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ortho-Silylation of 2,2′-bis(oxazolinyl)-1,1′-bis(diphenylphosphino)ferrocenes and remarkable effect of the silyl groups on the enantioselectivity in Pd-catalyzed asymmetric allylic alkylation

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Abstract

ortho-Silylation of chiral 2,2′-bis(oxazolinyl)-1,1′-bis(diphenylphosphino)ferrocenes (**1**) provided monosilylated derivatives, which were employed as chiral ligands in the Pd-catalyzed asymmetric allylic alkylation of 1,3-diphenylprop-2-enyl acetate with dimethyl malonate. The major product has (*S*)-configuration in the reactions employing three diastereomers **1** and the monosilylated ligand derived from the (S,S,$_P S$,$_P S$)-diastereomer (up to 99% *ee*). In sharp contrast, the enantioselectivity was reversed to give (*R*)-product in the reactions with the ligands derived from the (S,S,$_P R$,$_P R$)-diastereomer (up to 96% ee).

Keywords: Catalysis; Palladium; Ferrocene; Silylation; Enantioselectivity

1. Introduction

Various chiral ferrocene derivatives have been proved as effective ligands in many asymmetric catalytic reactions [1]. In particular, those with chiral oxazolinyl substituents are attractive due to easy preparation from readily available chiral aminoalcohols and selective derivatization by oxazoline-directed *ortho*-lithiations followed by the reactions with diverse electrophiles. Recently, several groups including ours have reported the synthesis of such ferrocene-based chiral ligands [2]. Of particular interest are three 1,1′-diphosphorylated diastereomers: ($_P S$,$_P S$)-, ($_P R$,$_P R$)-, and ($_P R$,$_P S$)-**1**. These can be stereoselectively synthesized by simple variation of reaction conditions for the phosphorylation of 1,1′-bis[(*S*)-(4-isopropyloxazolin-2-yl)ferrocene (Fig. 1) [3].

In Pd-catalyzed asymmetric allylic alkylations with **1** (Scheme 1) [4,5], (*S*)-**5** is given as the major product despite the difference in their planar chiralities. Meanwhile, the enantioselectivity was reversed when 1,1′,3,3′-tetraphosphorylated derivative **2** was employed as a chiral ligand, although the selectivity for (*R*)-**5** is only 27% ee. However, this result is one of the rare examples that demonstrates the control of absolute configuration in metal-catalyzed asymmetric reactions by using the ligands derived from a single enantiomer [6]. Now we describe the success in enhancing the selectivity for (*R*)-**5** up to 96% ee by the use of new ligands ($_P R$,$_P R$)-**3** readily derived from ($_P R$,$_P R$)-**1**.

2. Results and discussion

Tetraphosphorylated ligand **2** was synthesized from 1,1′-bis((*S*)-(4-isopropyloxazolin-2-yl))ferrocene by treatment with four equivalents of *tert*-butyllithium and subsequent reaction with excess chlorodiphenylphosphine. Ligands **3**, **6**, and **7** were prepared from **1** as shown in Scheme 2. Monophosphorylations of ($_P R$,$_P R$)-**1** and ($_P S$,$_P S$)-1 provided 1,1′,3-triphosphorylated derivatives ($_P R$)-**6** and ($_P S$)-**6**, respectively. Notably, the

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monophosphorylation of ($_P R,_P S$)-**1** afforded a mixture of ($_P R$)-**6** and ($_P S$)-**6** in a 13:1 ratio. Silylated derivatives **3** and **7** were also prepared through the lithiation of **1** by controlling the equivalents of *sec*-butyllithium: ($_P S,_P S$)-**3a** was prepared from ($_P S,_P S$)-**1**, and ($_P R,_P R$)-**3a**–**c** and **7** from ($_P R,_P R$)-**1**.

Bis(π-allylpalladium chloride) and the new ligands (**2**, **3**, **6**, and **7**) were combined in a 1:2 molar ratio to form the corresponding 1:1 Pd-complexes as the chiral catalysts in the asymmetric allylic alkylation reactions. In Table 1, the results are summarized and compared with the previous ones from the reactions with ($_P S,_P S$)-**1**, ($_P R,_P R$)-**1**, and ($_P R,_P S$)-**1**. In all reactions, alkylation product **5** was formed in excellent yields within 10 min at room temperature. Remarkably, (*R*)-**5** was produced in 88% ee in the reaction with ($_P R$)-**6** while the use of ($_P S$)-**6** led to the production of (*S*)-**5** in 96% ee. A similar contrast in enantioselectivity was observed in the reactions with silylated ligands ($_P R,_P R$)-**3a** and ($_P S,_P S$)-**3a**. The selectivity for (*R*)-**5** was slightly increased when the trimethylsilyl substituent of ($_P R,_P R$)-**3a** was replaced with a triethylsilyl group, but a negligible change was resulted from the replacement of the triethylsilyl group with triphenylsilyl one. Lowering reaction temperature enhanced the selectivity, although extension of reaction time was needed: The selectivity for (*R*)-**5** was increased to 96% ee by using ($_P R,_P R$)-**3b** at 0 °C. Disilylated ligand **7** behaved like tetraphosphorylated ligand **2** to give (*R*)-**5** only in 27% ee. Above results implicate that introducing steric substituents at 3-position of ($_P R,_P R$)-**1** is crucial to reverse the enantioselectivity in the alkylation reaction, but the additional steric effect of the 3′-substituent counterbalances the reversal. Meanwhile, the steric effect of 3-substituent of ($_P S,_P S$)-**1** increases the reactivity as well as the enantioselectivity for the (*R*)-product.

For the allylpalladium complexes coordination modes of our ligands were estimated by ^{31}P-NMR. The

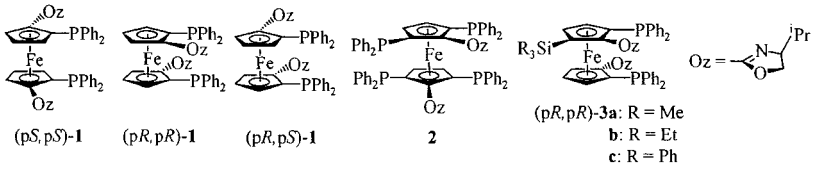
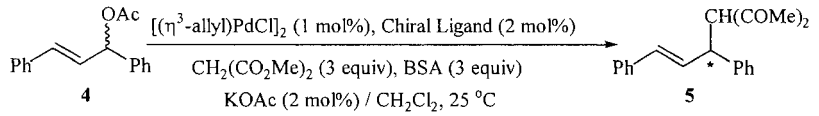
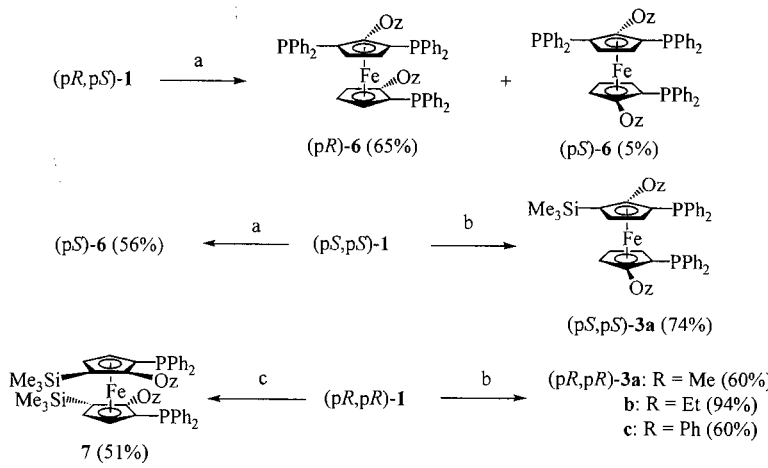


Fig. 1. Chiral ferrocene ligands derived from 1,1′-bis(oxazolinyl)ferrocene.



Scheme 1. Pd-catalyzed allylic alkylation of *rac*-(*E*)-1,3-diphenylpro-2-enyl acetate.



a: 1) *sec*-BuLi (1.2 equiv)/Et_2O, -78-25 °C, 2 h. 2) $ClPPh_2$ (1.3 equiv)

b: 1) *sec*-BuLi (1.2 equiv)/Et_2O, -78-25 °C, 2 h. 2) $ClSiR_3$ (1.3 equiv)

c: 1) *sec*-BuLi (2.2 equiv)/Et_2O, -78-25 °C, 3.5 h. 2) $ClSiR_3$ (2.3 equiv)

Scheme 2. Selective derivatization of diphosphorylated derivatives **1**.

Table 1
Enantioselective Pd-catalyzed allylic alkylations with chiral ferrocene ligands

Entry	Ligand	Reaction time (min) [a]	% ee [b] (abs. config.) [c]	Yield (%) [d]
1 [e]	($_P S$,$_P S$)-**1**	30	92 (*S*)	92
2 [e]	($_P R$,$_P S$)-**1**	10	99 (*S*)	99
3 [e]	($_P R$,$_P R$)-**1**	10	38 (*S*)	99
4	**2**	10	27 (*R*)	97
5	($_P S$)-**6**	10	96 (*S*)	98
6	($_P R$)-**6**	10	88 (*R*)	97
7	($_P S$,$_P S$)-**3a**	10	96 (*S*)	99
8	($_P R$,$_P R$)-**3a**	10	89 (*R*)	99
9	($_P R$,$_P R$)-**3b**	10	91 (*R*)	99
10	($_P R$,$_P R$)-**3c**	10	91 (*R*)	98
11	($_P R$,$_P R$)-**3b** [f]	120	96 (*R*)	98
12	**7**	10	27 (*R*)	99

[a] 0.3 M allylic acetate in CH_2Cl_2.
[b] Determined by HPLC (Chiralcel OD).
[c] The absolute configuration was assigned by comparison of the optical rotation with literature values.
[d] Isolated yields by column chromatography on SiO_2.
[e] See Ref. [5].
[f] At 0 °C.

resonance peaks for coordinated phosphino groups were shifted distinctly to down fields from those of free phosphino groups. Apparently, X-ray diffraction analysis revealed that the *tert*-butyl analog of ($_P S$,$_P S$)-**1**, which showed a parallel complexation behavior and afforded an almost same reactivity (94% ee for (*S*)-**5** in 99% yield) as ($_P S$,$_P S$)-**1**, is a P,P-chelate in its π-allylpalladium complex **8** (Fig. 2) [7]. Thus, the coordination modes of silylated ligands **3** and **7** in their allylpalladium complexes were assigned as P,P-chelations. The P,P-chelating phosphino groups and free ones were distinguished clearly in the ^{31}P-NMR spectra of the π-allylpalladium complexes of **2**, ($_P R$)-**6**, and ($_P S$)-**6**. However, the complexations with [(η^3-1,3-diphenylallyl)PdCl]$_2$ produced mixtures to complicate the regions for N,P-chelations [8]. N,P-Chelations appeared to be major in the case of ($_P R$,$_P R$)-**3a**, while a P,P-chelation was predominant for ($_P S$,$_P S$)-**3a** with reflecting the P,P-chelation in the resonance coupling between two phosphorus atoms (Fig. 3). For **7** populations of a P,P-chelation and N,P-chelations were comparable.

The enantioselectivity of the alkylation reaction was little affected by the palladium source, [(η^3-allyl)PdCl]$_2$ or [(η^3-1,3-diphenylallyl)PdCl]$_2$. Thus, the characteristic difference in complexation behavior observed in the ^{31}P-NMR spectra of the (η^3-1,3-diphenylallyl)palladium complexes would be responsible for the enantioselectivity change, although the composition of palladium species is not directly correlated with the resulting enantioselectivity. In fact, a reversal of enantioselectivity has been reported for the same alkylation reaction using N,P-ligands that have a chiral oxazolinyl group and a binaphthyl or a ferrocene backbone [6a,9]. Particularly, the reversal has been explained by the change in the ratio of two rotomers formed by the complexation with $Pd(CH_3CN)_2Cl_2$ for the 1,1′-*N*,*P*-ferrocene ligands having a trimethylsilyl group adjacent to the oxazolinyl group [6a]. This example provides a clue to the connection between the selectivity for (*R*)-**5** and the N,P-chelating behavior of ($_P R$,$_P R$)-**3**.

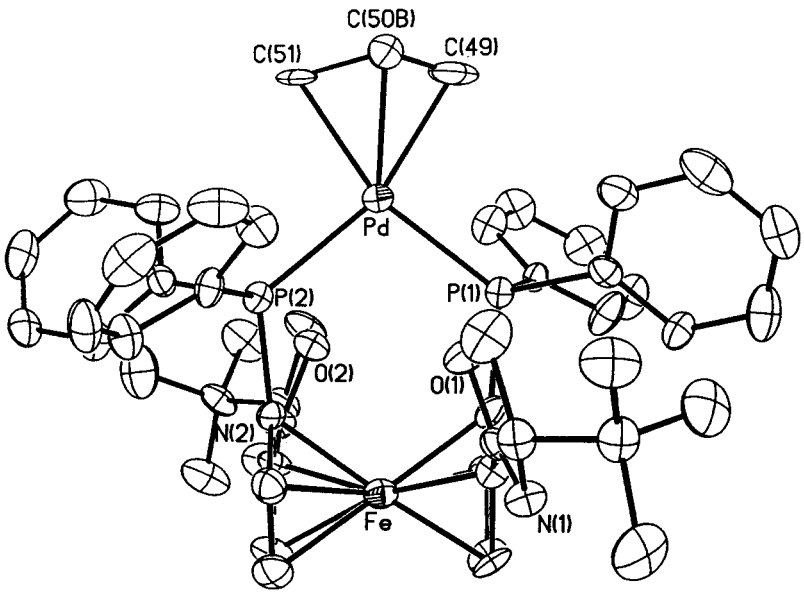


Fig. 2. X-ray structure of **8**. Selected bond distances (Å): Pd–P(1) = 2.336(3), Pd–P(2) = 2.337(4), Pd–C(49) = 2.218(13), Pd–C(50B) = 2.23(3), Pd–C(51) = 2.197(13), C(49)–C(50B) = 1.34(3), C(50B)–C(51) = 1.41(3). Selected bond angles (°): P(1)–Pd–P(2) = 102.77(12), P(1)–Pd–C(49) = 99.6(5), P(2)–Pd–C(51) = 95.1(4), C(49)–C(50B)–C(51) = 121(2). Counter anion (PF_6^-), two solvent molecules (CH_2Cl_2), and the disordered central carbon atom (C(50A)) of the allyl moiety are omitted for clarity.

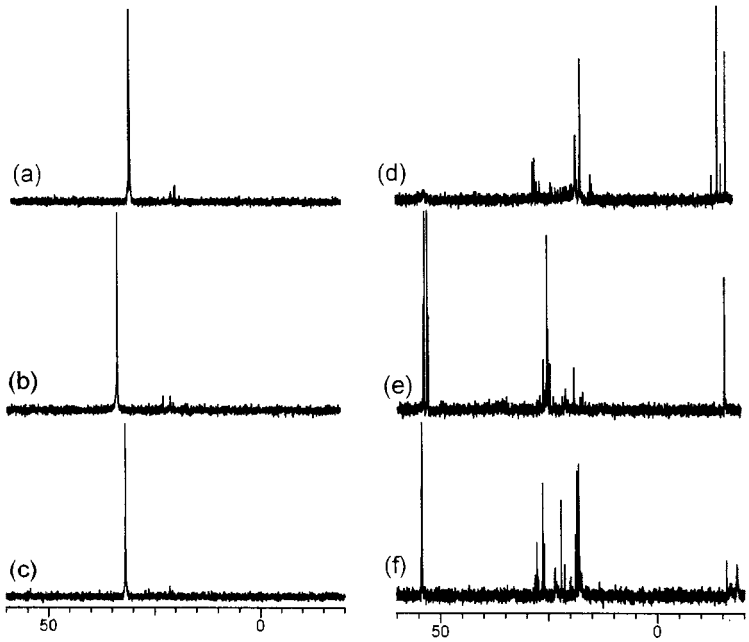


Fig. 3. ^{31}P-NMR spectra of π-allylpalladium complexes chelated with chiral ligands: (a) [(η^3-allyl)Pd(($_P R,_P R$)-**3a**)]Cl; (b) [(η^3-allyl)Pd(($_P S,_P S$)-**3a**)]Cl; (c) [(η^3-allyl)Pd(7)]Cl; (d) [(η^3-1,3-diphenylallyl)Pd(($_P R,_P R$)-**3a**)]Cl; (e) [(η^3-1,3-diphenylallyl)Pd(($_P S,_P S$)-**3a**)]Cl; (f) [(η^3-1,3-diphenylallyl)Pd(**7**)]Cl.

3. Conclusions

In summary, we have synthesized new ferrocene-based chiral ligands **2**, **3**, **6**, and **7** through phosphorylation and silylation of 2,2′-bis(oxazolinyl)-1,2′-bis(diphenylphosphino)ferrocenes **1**. A remarkable reversal of enantioselectivity to give the (*R*)-product has been demonstrated in the standard Pd-catalyzed allylic alkylation by using monosilylated ligands ($_P R,_P R$)-**3** and triphosphorylated ligand ($_P R$)-**6**. The complexation behaviors of the ligands have been investigated by ^{31}P-NMR to show that N,P-chelations in the (1,3-diphenylallyl)palladium complexes of ($_P R,_P R$)-**3a** are distinctive feature in comparison with the predominant P,P-chelation mode of ($_P S,_P S$)-**3a**.

4. Experimental

4.1. General

All manipulations except workup and purification were carried out under an atmosphere of argon using standard Schlenk techniques. Et_2O and THF were distilled from sodium–benzophenone ketyl. 2,2′-Bis(oxazolinyl)-1,1′-bis(diphenylphosphino)ferrocenes **1** and the *tert*-butyl analog of ($_P S,_P S$)-**1** [3], [(η^3-allyl)PdCl]$_2$ [10], and [(η^3-1,3-diphenylallyl)PdCl]$_2$ [11] were prepared according to the literature procedures. Butyllithiums were purchased from Aldrich and titrated with diphenylacetic acid.

If not otherwise stated, all NMR spectra were recorded in $CDCl_3$ with a Bruker AM 300 or DPX 300 spectrometer. Chemical shifts are given in δ ppm downfield from Me_4Si (δ 0, ^{1}H) or $CDCl_3$ (δ 77, ^{13}C) as an internal standard, and from aqueous 85% phosphoric acid solution (δ 0, ^{31}P) as an external standard. IR spectra were taken for the thin films of samples on NaCl plates. Optical rotations were measured at 589 nm (sodium D line). Specific rotations ([α]) are reported in degrees per decimeter at room temperature (r.t.), and the concentration (c) is given in grams per 100 ml in the specified solvent. Electron impact mass spectra were recorded on a JEOL JMS-AX505WA. Melting points were measured on a Thomas Hoover capillary melting point apparatus and are not corrected. Elemental analyses were performed by the Center for Biofunctional Molecules, Pohang University of Science and Technology.

4.2. 2,2′-Bis[(S)-(4-isopropyloxazolin-2-yl)]-1,1′,3,3′-tetra(diphenylphosphino)ferrocene (2)

To a solution of 1,1′-bis((*S*)-(4-isopropyloxazolin-2-yl))ferrocene (280 mg, 0.686 mmol) in Et_2O (12 ml) *tert*-butyllithium (1.7 M, 1.69 ml, 2.9 mmol) was added dropwise at −78 °C, and the resulting mixture was stirred at −78 °C for 2 h, and at 25 °C for 0.5 h. Then, chlorodiphenylphosphine (0.542 ml, 3.02 mmol) was added, and the resulting mixture was stirred at 25 °C for 1 h. The product mixture was diluted with Et_2O and quenched with the saturated aqueous

$NaHCO_3$ solution. The organic layer was separated and the aqueous layer was extracted twice with Et_2O. The combined ether solution was dried over $MgSO_4$, concentrated, and chromatographed on silica gel (elution solvent: hexane–ethyl acetate) under an argon atmosphere to give 188 mg (0.165 mmol, 24%) of **2** as a red gum, which was recrystallized from hexane at 0 °C; m.p. = 141–143 °C. ^{1}H-NMR: $\delta = 7.50$ (m, 4H), 7.37–7.16 (m, 28H), 7.02 (m, 8H), 4.46 (m, 2H), 4.01 (d, $J = 2.4$ Hz, 2H), 3.91 (m, 2H), 3.23 (t, $J = 8.1$ Hz, 2H), 3.16 (br s, 2H), 1.10 (m, 2H), 0.30 (d, $J = 6.7$ Hz, 6H), 0.20 (d, $J = 6.7$ Hz, 6H). ^{13}C-NMR: $\delta = 163.15$, 140.61 (d, $J_{C-P} = 13.5$ Hz), 139.81 (d, $J_{C-P} = 11.3$ Hz), 139.61 (d, $J_{C-P} = 14.6$ Hz), 139.26 (d, $J_{C-P} = 17.4$ Hz), 135.25 (d, $J_{C-P} = 21.8$ Hz), 134.99 (d, $J_{C-P} = 20.7$ Hz), 134.45 (d, $J_{C-P} = 22.0$ Hz), 133.28 (d, $J_{C-P} = 18.9$ Hz), 129.23, 128.94 (d, $J_{C-P} = 8.6$ Hz), 128.92, 128.75 (d, $J_{C-P} = 8.1$ Hz), 128.66, 128.41 (d, $J_{C-P} = 6.6$ Hz), 128.16 (d, $J_{C-P} = 6.3$ Hz), 127.97, 90.92 (d, $J_{C-P} = 27.3$ Hz), 84.16 (d, $J_{C-P} = 2.1$ Hz), 81.29 (m), 78.51, 74.61, 72.87, 70.45, 32.71, 18.82, 18.12. ^{31}P-NMR: $\delta = -16.70$, -17.78. IR (NaCl, cm^{-1}): ν(C=N) 1648 (s). $[\alpha]_D^{18} = +384.2°$ ($c = 0.43$, $CHCl_3$); FABMS; m/z: 1145. Anal. Found: C, 73.53; H, 5.74; N, 2.41. Calc. for $C_{70}H_{64}N_2O_2P_4Fe$: C, 73.43; H, 5.63; N, 2.45%.

*4.3. 2,2′-Bis[(S)-(4-isopropyloxazolin-2-yl)]-($_P$R,$_P$R)-1,1′-bis(diphenylphosphino)-3-(trimethylsilyl)ferrocene (($_P$R,$_P$R)-**3a**)*

To a solution of ($_P$R,$_P$R)-**1** (200 mg, 0.258 mmol) in Et_2O (6 ml) *sec*-butyllithium (1.3 M, 0.26 ml, 0.34 mmol) was added dropwise at −78 °C, and the resulting solution was stirred at −78 °C for 1.5 h, and at 25 °C for 0.5 h. Then, chlorotrimethylsilane (0.046 ml, 0.36 mmol) was added, and the resulting mixture was stirred at 25 °C for 3 h. The reaction mixture was diluted with Et_2O and quenched with saturated aqueous $NaHCO_3$ solution. The organic layer was separated and the aqueous layer was extracted twice with ether. The combined ether solution were dried over $MgSO_4$, concentrated, and chromatographed on silica gel (elution solvent: hexane–ethyl acetate) under an argon atmosphere to give 131 mg (0.155 mmol, 60%) of ($_P$R,$_P$R)-**3a** as a red gum, which was crystallized from hexane at −20 °C; m.p. = 146–148 °C; ^{1}H-NMR: $\delta = 7.29–7.24$ (m, 6H), 7.17–7.08 (m, 14H), 4.92 (t, $J = 1.2$ Hz, 1H), 4.71 (t, $J = 2.5$ Hz, 1H), 4.63 (d, $J = 2.4$ Hz, 1H), 3.93 (dd, $J = 9.2$, 7.6 Hz, 1H), 3.83 (m, 1H), 3.78–3.65 (m, 6H) 1.43 (m, 1H), 1.30 (m, 1H), 0.70 (d, $J = 6.7$ Hz, 3H), 0.59 (d, $J = 6.7$ Hz, 3H), 0.55 (d, $J = 6.7$ Hz, 3H), 0.48 (d, $J = 6.7$ Hz, 3H), 0.32 (s, 9H). ^{13}C-NMR: $\delta = 164.51$, 164.13, 140.38 (d, $J_{C-P} = 12.1$ Hz), 140.27 (d, $J_{C-P} = 12.3$ Hz), 138.59 (d, $J_{C-P} = 13.7$ Hz), 138.42 (d, $J_{C-P} = 12.2$ Hz), 135.69 (d, $J_{C-P} = 22.5$ Hz), 135.67 (d, $J_{C-P} = 22.7$ Hz), 132.89 (d, $^2J_{C-P} = 19.6$ Hz), 132.75 (d, $J_{C-P} = 19.9$ Hz), 129.67, 128.91, 128.81, 128.76, 128.65, 128.54, 128.45, 128.30, 84.25, 80.97 (d, $J_{C-P} = 11.4$ Hz), 80.71 ($J_{C-P} = 20.1$ Hz), 78.35, 76.25, 75.27, 73.82, 73.42, 69.95, 69.81, 33.45, 33.08, 19.39, 19.23, 18.75, 18.46, 0.92. ^{31}P-NMR: $\delta = -16.10$ (d, $J = 3.3$ Hz), -18.16 (d, $J = 3.3$ Hz). IR (NaCl, cm^{-1}): ν(C=N) 1652. FABMS; m/z: 849. Anal. Found: C, 69.01; H, 6.91; N, 3.10. Calc. for $C_{49}H_{54}N_2O_2P_2SiFe$: C, 69.33; H, 6.41; N, 3.30%.

*4.4. 2,2′-Bis[(S)-(4-isopropyloxazolin-2-yl)]-($_P$S,$_P$S)-1,1′-bis(diphenylphosphino)-3-(trimethylsilyl)ferrocene (($_P$S,$_P$S)-**3a**)*

Compound ($_P$S,$_P$S)-**3a** (162 mg, 0.191 mmol, 74%) was obtained as a red solid from ($_P$S,$_P$S)-**1** (200 mg, 0.258 mmol) and chlorotrimethylsilane (0.046 ml, 0.3 6 mmol) according to the procedure for ($_P$R,$_P$R)-**3a**; m.p. = 82–85 °C. ^{1}H-NMR: $\delta = 7.31–7.10$ (m, 20H), 5.07 (br s, 1H), 4.69 (t, $J = 2.5$ Hz, 1H), 4.14 (dd, $J = 9.4$, 8.5 Hz, 1H) 4.10 (dd, $J = 9.2$, 8.3 Hz, 1H), 3.78 (d, $J = 2.1$ Hz, 1H), 3.71 (m, 1H), 3.70 (br s, 1H), 3.70 (br s, 1H), 3.58 (m, 1H), 3.21 (dd, $J = 8.6$, 6.3 Hz, 1H), 3.18 (dd, $J = 8.4$, 6.1 Hz, 1H), 1.55 (m, 1H), 1.29 (m, 1H), 0.75 (d, $J = 6.6$ Hz, 3H), 0.73 (d, $J = 6.7$ Hz, 3H), 0.68 (d, $J = 6.7$ Hz, 3H), 0.47 (d, $J = 6.8$ Hz, 3H), 0.31 (s, 9H). ^{13}C-NMR: $\delta = 165.31$, 163.93, 140.11 (d, $J_{C-P} = 13.2$ Hz), 140.06 (d, $J_{C-P} = 11.9$ Hz), 138.44 (d, $J_{C-P} = 15.8$ Hz), 137.96 (d, $J_{C-P} = 13.2$ Hz), 135.40 (d, $J_{C-P} = 22.3$ Hz), 132.94 (d, $J_{C-P} = 20.3$ Hz), 129.65 (d, $J_{C-P} = 3.4$ Hz), 128.91, 128.81, 128.72, 128.63, 128.51, 84.54 (d, $J_{C-P} = 15.4$ Hz), 81.19 (d, $J_{C-P} = 3.8$ Hz), 80.92 (d, $J_{C-P} = 15.5$ Hz), 78.24, 77.91, 76.73 (d, $J_{C-P} = 6.4$ Hz), 76.34, 74.75, 73.34, 72.59, 70.74, 69.83 33.01, 32.22, 19.84, 19.41, 17.88, 0.45. ^{31}P-NMR: $\delta = -15.39$ (d, $J = 2.1$ Hz), -15.75 (d, $J = 2.6$ Hz). IR (NaCl, cm^{-1}) ν(C=N) 1651. $[\alpha]_D^{22} = -39.4°$ ($c = 0.80$, $CHCl_3$). FABMS; m/z: 849. Anal. Found: C, 70.1; H, 6.32; N, 3.14. Calc. for $C_{49}H_{54}N_2O_2P_2SiFe$: C, 69.33; H, 6.41; N, 3.30%.

*4.5. 2,2′-Bis[(S)-(4-isopropyloxazolin-2-yl)]-($_P$R,$_P$R)-1,1′-bis(diphenylphosphino)-3-(triethylsilyl)ferrocene (($_P$R,$_P$R)-**3b**)*

Compound ($_P$R,$_P$R)-**3b** (193 mg, 0.217 mmol, 94%) was obtained as a red solid from ($_P$R,$_P$R)-1 (180 mg, 0.231 mmol) and chlorotriethylsilane (0.054 ml, 0.32 mmol) according to the procedure for ($_P$R)-**3a**; m.p. = 83–85 °C. ^{1}H-NMR: $\delta = 7.35–7.25$ (m, 6H), 7.17–7.07 (m, 14H), 4.87 (t, $J = 1.2$ Hz, 1H), 4.69 (t, $J = 2.5$ Hz, 1H), 4.58 (d, $J = 2.5$ Hz, 1H), 3.88 (dd, $J = 9.5$, 7.8 Hz, 1H), 3.83–3.66 (m, 5H), 3.75 (d, $J = 2.5$ Hz, 1H), 3.68 (br s, 1H), 1.39 (m, 1H), 1.33 (m, 1H), 1.00–0.84 (m, 15H), 0.64 (d, $J = 6.7$ Hz, 3H), 0.59 (d, $J = 6.6$ Hz, 3H), 0.57 (d, $J = 6.7$ Hz, 3H), 0.49 (d, $J = 6.7$ Hz, 3H).

^{13}C-NMR: $\delta = 164.53$, 164.21, 140.60 (d, $J_{C-P} = 10.6$ Hz), 140.33 (d, $J_{C-P} = 12.6$ Hz), 138.76 (d, $J_{C-P} = 14.0$ Hz), 138.55 (d, $J_{C-P} = 14.0$ Hz), 135.76 (d, $J_{C-P} = 22.1$ Hz), 132.95 (d, $J_{C-P} = 19.7$ Hz), 132.92 (d, $J_{C-P} = 19.7$ Hz), 129.58 (d, $J_{C-P} = 4.8$ Hz), 128.82, 128.72, 128.62, 128.53, 128.44, 128.29, 128.26, 84.95 (d, $J_{C-P} = 16.5$ Hz), 81.32, 80.83 ($J_{C-P} = 17.8$ Hz), 80.28 ($J_{C-P} = 12.0$ Hz), 79.03, 78.66, 77.90, 76.32, 75.54, 74.91, 73.83, 73.30, 70.00, 69.84, 33.38, 33.08, 19.27, 19.11, 18.69, 18.55, 8.73, 4.98. ^{31}P-NMR: $\delta = -17.36$ (d, $J = 6.5$ Hz), -18.60 (d, $J = 6.7$ Hz). IR (NaCl, cm^{-1}): ν(C=N) 1653. $[\alpha]_D^{20} = +190.6$ ° ($c = 0.65$, $CHCl_3$). FABMS; m/z: 891. Anal. Found: C, 70.21; H, 6.53; N, 3.02. Calc. for $C_{52}H_{60}N_2O_2P_2SiFe$: C, 70.10; H, 6.79; N, 3.14%.

4.6. 2,2′-Bis[(S)-(4-isopropyloxazolin-2-yl)]-($_P$R,$_P$R)-1,1′-bis(diphenylphosphino)-3-(triphenylsilyl)ferrocene (($_P$R,$_P$R)-**3c**)

Compound ($_P$R,$_P$R)-**3c** (132 mg, 0.128 mmol, 60%) was obtained as a red solid from ($_P$R,$_P$R)-**1** (165 mg, 0.213 mmol) and chlorotriphenylsilane (78 mg, 0.30 mmol) according to the procedure for ($_P$R, $_P$R)-**3a**; m.p. = 158 °C (dec.). ^{1}H-NMR: $\delta = 7.62–7.16$ (m, 35H), 4.83 (s, 1H), 4.62 (t, $J = 2.4$ Hz, 1H), 4.48 (d, $J = 2.4$ Hz, 1H), 3.84 (d, $J = 2.4$ Hz, 1H), 3.65 (br s, 1H), 3.56 (m, 2H), 3.24 (m, 2H) 2.97 (m, 1H), 2.84 (m, 1H), 0.90 (m, 1H), 0.83 (m, 1H), 0.53 (d, $J = 6.6$ Hz, 3H), 0.42 (d, $J = 6.7$ Hz, 3H), 0.22 (d, $J = 6.7$ Hz, 6H). ^{13}C-NMR: $\delta = 163.48$ (d, $J_{C-P} = 3.3$ Hz), 163.32 (d, $J_{C-P} = 3.3$ Hz), 140.68 (d, $J_{C-P} = 11.2$ Hz), 140.08 (d, $J_{C-P} = 14.4$ Hz), 139.00 (d, $J_{C-P} = 15.9$ Hz), 138.91 (d, $J_{C-P} = 15.9$ Hz), 137.10, 136.71, 136.60, 136.34, 135.91, 135.67, 135.45, 133.45 (d, $J_{C-P} = 20.4$ Hz), 133.24 (d, $J_{C-P} = 19.7$ Hz), 130.77, 129.47, 129.18, 128.70, 128.61, 128.52, 128.41, 128.32, 128.19, 128.02, 86.64 (d, $J_{C-P} = 19.7$ Hz), 83.40, 82.73 (d, $J_{C-P} = 21.2$ Hz), 82.43 (d, $J_{C-P} = 13.2$ Hz), 79.44, 78.39, 76.12 (d, $J_{C-P} = 3.4$ Hz), 75.35, 75.03, 73.71, 73.55, 73.00, 70.34, 69.28, 33.17, 32.99, 19.35, 19.02, 18.99, 18.60. ^{31}P-NMR: $\delta = -19.80$ (d, $J = 18.3$ Hz), -21.05 (d, $J = 18.4$ Hz). IR (NaCl, cm^{-1}): ν(C=N) 1654. $[\alpha]_D^{20} = +95.0°$ ($c = 0.20$, $CHCl_3$). FABMS; m/z: 1036. Anal. Found: C, 74.17; H, 5.65; N, 2.84. Calc. for $C_{64}H_{60}N_2O_2P_2SiFe$: C, 74.27; H, 5.84; N, 2.71%.

4.7. 2,2′-Bis[(S)-(4-isopropyloxazolin-2-yl)]-($_P$S)-1,1′,3-tris(diphenylphosphino)ferrocene (($_P$S)-**6**)

Compound ($_P$S)-**6** (146 mg, 0.152 mmol, 56%) was obtained as a red solid from ($_P$S,$_P$S)-1 (210 mg, 0.271 mmol) and chlorodiphenylphosphine (0.065 ml, 0.36 mmol) according to the procedure for ($_P$R,$_P$R)-**3a**; m.p. = 117–120°C. ^{1}H-NMR: $\delta = 7.54$ (m, 4H), 7.44 (m, 2H), 7.31–7.20 (m, 24H), 4.89 (s, 1H), 4.59 (t, $J = 2.5$ Hz, 1H), 4.09 (dd, $J = 9.5$, 8.3 Hz, 1H), 4.00 (d, $J = 2.5$Hz, 1H), 3.88 (dd, $J = 9.5$, 8.0 Hz, 1H), 3.75 (s, 1H), 3.74 (m, 1H), 3.65 (m, 1H), 3.63 (d, $J = 2.6$ Hz, 1H), 3.67 (t, $J = 8.5$ Hz, 1H), 3.30 (t, $J = 7.7$ Hz, 1H), 1.51 (m, 1H), 1.06 (m, 1H), 0.75 (d, $J = 6.8$ Hz, 3H), 0.48 (d, $J = 6.7$ Hz, 3H), 0.31 (d, $J = 6.7$ Hz, 3H), 0.26 (d, $J = 6.7$ Hz). ^{13}C-NMR: $\delta = 164.78$, 163.33, 140.31 (d, $J_{C-P} = 13.0$ Hz), 140.14 (d, $J_{C-P} = 12.6$ Hz), 139.25 (d, $J_{C-P} = 15.6$ Hz), 138.89 (d, $J_{C-P} = 15.4$ Hz), 138.57 (d, $J_{C-P} = 15.0$ Hz), 135.86 (d, $J_{C-P} = 16.2$ Hz), 135.74 (d, $J_{C-P} = 23.5$ Hz), 135.62 (d, $J_{C-P} = 20.7$ Hz), 133.61 (d, $J_{C-P} = 20.2$ Hz), 133.56 (d, $J_{C-P} = 20.9$ Hz), 133.49 (d, $J_{C-P} = 19.9$ Hz), 129.35, 129.28, 128.94, 128.85, 128.67, 128.58, 128.44, 128.36, 87.40 (d, $J_{C-P} = 22.0$ Hz), 85.48 (d, $J_{C-P} = 21.1$ Hz), 84.20 (d, $J_{C-P} = 21.1$ Hz), 77.93, 77.15, 76.68, 76.23, 75.54, 74.23, 72.72, 72.61, 70.03, 32.80, 32.57, 19.89, 18.58, 18.19, 18.00. ^{31}P-NMR: $\delta = -17.59$, -19.67 (d, $J = 17.1$ Hz), -20.29 (d, $J = 17.0$ Hz). IR (NaCl, cm^{-1}): ν(C=N) 1650. $[\alpha]_D^{18} = +205.5°$ ($c = 0.82$, $CHCl_3$). FABMS; m/z: 961. Anal. Found: C, 72.10; H, 5.82; N, 2.83. Calc. for $C_{58}H_{55}N_2O_2P_3Fe$: C, 72.50; H, 5.71; N, 2.91%.

4.8. 2,2′-Bis[(S)-(4-isopropyloxazolin-2-yl)]-($_P$R)-1,1′,3-tris(diphenylphosphino)ferrocene (($_P$R)-**6**)

Compound ($_P$R)-**6** was obtained as a red solid from ($_P$R,$_P$R)-**1** (200 mg, 0.258 mmol) and chlorodiphenylphosphine (0.065 ml, 0.36 mmol) according to the procedure for ($_P$R,$_P$R)-**3a**; m.p. = 118–120°C. ^{1}H-NMR: $\delta = 7.61$ (m, 2H), 7.40–7.06 (m, 28H), 4.96 (s, 1H), 4.75 (t, $J = 2.5$ Hz, 1H), 4.40 (m, 1H), 4.05–3.94 (m, 3H), 4.02 (br s, 1H), 3.70 (m, 1H), 3.36 (t, $J = 1.8$ Hz, 1H), 3.28 (d, $J = 2.5$ Hz, 1H), 3.13 (t, $J = 8.0$ Hz), 1.56 (m, 1H), 0.97 (m, 1H), 0.66 (d, $J = 6.7$ Hz, 3H), 0.26 (d, $J = 6.7$ Hz, 3H), 0.15 (d, $J = 6.7$ Hz, 3H). ^{13}C-NMR: $\delta = 163.83$, 163.24, 140.07 (d, $J_{C-P} = 14.5$ Hz), 139.78 (d, $J_{C-P} = 9.5$ Hz), 139.46 (d, $J_{C-P} = 13.1$ Hz), 139.20 (d, $J_{C-P} = 16.6$ Hz), 139.16 (d, $J_{C-P} = 17.2$ Hz), 138.66 (d, $J_{C-P} = 14.6$ Hz), 135.35 (d, $J_{C-P} = 21.3$ Hz), 135.15 (d, $J_{C-P} = 22.0$ Hz), 134.97 (d, $J_{C-P} = 19.8$ Hz), 134.36 (d, $J_{C-P} = 21.7$ Hz), 133.21 (d, $J_{C-P} = 19.8$ Hz), 133.15 (d, $J_{C-P} = 20.3$ Hz), 129.43, 129.21, 128.99, 128.91, 128.85, 128.78, 128.68, 128.53, 128.48, 128.45, 128.39, 128.28, 89.87 (d, $J_{C-P} = 25.7$ Hz), 83.61 (d, $J_{C-P} = 17.1$ Hz), 81.00 (d, $J_{C-P} = 22.2$ Hz), 79.85 (d, $J_{C-P} = 13.8$ Hz), 78.35, 77.23, 76.88 (d, $J_{C-P} = 7.1$ Hz), 75.81, 75.65, 73.56, 72.66, 70.54, 70.20, 33.54, 32.92, 19.14, 18.93, 18.66, 18.00. ^{31}P-NMR: $\delta = -17.63$, -18.38. IR (NaCl, cm^{-1}): ν(C=N) 1653. $[\alpha]_D^{19} = +492.1°$ ($c = 0.80$, $CHCl_3$). FABMS; m/z: 961. Anal. Found: C, 72.81; H, 6.01; N, 3.00. Calc. for $C_{58}H_{55}N_2O_2P_3Fe$: C, 72.50; H, 5.71; N, 2.91%.

4.9. 2,2′-Bis[(S)-(4-isopropyloxazolin-2-yl)]-($_P$R,$_P$R)-1,1′-bis(diphenylphosphino)-3,3′-bis(trimethylsilyl)-ferrocene (7)

Compound **7** (72 mg, 0.078 mmol, 51%) was obtained as a red solid from ($_P$R,$_P$R)-**1** (120 mg, 0.154 mmol) and chlorotrimethylsilane (0.051 ml, 0.40 mmol) according to the procedure for ($_P$R,$_P$R)-**3a**; m.p. = 220 °C (dec.). ^{1}H-NMR: $\delta = 7.32–6.99$ (m, 20H), 4.63 (d, 2.3 Hz, 2H), 3.91 (m, 2H), 3.67–3.56 (m, 4H), 3.39 (d, 2.3 Hz, 2H), 1.17 (m, 2H), 0.56 (d, $J = 6.7$ Hz, 6H), 0.49 (d, $J = 6.70$ Hz, 6H), 0.28 (s, 18H). ^{13}C-NMR: $\delta = 164.45$, 140.71 (d, $J_{C-P} = 16.5$ Hz), 139.72 (d, $J_{C-P} = 16.2$ Hz), 135.96 (t, $J_{C-P} = 11.5$ Hz), 132.85 (t, $J_{C-P} = 9.7$ Hz), 129.46, 128.52 (t, $J_{C-P} = 3.2$ Hz), 128.34 (t, $J_{C-P} = 3.2$ Hz), 127.96, 81.57, 80.97, 77.90, 76.97, 73.82, 69.95, 33.42, 19.42, 19.00, 1.20. ^{31}P-NMR: $\delta = -17.86$ (br s). IR (NaCl, cm^{-1}): ν(C=N) 1651. $[\alpha]_D^{22} = +714.6°$ ($c = 0.80$, $CHCl_3$). FABMS; m/z: 921. Anal. Found: C, 68.01; H, 6.43; N, 2.91. Calc. for $C_{52}H_{62}N_2O_2P_2Si_2Fe$: C, 67.81; H, 6.78; N, 3.04%.

4.10. General procedure for the Pd-catalyzed allylic alkylation

A mixture of [(η^3-allyl)PdCl]$_2$ (3.7 mg, 0.01 mmol) and a chiral ligand (0.025 mmol) in CH_2Cl_2 (1.7 ml) was stirred at 25°C for 30 min. The resulting solution was added to (*E*)-1,3-diphenylprop-2-enyl acetate (252 mg, 1.0 mmol) in CH_2Cl_2 (1.7 ml). Then, dimethyl malonate (0.34 ml, 3.0 mmol), *N*,*O*-bis(trimethylsilyl)acetamide (0.74 ml, 3.0 mmol), and potassium acetate (2.0 mg, 0.02 mmol) were added sequentially. The reaction was monitored by TLC (4:1 hexane–ethyl acetate, $R_f = 0.4$). After the reaction was completed, the reaction mixture was diluted with CH_2Cl_2 (20 ml), washed with saturated aqueous NH_4Cl (15 ml), and dried over $MgSO_4$. The solvent was evaporated, and the resulting residue was chromatographed on silica gel (4:1 hexane–ethyl acetate). For the alkylated products, enantioselectivity was determined by HPLC with a chiral column [Chiralcel OD® 25 cm × 0.46 cm; 99:1 hexane–*i*-PrOH; flow rate = 0.9 ml min^{-1}; $t_R = 14.10$ (*R*), 15.44 (*S*) min].

4.11. General procedure for the preparation of π-allyl palladium complexes

A chiral ligand (0.056 mmol) and [(η^3-C_3H_5)PdCl]$_2$ or [(η^3-1,3-diphenylallyl)PdCl]$_2$ (0.028 mmol) were dissolved in CD_2Cl_2 (0.5 ml), and the resulting solution was stirred for 30 min at r.t. Then the solution was transferred to a 5 mm NMR tube to get the ^{31}P-NMR data: [(η^3-allyl)Pd(**2**)]Cl $\delta = 29.3$, -16.5; [(η^3-allyl)Pd(($_P$R,$_P$R)-**3a**)]Cl $\delta = 31.4$; [(η^3-allyl)Pd(($_P$S,$_P$S)-**3a**)]Cl $\delta = 33.5$; [(η^3-allyl)Pd(($_P$R)-**6**)]Cl $\delta = 30.4$ (br s), -14.9 (br s); [(η^3-allyl)Pd(($_P$S)-**6**)]Cl $\delta = 33.6$ (d, $J = 40.8$ Hz), 32.7 (d, $J = 40.8$ Hz), -17.3 (br s); [(η^3-allyl)Pd(**7**)]Cl $\delta = 31.8$; [(η^3-diphenylallyl)Pd(($_P$R,$_P$R)-**3a**)]Cl $\delta = 53.2$ (br s), 17.3, 16.1, -16.3 (d, $J = 5.7$ Hz), -18.3 (d, $J = 5.7$ Hz); [(η^3-diphenylallyl)Pd(($_P$S,$_P$S)-**3a**)]Cl $\delta = 53.9$ (d, $J = 27.7$ Hz), 52.9 (d, $J = 27.7$ Hz), 25.1, -16.3; [(η^3-diphenylallyl)Pd(**7**)]Cl $\delta = 54.2$, 26.4, 26.0, 23.3, 18.5, 18.0, -16.0 (br s), -18.2 (br s). Minor peaks for (η^3-diphenylallyl)palladium complexes are omitted (see Fig. 2).

4.12. X-ray crystallography of 8

2,2′-Bis[(*S*)-(4-*tert*-butyloxazolin-2-yl)]-($_P$S,$_P$S)-1,1′-bis(diphenylphosphino)ferrocene (94 mg, 0.12 mmol) and [(η^3-C_3H_5)PdCl]$_2$ (21 mg, 0.057 mmol) were dissolved in CD_2Cl_2 (1 ml), and the resulting solution was stirred for 30 min at r.t. ^{31}P-NMR (CD_2Cl_2): $\delta = 33.1$ ppm.

A solution of $AgPF_6$ (30 mg, 0.12 mmol) in THF (0.5 ml) was added into the solution of the allylpalladium complex at 0 °C. A brown precipitate was filtered off, and solvents were evaporated to give an orange solid (100 mg), which was recrystallized from CH_2Cl_2 and hexane at -18 °C to give orange crystals of **8**. ^{31}P-NMR (CD_2Cl_2): $\delta = 33.4$, -141.8 (septet for PF_6^-) ppm.

The crystals were sealed in capillaries before the intensity data were collected with an Enraf–Nonius CAD4 diffractometer using monochromated Mo–K_α ($\lambda = 0.71013$ Å) radiation. The raw data collected were processed to produce conventional intensity data by the program SAINT. The intensity data were corrected for Lorenz and polarization effects. The structure was solved by a combination of Patterson and difference Fourier methods provided by the program package SHELEXTL. All the non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated and included in the final cycle of refinement. Crystal data for **8**: $C_{53}H_{59}Cl_4F_6FeN_2O_2P_3Pd$, mol. wt. = 1267.06, orange, 0.3 × 0.3 × 0.5 mm^3, orthorhombic, $P2_12_12_1$, $a = 10.069(2)$, $b = 20.956$ (4), $c = 26.825(7)$ Å, $V = 5660(2)$ Å^3, $Z = 4$, density = 1.487 mg cm^{-3}, absorption coefficient = 0.908 mm^{-1}, $T = 293(2)$ K, 3916 unique reflections measured, $R(F)$ for all data = 0.0838, $R_w(F)$ for all data = 0.1303, goodness-of-fit = 1.086.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 154930 for compound **8**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road,

Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://ccdc.cam.ac.uk).

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