

# Chiral Bis(pyridylimino)isoindoles: A Highly Modular Class of Pincer Ligands for Enantioselective Catalysis\*\*

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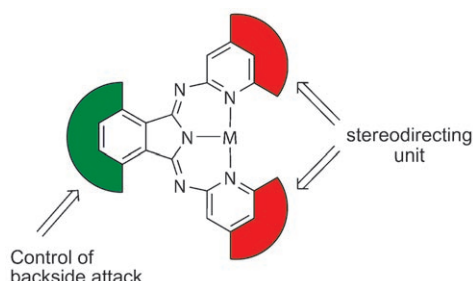
The control of stereoselective catalytic transformations that use metal complexes rests upon the development of efficient structural platforms for ancillary stereodirecting ligands.<sup>[1]</sup> Essential for the rapid identification of an optimized system for a given lead structure and catalytic reaction is modularity of the ligand and thus, catalyst assembly.<sup>[2]</sup> Apart from the ubiquitous chiral chelates, monoanionic, meridionally coordinating tridentate ligand systems are expected to enhance catalyst stability and to offer a structural platform for the construction of efficient stereodirecting elements.

Whereas Nishiyama's phebox ligands (phebox = bis(oxazolinyl)phenyl) have been proven to act as efficient stereodirecting ligands in a variety of applications,<sup>[3]</sup> the majority of the known pincer-type chiral systems perform relatively poorly in enantioselective catalysis.<sup>[4]</sup> This poor selectivity may be in part due to a certain lack of control of the substrate orientation for reactions that proceed by backside attack at the metal center; that is, the stereodirection by the chiral units in the wing positions may be ineffective.

Bis(2-pyridylimino)isoindoles (bpi) are highly modular and readily accessible pincer ligands.<sup>[5]</sup> These compounds were first employed as ligands for the cobalt-catalyzed aerobic oxidation of hydrocarbons three decades ago,<sup>[6]</sup> and their coordination chemistry with 3d metals in particular has been studied in some detail.<sup>[7]</sup> However they have not been studied as new lead structures for enantioselective catalysts.

Herein we report the synthesis of a series of chiral bpi ligands. Whereas the chirally modified pyridyl units act as stereodirecting elements,<sup>[8]</sup> the appropriate substitution pattern in the backbone will provide a protective hedge for backside attack on the metal center (Figure 1). Their versatility as efficient stereodirecting ligands will be demonstrated for the iron-catalyzed asymmetric hydrosilylation of ketones and the cobalt-catalyzed enantioselective inter- and intramolecular cyclopropanation of alkenes.

Three types of chiral bpi derivatives, depicted in Scheme 1, were prepared by the established one-pot procedure with chiral aminopyridines derived from commercially



**Figure 1.** Construction principle of chiral bpi ligands: stereodirecting units attached to the pyridyl wings of the meridionally coordinating ligand (red) and substituents within the ligand backbone to control access from the backside of the metal center (green).

available terpenes. Starting from myrtenal, the corresponding bpi derivatives **2a–b** (denoted myrbpi) were synthesized by using 2-aminopyridine derivative **1a**, which was first reported by von Zelewsky and co-workers.<sup>[9]</sup> A series of constitutional isomers of **2a–c**, compounds **3a–c** (denoted pinbpi), was obtained by using **1b**, which was derived from (–)-β-pinene,<sup>[10]</sup> and the (+)-2-carene-derived series (**4a–c**; denoted carbpi) was prepared from **1c**, which was synthesized from the corresponding 2-triflatopyridine (see the Supporting Information).<sup>[11]</sup>

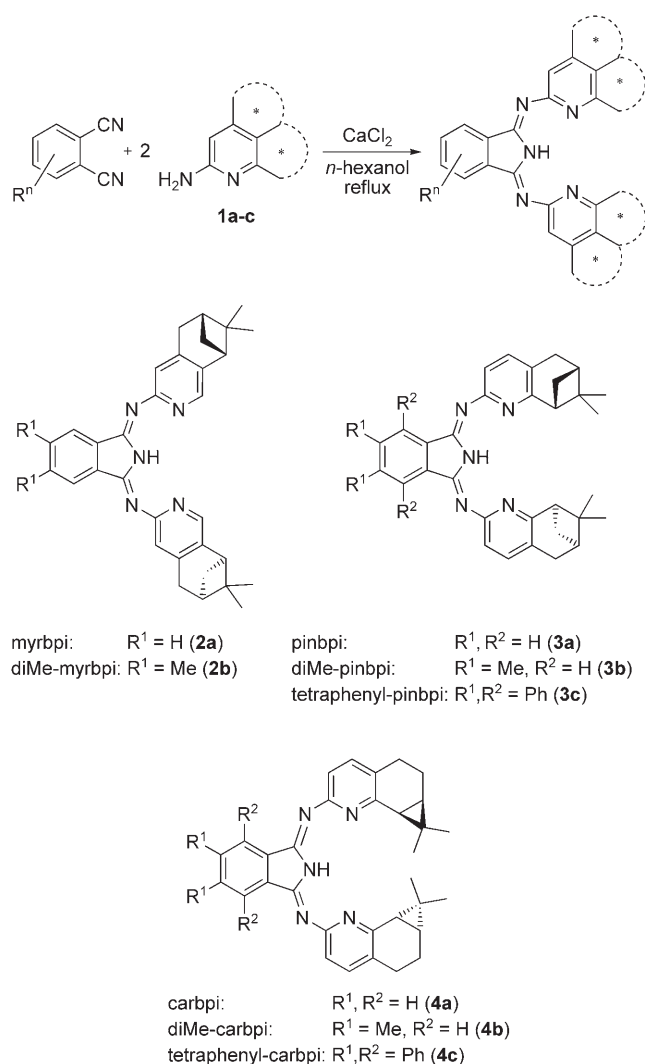
The bpi ligands for each of the three series were used for the preparation of iron(II) and cobalt(II) acetato complexes **5a–9c** (Scheme 2) by either direct complexation of the metal diacetate or by reaction with the corresponding dichloride with subsequent anion exchange. All metal compounds are assumed to adopt distorted octahedral coordination geometries with one solvent molecule (MeOH or THF) occupying the sixth coordination site as indicated by the mass spectrometric and analytical data. An X-ray diffraction study has established this type of coordination geometry for a related Co complex bearing an achiral bpi ligand (see the Supporting Information).

To gain insight into the structural details of this new class of stereodirecting ligands, single crystal X-ray structure analyses of carbpi (**4a**) (Figure 2a) and [Cu(tetraphenylpinbpi)(OAc)] (**12**) (Figure 2b) were obtained. The latter has been the only transition-metal complex with this type of ligand to give X-ray quality crystals.<sup>[12]</sup> Whereas the structures of both the ligand precursor and the metal complex illustrate the orientation of the chiral wedges of the pyridyl units, which are introduced as stereodirecting elements, the tetraphenylated backbone of the Cu complex (Figure 2b) nicely depicts the protective hedge on the backside of the reactive metal center.

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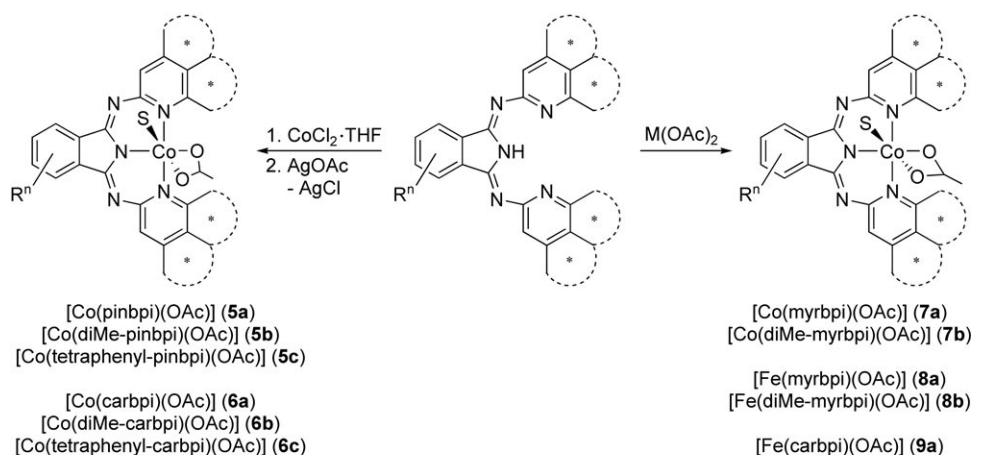
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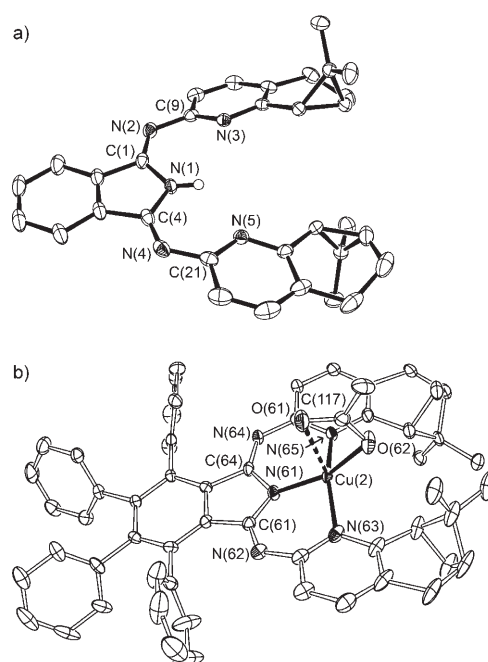


**Scheme 1.** Modular assembly of chiral bis(2-pyridylimino)isoindole ligand (precursors) by condensation of a substituted phthalonitrile and two molar equivalents of a chiral 2-aminopyridine derivative. The acronyms are derived from the underlying terpene structures and a prefix designating the substitution pattern of the isoindole backbone.

There has recently been a burgeoning interest in replacing established noble-metal catalysts by systems containing nonprecious metals.<sup>[13]</sup> Much of the focus has been on catalysts containing iron, a transition metal still comparatively underdeveloped in molecular catalysis.<sup>[14]</sup> In the first report on the application of iron catalysts in asymmetric hydrosilylations of ketones,<sup>[15]</sup> Nishiyama and Furuta employed pyridylbi-



**Scheme 2.** Synthesis of a series of chiral  $Fe^{II}$ -bpi and  $Co^{II}$ -bpi complexes containing three different classes of stereodirecting bpi ligands.



**Figure 2.** Molecular structure of: a) carbpi **4a** and b) [Cu(tetraphenyl-pinbpi)(OAc)] (**12**); hydrogen atoms omitted for clarity. Selected bond lengths [Å] and angles [°] of carbpi (**4a**): N(1)–C(1) 1.391(2), N(1)–C(4) 1.393(2), C(1)–N(2) 1.282(3), C(4)–N(4) 1.280(3), N(2)–C(9) 1.403(2), N(4)–C(21) 1.403(3), C(9)–N(3) 1.338(2), C(21)–N(5) 1.338(2); N(1)–C(1)–N(2) 131.2(2), N(1)–C(4)–N(4) 131.5(2); selected bond length [Å] and angles [°] of [Cu(tetraphenyl-pinbpi)(OAc)] **12**: N(61)–Cu(2) 1.883(3), N(63)–Cu(2) 2.098(3), N(65)–Cu(2) 2.089(3), O(61)–Cu(2) 2.480(3), O(62)–Cu(2) 1.945(2), O(61)–C(117) 1.226(4), O(62)–C(117) 1.283(4); N(61)–Cu(2)–O(62) 155.0(1), N(63)–Cu(2)–N(65) 156.7(1), N(61)–Cu(2)–O(61) 97.2(1), N(61)–Cu(2)–N(63) 90.7(1), N(61)–Cu(2)–N(65) 90.5(1).

soxazoline (pybox) and bis(oxazolynyl)diphenylamine (bopa) ligands and reported enantioselectivities of up to 79% for highly substituted aryl(alkyl)ketones.<sup>[16]</sup> Recently Beller and co-workers have extended the scope of this reaction by using

chiral diphosphine-based catalysts which were optimized in an extensive screening process.<sup>[17]</sup>

The first test of iron complexes **8a** and **b**, and **9a–c** as catalysts in the asymmetric hydrosilylation of acetophenone (Table 1) established carene derivatives **9a–c** as the most

**Table 1:** Chiral Fe<sup>II</sup>-complex catalysts for asymmetric hydrosilylation of acetophenone.<sup>[a]</sup>

| Entry | Catalyst                                    | Yield [%] <sup>[b]</sup> | T [°C] | t [h] | ee [%] <sup>[c]</sup> |
|-------|---------------------------------------------|--------------------------|--------|-------|-----------------------|
| 1     | [Fe(myrbpi)(OAc)] ( <b>8a</b> )             | 93                       | 65     | 16    | 27 (R)                |
| 2     | [Fe(diMe-myrbpi)(OAc)] ( <b>8b</b> )        | 92                       | 65     | 16    | 28 (R)                |
| 3     | [Fe(carbpi)(OAc)] ( <b>9a</b> )             | 94                       | 65     | 16    | 77 (S)                |
| 4     | [Fe(carbpi)(OAc)] ( <b>9a</b> )             | 84                       | 40     | 40    | 84 (S)                |
| 5     | [Fe(diMe-carbpi)(OAc)] ( <b>9b</b> )        | 95                       | 65     | 16    | 77 (S)                |
| 6     | [Fe(diMe-carbpi)(OAc)] ( <b>9b</b> )        | 86                       | 40     | 40    | 84 (S)                |
| 7     | [Fe(tetraphenyl-carbpi)(OAc)] ( <b>9c</b> ) | 91                       | 65     | 16    | 78 (S)                |
| 8     | [Fe(tetraphenyl-carbpi)(OAc)] ( <b>9c</b> ) | 85                       | 40     | 40    | 86 (S)                |

[a] General conditions: Fe<sup>II</sup>-complex (5 mol%), acetophenone (1 equiv), (diethoxy) methyl silane (2 equiv) in THF (2 mL). Work-up with K<sub>2</sub>CO<sub>3</sub> (1% in methanol). [b] Yield of isolated pure product. [c] Determined by chiral GC analysis on a  $\beta$ -PM column; absolute configuration of the secondary alcohol was determined by comparison with literature.

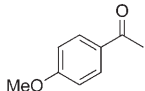
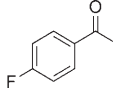
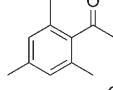
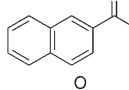
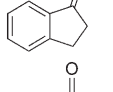
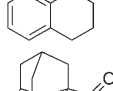
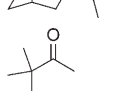
selective systems, which gave the reaction product in enantioselectivities of up to 86% (Table 1, entry 8); this result was superior to previously reported iron catalysts that were tested for this reference reaction.<sup>[16,17]</sup> Notably, the reaction is relatively insensitive to the backbone substitution, but the type of chiral pyridyl unit seems to determine the stereoselectivities.

By using the optimized iron-based system (**9c**) for the hydrosilylation of a range of aryl(alkyl) ketones, the reaction products were determined to have enantiomeric excesses of up to 93% (Table 2). In contrast, dialkyl ketones appeared to be reduced with somewhat lower selectivities (55–60% ee), mirroring the behavior of most of the established precious-metal-based systems.

The importance of controlling a potential backside attack at the active site of the molecular catalyst should be apparent in catalytic reactions in which the key stereochemically determining step involves a side-on approach of the substrate, which should be sensitively dependent upon the backbone structure. This aspect has been probed in the cobalt-catalyzed asymmetric cyclopropanation of alkenes with diazoalkanes previously developed in the groups of Katsuki and Yamada.<sup>[18]</sup> A major advantage of the cobalt system is the complete suppression of diazoalkane dimerization (giving the undesired corresponding alkenes), a problem that complicates the use of copper (and most of the Ru and Rh) catalysts and necessitates the use of syringe pumps or similar devices.<sup>[19]</sup>

Cobalt complexes **5a–c**, **6a–c**, and **7a** and **7b** were first tested in the reference reaction of styrene with ethyl diazoacetate. The results displayed in Table 3 are instructive as to how the different structural elements in the bpi ligand platform influence the catalyst performance. Complexes **7a** and **7b**, both of which contain the chiral units at the pyridyl groups oriented furthest away from the active site, gave the cyclopropane products in both low diastereo- and enantioselectivities.

**Table 2:** Scope of the [Fe(tetraphenyl-carbpi)(OAc)]-catalyzed asymmetric hydrosilylation of ketones.<sup>[a]</sup>

| Entry | ketone                                                                             | Yield [%] <sup>[b]</sup> | T [°C]   | t [h]    | ee [%] <sup>[c]</sup> |
|-------|------------------------------------------------------------------------------------|--------------------------|----------|----------|-----------------------|
| 1     |  | 91<br>80                 | 65<br>40 | 16<br>40 | 75<br>86 (S)          |
| 2     |  | 92<br>79                 | 65<br>40 | 16<br>40 | 73<br>85 (S)          |
| 3     |  | 92<br>83                 | 65<br>40 | 48<br>40 | 85<br>93              |
| 4     |  | 87<br>77                 | 65<br>40 | 16<br>40 | 71<br>83 (S)          |
| 5     |  | 88<br>72                 | 65<br>40 | 16<br>40 | 75<br>85 (S)          |
| 6     |  | 89<br>72                 | 65<br>40 | 16<br>40 | 74<br>80 (S)          |
| 7     |  | 65<br>50                 | 65<br>40 | 16<br>40 | 50<br>56 (S)          |
| 8     |  | 67<br>51                 | 65<br>40 | 16<br>40 | 54<br>59 (S)          |

[a] General conditions: Fe<sup>II</sup>-complex **9c** (5 mol%), ketone (1 equiv), (diethoxy) methyl silane (2 equiv) in 2 equiv THF (2 equiv). Work-up with K<sub>2</sub>CO<sub>3</sub> (1% in methanol). [b] Yield of isolated pure product. [c] Determined by chiral GC or HPLC analysis; absolute configuration of the secondary alcohol was determined by comparison with literature.

**Table 3:** Various Co<sup>II</sup>-complex catalysts for asymmetric cyclopropanation of styrene.<sup>[a]</sup>

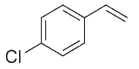
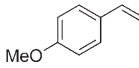
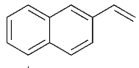
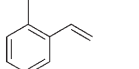
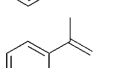
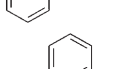
| Entry | Catalyst                                    | Yield [%] <sup>[b]</sup> | trans:cis <sup>[c]</sup> | ee [%] <sup>[d]</sup> |
|-------|---------------------------------------------|--------------------------|--------------------------|-----------------------|
| 1     | [Co(myrbpi)(OAc)] ( <b>7a</b> )             | 96                       | 80:20                    | 45<br>(1S,2S)         |
| 2     | [Co(diMe-myrbpi)(OAc)] ( <b>7b</b> )        | 95                       | 81:19                    | 44<br>(1S,2S)         |
| 3     | [Co(pinbpi)(OAc)] ( <b>5a</b> )             | 94                       | 91:9                     | 63 (1S,2S)            |
| 4     | [Co(diMe-pinbpi)(OAc)] ( <b>5b</b> )        | 96                       | 91:9                     | 62<br>(1S,2S)         |
| 5     | [Co(tetraphenyl-pinbpi)(OAc)] ( <b>5c</b> ) | 95                       | 94:6                     | 68<br>(1S,2S)         |
| 6     | [Co(carbpi)(OAc)] ( <b>6a</b> )             | 95                       | 92:8                     | 84<br>(1R,2R)         |
| 7     | [Co(diMe-carbpi)(OAc)] ( <b>6b</b> )        | 94                       | 91:9                     | 84<br>(1R,2R)         |
| 8     | [Co(tetraphenyl-carbpi)(OAc)] ( <b>6c</b> ) | 97                       | 95:5                     | 90<br>(1R,2R)         |

[a] General conditions: Co<sup>II</sup>-complex (2 mol%), styrene (1 equiv), ethyl diazoacetate (1.2 equiv) in toluene (2 mL) for a reaction time of 16 h. [b] Yield of isolated pure product. [c] Determined by GC analysis. [d] Determined by chiral GC analysis on a  $\beta$ -PM column; absolute configuration of the secondary alcohol was determined by comparison with literature.

lectivities (ca. 45% *ee*, Table 3, entries 1 and 2). The rotation of the chiral bicyclic terpene-derived unit towards the metal center, as achieved in the pinbpi derivatives (**5a–c**) gives the product with improved stereoselectivity. The introduction of the tetraphenyl-substituted backbone significantly improves the enantiomeric excess (compare Table 3, entries 5 and 4). The highest enantio- and diastereoselectivities were obtained by using the carene-derived catalysts (**6a–c**), in which the chiral stereodirecting elements control the active chiral space most effectively. Again, protection of the backside of the metal center by the tetraphenyl-substituted isoindole groups leads to an improved selectivity (compare Table 3, entries 8 and 7).

The optimized catalyst, [Co(tetraphenyl-carbpi)(OAc)] (**6c**), has been employed in the cyclopropanation of a variety of arylalkenes to give cyclopropane products with enantioselectivities of up to 94% (Table 4). Not unexpectedly, the system is somewhat less efficient for 1,1-disubstituted alkenes (Table 4, entries 5 and 6). Dimerization of the diazoalkane

**Table 4:** Scope of the [Co(tetraphenyl-carbpi)(OAc)]-catalyzed asymmetric inter molecular cyclopropanation.<sup>[a]</sup>

| Entry | Alkene                                                                              | Yield [%] <sup>[b]</sup> | <i>trans</i> : <i>cis</i> <sup>[c]</sup> | <i>ee</i> [%] <sup>[d]</sup> |
|-------|-------------------------------------------------------------------------------------|--------------------------|------------------------------------------|------------------------------|
| 1     |    | 97                       | 95:5                                     | 91                           |
| 2     |   | 96                       | 94:6                                     | 91                           |
| 3     |  | 93                       | 96:4                                     | 94                           |
| 4     |  | 92                       | 94:6                                     | 91                           |
| 5     |  | 78                       | 75:25                                    | 88                           |
| 6     |  | 71                       | –                                        | 80                           |

[a] General conditions: Co<sup>II</sup>-complex **6c** (2 mol%), alkene (1 equiv), ethyl diazoacetate (1.2 equiv) in toluene (2 mL) for a reaction time of 16 h. [b] Yield of isolated pure product. [c] Determined by either GC or NMR analysis. [d] Determined by chiral GC or HPLC analysis; absolute configuration of the cyclopropane rings was 1*R*,2*R*.

was not observed, conveniently allowing its addition to the alkene in one portion at the beginning of the reaction. Similarly high enantioselectivities (up to 94% *ee*) were observed in the intramolecular cyclopropanation of aryl-2-propen-1-yl diazoacetates (Table 5), demonstrating the versatility of the new catalyst system.<sup>[18d]</sup>

This is the first study of chiral bpi ligands in enantioselective catalysis with 3d-metal complexes, and the results demonstrate their efficiency as stereodirecting ligands in two mechanistically different reactions. Their modular assembly allows the facile variation of the key structural units that control the active space of the catalysts. The investigation of

**Table 5:** Scope of the [Co(tetraphenyl-carbpi)(OAc)]-catalyzed asymmetric intramolecular cyclopropanation.<sup>[a]</sup>

| Entry | R <sup>1</sup> | R <sup>2</sup>                             | R <sup>3</sup> | Yield [%] <sup>[b]</sup> | <i>ee</i> [%] <sup>[c]</sup> |
|-------|----------------|--------------------------------------------|----------------|--------------------------|------------------------------|
| 1     | H              | Ph                                         | H              | 83                       | 93                           |
| 2     | H              | <i>p</i> -ClC <sub>6</sub> H <sub>4</sub>  | H              | 81                       | 93                           |
| 3     | H              | <i>p</i> -BrC <sub>6</sub> H <sub>4</sub>  | H              | 84                       | 94                           |
| 4     | H              | <i>p</i> -MeOC <sub>6</sub> H <sub>4</sub> | H              | 79                       | 93                           |
| 5     | H              | <i>p</i> -MeC <sub>6</sub> H <sub>4</sub>  | H              | 83                       | 93                           |
| 6     | Me             | Ph                                         | H              | 74                       | 88                           |
| 7     | Ph             | Ph                                         | H              | 64                       | 77                           |
| 8     | Ph             | H                                          | H              | 42                       | 65                           |

[a] General conditions: Co<sup>II</sup>-complex **6c** (2 mol%), diazo compound (1 equiv) in toluene (2 mL) for a reaction time of 16–48 h. [b] Yield of isolated pure product. [c] Determined by chiral GC or HPLC analysis.

the scope of this new lead structure and the potential strategy it provides for discovering new catalysts is ongoing.

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- [12] *Crystal data*: **4a** C<sub>32</sub>H<sub>33</sub>N<sub>5</sub>, orthorhombic, space group *P*2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>, *a* = 12.9641(7), *b* = 13.0908(7), *c* = 15.3367(8) Å, *V* = 2602.8(2) Å<sup>3</sup>, *Z* = 4,  $\mu$  = 0.057 mm<sup>-1</sup>, *F*<sub>000</sub> = 1040.  $\theta$  range 2.1 to 30.5°. Index ranges *h*, *k*, *l* (indep. set): 0...18, 0...18, 0...21. Reflections measd.: 63065, indep.: 4413 [*R*<sub>int</sub> = 0.0542], obsvd. [*I* > 2 $\sigma$ (*I*)]: 3844. Final *R* indices [*F*<sub>o</sub> > 4 $\sigma$ (*F*<sub>o</sub>)]: *R*(*F*) = 0.0447, *wR*(*F*<sup>2</sup>) = 0.1190, *Goof* = 1.088. **12** C<sub>58.35</sub>H<sub>51.70</sub>Cl<sub>0.70</sub>CuN<sub>5</sub>O<sub>2</sub>, monoclinic, 7% pseudo-merohedral twin, space group *P*2<sub>1</sub>, *a* = 15.8992(8), *b* = 18.4526(9), *c* = 16.1443(8) Å,  $\beta$  = 90.276(1)°, *V* = 4736.4(4) Å<sup>3</sup>, *Z* = 4,  $\mu$  = 0.551 mm<sup>-1</sup>, *F*<sub>000</sub> = 1975.  $\theta$  range 1.3 to 31.0°. Index ranges *h*, *k*, *l* (indep. set): -23...23, -26...26, 0...23. Reflections measd.: 115862, indep.: 29873 [*R*<sub>int</sub> = 0.0719], obsvd. [*I* > 2 $\sigma$ (*I*)]: 24247. Final *R* indices [*F*<sub>o</sub> > 4 $\sigma$ (*F*<sub>o</sub>)]: *R*(*F*) = 0.0786, *wR*(*F*<sup>2</sup>) = 0.1488, *Goof* = 1.076; Flack parameters for the two twin individuals 0.024(8) and 0.008(6). Details of the structure solution are given in the Supporting Information. CCDC-680375 (**4a**) and CCDC-680376 (**12**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).
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