

## Synthesis of new enantiomerically pure 1,3-bis-(2'-oxazoliny)ferrocenes as potential pincer ligands

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Dedicated to Professor Giuseppe Bartoli on his 65<sup>th</sup> birthday

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### Abstract

New enantiomerically pure 1,3-bis(2'-oxazoliny)ferrocenes have been synthesized in good yields starting from 1,3-ferrocene dicarboxylic acid. Moreover, the possibility of performing a regioselective lithiation in position 2 of the disubstituted cyclopentadienyl ring of these compounds has been demonstrated.

**Keywords:** Ferrocene, bis-oxazolines, regioselective lithiation, pincer ligands

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### Introduction

Since the first reports in the late 1970s on transition metal complexes containing pincer-type ligands, so called because of their particular coordination mode, these systems have attracted increasing interest owing to the unusual properties imparted to the metal centers by the pincer ligand.<sup>1</sup> The control of the properties of metal centers by a well defined ligand system is an ultimate goal of inorganic and organometallic chemistry. In organometallic complexes containing a direct (transition) metal-carbon bond, chelation leads to the formation of metallacycles, which provide additional stabilization of the M–C bond. Typically, these so-called pincer ligands have a general formula  $[2,6-(E\text{CH}_2)_2\text{C}_6\text{H}_3]^-$  and comprise an anionic aryl ring which is *ortho*, *ortho*-disubstituted with heteroatom based substituents, for example,  $\text{CH}_2\text{NR}_2$ ,  $\text{CH}_2\text{PR}_2$  or  $\text{CH}_2\text{SR}$ . These generally coordinate to the metal center, and therefore support the formation of M–C  $\sigma$  bond. Metal complexation with pincer ligands usually occurs with formation of two five-membered metallacycles which share the M–C bond. Pincer-based metal complexes possess an unique balance of stability vs. reactivity which can be controlled by systematic ligand modifications and /or variation of the metal center, allowing enhancement of

metal complex reactivity, stability, reaction selectivity and simultaneously provide a flurry of new fundamental insights.

Various homogeneous catalytic processes with pincer complexes have been reported,<sup>2</sup> including Kharasch addition,<sup>3</sup> Heck olefin arylation,<sup>4</sup> Suzuki biaryl coupling,<sup>5</sup> dehydrogenation of alkanes,<sup>6</sup> transfer hydrogenation<sup>7</sup> and stannyl and silyl transfer to propargylic substrates.<sup>8</sup>

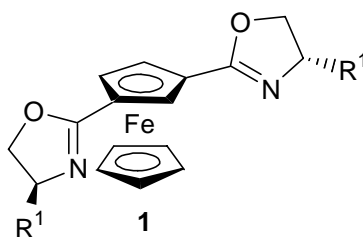
Chiral variants of pincer ligands have been less studied. The stereochemical information can be introduced, for example, at the benzylic carbons or by the donor atom substituents, creating potential stereoselective catalysts. Proline-derived NCN-pincer complexes have been applied as catalysts for Kharasch addition<sup>9</sup> with modest enantioselectivity whereas PCP-containing complexes<sup>10</sup> have been used for the asymmetric aldol reaction between aldehydes and methyl isocynoacetate obtaining e.e. up to 65%. Richards and co-authors have investigated anionic terdentate ligands derived from 1,3-bis(2'-oxazolinyl)benzenes readily obtained from optically pure  $\beta$ -amino alcohols.<sup>11</sup> These pincer ligands provide a series of palladium and platinum pincer complexes that have found application as catalysts for Michael reaction, Diels–Alder reaction and aldehyde and imine silylcyanation. Chiral bis(oxazolinyl)phenyl platinum complexes have also been used in asymmetric alkylation of aldimine with organolithium reagents affording enantiomeric excess up to 82%,<sup>12</sup> whereas the corresponding rhodium complexes act as asymmetric catalysts for enantioselective allylation of aldehydes in up to 80% ee.<sup>13</sup>

It is rather remarkable that there have been only few reports until now on attempts to design pincer complexes based on aromatic homocyclic systems other than benzene: viz. cyclopentadienyl ring of metallocenes. Koridze, Poli and co-workers<sup>14</sup> and simultaneously van Koten, Brown and co-workers<sup>15</sup> reported on the synthesis of the first representative ferrocene PCP pincer complexes of rhodium and palladium. Togni reported in 2004<sup>16</sup> the preparation of a new chiral tridentate PCP *N*-heterocyclic carbene ligand based on a ferrocene backbone and of the corresponding palladium and ruthenium complexes.

Ferrocene derivatives have found widespread application in various fields such as asymmetric catalysis,<sup>17</sup> electrochemistry<sup>18</sup> and development of new pharmaceuticals against malaria.<sup>19</sup> Furthermore, the sandwich structure of the ferrocene and the planar chirality, present in derivatives with at least two different substituents in the same ring,<sup>17b,c</sup> render these derivatives completely different from conventional aromatic molecules and increase their interest as chiral ligands. Among the plethora of chiral ferrocene derivatives that have been synthesized in the last century, only few examples have been reported so far concerning the synthesis of 1,3-disubstituted derivatives.<sup>20</sup>

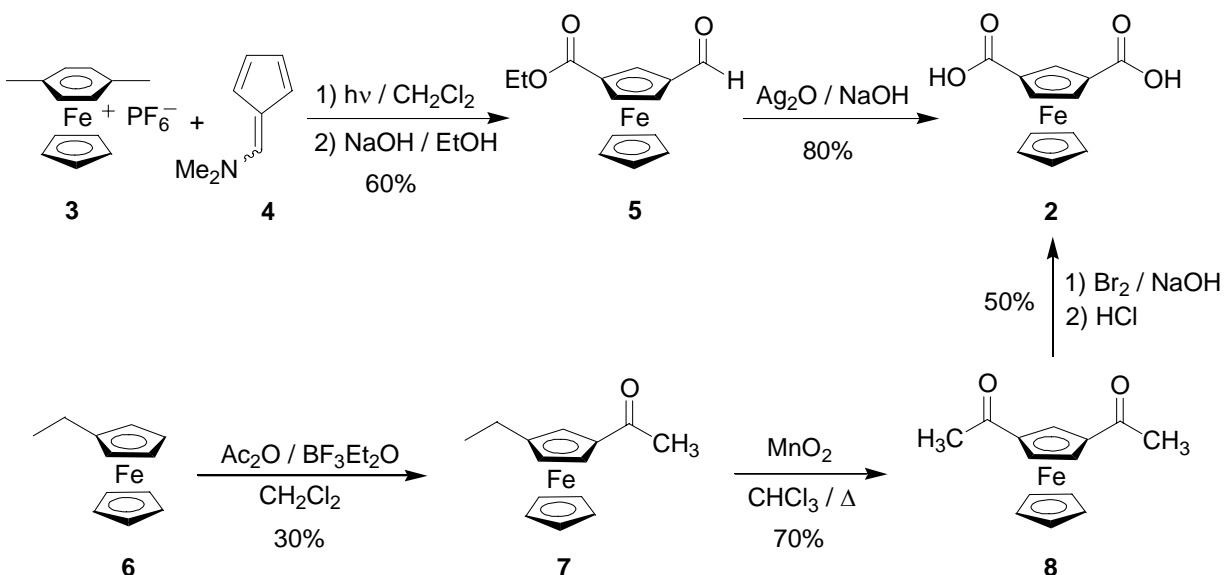
As a part of our ongoing interest in ferrocene containing molecules, we have recently synthesized enantiomerically pure ferrocenoylsilanes and thioferrocenoylsilanes,<sup>21</sup> 4-ferrocenyl- $\beta$ -lactams,<sup>22</sup>  $\beta$ -hydroxyalkyl,  $\beta$ -aminoalkyl and  $\beta$ -iminoalkyl ferrocenyl sulfides,<sup>23</sup> alcohols, imines, cyanohydrins, amino alcohols, oxazolines and thiazolines bearing the ferrocene moiety.<sup>24</sup> Some of these derivatives were successfully employed as ligands in asymmetric catalysis affording high level of enantioselectivity in palladium-catalyzed allylic substitution,<sup>23a,24a</sup> in diethylzinc addition to aldehydes<sup>24a</sup> and in asymmetric transformation of aldehydes into

epoxides.<sup>23b</sup> Herein we report the synthesis of unprecedented reported enantiomerically pure 1,3-bis(2'-oxazoliny)ferrocenes **1** as possible precursor of pincer complexes.



## Results and Discussion

General methods for the preparation of 1,3-disubstituted ferrocenes are severely lacking. In order to synthesize a suitable precursor for 1,3-bis(oxazoliny)ferrocenes **1**, we prepared 1,3-ferrocenedicarboxylic acid **2** following two different synthetic strategy according to published procedures<sup>25a,b</sup> as depicted in scheme 1. The first methodology consists in a two steps procedure involving the photochemical displacement of *p*-xylene from CpFe[*p*-xylene]<sup>+</sup>PF<sub>6</sub><sup>-</sup> **3**<sup>26</sup> in the presence of 3-methoxycarbonyl-6-dimethylaminofulvene **4**<sup>25a</sup> and the subsequent oxidation of 1-ethoxycarbonyl-3-formylferrocene **5** with Ag<sub>2</sub>O.<sup>25b</sup>

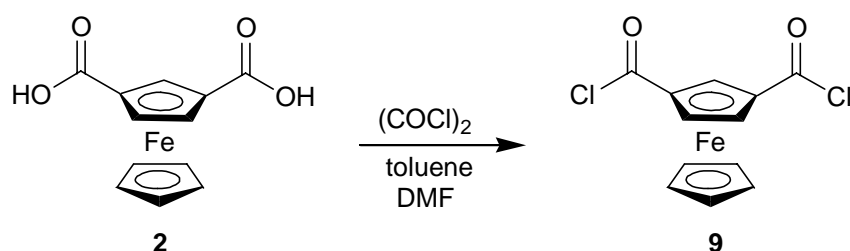


**Scheme 1.** Synthesis of 1,3-ferrocenedicarboxylic acid **2**.

The second route to 1,3-ferrocenedicarboxylic acid **2** involves a lengthy set of sequential reactions<sup>27a-d</sup> from ethylferrocene, namely (*i*) the Friedel Crafts acetylation that furnished the desired 1,3-disubstituted derivative **7** in 30% yield besides 1-acetyl-2-ethylferrocene and 1-

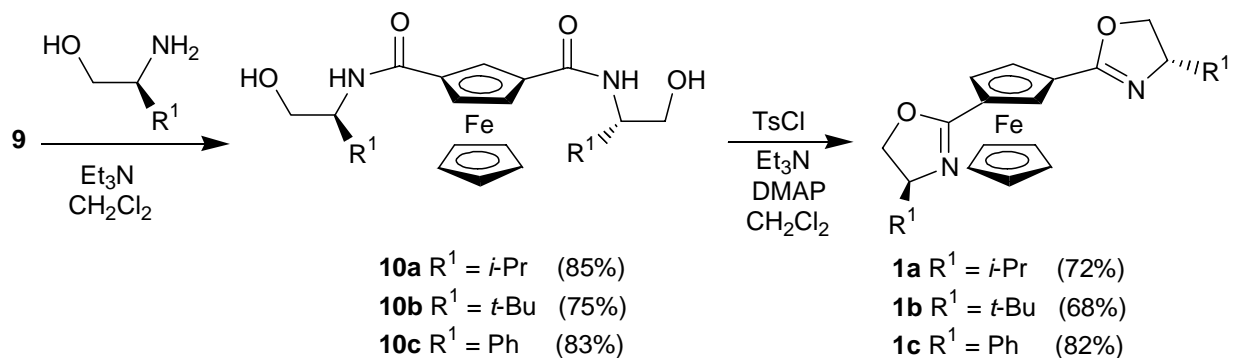
acetyl-1'-ethylferrocene, (ii) the oxidation of compound **7** to the diacyl derivative **8** with  $\text{MnO}_2$  in refluxing chloroform for 17 days, and the final haloform reaction. The first methodology has been preferred to the second one due to possibility of preparing the desired diacid **2** in a higher yield and quicker manner.

The dicarboxylic acid **2** was then transformed in quantitative yields into the corresponding ferrocene-1,3-diacid chloride **9** by reaction with oxalyl chloride in toluene (Scheme 2).



**Scheme 2.** Synthesis of ferrocene-1,3-diacid chloride **9**.

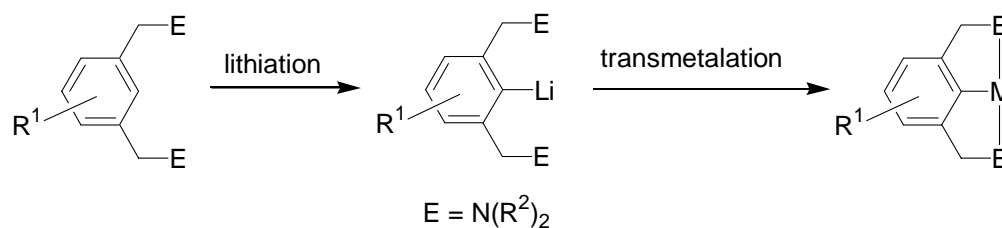
Among the available procedures described in the literature for the synthesis of oxazolines starting from  $\beta$ -amino alcohols, the most common are (i) single step methodologies<sup>28</sup> or (ii) cyclic dehydration reactions of a  $\beta$ -hydroxy amide (by converting the hydroxyl group into a good leaving group using different reagents).<sup>29</sup> The bis- $\beta$ -hydroxy amides **10a-c** were successfully prepared in very good yield by reaction of 1,3-ferrocenoyl dichloride **9** with three different enantiomerically pure  $\beta$ -amino alcohols in  $\text{CH}_2\text{Cl}_2$  in the presence of  $\text{Et}_3\text{N}$  at 30 °C (Scheme 3). Bis-amides **10a-c** were then cyclodehydrated using  $\text{TsCl}/\text{DMAP}/\text{Et}_3\text{N}$  affording the corresponding 1,3-bis-oxazolines **1a-c** in good isolated yield.



**Scheme 3.** Synthesis of 1,3-bis(2'-oxazoliny)ferrocenes **1**.

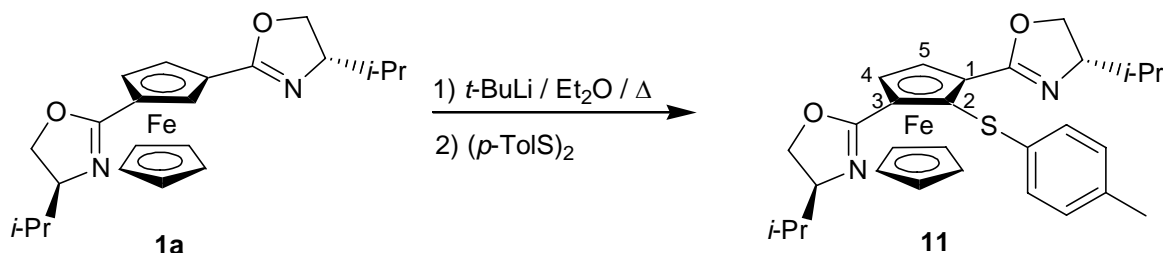
Various methods such as direct cyclometalation, oxidative addition, transmetalation and transcyclometalation have been developed for metalation of aryl pincer ligands and the creation of a new transition metal-carbon  $\sigma$  bond.<sup>1a</sup> The application of each of these methods is strongly dependent on the metal and the donor site of the pincer ligand. Lithiation of the  $\text{NC(H)N}$  ligand

precursors has been applied extensively to the preparation of suitable substrates for transmetalation (Scheme 4).



#### Scheme 4

Accordingly, we have started an investigation on the possibility of performing lithiation of 1,3-bis(2'-oxazolanyl)ferrocenes **1** in position 2 of the disubstituted cyclopentadienyl ring using product **1a** as model compound. The use of LDA in the presence of TMEDA,<sup>30</sup> *n*-BuLi or *t*-BuLi at room temperature failed and the 1,3-bis oxazoline **1a** was recovered unchanged. The use of 1.5 equivalents of *t*-BuLi in Et<sub>2</sub>O at reflux afforded the desired lithium derivative as demonstrated by quenching the reaction mixture with *p*-tolyl disulfide which leads to product **11** in 60% yield (Scheme 5).



#### Scheme 5

The structure of **11** was verified by the absence from the <sup>1</sup>H-NMR spectrum of the proton *ortho* to both the oxazoline rings. It is interesting to remark that the lithiation of **1a** occurs in a regioselective fashion and no trace of lithiation at C<sup>4</sup> or C<sup>5</sup> of the disubstituted cyclopentadienyl ring was found. This fact is extremely important in view of the preparation of pincer complexes since these latter kind of lithium derivatives would lead to simple cyclopalladated products decreasing the selectivity in the pincer complex formation.

In conclusion new enantiomerically pure 1,3-bis(2'-oxazolanyl)ferrocenes **1** have been synthesized starting from 1,3-ferrocene dicarboxylic acid and the possibility of performing a regioselective lithiation in position 2 of the disubstituted cyclopentadienyl ring of these compounds has been demonstrated. Further studies are in progress in our laboratories in order to obtain pincer complexes via transmetalation of the lithium species.

## Experimental Section

**General Procedures.** Reactions were conducted in oven-dried (120 °C) glassware under a positive pressure of argon. The transfer of anhydrous solvents or mixtures was accomplished with oven-dried syringes/septum techniques. THF was distilled from sodium/benzophenone prior to use and stored under argon. CH<sub>2</sub>Cl<sub>2</sub> was passed through basic alumina and distilled from CaH<sub>2</sub> prior to use. Other solvents were purified by standard procedures. Light petroleum ether refers to the fraction with a boiling range of 40–60 °C. Unless otherwise noted, all reagents were obtained from commercial suppliers and used without further purification. Thin-layer chromatography (TLC) was performed with plastic plates coated with (0.20 mm) silica gel 60 F<sub>254</sub> or aluminum oxide 60 F<sub>254</sub> neutral. Column chromatography was carried out with 70–230 mesh silica gel or 70–230 mesh aluminum oxide 90 active neutral. Preparative thick-layer chromatography was carried out with glass plates using a 1 mm layer of silica gel 60 PF<sub>254</sub>. Melting points are uncorrected. IR spectra were recorded on a Perkin-Elmer model 257 grating spectrometer. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded at 400 and 100 MHz, respectively, in CDCl<sub>3</sub> as solvent. Chemical shifts are reported on the δ scale and measured in ppm relative to residual CHCl<sub>3</sub> (δ=7.26 ppm) for <sup>1</sup>H NMR and to the central line of CDCl<sub>3</sub> (δ=77.0 ppm) for <sup>13</sup>C NMR spectra. *J* values are given in Hz. <sup>13</sup>C NMR spectral assignments were based on the results of DEPT experiments. The manufacturer's software was used for DEPT, gradient-enhanced COSY, as well as for the inversely-detected gradient selected heteronuclear correlations gHMBC and gHSQC data analysis. Mass spectra (MS) were obtained using an electrospray ionization source (ESIMS). All the ESIMS spectra were performed by using MeOH as the solvent. [α]<sub>D</sub> values are given in 10<sup>-1</sup> deg cm<sup>2</sup>g<sup>-1</sup>. Elemental analyses were performed using Flash EA1112 Automatic Elemental Analyzer CE instruments. The originality of all compounds was checked by a CAS on-line structure search.

### Compound characterization

**Ferrocene-1,3-diacid chloride (9).** Oxalyl chloride (3.5 mmol, 0.3 mL) and a drop of DMF were added to a suspension of 1,3-ferrocene dicarboxylic acid (1.1 mmol, 300 mg) in toluene (25 mL). The mixture was reacted for 1 h at 60 °C and then the solvent was evaporated under vacuum. The obtained dichloride was dissolved with a mixture of dry Et<sub>2</sub>O/pentane 1:5 and filtered. The filtrate was concentrated under vacuum affording the title compound in quantitative yield (335 mg). The dichloride was used immediately without further purification, owing to its low stability.

**General procedure for the synthesis of the bis-β-hydroxy amides (10a-c).** To a solution of amino alcohol (1.42 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (5 mL), Et<sub>3</sub>N (1.9 mmol, 0.27 mL) and the dichloride (0.64 mmol, 200 mg) were added. The mixture was reacted overnight at 30 °C, then quenched with saturated NaHCO<sub>3</sub> solution. The organic layer was extracted with CH<sub>2</sub>Cl<sub>2</sub>/MeOH 10:1 and then dried over magnesium sulfate and concentrated under reduced pressure. The reaction mixture was purified by column chromatography on silica gel (CH<sub>2</sub>Cl<sub>2</sub>/MeOH 20:1 as the eluent)

affording the title compound as a yellow solid. Protons and carbons assignments were made by gCOSY, gHSQC and gHMBC.

**Ferrocene-1,3-*N*<sup>1</sup>,*N*<sup>3</sup>-bis((*S*)-1-hydroxy-3-methylbutan-2-yl)carboxamide (10a).** Starting from 146 mg of (*S*)-2-amino-3-methyl-butanol, the title compound was obtained in 85% yield (242 mg, 0.54 mmol); <sup>1</sup>H-NMR (400 MHz, CD<sub>3</sub>OD) δ 1.01 (12H, m, 4 CH<sub>3</sub>-*i*Pr), 1.96 (2H, m, 2 CH-*i*Pr), 3.68 (4H, m, 2 CH<sub>2</sub>), 3.86 (2H, m, 2 CH), 4.27 (5H, s, C<sub>5</sub>H<sub>5</sub>), 5.03 (1H, br. s, H<sup>4</sup> or H<sup>5</sup>-C<sub>5</sub>H<sub>3</sub>), 5.05 (1H, br. s, H<sup>4</sup> or H<sup>5</sup>-C<sub>5</sub>H<sub>3</sub>), 5.48 (1H, br. s, H<sup>2</sup>-C<sub>5</sub>H<sub>3</sub>), 7.50 (2H, br. t, *J* = 7.8 Hz, 2 NH); <sup>13</sup>C-NMR (100 MHz, CD<sub>3</sub>OD) δ 19.47, 20.19 (CH<sub>3</sub>), 30.13, 58.45 (CH), 63.16 (CH<sub>2</sub>), 69.61, 71.25, 71.90, (CH-C<sub>5</sub>H<sub>3</sub>), 72.57 (CH-C<sub>5</sub>H<sub>5</sub>), 79.60, 79.70 (C), 172.02 (CO); MS (ESI) *m/z*: 467 (M<sup>+</sup>+Na), 445 (M<sup>+</sup>+1); *Anal Calcd.* C<sub>22</sub>H<sub>32</sub>FeN<sub>2</sub>O<sub>4</sub>: C, 59.47; H, 7.26; N, 6.30. Found: C, 59.51; H, 7.22; N, 6.38.

**Ferrocene-1,3-*N*<sup>1</sup>,*N*<sup>3</sup>-bis((*S*)-1-hydroxy-3,3-dimethylbutan-2-yl)carboxamide (10b).** Starting from 166 mg of (*S*)-2-amino-3,3-dimethylbutanol, the title compound was obtained in 75% yield (227 mg, 0.48 mmol); <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ 1.00 (9H, s, CH<sub>3</sub>), 1.02 (9H, s, CH<sub>3</sub>), 3.31 – 4.05 (6H, m, 2CH<sub>2</sub> and 2CH), 4.21 (5H, s, C<sub>5</sub>H<sub>5</sub>), 4.77 (1H, br. s, H<sup>4</sup> or rH<sup>5</sup>-C<sub>5</sub>H<sub>3</sub>), 4.82 (1H, br. s, H<sup>4</sup> or H<sup>5</sup>-C<sub>5</sub>H<sub>3</sub>), 5.46 (1H, br. s, H<sup>2</sup>-C<sub>5</sub>H<sub>3</sub>), 6.51 (1H, br. d, NH), 6.76 (1H, br. d, NH); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ 19.57, 20.12 (CH<sub>3</sub>), 58.65 (CH), 62.18 (CH<sub>2</sub>), 69.71, 71.40, 71.85, (CH-C<sub>5</sub>H<sub>3</sub>), 73.14 (CH-C<sub>5</sub>H<sub>5</sub>), 78.12, 78.89 (C), 171.18, 173.00 (CO); MS (ESI) *m/z*: 495 (M<sup>+</sup>+Na), 473 (M<sup>+</sup>+1); *Anal Calcd.* C<sub>24</sub>H<sub>36</sub>FeN<sub>2</sub>O<sub>4</sub>: C, 61.02; H, 7.68; N, 5.93. Found: C, 61.11; H, 7.61; N, 5.99.

**Ferrocene-1,3-*N*<sup>1</sup>,*N*<sup>3</sup>-bis((*S*)-2-hydroxy-1-phenylethyl)carboxamide (10c).** Starting from 195 mg of (*S*)-2-amino-2-phenyl-ethanol, the title compound was obtained in 83% yield (272 mg, 0.53 mmol); <sup>1</sup>H-NMR (400 MHz, CD<sub>3</sub>OD) δ 3.85 (4H, d, *J* = 6.8 Hz, 2 CH<sub>2</sub>), 4.07 (5H, s, C<sub>5</sub>H<sub>5</sub>), 5.04 (1H, m, H<sup>4</sup> o H<sup>5</sup>-C<sub>5</sub>H<sub>3</sub>) 5.15 (3H, m, H<sup>4</sup> o H<sup>5</sup>-C<sub>5</sub>H<sub>3</sub> e 2CH), 5.55 (1H, br. s, H<sup>2</sup>-C<sub>5</sub>H<sub>3</sub>), 7.22 – 7.49 (12H, complex m, Ar-H and NH); <sup>13</sup>C-NMR (100 MHz, CD<sub>3</sub>OD) δ: 57.39 (CH), 65.72 (CH<sub>2</sub>) 69.83, 71.15, 72.34 (CH-C<sub>5</sub>H<sub>3</sub>), 72.44 (CH-C<sub>5</sub>H<sub>5</sub>), 79.12, 79.19 (C), 128.13, 128.51, 129.52 (Ar-CH) 141.63 (Ar-C), 171.67 (CO); MS (ESI) *m/z*: 535 (M<sup>+</sup>+Na); *Anal Calcd.* C<sub>28</sub>H<sub>28</sub>FeN<sub>2</sub>O<sub>4</sub>: C, 65.64; H, 5.51; N, 5.47. Found: C, 65.59; H, 5.60; N, 5.39.

**General procedure for the synthesis of 1,3-bis oxazolines (1a-c).** *p*-Tosyl chloride (230 mg, 1.2 mmol) and 4-dimethylaminopyridine (DMAP) (10 mg, 0.08 mmol) were added to a solution of hydroxy amide **7** (0.4 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (6 mL). After 15 min. triethylamine (3.3 mL, 2.4 mmol) was added dropwise and the reaction was stirred for 24h at 30 °C. The reaction was poured into saturated aqueous NaHCO<sub>3</sub>, and extracted with CH<sub>2</sub>Cl<sub>2</sub>. The combined organic layers were washed with brine, dried (MgSO<sub>4</sub>), filtered and concentrated in vacuum. Purification of the crude by column chromatography on silica gel (CH<sub>2</sub>Cl<sub>2</sub>/MeOH 20:1 as the eluent) afforded the title compound as a yellow solid. Protons and carbons assignments were made by gCOSY, gHSQC and gHMBC.

**1,3-Bis[(4*S*)-(4-(2-methyl)ethyl)oxazolin-2-yl]-ferrocene (1a).** Starting from 178 mg of **7a**, the title compound was obtained in 72% yield (128 mg, 0.31 mmol); mp 85 – 87 °C;  $[\alpha]_{\text{D}}^{20} = -115.3$  (c 0.5, CHCl<sub>3</sub>); IR (CCl<sub>4</sub>):  $\nu$  1660 cm<sup>-1</sup>; <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  0.92 (3H, d,  $J = 6.8$  Hz, CH<sub>3</sub>-<sup>*i*</sup>Pr), 0.93 (3H, d,  $J = 6.8$  Hz, CH<sub>3</sub>-<sup>*i*</sup>Pr), 0.99 (6H, d,  $J = 6.8$  Hz, 2 CH<sub>3</sub>-<sup>*i*</sup>Pr), 1.84 (2H, m, 2 CH-<sup>*i*</sup>Pr), 3.99 (2H, m, 2 CH), 4.06 (2H, m, 2H<sub>a</sub>-CH<sub>2</sub>), 4.21 (5H, s, C<sub>5</sub>H<sub>5</sub>), 4.30 (2H, m, 2H<sub>b</sub>-CH<sub>2</sub>), 4.87 (1H, br. dd,  $J_1 = 2.6, J_2 = 1.4$  Hz, H<sup>4</sup> or H<sup>5</sup>-C<sub>5</sub>H<sub>3</sub>), 4.91 (1H, br. dd,  $J_1 = 2.6, J_2 = 1.4$  Hz, H<sup>4</sup> or H<sup>5</sup>-C<sub>5</sub>H<sub>3</sub>), 5.32 (1H, br. t,  $J = 1.4$  Hz, H<sup>2</sup>-C<sub>5</sub>H<sub>3</sub>); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  17.90, 17.91, 18.77, 18.80 (CH<sub>3</sub>-<sup>*i*</sup>Pr), 32.33, 32.42 (CH-<sup>*i*</sup>Pr), 69.57, 69.62 (CH<sub>2</sub>), 69.95, 70.66, 70.71 (CH-C<sub>5</sub>H<sub>3</sub>), 71.08 (CH-C<sub>5</sub>H<sub>5</sub>), 72.32, 72.39 (CH) 72.67, 73.05 (C), 164.56, 164.58 (CON); MS (ESI)  $m/z$ : 431 (M<sup>+</sup>+Na), 409 (M<sup>+</sup>+1); Anal Calcd. C<sub>22</sub>H<sub>28</sub>FeN<sub>2</sub>O<sub>2</sub>: C, 64.71; H, 6.91; N, 6.86. Found: C, 64.65; H, 6.99; N, 6.78.

**1,3-Bis[(4*S*)-(4-(2,2-dimethyl)ethyl)oxazolin-2-yl]-ferrocene (1b).** Starting from 190 mg of **7b**, the title compound was obtained in 68% yield (118 mg, 0.27 mmol); mp 88 – 87 °C; with  $[\alpha]_{\text{D}}^{20} = -137.5$  (c 0.5, CHCl<sub>3</sub>); IR (CCl<sub>4</sub>):  $\nu$  1661 cm<sup>-1</sup>; <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  0.93 (18H, s, 6xCH<sub>3</sub>), 3.89 (2H, 2 superimposed dd, 2 CH), 4.15 (2H, m, 2H<sub>a</sub>-CH<sub>2</sub>), 4.20 (5H, s, C<sub>5</sub>H<sub>5</sub>), 4.25 (2H, m, 2H<sub>b</sub>-CH<sub>2</sub>), 4.83 (1H, br. s, H<sup>4</sup> o H<sup>5</sup>-C<sub>5</sub>H<sub>3</sub>), 4.90 (1H, br. s, H<sup>4</sup> o H<sup>5</sup>-C<sub>5</sub>H<sub>3</sub>), 5.34 (1H, br. s, H<sup>2</sup>-C<sub>5</sub>H<sub>3</sub>); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  26.11 (CH<sub>3</sub>), 68.73 (CH<sub>2</sub>) 70.16, 70.77, 70.92 (CH-C<sub>5</sub>H<sub>3</sub>), 71.20 (CH-C<sub>5</sub>H<sub>5</sub>), 72.99, 73.02 (C-C<sub>5</sub>H<sub>3</sub>), 76.31 (CH); MS (ESI)  $m/z$ : 459 (M<sup>+</sup>+Na), 437 (M<sup>+</sup>+1); Anal Calcd. C<sub>24</sub>H<sub>32</sub>FeN<sub>2</sub>O<sub>2</sub>: C, 66.06; H, 7.39; N, 6.42. Found: C, 66.01; H, 7.31; N, 6.49.

**1,3-Bis[(4*S*)-(4-phenyl)oxazolin-2-yl]-ferrocene (1c).** Starting from 205 mg of **7c**, the title compound was obtained in 82% yield (157 mg, 0.33 mmol); mp 108 – 110 °C;  $[\alpha]_{\text{D}}^{20} = -98.6$  (c 0.5, CHCl<sub>3</sub>); IR (CCl<sub>4</sub>):  $\nu$  1652 cm<sup>-1</sup>; <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  4.21 (2H, dd,  $J_1 = J_2 = 8.3$  Hz, 2H<sub>a</sub> -CH<sub>2</sub>), 4.31 (5H, s, C<sub>5</sub>H<sub>5</sub>) 4.71 (2H, 2dd,  $J_1 = 8.3 J_2 = 5.4$  Hz, 2H<sub>b</sub> -CH<sub>2</sub>), 5.02 (1H, dd,  $J_1 = 2.6 J_2 = 1.4$  Hz, H<sup>4</sup> or H<sup>5</sup>-C<sub>5</sub>H<sub>3</sub>), 5.05 (1H, dd,  $J_1 = 2.6 J_2 = 1.4$  Hz, H<sup>4</sup> or H<sup>5</sup>-C<sub>5</sub>H<sub>3</sub>), 5.25 (2H, 2 dd, 2CH) 5.48 (1H, t,  $J = 1.4$  Hz, H<sup>2</sup>-C<sub>5</sub>H<sub>3</sub>), 7.28 – 7.40 (10H, m, Ar-H); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  69.94, 70.00 (CH), 70.26 71.16 (CH-C<sub>5</sub>H<sub>3</sub>), 71.27 (CH-C<sub>5</sub>H<sub>3</sub> and CH-C<sub>5</sub>H<sub>5</sub>), 72.28, 72.32 (C-C<sub>5</sub>H<sub>3</sub>), 74.67 (CH<sub>2</sub>) 126.58, 126.62, 127.58, 128.72, 128.76 (Ar-CH) 142.39, 142.49 (Ar-C), 166.17, 166.22 (CON); MS (ESI)  $m/z$ : 499 (M<sup>+</sup>+Na), 477 (M<sup>+</sup>+1). Anal Calcd. C<sub>28</sub>H<sub>24</sub>FeN<sub>2</sub>O<sub>2</sub>: C, 70.60; H, 5.08; N, 5.88. Found: C, 70.69; H, 5.02; N, 5.92.

**1,3-Bis[(4*S*)-(4-(2methyl)ethyl)oxazolin-2-yl]-2-*p*-tolylsulfanyl-ferrocene (11).** To a solution of **1a** (41 mg, 0.1 mmol) in dry Et<sub>2</sub>O (6 mL) 90  $\mu$ L of *t*-BuLi (0.15 mmol) were slowly added. The deep red mixture were refluxed for 1h and then quenched by addition of a solution of *p*-tolyl disulfide (50 mg, 0.2 mmol) in dry Et<sub>2</sub>O (2 mL). After the addition was completed, the mixture was stirred at room temperature for 1 h and then poured into saturated aqueous NaHCO<sub>3</sub>, and extracted with EtOAc. The organic layer was dried (MgSO<sub>4</sub>), filtered and concentrated in vacuum. Purification of the crude by column chromatography on silica gel (CH<sub>2</sub>Cl<sub>2</sub>/MeOH 20:1 as the eluent) afforded the title compound as a yellow solid in 60% yield (32 mg, 0.06 mmol). mp 122–125 °C (dec.);  $[\alpha]_{\text{D}}^{20} = -69.3$  (c 0.5, CHCl<sub>3</sub>); IR (CCl<sub>4</sub>):  $\nu$  1659 cm<sup>-1</sup>; <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  0.77 (3H, d,  $J = 6.8$  Hz, CH<sub>3</sub>-<sup>*i*</sup>Pr), 0.85 (3H, d,  $J = 6.8$  Hz, CH<sub>3</sub>-<sup>*i*</sup>Pr), 0.894 (3H,



d,  $J = 6.8$  Hz,  $\text{CH}_3\text{-}^i\text{Pr}$ ), 0.898 (3H, d,  $J = 6.8$  Hz,  $\text{CH}_3\text{-}^i\text{Pr}$ ), 1.69 (2H, m, 2  $\text{CH-}^i\text{Pr}$ ), 2.20 (3H, s,  $\text{CH}_3$ ), 3.89-4.00 (2H, m, 2 CH), 4.06-4.18 (4H, m, 2  $\text{CH}_2$ ), 4.32 (5H, s,  $\text{C}_5\text{H}_5$ ), 4.99 (1H, d,  $J = 2.9$  Hz,  $\text{H}^4$  or  $\text{H}^5\text{-C}_5\text{H}_3$ ), 5.04 (1H, d,  $J = 2.9$  Hz,  $\text{H}^4$  or  $\text{H}^5\text{-C}_5\text{H}_3$ ), 6.91 (2H, d,  $J = 8.4$  Hz, Ar-H), 7.00 (2H, d,  $J = 8.4$  Hz, Ar-H);  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  17.45, 17.48, 18.20, 18.35 ( $\text{CH}_3\text{-}^i\text{Pr}$ ), 31.89, 32.12 ( $\text{CH-}^i\text{Pr}$ ), 67.27, 68.89 ( $\text{CH}_2$ ), 68.95, 71.01, ( $\text{CH-C}_5\text{H}_3$ ), 72.12 ( $\text{CH-C}_5\text{H}_3$ ), 72.28, 72.95 (CH) 72.18, 73.28 (C), 121.18, 125.39, 127.18 (ArCH), 132.18, 133.86 (ArC), 164.56, 164.58 (CON); MS (ESI)  $m/z$ : 553 ( $\text{M}^+\text{+Na}$ ), 531 ( $\text{M}^+\text{+1}$ ); *Anal Calcd.*  $\text{C}_{29}\text{H}_{34}\text{FeN}_2\text{O}_2\text{S}$ : C, 65.66; H, 6.46; N, 5.28. Found: C, 65.68; H, 6.51; N, 5.21.

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