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Reusable Catalysts for the Asymmetric Diels–Alder Reaction

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Abstract: A new method for recycling chiral bis(oxazoline)–copper complexes is described based on the formation of charge-transfer complexes, their subsequent precipitation, and reuse after addition of new substrates. The conditions to perform this procedure were optimized in the presence of three bis(oxazoline)-based ligands. When associated with copper salts, these ligands efficiently catalyzed the Diels–Alder reaction between cyclopentadiene and α,β-unsaturated acyloxazolidinones. These catalysts were successfully recycled up to ten times while maintaining their high activities and enantioselectivities.

Keywords: asymmetric catalysis · catalyst recycling · charge transfer · cycloaddition · N ligands

Introduction

Asymmetric catalysis performed with dedicated chiral complexes has been widely developed for the preparation of enantiomerically enriched valuable synthons. Intensive research in this area has allowed the application of optimized methodologies on an industrial scale, mainly for reactions involving C–H bond formation.[1] However, very few industrial applications for the creation of new C–C bonds have been described, probably as a result of the low substrate to catalyst ratio that is often required for full conversion over a reasonable timescale.[2] In such a context, easy catalyst recovery (both the chiral ligand and the precious metal) and its efficient recycling can provide a solution to lower the global process cost. Chiral bis(oxazolines) proved to be the ligands of choice for the enantioselective formation of numerous C–C bonds by employing, for example, a Diels–Alder reaction, cyclopropanation, nucleophilic allylic substitution, an ene reaction, or hydrocyanation of aldehydes.[3,4] Various novel methods have been reported to allow the recovery and reuse of such efficient catalysts that are mainly based on covalent grafting to organic[5] or inorganic supports.[6] Other procedures involving the polymerization of the targeted modified ligands[7] have also been described in addition to papers reporting immobilization methodologies based on noncovalent interactions.[8] These procedures have been applied in numerous catalytic transformations leading to some success in terms of product enantioselectivity and the activity of the immobilized complexes. However, the number of catalytic cycles remained limited mainly as a result of metal leaching. These results have been presented recently in a comprehensive review.[9]

During our studies dedicated to the search for new methodologies towards efficient recycling of chiral catalysts, we recently reported a new procedure for the reuse of bis(oxazoline)–copper complexes through the formation of charge-transfer complexes.[10] This new concept was tested by performing Diels–Alder reactions between unsaturated acyloxazolidinones and cyclopentadiene in the presence of a copper complex chelated by modified bis(oxazoline) arising from (1*R*,2*S*)-(+)-*cis*-1-amino-2-indanol.

Recycling of the chiral catalyst is based on the formation of the corresponding charge-transfer complex arising from an electronic transfer between the anthracene functionality of the new bis(oxazoline)-type ligand and 2,4,7-trinitrofluorenone (TNF). At the end of the catalytic transformation, pentane is poured into the reaction mixture, which results in the precipitation of the catalyst. Products are then removed for analysis before additional solvent and substrates are added for the reuse of the catalyst. Complex **1** depicted in Scheme 1 was thus successfully used 12 times leading to the formation of the Diels–Alder *endo* products, as expected, with high yields and enantioselectivities. The formation of charge-transfer complexes to recover chiral catalysts proved to be a very efficient method, with overall high recovery of both the precious chiral ligand and metal. In this paper we report our results concerning the application of this proce-

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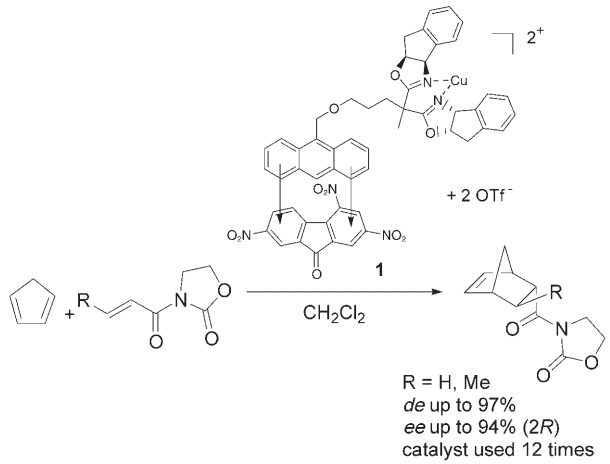


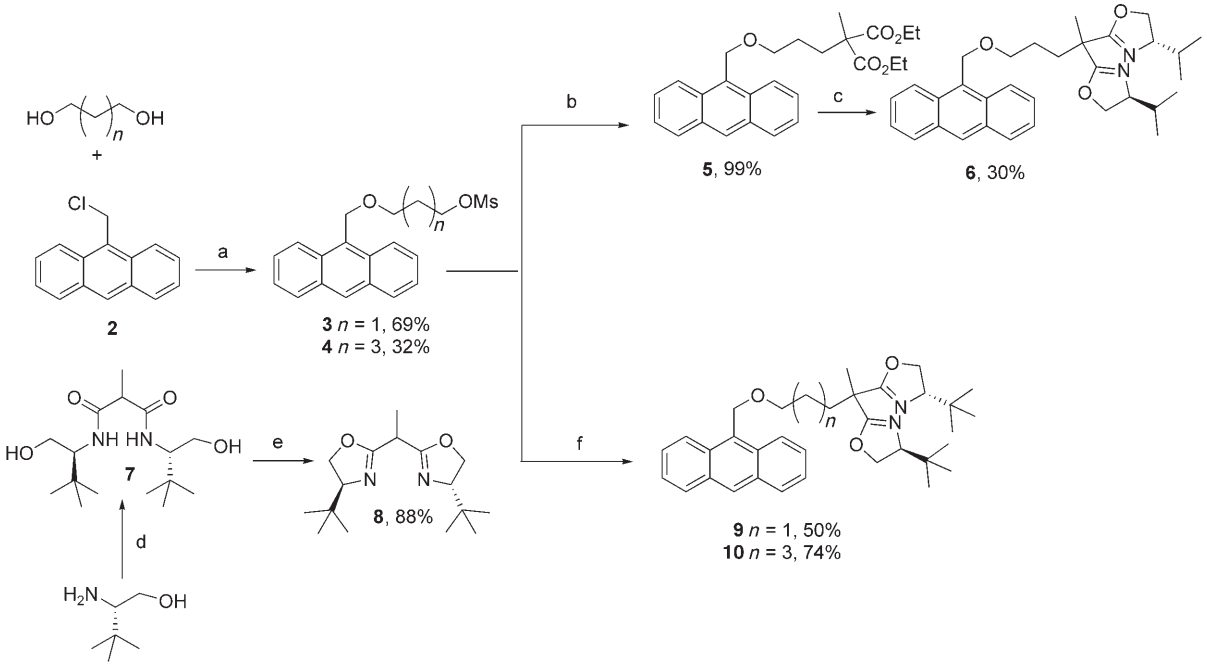
Scheme 1. Charge-transfer complex formation for recycling a bis(oxazoline)–copper catalyst.

dure to other C_2-symmetric bis(oxazolines) and especially those derived from L-valinol and (*S*)-*tert*-leucinol.

Results and Discussion

Synthesis of new modified bis(oxazolines): Three bis(oxazolines) covalently modified by an anthracene derivative have been synthesized by following a straightforward synthesis as depicted in Scheme 2. Commercially available 9-chloromethylanthracene (**2**) was transformed into the mesylated analogues **3** and **4** by means of nucleophilic substitution using 1,3-propanediol and 1,5-pentanediol, respectively, followed by subsequent mesylation. Two different strategies were tested for the introduction of the chelating bis(oxazoline) moiety. First, the synthesis of compound **6** involved the reaction between **3** and the sodium salt of diethyl methylmalonate[11] to afford the modified anthracene derivative **5** in high yield. The introduction of the bis(oxazoline) moiety was then performed through direct reaction of **5** with 4 equiv of enantiomerically pure L-valinol and sodium hydride by following a procedure described by Dodd et al. for the synthesis of mono(oxazolines).[12] The intermediate diamide was finally cyclized via its mesylated analogue in the presence of a base.[13,14] The targeted anthracene-modified bis(oxazoline) **6** was thus obtained in 20% overall yield. In the second strategy a more convergent synthesis was developed for the preparation of *tert*-leucinol derived bis(oxazolines). *tert*-Leucinol was heated in the presence of diethyl methylmalonate without solvent to yield the corresponding diamide **7**.[15] After cyclization under basic conditions and subsequent deprotonation, this methylated bis(oxazoline) (**8**) was reacted with mesylates **3** and **4** to give compounds **9** and **10**, respectively, in good yields.[16] These three new ligands were purified by using flash chromatography and were also fully characterized.

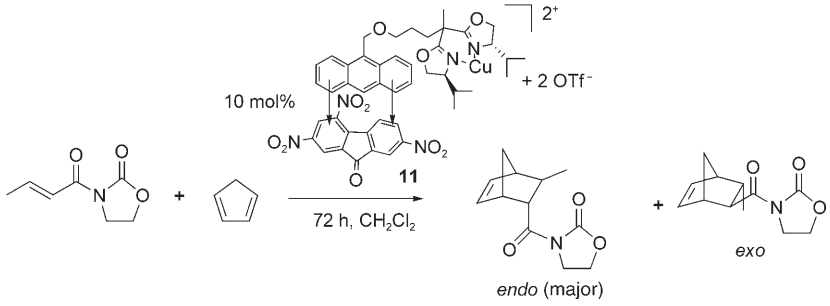
Catalytic tests: The new enantiomerically pure bis(oxazolines) were tested as copper ligands in the asymmetric Diels–Alder reactions between cyclopentadiene and α,β-unsaturated acyloxazolidinones. The new ligands were first used in the Diels–Alder reaction under homogeneous conditions. In our hands, 2,2′-isopropylidenebis[(4*S*)-4-isopropyl-



Scheme 2. Synthesis of modified anthracene-linked bis(oxazolines). Reagents and conditions: a) 1) NaH, tBu$_4$NI, THF; 2) NEt$_3$, DMAP, MsCl, CH_2Cl_2. b) $CH_3CH(CO_2Et)_2$, NaH, THF. c) 1) L-valinol, NaH, toluene; 2) NEt$_3$, MsCl, CH_2Cl_2; 3) NaOH (0.5 M). d) $CH_3CH(CO_2Et)_2$, 110 °C, 3 d. e) 1) NEt$_3$, MsCl; 2) NaOH. f) LDA, THF, 60 °C.

2-oxazoline] associated to copper(II) triflate allowed the reaction between 3-(but-2-enoyl)oxazolidin-2-one and cyclopentadiene to be performed at 0°C in dichloromethane, and the expected *endo* major product was obtained with an enantioselectivity (*ee*) of 40%. Analogous conditions were applied for the same transformation in the presence of ligand **6**, which led to the desired product, but with a significant loss of enantioselectivity (22% *ee*). It turns out that the partial loss of C_2 symmetry as a result of the monofunctionalization of the bis(oxazoline) ligand, albeit on the *gem*-dimethyl group, is detrimental to enantiofacial discrimination during the catalytic transformation.

Table 1. Recycling chiral copper complex **11** for a Diels–Alder transformation.



Cycle	*T* [°C]	Conversion[a] [%]	*de*[b] [%]	*ee*[b] (*endo*) [%]
1	0	47	63	25 (2*S*)
2	0	88	63	22 (2*S*)
3	0	81	61	22 (2*S*)
4	0	88	67	21 (2*S*)
5	−20	32	71	25 (2*S*)
6	0	63	66	22 (2*S*)

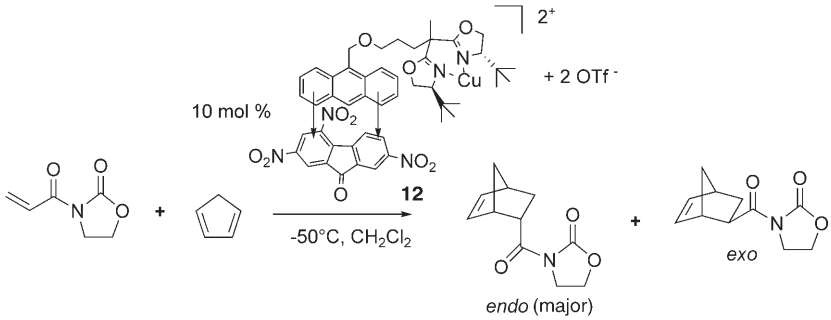
[a] Determined by GC. [b] Determined by HPLC chromatography (Whelk, hexane/ethanol).

The procedure for the recovery and recycling of the chiral copper catalyst arising from **6** and copper(II) triflate first involved the ex situ preparation of charge-transfer complex **11** from equimolar amounts of chiral copper catalyst and TNF dissolved in dichloromethane. Substrates were then added to the homogeneous red solution and the reaction was performed at 0°C. The results are reported in Table 1.

The first use of the catalyst yielded the expected *endo* product with an enantioselectivity similar to that reported in the absence of the electron-deficient molecule. Thus, the presence of the charge-transfer complex does not modify the efficiency of the catalyst. As the complex was soluble in dichloromethane, pentane was added directly to the reaction mixture at the end of the transformation, which resulted in the immediate precipitation of a red powder. Products and solvents were removed; the precipitated charge-transfer complex was washed with pentane and dried under vacuum before new substrates and solvent were added to reuse the catalyst. This procedure was repeated five times, which allowed the formation of the expected product with no loss of enantiomeric excess. A lower reaction temperature (Table 1, 5th cycle, −20°C) led to a lower conversion of the substrates in the same reaction time (72 h) and the sixth cycle was accompanied by a decreased activity of the catalyst.

This procedure was then tested with other ligands, compounds **9** and **10** in Scheme 2, derived from the well-known 2,2′-isopropylidenebis[(4*S*)-4-*tert*-butyl-2-oxazoline] ligand developed by Evans and co-workers as an efficient copper(II) ligand for the simultaneous formation of two new C–C bonds in a highly diastereo- and enantioselective fashion.[17,18] We used this catalytic system to perform the Diels–Alder reaction between cyclopentadiene and 3-acryloyloxazolidin-2-one dissolved in dichloromethane, at −50°C, with a high diastereoselectivity in favor of the *endo* isomer (94% *de*) with an enantioselectivity of 97%. Both ligands **9** and **10** were tested under these conditions and led to the same major isomer with similar enantioselectivities (90% *ee* in both cases). The partial loss of C_2-symmetry appeared to be less important for the *tert*-leucinol-derived ligands relative to structure **6**. A similar procedure was then used for the synthesis of the chiral complex arising from **9** towards its recycling, that is, the preliminary ex situ preparation of the corresponding charge-transfer complex with TNF. Complex **12** was tested as a catalyst for the Diels–Alder reaction depicted in Table 2, in dichloromethane at −50°C. Its recov-

Table 2. Recycling chiral copper complex **12** for a Diels–Alder transformation.



Cycle	*t* [h]	Conversion[a] [%]	*de*[b] [%]	*ee*[b] (*endo*) [%]
1	33	64	87	15 (2*S*)
2	44	83	84	44 (2*S*)
3	44	90	86	49 (2*S*)
4	44	90	89	54 (2*S*)

[a] Determined by GC. [b] Determined by HPLC chromatography (ODH, hexane/isopropanol).

ery again involved the addition of pentane at the end of the catalytic transformation for its precipitation.

Surprisingly, complex **12** behaved differently to **11** in that its first use led to the preparation of the desired product with a very low enantiomeric excess. Long reaction times were necessary to afford high conversions and interestingly, the enantioselectivity of the transformation increased with successive cycles. Complex **13**, the copper complex arising from ligand **10** and TNF, behaved similarly, that is, the first cycle afforded the product with an enantioselectivity of 33%, whereas the second cycle allowed its isolation with an enantioselectivity of 86%. Thus, the length of the spacer between the active catalytic site and the charge-transfer complex is not the major factor in determining the enantioselectivity of the transformation. The *tert*-leucinol derived bis(oxazolines) are strongly sterically hindered around the coordination site and these experiments indicate that either the chiral catalytic species is formed slowly or that the efficient chiral catalyst is purified during successive cycles.

To check this proposal, the copper complex prepared directly from **9** was used in a catalytic transformation. After total conversion of the substrates, TNF was added and led to the immediate formation of complex **12**. As expected, products isolated from this first transformation were obtained with high enantiomeric excess (85% *ee*, Table 3).

Catalyst **12,** formed in situ, was subsequently reused five times and showed that only 19 h reaction time was necessary to obtain total conversion of the substrates. Although this recycling was performed without loss of activity, a substantial decrease in enantioselectivity occurred. The detrimental effect of water on the copper catalyst prepared from *tert*-leucinol derived bis(oxazolines) and copper triflate has been unambiguously demonstrated by Evans and co-workers.[17] Therefore, 4 Å molecular sieves were added prior to the sixth cycle of the catalyst and to our delight the product was subsequently isolated with a high enantioselectivity (91% *ee*). Catalyst **12** maintained its performance for four additional runs. A similar behavior was observed for catalyst **13**, formed from ligand **10** and these results are described in the Experimental Section.

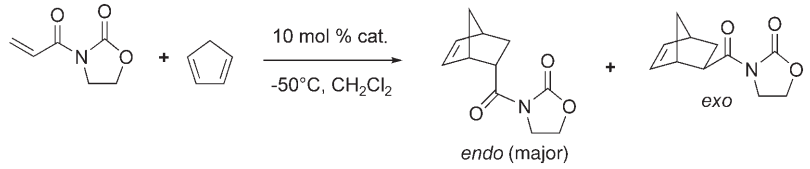
To study the difference in stability between the complexes derived from *tert*-leucinol or indanol, calculations were performed to provide representations of the catalyst–substrate complexes. Previously, Evans and co-workers[17,18] reported detailed investigations on copper–*tert*-leucinol–bis(oxazoline) complexes based on X-ray analyses of bis(aquo) or dichloride analogues. The crystallographic data revealed a distorted square-pyramidal geometry at the copper atom with one triflate molecule acting as a counteranion placed in the apical position and the other one fully dissociated. Crystals of [CuX_2{indane–bis(oxazoline)}], in which X = Cl or Br, were prepared and analyzed by Jørgensen and co-workers[19] who arrived at the same conclusion. However, their attempts to obtain complex–substrate crystals suitable to perform X-ray analyses failed. PM3 calculations were performed by Evans et al. in the presence of the dienophile, which used a two-point chelation to the copper metal center in an s-*cis* dienophile conformation to account for the stereochemical outcome of the cycloaddition. To mimic copper complexes coordinated to methyl glyoxylate as a substrate, Jørgensen carried out calculations by using the restricted open-shell Hartree–Fock method. The data obtained are similar to those determined by X-ray analyses for related complexes.

Starting from these results, we have performed calculations with the PM3 semiempirical method using the Hyperchem 5.11 Standard package[20] with the unrestricted Hartree–Fock method. We have modeled complexes derived from two bis(oxazoline) molecules coordinated to dienophile substrates for a comparison of their structure. Complexes **14** and **15** shown in Scheme 3 represent the structures of minimal energy obtained with a good convergence.

Both calculated complexes possess a similar structure with the copper atom in a distorted square-planar geometry. Surprisingly, the anthracene moiety is placed on the same side facing the oxazoline substituent. Calculated bond lengths and dihedral angles are quite similar, but the average degree of distortion of the coordinated substrate in complex **14** is larger than that in complex **15**. This difference may explain the lower stability of complex **14** relative to **15** and the catalytic results obtained. Furthermore, the absolute configuration observed in the catalytic transformation is in agreement with the calculated predictions.

Finally, the ability of catalyst **12** to perform a multisubstrate

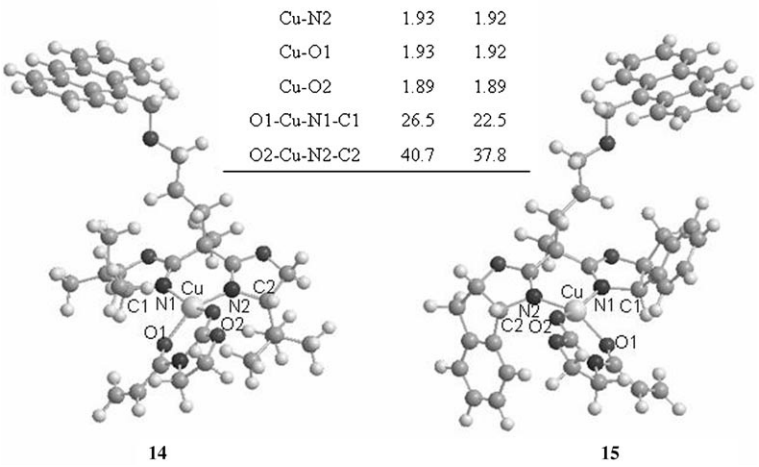
Table 3. New procedure for recycling chiral copper complex **12**.



Catalyst	Cycle	*t* [h]	Conversion[a] [%]	Yield [%]	*de*[b] [%]	*ee* (*endo*) [%][b]
[Cu(**9**)]	0	44	100	95	87	85 (2*S*)
12	1	44	100	91	87	76 (2*S*)
12	2	44	100	88	82	70 (2*S*)
12	3	30	100	88	84	69 (2*S*)
12	4	20	100	83	83	67 (2*S*)
12	5	19	100	95	84	64 (2*S*)
12[c]	6	19	100	96	90	91 (2*S*)
12	7	19	100	90	90	92 (2*S*)
12	8	19	100	87	85	90 (2*S*)
12	9	19	100	85	89	91 (2*S*)
12	10	19	94	76	90	86 (2*S*)

[a] Determined by GC. [b] Determined by HPLC chromatography (ODH, hexane/isopropanol). [c] After addition of 4 Å molecular sieves.

Measurement	14	15
Cu-N1	1.92	1.91
Cu-N2	1.93	1.92
Cu-O1	1.93	1.92
Cu-O2	1.89	1.89
O1-Cu-N1-C1	26.5	22.5
O2-Cu-N2-C2	40.7	37.8



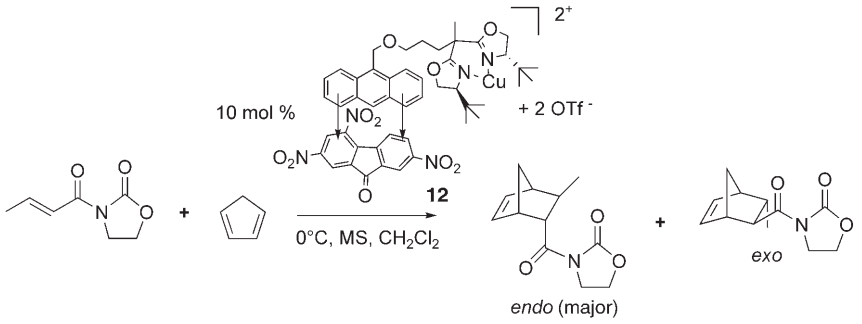
14 15

Scheme 3. Calculated PM3 structures and selected bond lengths [Å] and dihedral angles [°] for **14** and **15**.

transformation was studied. The efficient recycling of asymmetric catalysts is essential for the increase of the substrate to catalyst ratio. It is also important to check if the immobilized catalyst is able to perform reactions involving different substrates during the recycling procedure. Rarely has such a concept been demonstrated, despite the abundant literature regarding methodologies for asymmetric heterogeneous catalysts.[21]

The [Cu(**9**)] catalyst was first used for the efficient transformation of 3-(but-2-enoyl)-oxazolidin-2-one into 3-(3-methylbicyclo[2.2.1]hept-5-ene-2-carbonyl)oxazolidin-2-one at 0 °C. The subsequent addition of TNF, followed by precipitation of the charge-transfer complex **12** by pentane, allowed its reuse for three additional cycles (Table 4). A slight decrease in enantioselectivity was observed after the third cycle, therefore, now molecular sieves were added. The fourth cycle of the catalyst was performed at −50 °C by using 3-acryloyloxazolidin-2-one and 3-(bicyclo[2.2.1]hept-5-ene-2-carbonyl)oxazolidin-2-one and the product was isolated in high yield and enantioselectivity (Table 5). However, this product was obtained together with traces of 3-(3-methylbicyclo[2.2.1]hept-5-ene-2-carbonyl)oxazolidin-2-one, probably arising from coordination to the copper center during the previous cycle. Additional cycles were successfully performed by using 3-acryloyl-oxazolidin-2-one and the corresponding product was isolated in its pure form. Unfortunately, reusing the complex led to the expected product with a significant loss of activity and enantioselectivity. As previously mentioned, the bis(oxazoline)

Table 4. Multisubstrate recycling of chiral copper complex **12**.



Catalyst	Cycle	*t* [h]	Conversion[a] [%]	Yield [%]	*de*[b] [%]	*ee* (*endo*) [%][b]
[Cu(**9**)]	0	42	56	42	96	87 (2*S*)
12	1	66	100	89	76	87 (2*S*)
12	2	66	100	87	73	84 (2*S*)
12	3	66	82	75	80	78 (2*S*)

[a] Determined by NMR spectroscopy. [b] Determined by HPLC chromatography (Whelk, hexane/ethanol).

Table 5. Multisubstrate recycling of chiral copper complex **12**.

Catalyst	Cycle	*t* [h]	Conversion[a] [%]	Yield [%]	*de*[b] [%]	*ee* (*endo*) [%][b]
12[c]	4	18	100	91	88	89 (2*S*)
12	5	18	91	80	91	84 (2*S*)
12	6	18	64	62	90	71 (2*S*)

[a] Determined by NMR spectroscopy. [b] Determined by HPLC chromatography (ODH, hexane/isopropanol). [c] After addition of 4 Å molecular sieves.

arising from the *tert*-butyl-substituted aminoalcohol led to a more sensitive catalyst relative to the complex derived from enantiomerically pure indanol.

Conclusion

We have prepared three new bis(oxazoline)-based ligands for use in asymmetric Diels–Alder reactions, which result in high activities and enantioselectivities. All these catalysts were easily recovered and reused by the formation of charge-transfer complexes between their anthracene moiety and TNF. After precipitation with pentane and removal of the product solution, new substrates could be added for a new reaction run. The valinol-modified bis(oxazoline) led to poor results in terms of enantiofacial discrimination for this catalytic transformation even if the catalytic system was highly stable under the recycling conditions. The *tert*-leucinol derivatives yielded the expected *endo* product with much higher enantioselectivity. However, preparation of the copper catalyst and the corresponding charge-transfer complex was more dependent on the synthetic procedure. We have demonstrated that in this case the active and enantioselective species had to be prepared in the absence of the electron deficient molecule for efficient recycling after a first catalytic transformation. PM3 calculations on this complex and on the analogous indanol derivative attached to the dienophile substrate have been performed, and showed similar structures with an average degree of distortion of the coordinated substrate in the *tert*-leucinol complex slightly larger than that in the indanol derivative. We assume that the different behavior of complexes **12** and **13** relative to the other catalysts derived from valinol or indanol is owing to a more sterically hindered coordination site around the copper atom. These new chiral catalysts have been efficiently used and recycled as enantioselective and active copper species to perform up to eleven Diels–Alder reactions without loss of enantioselectivity or activity.

Experimental Section

General remarks: All reactions were carried out under an argon atmosphere in oven-dried glassware with magnetic stirring. Solvents were distilled before use: THF from sodium metal/benzophenone, Et_3N and CH_2Cl_2 from calcium hydride. Cyclopentadiene was distilled by cracking dicyclopentadiene over calcium hydride. ^{1}H NMR spectra were recorded on either a Bruker AM 200 (200 MHz) or an AM 250 (250 MHz) instrument with samples dissolved in $CDCl_3$ and data are reported in ppm relative to the solvent (7.27 ppm). ^{13}C NMR spectra were recorded on a Bruker AM 250 (62.5 MHz) instrument with samples dissolved in $CDCl_3$ and data are reported in ppm relative to the solvent (77.0 ppm). Optical rotations were measured for sample solutions in 10 cm cells at the sodium D line by using a Perkin–Elmer 241 polarimeter. Melting points were measured with a Reichert instrument. Gas chromatography analyses were performed on a Fisons 9000 gas chromatograph, using a BP1 column (15 m × 0.32 mm × 0.5 μm). Mass spectra were recorded on a Finnigan MAT 95 S spectrometer. HPLC analyses were carried out on a Perkin–Elmer chromatograph equipped with a diode array UV detector using an ODH or a WHELK column.

3-[(Anthracen-9-yl)methoxy]propan-1-ol: Freshly distilled 1,3-propanediol (942 μL, 13 mmol) was added to a suspension of NaH (529 mg, 13 mmol, 60% in mineral oil) in dry THF (60 mL) at 0°C. The mixture was stirred for 3 h at room temperature before tetrabutylammonium iodide (814 mg, 2.08 mmol) and a solution of 9-chloromethylanthracene (3 g, 13 mmol) in THF (30 mL) were added at 0°C. The mixture was stirred overnight at room temperature. The resulting suspension was treated with a saturated aqueous NH_4Cl solution and extracted with Et_2O (3× 30 mL). The combined organic phases were washed with water, saturated aqueous NaCl solution, and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by using flash chromatography (cyclohexane/EtOAc, 1:1) to give the expected alcohol as a yellow oil (2.9 g, 84%). R_f = 0.36 (cyclohexane/EtOAc 1:1); ^{1}H NMR (250 MHz, $CDCl_3$): δ = 8.47 (s, 1H), 8.37 (d, J = 8.8 Hz, 2H), 8.02 (d, J = 7.8 Hz, 2H), 7.52–7.48 (m, 4H), 5.49 (s, 2H), 3.83 (t, J = 5.6 Hz, 2H), 3.72 (t, J = 5.6 Hz, 2H), 2.30 (br s, 1H), 1.90–1.85 ppm (m, 2H); ^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 131.5 (C_q^{arom}), 131.0 (C_q^{arom}), 129.4 (C_H^{arom}), 128.8 (C_H^{arom}), 126.7 (C_H^{arom}), 125.3 (C_H^{arom}), 124.4 (C_H^{arom}), 69.7 (CH_2), 66.3 (CH_2), 62.1 (CH_2), 32.6 ppm (CH_2); HRMS (ESI): m/z: calcd for $C_{18}H_{18}NaO_2$: 289.1199; found: 289.1202 [M+Na$^+$].

5-[(Anthracen-9-yl)methoxy]pentan-1-ol: Freshly distilled 1,5-pentanediol (460 μL, 4.4 mmol) was added to a suspension of NaH (176 mg, 4.4 mmol, 60% in mineral oil) in dry THF (10 mL) at 0°C. The mixture was stirred for 3 h at room temperature before tetrabutylammonium iodide (260 mg, 0.7 mmol) and a solution of 9-chloromethylanthracene (1 g, 4.4 mmol) dissolved in THF (20 mL) were added at 0°C. The mixture was stirred overnight at room temperature. The resulting suspension was treated with a saturated NH_4Cl solution and extracted with Et_2O (3× 30 mL). The combined organic phases were washed with water, saturated aqueous NaCl solution, and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by using flash chromatography (cyclohexane/EtOAc, 2:1) to give the expected alcohol as a yellow oil (601 mg, 46%). R_f = 0.33 (cyclohexane/EtOAc, 1:1); ^{1}H NMR (250 MHz, $CDCl_3$): δ = 8.46 (s, 1H), 8.40 (d, J = 8.8 Hz, 2H), 8.02 (d, J = 8.8 Hz, 2H), 7.57–7.46 (m, 4H), 5.47 (s, 2H), 3.68 (t, J = 6.3 Hz, 2H), 3.54 (t, J = 6.3 Hz, 2H), 1.68–1.62 (m, 2H), 1.54–1.42 ppm (m, 4H); ^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 131.5 (C_q^{arom}), 131.0 (C_q^{arom}), 128.9 (C_H^{arom}), 128.2 (C_H^{arom}), 126.1 (C_H^{arom}), 124.9 (C_H^{arom}), 124.4 (C_H^{arom}), 70.5 (CH_2), 65.0 (CH_2), 62.7 (CH_2), 32.4 (CH_2), 29.5 (CH_2), 22.4 ppm (CH_2); HRMS (ESI): m/z: calcd for $C_{20}H_{22}NaO_2$: 317.1512; found: 317.1518 [M+Na$^+$].

3-[(Anthracen-9-yl)methoxy]propyl methanesulfonate (3): 3-[(Anthracen-9-yl)methoxy]propan-1-ol (1.59 g, 5.98 mmol), dry CH_2Cl_2 (48 mL), Et_3N (1.23 mL, 8.97 mmol), and dimethylaminopyridine (DMAP) (37 mg, 0.3 mmol) were added to a flask. After cooling the solution in an ice bath, mesyl chloride (1.23 mL, 10.7 mmol) was added dropwise and the mixture was stirred at room temperature for 1.5 h. The resulting suspension was washed with cold water and extracted with CH_2Cl_2 (3×30 mL). The combined organic phases were washed with 0.1 N aqueous HCl, saturated aqueous $NaHCO_3$ solution, saturated aqueous NaCl solution, dried over $MgSO_4$, and the solvent was removed under reduced pressure. The residue was purified by using flash chromatography (cyclohexane/EtOAc, 1:1) to give product **3** as a yellow solid (1.68 g, 4.9 mmol, 82%). R_f = 0.59 (cyclohexane/EtOAc, 1:1); m.p. 78°C; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 8.48 (s, 1H), 8.38 (d, J = 8.8 Hz, 2H), 8.02 (d, J = 8.3 Hz, 2H), 7.57–7.48 (m, 4H), 5.51 (s, 2H), 4.26 (t, J = 6.3 Hz, 2H), 3.77 (t, J = 5.8 Hz, 2H), 2.74 (s, 3H), 2.04–2.00 ppm (m, 2H); ^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 131.4 (C_q^{arom}), 131.1 (C_q^{arom}), 129.1 (C_H^{arom}), 128.5 (C_H^{arom}), 126.3 (C_H^{arom}), 125.1 (C_H^{arom}), 124.2 (C_H^{arom}), 67.4 (CH_2), 65.5 (CH_2), 65.0 (CH_2), 36.7 (CH_3), 29.6 ppm (CH_2); HRMS (ESI): m/z: calcd for $C_{19}H_{20}NaO_4S$: 367.0975; found: 367.0983 [M+Na$^+$].

5-[(Anthracen-9-yl)methoxy]pentyl methanesulfonate (4): 5-[(Anthracen-9-yl)methoxy]pentan-1-ol (570 mg, 1.9 mmol), dry CH_2Cl_2 (5 mL), Et_3N (409 μL, 2.8 mmol), and DMAP (12 mg, 0.1 mmol) were added to a flask. After cooling the solution in an ice bath, mesyl chloride (270 μL, 3.4 mmol) was added dropwise and the mixture was stirred at room temperature for 1.5 h. The resulting suspension was washed with cold water and extracted with CH_2Cl_2 (3×30 mL). The combined organic phases were washed with 0.1 N aqueous HCl, saturated aqueous $NaHCO_3$ solu-

tion, saturated aqueous NaCl solution, dried over $MgSO_4$, and the solvent was removed under reduced pressure. The residue was purified by using flash chromatography (cyclohexane/EtOAc, 2:1) to give product **4** as a yellow solid (497 mg, 1.3 mmol, 69%). R_f = 0.55 (cyclohexane/EtOAc, 1:1); m.p. 84 °C; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 8.41 (s, 1H), 8.38 (d, J = 8.8 Hz, 2H), 7.99 (d, J = 8.2 Hz, 2H), 7.60–7.45 (m, 4H), 5.41 (s, 2H), 4.07 (t, J = 6.3 Hz, 2H), 3.64 (t, J = 6.3 Hz, 2H), 2.83 (s, 3H), 1.68–1.59 (m, 4H), 1.45–1.41 ppm (m, 2H); ^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 131.2 (C_q^{arom}), 130.5 (C_q^{arom}), 128.6 (C_H^{arom}), 127.8 (C_H^{arom}), 125.7 (C_H^{arom}), 124.6 (C_H^{arom}), 123.9 (C_H^{arom}), 69.8 (CH_2), 69.6 (CH_2), 64.5 (CH_2), 36.6 (CH_3), 28.7 (CH_2), 28.3 (CH_2), 21.8 ppm (CH_2); HRMS (ESI): m/z: calcd for $C_{21}H_{24}NaO_4S$: 395.1288; found: 395.1290 [M+Na$^+$].

Diethyl 2-{3-[(anthracen-9-yl)methoxy]propyl}-2-methylmalonate (5): Freshly distilled diethyl methylmalonate (857 μL, 5 mmol) was added to a suspension of NaH (239 mg, 6.0 mmol, 60% in mineral oil) in dry THF (5 mL). The mixture was stirred for 2 h at room temperature before compound **3** (1.9 g, 5.5 mmol) dissolved in THF (20 mL) was added dropwise and the mixture was stirred at 60 °C overnight. The solution was cooled, washed with a saturated aqueous NaCl solution, and extracted with Et_2O (3×20 mL). The combined organic phases were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The residue was purified by using flash chromatography (cyclohexane/EtOAc, 2:1) to give product **5** as a yellow solid (2.07 g, 99%). R_f = 0.67 (cyclohexane/EtOAc, 1:1); m.p. 44 °C; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 8.47 (s, 1H), 8.39 (d, J = 8.8 Hz, 2H), 8.02 (d, J = 8.3 Hz, 2H), 7.59–7.44 (m, 4H), 5.47 (s, 2H), 4.15 (q, J = 6.8 Hz, 4H), 3.67 (t, J = 6.8 Hz, 2H), 1.97–1.88 (m, 2H), 1.65–1.57 (m, 2H), 1.37 (s, 3H), 1.21 ppm (t, J = 6.8 Hz, 6H); ^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 171.9 (CO_2Me), 131.1 (C_q^{arom}), 130.7 (C_q^{arom}), 128.7 (C_H^{arom}), 127.9 (C_H^{arom}), 125.8 (C_H^{arom}), 124.6 (C_H^{arom}), 124.1 (C_H^{arom}), 70.1 (CH_2), 64.6 (CH_2), 60.8 (*C*H$_2$-CH$_3$), 53.1 (Cq), 32.1 (CH_2), 24.7 (CH_2), 19.6 (CH_3), 13.7 ppm (CH$_2$-*C*H$_3$); HRMS (ESI): m/z: calcd for $C_{26}H_{30}NaO_5$: 445.1985; found: 445.1992 [M+Na$^+$].

2-{3-[(Anthracen-9-yl)methoxy]propyl}-N^1,N^3-bis[(S)-1-hydroxy-3-methylbut-2-yl]-2-methylmalonamide: (*S*)-2-Amino-3-methylbutan-1-ol (4.4 g, 40 mmol, 4 equiv) was added to a suspension of NaH (1.88 g, 44 mmol, 60% in mineral oil) in toluene (30 mL). The mixture was stirred for 1 h at room temperature. Then compound **5** (4.5 g, 10 mmol) in toluene (46 mL) was added dropwise. The mixture was stirred overnight at room temperature. The solution was washed with a saturated aqueous NaCl solution then extracted with CH_2Cl_2. The combined organic phases were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The residue was purified by distillation to give the diamide product as a white solid (2.26 g, 42%). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 8.47 (s, 1H), 8.34 (d, J = 8.3 Hz, 2H), 8.02 (d, J = 8.3 Hz, 2H), 7.59–7.44 (m, 4H), 6.95 (d, J = 8.8 Hz, 1H), 6.57 (d, J = 8.8 Hz, 1H), 5.48 (s, 2H), 3.77–3.71 (m, 2H), 3.62- 3.51 (m, 4H), 3.09- 3.00 (m, 2H), 2.06–2.00 (m, 2H), 1.69–1.58 (m, 4H), 1.38 (s, 3H), 0.77 (d, J = 6.8 Hz, 6H), 0.60 ppm (d, J = 6.8 Hz, 6H).

Bis(oxazoline) 6: The above-mentioned diamide (862 mg, 1.6 mmol) and NEt_3 (1.12 mL, 8 mmol) were dissolved in dry CH_2Cl_2 (11 mL). After cooling the solution in an ice bath, mesyl chloride (309 μL, 4 mmol) was added dropwise and the mixture was stirred at room temperature for 2 h. The solution was washed with saturated aqueous NH_4Cl and NaCl solutions, and extracted with CH_2Cl_2. The combined organic phases were dried over $MgSO_4$ and the solvent was removed under reduced pressure. A solution of NaOH (0.5 M, 11 mL) was added to the resulting oil and the mixture was stirred at reflux for 3 h. The solution was cooled, extracted with CH_2Cl_2, and washed with saturated aqueous NaCl solution. The combined organic phases were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The residue was purified by using flash chromatography (cyclohexane/EtOAc, 2:1) to give product **6** as a yellow oil (149 mg, 71%). R_f = 0.67 (cyclohexane/EtOAc, 1:1); $[\alpha]_D$ = −46 (c = 1 in $CHCl_3$); ^{1}H NMR (250 MHz, $CDCl_3$): δ = 8.44 (s, 1H), 8.40 (d, J = 7.8 Hz, 2H), 8.00 (d, J = 7.8 Hz, 2H), 7.52–7.48 (m, 4H), 5.46 (s, 2H), 4.19–4.13 (m, 2H), 3.98–3.92 (m, 4H), 3.68 (t, J = 6.8 Hz, 2H), 2.05–1.95 (m, 2H), 1.78–1.60 (m, 4H), 1.49 (s, 3H), 0.89 (d, J = 6.8 Hz, 6H), 0.83 ppm (d, J = 6.8 Hz, 6H); ^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 168.0 (CN), 167.9 (CN), 131.4 (C_q^{arom}), 131.0 (C_q^{arom}), 128.9 (C_H^{arom}), 128.2 (C_H^{arom}), 126.1 (C_H^{arom}), 124.9 (C_H^{arom}), 124.5 (C_H^{arom}), 71.7 (CH-N), 71.5 (CH-N), 70.8 (CH_2), 69.9 (CH_2), 69.7 (CH_2), 64.9 (CH_2), 42.1 (C_q), 33.2 (CH_2), 32.4 (CH), 32.3 (CH), 24.9 (CH_2), 21.5 (CH_3), 18.8 (CH_3), 18.7 (CH_3), 17.7 (CH_3), 17.5 ppm (CH_3); HRMS (ESI): m/z: calcd for $C_{32}H_{40}NaN_2O_3$: 523.2931; found: 523.2957 [M+Na$^+$].

Diamide 7: Diethyl methylmalonate (495 mL, 2.8 mmol) and (*S*)-*tert*-leucinol (706 mg, 5.9 mmol) were added to a Schlenk tube. The mixture was stirred for 3 days at 110 °C. The product was obtained quantitatively as a white solid. M.p. 138 °C; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.41 (d, J = 9.7 Hz, 1H), 7.31 (d, J = 9.7 Hz, 1H), 3.98–3.34 (m, 7H), 1.53 (d, J = 6.7 Hz, 3H), 0.96 (s, 9H), 0.91 ppm (s, 9H); ^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 173.8 (CO), 173.0 (CO), 61.8 (CH_2), 61.5 (CH_2), 59.4 (2× CH), 48.9 (CH), 33.4 (2×Cq), 26.7 (6×CH_3), 17.3 ppm (CH_3); HRMS (ESI): m/z: calcd for $C_{16}H_{32}NaN_2O_4$: 339.2254; found: 339.2257 [M+Na$^+$].

Bis(oxazoline) 8: Compound **7** (524 mg, 1.7 mmol) and NEt_3 (1.18 mL, 8.5 mmol) were dissolved in dry CH_2Cl_2 (12 mL). After cooling the solution in an ice bath, mesyl chloride (325 μL, 4.25 mmol) was added dropwise and the mixture was stirred at room temperature for 2 h. The solution was washed with saturated aqueous NH_4Cl and NaCl solutions, and extracted with CH_2Cl_2. The combined organic phases were dried over $MgSO_4$ and the solvent was removed under reduced pressure. A solution of NaOH (0.5 M, 12 mL) was added to the resulting oil and the mixture was stirred at reflux for 3 h. The solution was cooled, extracted with CH_2Cl_2, and washed with saturated aqueous NaCl solution. The combined organic phases were dried over $MgSO_4$ and the solvent was removed under reduced pressure. Product **8** was obtained as a bluish oil (415 mg, 88%). The product was pure enough to be used in the following step without further purification. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 4.11–3.96 (m, 4H), 3.77 (t, J = 8.5 Hz, 2H), 3.45 (q, J = 7.5 Hz, 1H), 1.38 (d, J = 7.5 Hz, 3H), 0.79 ppm (s, 18H); ^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 166.2 (CN), 165.9 (CN), 76.1 (2×CH-N), 69.6 (2×CH_2), 34.6 (CH), 34.3 (2×Cq), 26.3 (6×CH_3), 15.9 ppm (CH_3); HRMS (ESI): m/z: calcd for $C_{16}H_{29}N_2O_2$: 281.2224; found: 281.2231 [M+H$^+$].

Bis(oxazoline) 9: *N*,*N*,*N*′,*N*′-Tetramethylethane-1,2-diamine (TMEDA) (145 μL, 0.96 mmol) and *i*Pr$_2$NH (271 μL, 1.92 mmol) were dissolved in dry THF (3 mL) before *n*BuLi (1.21 mL, 1.6 M in hexanes) was added at −20 °C. The mixture was stirred at −20 °C for 1 h and added at −20 °C to a solution of **8** (270 mg, 0.96 mmol) dissolved in THF (20 mL). The mixture was stirred for 3 h at room temperature before mesylate **3** (498 mg, 1.44 mmol) was added at −20 °C. The mixture was heated at 60 °C for 24 h. The solution was cooled, washed with saturated aqueous NH_4Cl solution, and extracted with EtOAc (3×30 mL). The combined organic phases were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The residue was purified by using flash chromatography (cyclohexane/EtOAc, 4:1) to give product **9** as a yellow oil (255 mg, 0.48 mmol, 50%). R_f = 0.51 (cyclohexane/EtOAc, 1:1); $[\alpha]_D$ = −62 (c = 1 in $CHCl_3$); ^{1}H NMR (250 MHz, $CDCl_3$): δ = 8.46 (s, 1H), 8.40 (d, J = 7.8 Hz, 2H), 8.01 (d, J = 7.8 Hz, 2H), 7.53–7.45 (m, 4H), 5.47 (s, 2H), 4.15–3.98 (m, 4H), 3.89–3.78 (m, 2H), 3.68 (t, J = 6.8 Hz, 2H), 2.13–2.00 (m, 2H,), 1.78–1.62 (m, 2H), 1.45 (s, 3H), 0.86 ppm (s, 18H); ^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 168.3 (CN), 168.1 (CN), 131.8 (C_q^{arom}), 131.4 (C_q^{arom}), 129.3 (C_H^{arom}), 128.6 (C_H^{arom}), 126.4 (C_H^{arom}), 125.3 (C_H^{arom}), 124.8 (C_H^{arom}), 75.8 (CH-N), 75.7 (CH-N), 71.1 (CH_2), 69.1 (2×CH_2), 65.1 (CH_2), 42.5 (Cq), 34.3 (2×Cq), 33.6 (CH_2), 26.2 (6×CH_3), 25.3 (CH_2), 21.8 ppm (CH_3); HRMS (ESI): m/z: calcd for $C_{34}H_{44}NaN_2O_3$: 551.3244; found: 551.3245 [M+Na$^+$].

Bis(oxazoline) 10: TMEDA (43 μL, 0.29 mmol) and *i*Pr$_2$NH (80 μL, 0.57 mmol) were dissolved in dry THF (2 mL) before *n*BuLi (359 μL, 1.6 M in hexanes) was added at −20 °C. The mixture was stirred at −20 °C for 1 h and added at −20 °C to a solution of **8** (80 mg, 0.29 mmol) dissolved in THF (7 mL). The mixture was stirred for 3 h at room temperature before mesylate **4** (160 mg, 0.43 mmol) was added at −20 °C. The mixture was heated at 60 °C for 24 h. The solution was cooled, washed with saturated aqueous NH_4Cl solution, and extracted with EtOAc (3× 30 mL). The combined organic phases were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The residue was purified by using flash chromatography (cyclohexane/EtOAc, 4:1) to give product

10 as a yellow oil (117 mg, 0.21 mmol, 74%). $R_f = 0.42$ (cyclohexane/EtOAc, 1:1); $[\alpha]_D = -50.3$ ($c = 1$ in $CHCl_3$); ^1H NMR (250 MHz, $CDCl_3$): $\delta = 8.45$ (s, 1H), 8.39 (d, $J = 8.8$ Hz, 2H), 7.99 (d, $J = 8.2$ Hz, 2H), 7.60–7.45 (m, 4H), 5.45 (s, 2H), 4.17–4.01 (m, 4H), 3.90–3.85 (m, 2H), 3.68 (t, $J = 6.3$ Hz, 2H), 1.99–1.86 (m, 2H), 1.74–1.64 (m, 2H), 1.49 (s, 3H), 1.43–1.27 (m, 4H), 0.89 ppm (s, 18H); ^{13}C NMR (62.5 MHz, $CDCl_3$): $\delta = 168.3$ (CN), 167.8 (CN), 131.4 (C_q^{arom}), 130.9 (C_q^{arom}), 128.9 (C_H^{arom}), 128.1 (C_H^{arom}), 126.0 (C_H^{arom}), 124.8 (C_H^{arom}), 124.7 (C_H^{arom}), 75.4 (CH-N), 75.2 (CH-N), 70.6 (CH_2), 68.6 ($2\times CH_2$), 64.9 (CH_2), 42.2 (Cq), 36.3 (CH_2), 33.8 (Cq), 33.7 (Cq), 29.7 (CH_2), 26.4 (CH_2), 25.7 ($6\times CH_3$), 24.1 (CH_2), 21.4 ppm (CH_3); HRMS (ESI): m/z: calcd for $C_{36}H_{49}N_2O_3$: 557.3738; found: 557.3739 [$M+H^+$].

Diels–Alder reaction between cyclopentadiene and 3-(but-2-enoyl)-oxazolidin-2-one

*Procedure for the catalytic tests with **6***: $Cu(OTf)_2$ (0.033 mmol) was added to a Schlenk tube before ligand **6** (0.036 mmol) dissolved in CH_2Cl_2 (650 μL) was added dropwise. The solution was stirred for 1 h. 3-(But-2-enoyl)oxazolidin-2-one (0.33 mmol, 51 mg) was added as a solution in CH_2Cl_2 (650 μL) by using a syringe. Freshly cracked cyclopentadiene (200 μL, 2.4 mmol) was immediately added by using a syringe. The resulting solution was stirred at room temperature for the specified amount of time. The mixture was then washed with saturated aqueous NH_4Cl solution and extracted with CH_2Cl_2 (2×10 mL). The combined organic phases were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The residue was purified by using flash chromatography (toluene/EtOAc, 80:20).

*Procedure for catalytic tests with **11***: $Cu(OTf)_2$ (0.033 mmol) was added to a Schlenk tube before ligand **6** (0.036 mmol) dissolved in CH_2Cl_2 (650 μL) was added dropwise. The solution was stirred for 1 h. TNF (0.036 mmol) was added and the solution was stirred for 1 h before it was cooled to the desired temperature. 3-(But-2-enoyl)oxazolidin-2-one (0.33 mmol, 51 mg) was added as a solution in CH_2Cl_2 (650 μL) by using a syringe. Freshly cracked cyclopentadiene (200 μL, 2.4 mmol) was immediately added by using a syringe. The resulting solution was stirred at room temperature for the specified amount of time. When the reaction was finished, pentane (15 mL) was added to precipitate complex **11**. The solution was recovered and complex **11** could be reused in a new Diels–Alder reaction. The solvent was removed from the products by using reduced pressure and the solution was purified by using silica gel chromatography (toluene/EtOAc, 80:20).

3-(3-Methyl-bicyclo[2.2.1]hept-5-ene-2-carbonyl)oxazolidin-2-one: The *ee* for the major *endo* isomer was determined by means of HPLC analyses using a WHELK column (flow rate = 0.8 mL min^{-1}; 99% hexane, 1% ethanol), which resolved the four diastereoisomers (exo_1 $t_R = 35.4$ min, exo_2 $t_R = 36.8$ min, $endo_1$ $t_R = 40.3$ min, $endo_2$ $t_R = 42.8$ min). $R_f = 0.45$ and 0.57 (toluene/EtOAc, 4:1); ^1H NMR (250 MHz, $CDCl_3$): $\delta = 6.38$ (dd, $J =$ 5.8, 3.4 Hz, 1H), 5.82 (dd, $J = 5.8$, 3.4 Hz, 1H), 4.40 (t, $J = 7.8$ Hz, 2H), 4.03–3.87 (m, 2H), 3.55–3.47 (m, 1H), 3.29 (brs, 1H), 2.55 (brs, 1H), 2.13–2.09 (m, 1H), 1.73–1.70 (m, 1H), 1.48–1.45 (m, 1H), 1.16 ppm (d, $J = 6.3$ Hz, 3H); ^{13}C NMR (62.5 MHz, $CDCl_3$): $\delta = 175.3$ (Cq), 154.0 (Cq), 139.7 (CH), 130.9 (CH), 61.8 (CH_2), 51.3 (CH), 49.5 (CH), 47.4 (CH), 47.1 (CH_2), 43.0 (CH_2), 36.4 (CH), 20.4 ppm (CH_3).

Diels–Alder reaction between cyclopentadiene and 3-acryloyl-oxazolidin-2-one

*Procedure for the homogeneous catalytic tests with **9** or **10***: A Schlenk tube was charged with $Cu(OTf)_2$ (0.033 mmol) and the ligand **9** (or **10**) (0.036 mmol) dissolved in CH_2Cl_2 (650 μL) was added dropwise. The solution was stirred for 3 h before it was cooled to the desired temperature. 3-Acryloyloxazolidin-2-one (0.33 mmol, 46 mg) was added as a solution in CH_2Cl_2 (650 μL) by using a syringe. Freshly cracked cyclopentadiene (200 μL, 2.4 mmol) was immediately added by using a syringe. The resulting solution was stirred at the desired temperature for the specified amount of time. The mixture was then washed with saturated aqueous NH_4Cl solution and extracted with CH_2Cl_2 (2×10 mL). The combined organic phases were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The residue was purified by using flash chromatography (toluene/EtOAc, 80:20).

*Procedure for catalytic tests with **12** or **13** (ex situ preparation of the complex)*: $Cu(OTf)_2$ (0.033 mmol) was added to a Schlenk tube before ligand **9** (or **10**) (0.036 mmol) dissolved in CH_2Cl_2 (650 μL) was added dropwise. The solution was stirred for 3 h before TNF (0.036 mmol) was added and the solution was stirred for 1 h, and then cooled to the desired temperature. 3-Acryloyloxazolidin-2-one (0.33 mmol, 46 mg) was added as a solution in CH_2Cl_2 (650 μL) by using a syringe. Freshly cracked cyclopentadiene (200 μL, 2.4 mmol) was immediately added by using a syringe. The resulting solution was stirred at this temperature for the specified amount of time. When the reaction was finished, pentane (15 mL) was added to precipitate complex **12** (or **13**). The solution was recovered and complex **12** (or **13**) could be reused in a new Diels–Alder reaction. After removal of the solvents, the products were purified by using silica gel chromatography (toluene/EtOAc, 80:20). The catalytic results obtained with catalyst **13** at −50 °C for 19 h reaction time are given in Table 6.

Table 6. Catalytic results obtained for complex **13** at 50 °C after 19 h.

Cycle[a]	Conversion[b] [%]	Yield [%]	*de*[c] [%]	*ee*[c] (*endo*) [%]
1	100	85	75	83 (2*S*)
2	100	85	76	79 (2*S*)
3	100	89	84	75 (2*S*)
4	89	78	84	70 (2*S*)
5[d]	100	81	84	90 (2*S*)
6	100	91	88	90 (2*S*)
7	100	88	87	90 (2*S*)

[a] Catalyst **13**. [b] Determined by NMR spectroscopy. [c] Determined by HPLC chromatography (ODH, hexane/isopropanol). [d] After addition of 4 Å molecular sieves.

*Procedure for catalytic tests with **12** or **13** (in situ preparation of the complex)*: $Cu(OTf)_2$ (0.033 mmol) was added to a Schlenk tube before ligand **9** or **10** (0.036 mmol) dissolved in CH_2Cl_2 (650 μL) was added dropwise. The solution was stirred for 3 h before 3-acryloyloxazolidin-2-one (0.33 mmol, 46 mg) was added as a solution in CH_2Cl_2 (650 μL) by using a syringe. Freshly cracked cyclopentadiene (200 μL, 2.4 mmol) was immediately added by using a syringe. The resulting solution was stirred at this temperature for the specified amount of time. When the reaction was finished, TNF (0.036 mmol) was added. Pentane (15 mL) was added to precipitate complex **12** (or **13**). The solution was recovered and complex **12** (or **13**) could be reused in a new Diels–Alder reaction. After removal of the solvents, the products were purified by using silica gel chromatography (toluene/EtOAc, 80:20).

3-(Bicyclo[2.2.1]hept-5-ene-2-carbonyl)oxazolidin-2-one: The *ee* for the major *endo* isomer was determined by HPLC analyses using an ODH column (flow rate = 0.8 mL min^{-1}; 98% hexane, 2% isopropanol), which resolved the four diastereoisomers (exo_1 $t_R = 49.1$ min, exo_2 $t_R = 51.2$ min, $endo_1$ $t_R = 56.3$ min, $endo_2$ $t_R = 59.9$ min). $R_f = 0.45$ and 0.57 (toluene/EtOAc 4:1); ^1H NMR (250 MHz, $CDCl_3$): $\delta = 6.25$ (dd, $J = 5.8$, 3.4 Hz, 1H), 5.88 (dd, $J = 5.8$, 3.4 Hz, 1H), 4.40 (t, $J = 7.8$ Hz, 2H), 4.03–3.87 (m, 3H), 3.32 (brs, 1H), 2.95 (brs, 1H), 1.95 (m, 1H), 1.45 ppm (m, 3H); ^{13}C NMR (62.5 MHz, $CDCl_3$): $\delta = 175.3$ (Cq), 154.0 (Cq), 138.7 (CH), 132.2 (CH), 62.6 (CH_2), 50.8 (CH_2), 47.0 (CH), 43.8 (CH_2), 43.5 (CH), 43.4 (CH), 30.1 ppm (CH_2).

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