 1.77−1.65 (m, 2 H, CH_2), 1.58−1.49 (m, 1 H, CH_2), 1.37−1.30 (m, 1 H, CH_2). ^{13}C NMR (125 MHz, $CDCl_3$, 21 °C): δ 168.8, 168.7, 129.6, 127.2, 56.7, 52.3, 52.2, 35.3, 26.5, 24.8, 20.8. The analytical data are in agreement with literature data.[26]

(R)-Dimethyl 3-cyclopentenylmalonate: yield >99%, colorless oil; 91% ee (R)[25] as determined by ^{1}H NMR (300 MHz, C_6D_6) using (+)-Eu(hfc)$_3$ as a chiral shift reagent.

$C_{10}H_{14}O_4$, mol wt: 198.22. $[\alpha]_D^{23}$ = +73.5 (c 0.89 g dL^{-1}, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$, 21 °C): δ 5.82−5.80 (m, 1 H, HCCH), 5.64−5.62 (m, 1 H, HCC*H*), 3.71 (s, 6 H, OCH_3), 3.37−3.34 (m, 1 H, H_2CHCH), 3.26 (d, J = 9.5, 1 H, OC*H*CCO), 2.36−2.29 (m, 2 H, CH_2), 2.14−2.08 (m, 1 H, CH_2), 1.60−1.55 (m, 1 H, CH_2). ^{13}C NMR (125 MHz, $CDCl_3$, 21 °C): δ 169.1, 169.0, 133.0, 131.3, 56.6, 52.4, 52.3, 45.4, 31.7, 27.7. The analytical data are in agreement with literature data.[26]

(R)-Dimethyl 3-cycloheptenylmalonate: yield 80%, colorless oil; 90% ee (R)[25] as determined by GC (HRCG MEGA 2 serie HT system with a Bondex-UN-alpha+beta column; length of the column 20 m, i.d. 0.30 mm; film thickness 0.25 μm; carrier gas 0.4 bar of H_2; method 100 °C isotherm); R_t = 90.9 min (R) and 93.7 min (S).

$C_{12}H_{18}O_4$, mol wt: 226.27. $[\alpha]_D^{23}$ = +6.6° (c = 1.0 g dL^{-1}, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$, 21 °C): δ 5.82−5.77 (m, 1 H, HCCH), 5.57−5.54 (m, 1 H, HCC*H*), 3.71 (s, 3 H, OCH_3), 3.69 (s, 3 H, OCH_3), 3.44 (d, J = 8.5, 1 H, OC*H*CCO), 3.03−2.99 (m, 1 H, H_2CHCH), 2.12−2.10 (m, 2 H, CH_2), 1.93−1.89 (m, 1 H, CH_2), 1.66−1.56 (m, 3 H, CH_2), 1.37−1.28 (m, 2 H, CH_2). ^{13}C NMR (125 MHz, $CDCl_3$, 21 °C): δ 169.1, 168.9, 132.8, 132.7, 56.7, 52.3, 52.2, 39.6, 30.9, 30.1, 28.3, 26.2. The analytical data are in agreement with literature data.[26]

(R)-Dimethyl 2-(5,5-dimethylcyclohex-2-en-1-yl)malonate: yield >99%, colorless oil; 74% ee as determined by GC (HRCG MEGA 2 serie HT system with a Bondex-UN-alpha+beta column; length of the column 20 m, i.d. 0.30 mm; film thickness 0.25 μm; carrier gas 0.4 bar of H_2, method 50 °C 1 min, ramp @ 10 °C min^{-1} until 110 °C, isotherm hold 1 min); R_t = 44.7 min (S) and 45.6 min (R).

$C_{13}H_{20}O_4$, mol wt: 240.30. $[\alpha]_D^{23}$ = +2.1° (c = 1.0 g dL^{-1}, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$, 21 °C): δ 5.72−5.68 (m, 1 H, HCCH), 5.50−5.47 (m, 1 H, HCC*H*), 3.748 (s, 3 H, OCH_3), 3.743 (s, 3 H, OCH_3), 3.25 (d, J = 9.0, 1 H, OC*H*CCO), 2.98−2.86 (m, 1 H, H_2CHCH), 1.83−1.75 (m, 2 H, CH_2), 1.43−1.39 (m, 1 H, CH_2), 1.16 (m, 1 H, CH_2), 0.95 (s, 1 H, CH_3), 0.91 (s, 1 H, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$, 21 °C): δ169.1, 128.3, 126.0, 56.7, 52.5, 39.7, 38.8, 34.5, 32.0, 29.7, 25.2. HRMS (ESI): m/z calcd for $[M + Na]^+ = C_{13}H_{20}NaO_4$, 263.1254; found, 263.1263.

■ ASSOCIATED CONTENT

Supporting Information

Figures giving NMR spectra of new compounds and determinations of enantiomeric excesses and CIF files giving crystallographic data for **9a**,**b** and **13**. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail for R.P.: rene.peters@oc.uni-stuttgart.de.

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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