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Recyclable Copper Catalysts Based on Imidazolium-Tagged Bis(oxazolines): A Marked Enhancement in Rate and Enantioselectivity for Diels–Alder Reactions in Ionic Liquid

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Abstract: Imidazolium-tagged bis(oxazolines) have been prepared and used as chiral ligands in the copper(II)-catalysed Diels–Alder reaction of *N*-acryloyl- and *N*-crotonoyloxazolidinones with cyclopentadiene and 1,3-cyclohexadiene in the ionic liquid 1-ethyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]-imide, [emim][NTf_2]. A significant and substantial enhancement in the rate and enantioselectivity was achieved in [emim][NTf_2] compared with dichloromethane. For example, complete conversion and enantioselectivities up to 95% were obtained for the reaction between *N*-acryloyloxazolidinone and cyclopentadiene within 2 min in [emim][NTf_2] whereas the corresponding reaction in dichloromethane required 60 min to reach completion and gave an *ee* of only 16%. The enhanced rates obtained in the ionic liquid enabled a catalyst loading as low as 0.5 mol% to give complete conversion within 2 min while retaining the same level of enantioselectivity. The imidazolium-tagged catalysts can be recycled ten times without any loss in activity or enantioselectivity and showed much higher affinity for the ionic liquid phase during the recycle procedure than the analogous uncharged ligand.

Keywords: asymmetric Diels–Alder reaction; ionic liquids; rate and enantioselectivity enhancements; recyclability; task-specific ionic liquids

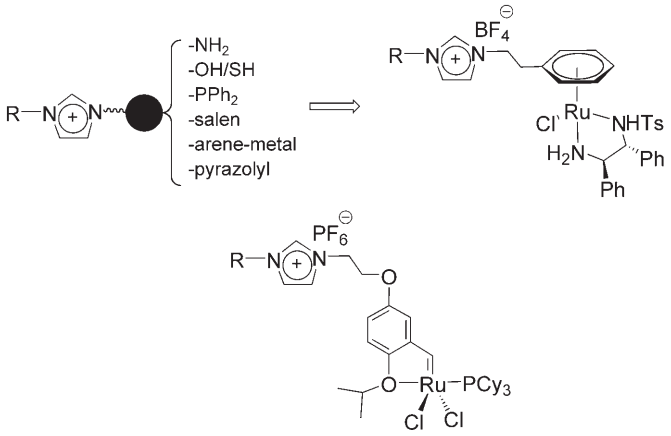
Introduction

Since their introduction, bis(oxazolines) have proven remarkably effective ligands for stereocontrol in a variety of enantioselective metal-catalysed reactions[1] and have been established as among the most versatile ligands in homogenous asymmetric catalysis. While the majority of bis(oxazolines) are prepared from naturally occurring starting materials and are relatively inexpensive, a number of highly effective catalysts require unnatural amino acids and are substantially more expensive. Since these expensive bis(oxazolines) are often the ligand of choice to achieve high levels of stereocontrol in Lewis acid catalysis; a number of approaches have been investigated for their immobilisation,[2] including covalent grafting onto soluble[3] and insoluble organic polymers,[4] amorphous and mesoporous crystalline silica,[5] electrostatic immobilisation/ion pairing on anionic supports,[6] and modification of nano-sized gold particles.[7] However, while catalyst separation is usually straightforward the process of immobilisation often results in a reduction in activity, due to poor mass transfer characteristics, and in the enantioselectivity, due to modification of the chiral environment by the large polymeric substituent.

The use of ionic liquids[8] as a medium for homogeneous catalysis[9] is a relatively new development and several additional benefits associated with this medium over conventional solvents have already been identified such as improved catalyst stability, facile product separation and an increase in activity and selectivity in many cases.[10] In addition, due to their low volatility and immiscibility with non-polar organic solvents ionic liquids have been extensively investigated for immobilisation and subsequent recy-

cle of the dissolved catalysts. In this regard, there has recently been an increasing number of reports utilising ionic liquids in asymmetric catalysis: however, despite their efficacy in molecular solvents, few examples of copper complexes of bis(oxazolines) have been reported.[11–13] In the first of these, copper(II) complexes of bis(oxazolines) and aza-bis(oxazolines) were shown to catalyse the enantioselective cyclopropanation between styrene and ethyl diazoacetate in ionic liquids to afford *ee*s as high as 92 and 82% for the *trans* and *cis* isomers, respectively, which were comparable to the selectivities obtained in dichloromethane.[11,12] More recently, Meracz and Oh have shown that ionic liquids can enhance the enantioselectivity and *endo*:*exo* ratio of the asymmetric Diels–Alder reaction between *N*-crotonoyloxazolidinone and cyclopentadiene compared with dichloromethane.[13] The *ee* of 92% and an *endo*:*exo* ratio of 93:7 obtained in 1,3-dibutylimidazolium tetrafluoroborate were significantly higher than 52% *ee* and an *endo*:*exo* ratio of 79:21, obtained in dichloromethane. This latter example is one of an increasing number of reports that show that ionic liquids can enhance the enantioselectivity of a catalytic asymmetric transformation compared with organic solvents.[14]

Although by using solvent extraction techniques ionic liquids can allow homogeneous catalysts to be recycled a number of times, often without reduction in selectivity, one drawback to this approach is the tendency of the catalyst or the ligand to leach into the extracting solvent. For asymmetric transformations using copper(II) complexes of bis(oxazolines) and aza-bis(oxazolines), extraction of the ligand is particularly problematic since the copper precursor remaining in the ionic liquid catalyses the background reaction and causes a reduction in the enantioselectivity.[12] In other ionic liquid systems, this problem has been addressed with varying levels of success by either designing new cationic ligands to increase the solubility of the catalyst and/or ligand in the ionic liquid[15] or by incorporating an imidazolium salt into the ligand to afford a "task-specific" ionic liquid,[16] two examples of which are illustrated in Scheme 1. In this latter approach a ligand is modified with an imidazolium group located remotely from the coordinating atoms (and hence the active site) such that the catalyst becomes an integral part of the ionic liquid and is retained during extraction. To date this strategy has been applied to a range of transformations including the rhodium-catalysed hydroformylation of alkenes,[17] ruthenium-catalysed asymmetric hydrogenation and transfer hydrogenations,[18] ruthenium-catalysed ring closing olefin metathesis,[19] vanadium-catalysed cyanosilylation of aldehydes,[20] titanium-promoted enantioselective addition of diethylzinc to aldehydes,[21] Heck,[22] Suzuki[23] and Negishi[24] couplings and asymmetric organocatalysis.[25] This strategy has been the subject of a recent and extensive review.[16]



Scheme 1.

Herein, we report the synthesis of imidazolium-tagged bis(oxazolines), a study of their performance in the copper-catalysed asymmetric Diels–Alder reaction in both an ionic liquid and dichloromethane and a comparison with their unmodified homogeneous counterparts. Particularly noteworthy features of this work include a distinct and significant enhancement in both rate and enantioselectivity for reactions carried out in the ionic liquid 1-ethyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide, [emim][NTf_2], compared with dichloromethane, highly reproducible selectivities with significantly reduced catalyst aging times for reactions conducted in the ionic liquid compared with dichloromethane (5 min *vs.* >3 h), excellent recyclability of catalysts based on task-specific imidazolium-tagged bis(oxazolines) and markedly better retention of the tagged bis(oxazolines) in the ionic liquid phase compared with their neutral counterparts.

Results and Discussion

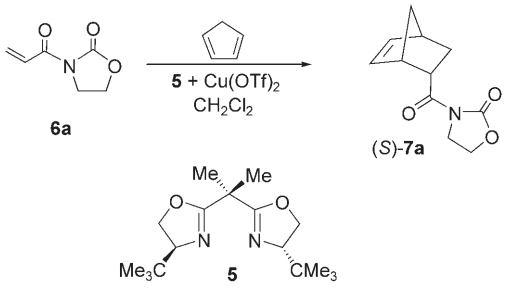
Synthesis of Imidazolium-Tagged Bis(oxazolines) 4a,b

Imidazolium-tagged bis(oxazolines) **4a**,**b** were identified as potential task-specific ionic liquids because they are relatively straightforward to prepare from inexpensive and readily available starting materials and the corresponding unfunctionalized bis(oxazoline) has often proven to be the optimum ligand for a wide range of Lewis acid-catalysed asymmetric transformations including; Diels–Alder[26] and hetero-Diels–Alder reactions,[27] the Mukaiyama aldol reaction,[28] enantioselective carbonyl-ene reactions,[29] Michael reactions,[30] the Henry reaction between α-keto esters and nitromethane[31] and the Mukaiyama–Michael addition of enol silanes to unsaturated imide deriva-

tives.[32] Moreover, the imidazolium group in **4a**,**b** is remote from the metal centre and the tether connecting the central carbon atom of the oxazoline to the imidazolium fragment can be systematically varied. The synthesis of bis(oxazolines) **4a**,**b** bearing a pendent imidazolium tag is shown in Scheme 2. Condensation of diethyl methylmalonate with (*S*)-valinol or (*S*)-*tert*-leucinol affords the corresponding bis(hydroxyamides) **1a** and **1b**, respectively, which are readily converted into the desired bis(oxazolines) **2a**,**b** *via* a DAST-mediated cyclisation.[33] The yields and spectroscopic properties of **2a** are similar to those previously reported for this compound, which was prepared from **1a** by cyclisation of the derived mesylate.[34] Deprotonation of **2a**,**b** in THF with BuLi at −78 °C and addition of the resulting solution to an excess of 1,5-dibromopentane in THF afforded the desired bromopentyl-substituted bis(oxazolines) **3a**,**b**, in excellent yield, after purification by column chromatography. The imidazolium tag was introduced in the final step by reaction of **3a**,**b** with 1-methylimidazole in toluene at 110 °C to afford the bromide salts of **4a**,**b**.

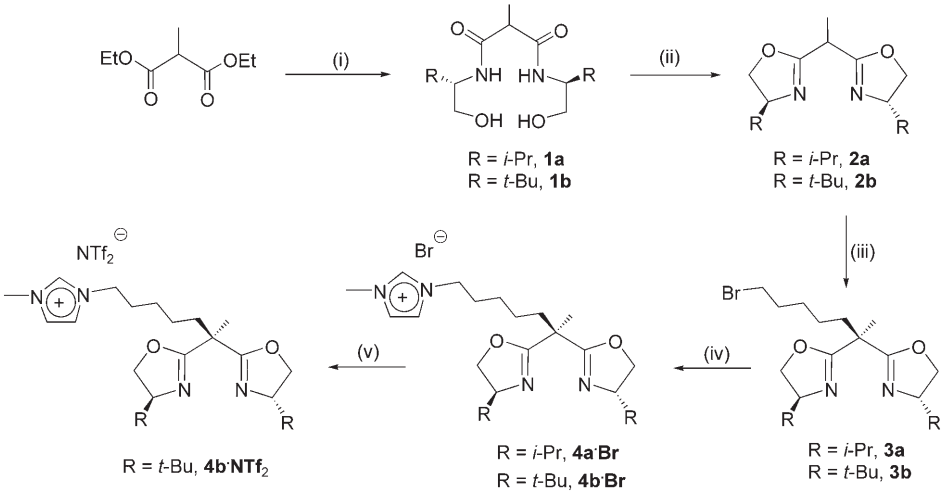
Asymmetric Diels–Alder Reactions

Table 1 summarizes the results of a comparative study of the performance of copper complexes based on 5-bromopentyl substituted bis(oxazolines) **3a**,**b**, Br^- and $[NTf_2]^-$ salts of imidazolium-tagged bis(oxazolines) **4a**,**b**, and unfunctionalized (*S*,*S*)-*t*-Bu-box, **5**, as Lewis acid catalysts for the Diels–Alder reaction between *N*-acryloyloxazolidinone **6a** and cyclopentadiene in [emim][NTf_2] and dichloromethane [Eq. (1)]. The catalysts were typically prepared by stirring a dichloromethane solution of $Cu(OTf)_2$ (10 mol %) and the appropriate bis(oxazoline) (11 mol %) at room temperature for 3 h, since Evans et al. has previously reported that catalyst performance depends dramatically on the metal-ligand complexation time, with short aging times leading to irreproducible results characterised by near racemic cycloadduct in low diastereoselectivity.[26] To ensure a direct and meaningful comparison all reactions, except where indicated, were performed at room temperature in both [emim][NTf_2] and dichloromethane.



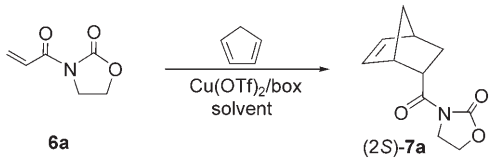
(1)

Not surprisingly, regardless of the solvent the *tert*-butyl-substituted bis(oxazolines) proved to be the optimum ligand, in the majority of cases giving significantly higher *ee*s than their isopropyl-substituted counterparts. For example, the catalyst derived from **3a** gave cycloadduct (2*S*)-**7a** in 29 and 2 % *ee* in [emim][NTf_2] and dichloromethane, respectively, whereas the corresponding *ee*s obtained with **3b**-$Cu(OTf)_2$ were 93 and 16 %, respectively (Table 1, entries 1–5). Reactions were also significantly faster in ionic liquid than those performed in dichloromethane; high or complete conversions were typically obtained with catalyst mixtures generated from $Cu(OTf)_2$ and **3b**, **4b·NTf₂** or **5** in less than 2 min, whereas reaction times in excess of 60 min were re-



Scheme 2. Synthesis of imidazolium-tagged bis(oxazolines) **4a,b**. (i) amino alcohol, toluene 120 °C; (ii) 2.1 equivs. DAST, −78 °C, 30 min; (iii) 1 equiv BuLi, −78 °C warm to −20 °C, 7 equivs. 1,5-dibromopentane; (iv) toluene, 1-methylimidazole 110 °C, 16 h; (v) CH_2Cl_2, Li[NTf_2], aqueous work-up.

Table 1. Enantioselective Diels–Alder reaction between imide **6a** and cyclopentadiene catalysed by 10 mol% $Cu(OTf)_2$/box in dichloromethane and [emim][NTf_2].



6a (2*S*)-**7a**

Entry	box	Solvent	Time [min]	Conversion [%][a,d]	*endo ee* [%][b,d]	% *endo*[c,d]
1	**3a**	[emim][NTf_2]	60	94	29	78
2	**3a**	CH_2Cl_2	60	100	2	90
3	**3a**	CH_2Cl_2 (−20 °C)	60	100	26	90
4	**3b**	[emim][NTf_2]	2	100	93	88
5	**3b**	CH_2Cl_2	60	90	16	85
6	**4a·Br**	[emim][NTf_2]	60	98	21	87
7	**4a·Br**	CH_2Cl_2	60	100	4	89
8	**4a·Br**	CH_2Cl_2 (−20 °C)	60	96	24	91
9	**4b·Br**	[emim][NTf_2]	2	33	48	88
10	**4b·Br**	CH_2Cl_2	60	40	2	87
11	**4b·NTf_2**	[emim][NTf_2]	2	100	84	88
12	**4b·NTf_2**	CH_2Cl_2	60	43	12	86
13	**5**	[emim][NTf_2]	2	100	95	90
14	**5**	CH_2Cl_2	60	78	78	88

[a] Determined by ^{1}H NMR spectroscopy.
[b] Enantiomeric excess determined by HPLC (Daicel Chiralcel OD-H).
[c] *Endo*/*exo* ratio determined by ^{1}H NMR spectroscopy.
[d] Average of three runs.

quired to reach the same level of conversion in dichloromethane. In addition, for each ligand pair studied significantly higher *ee*s were obtained in [emim][NTf_2] compared with dichloromethane. In the most dramatic cases, catalysts derived from **3b** and **4b·NTf_2** were highly selective in [emim][NTf_2] giving *endo*-**7a** in 93 and 84% *ee*, respectively, but markedly less selective in dichloromethane giving *ee*s of 16 and 12%, respectively. The absolute configuration of (2*S*)-**7a** was determined by comparison of the HPLC retention times with a sample generated using {Cu[(*S*,*S*)-*t*-Bu-box]}[OTf]$_2$, whose stereochemistry and optical rotation have previously been reported.[26]

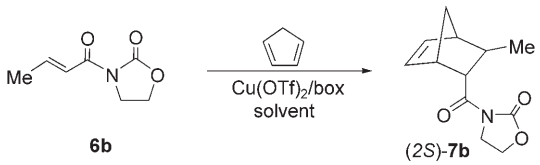
Although, the *ee* of 48% obtained with **4b·Br**-$Cu(OTf)_2$ in [emim][NTf_2] is significantly higher than that of the near racemic mixture (2% *ee*) obtained in dichloromethane (Table 1, entries 9 and 10), it is still markedly lower than those of 93 and 84% obtained with **3b** and **4b·NTf_2**, respectively (Table 1, entries 4 and 11). These unexpectedly low *ee* values were also accompanied by poor conversions, particularly for reaction in [emim][NTf_2] which achieved a conversion of only 33%. While the catalyst solutions based on **3b** and **4b·NTf_2** remained emerald green for the entire reaction, a colour commonly associated with Lewis acid [Cu(box)]X_2 complexes in organic solvent; that based on **4b·Br** immediately adopted a red-brown colour upon the addition of $Cu(OTf)_2$ to the ligand. A similar colour change was also reported by Fraile et al. whereby [Cu(box)][X]$_2$ (X = Cl, OTf) complexes formed red-brown solutions in [emim][BF_4]. These solutions were almost completely inactive for cyclopropanation of styrene but were found to decompose ethyl diazoacetate under the reaction conditions with the colour change thought to be associated with the formation of Cu(0).[11a] In the present case, whilst the presence of Cu(0) may be the cause of the low *ee* obtained with **4a·Br**, substitution of Br^- by $[NTf_2]^-$, by treatment of a dichloromethane solution of **4b·Br** with Li[NTf_2], markedly improved the catalyst performance to afford an *ee* of 84% in [emim][NTf_2]. This suggests that the presence of bromide could be responsible for the lower *ee* values and conversions. In order to investigate the possible influence of Br^- on catalyst performance a solution of [Cu((*S*,*S*)-*t*-Bu-box)][OTf]$_2$ in [emim][NTf_2] was treated with one mole equivalent of [emim]Br immediately prior to addition of substrate. The resulting solution rapidly turned deep red-brown, in much the same manner as that for **4b·Br**-$Cu(OTf)_2$, and gave cycloadduct **6a** in 6% *ee* and 78% conversion after 2 min, compared with 95% *ee* and 100% conversion in the absence of bromide (*vide infra*). However, while the poor performance of catalyst generated from **4b·Br** may be associated with the presence of bromide it is worth noting that Mayoral and co-workers recently demonstrated

that bis(oxazoline) complexes derived from $CuCl_2$ give similar *ee*s and conversions as those derived from $Cu(OTf)_2$ for the cyclopropanation of styrene with ethyl diazoacetate when the complex was dissolved in a bis[(trifluoromethyl)sulfonyl]imide-based ionic liquid. They proposed that in an ionic liquid the most abundant copper species will bear the counterion of the solvent.[11a]

An enhancement in both the rate and enantioselectivity of the reaction was also obtained with a catalyst based on (*S*,*S*)-*t*-Bu-box, **5**, in [emim][NTf_2] compared with dichloromethane. Specifically, under identical conditions the catalyst derived from **5** gave *endo*-(2*S*)-**7a** in 95% *ee* and complete conversion within 2 min at room temperature in [emim][NTf_2], whereas the corresponding reaction in dichloromethane gave 78% conversion and an *ee* of 78% after 60 min (Table 1, entries 13 and 14). This enhancement in enantioselectivity for reactions conducted in ionic liquid compared with dichloromethane was confirmed by removing the solvent from a reaction carried out in dichloromethane, extracting, analysing the product and recycling the catalyst in [emim][NTf_2], which gave (2*S*)-**7a** in 95% *ee* and 100% conversions, with subsequent recycles consistently giving 93% *ee*. It is worth noting here that although an *ee* of 78% was obtained with {Cu[(*S*,*S*)-*t*-Bu-box]}[SbF_6]$_2$ in dichloromethane at room temperature, the reproducibility was very poor and *ee* values were typically much lower ranging from 16 to 40%. In contrast, the same catalyst in [emim][NTf_2] was much more reliable and consistently gave high enantioselectivities regardless of metal-ligand complexation time. For example, in dichloromethane metal-ligand complexation times of >3 h are generally required to obtain high *ee*s, in contrast, a catalyst based on $Cu(OTf)_2$ with (*S*,*S*)-*t*-Bu-box, **5**, stirred for only 5 min in a mixture of [emim][NTf_2] and dichloromethane gave cycloadduct (2*S*)-**7a** in 95% *ee* and 100% conversion. For comparison, Evans et al. has previously reported that {Cu[(*S*,*S*)-*t*-Bu-box]}[$OTf]_2$ catalyses the reaction between oxazolidinone **6a** and cyclopentadiene to give cycloadduct (2*S*)-**7a** in 98% *ee* and 86% yield, albeit after 10 h at -78 °C and with extended complexation time.[26] An *ee* of 86%, high *endo*/*exo* selectivity and good yield were also obtained at 20 °C, although at this temperature the reaction was noticeably exothermic and still required 15 min to reach completion. Thus, there are clearly significant benefits associated with the use of ionic liquids over dichloromethane since the same reaction gave complete conversion, an *endo* enantioselectivity of 95% and high *endo*:*exo* selectivity in less than 2 min at room temperature in [emim][NTf_2].

Table 2 summarises the corresponding results for the Diels–Alder reaction between crotonoyl oxazolidinone **6b** and cyclopentadiene, catalysed by copper complexes of the same bis(oxazolines). Qualitatively, these results illustrate the same trend in that the optimum catalysts are generated from *tert*-butyl-substituted bis(oxazolines) and afford cycloadduct (2*S*)-**7b**

Table 2. Enantioselective Diels–Alder reaction between imide **6b** and cyclopentadiene catalysed by 10 mol% $Cu(OTf)_2$/box in dichloromethane and [emim][NTf_2] at room temperature.



6b (2*S*)-**7b**

Entry	Box	Solvent	Time [min]	Conversion [%][a,d]	*endo ee* [%][b,d]	% *endo*[c,d]
1	**3a**	[emim][NTf_2]	60	86	30	81
2	**3a**	CH_2Cl_2	60	no reaction	-	-
3	**3b**	[emim][NTf_2]	20	100	90	80
4	**3b**	CH_2Cl_2	120	no reaction	-	-
5	**4a·Br**	[emim][NTf_2]	60	2	10	80
6	**4a·Br**	CH_2Cl_2	120	no reaction	-	-
7	**4b·Br**	[emim][NTf_2]	20	54	47	83
8	**4b·Br**	CH_2Cl_2	120	no reaction	-	-
9	**4b·NTf_2**	[emim][NTf_2]	20	100	95	83
10	**4b·NTf_2**	CH_2Cl_2	120	no reaction	-	-
11	**5**	[emim][NTf_2]	20	100	97	87
12	**5**	CH_2Cl_2	120	no reaction	-	-

[a] Determined by ^{1}H NMR spectroscopy.
[b] Enantiomeric excess determined by HPLC (Daicel Chiralcel OD-H).
[c] The *endo*/*exo* ratio was determined by ^{1}H NMR spectroscopy.
[d] Average of three runs.

with enantioselectivities as high as 97% in [emim][NTf_2] whereas their isopropyl-substituted counterparts gave markedly lower *ee*s. The most striking feature of these [Cu(box)][X]$_2$-catalysed Diels–Alder reactions is the disparate levels of conversion obtained in dichloromethane and [emim][NTf_2]. For each of the bis(oxazolines) studied, with the exception of **4a·Br** and **4b·Br**, good to excellent conversions were obtained within 20 min in [emim][NTf_2] whereas there was no evidence of reaction in dichloromethane even after 2 h at room temperature. A similar enhancement in rate and enantioselectivity for the reaction between **6b** and cyclopentadiene catalysed by **5** in 1,3-dibutylimidazolium tetrafluoroborate compared with dichloromethane was shown by Meracz and Oh.[13] At room temperature, (2*S*)-**7b** was obtained in 65% yield with an *ee* of 92% and an *endo*:*exo* ratio of 93:7 in 1,3-dibutylimidazolium tetrafluoroborate compared with 4% yield, 52% *ee* and an *exo*:*endo* ratio of 76:24 in dichloromethane. Thus, even though *N*-crotonoyloxazolidinone **6b** is a much less reactive substrate than **6a** the rate enhancement obtained in ionic liquid allows high conversions to be obtained in relatively short reaction times. This is particularly apparent for the copper catalyst derived from **5**, which gave complete conversion within 20 min, an *endo* enantioselectivity of 97% and high *endo*/*exo* selectivity (Table 2, entry 11). In contrast, Evans reported that {Cu[(*S*,*S*)-*tert*-butyl-box]}[OTf]$_2$ requires 8 h to reach 95% conversion in dichloromethane with an *ee* of 94% and an *endo*:*exo* ratio of 87:13.[26]

A comparative study of the variation in conversion and enantioselectivity for the reaction between cyclopentadiene and *N*-crotonoyloxazolidinone for catalysts based on **3b**, **4b·Br** and **4b·NTf_2** (Figure 1) clearly showed that the catalyst generated from imidazolium-tagged **4b·NTf_2** is more efficient than that generated from **3b** as evidenced by the higher conversion and enantioselectivities. This study also highlighted the markedly different performance between catalysts based on Br^- and $[NTf_2]^-$ salts of imidazolium-tagged bis(oxazolines), the former reaching a maximum conversion of 51% after only 2 min before undergoing rapid catalyst deactivation. Surprisingly, the enantioselectivity also followed a similar profile in that the maximum *ee* of 47% obtained within 2 min was significantly lower than those of 90 and 95% obtained with **3b** and **4b·NTf_2**, respectively. The poor conversion and *ee* obtained with **4b·Br** was unsurprising since this catalyst also performed poorly in the reaction between **6a** and cyclopentadiene, with 33% conversion and an *ee* of 48%. Although the performance of catalysts based on the bromide salt of imidazolium-tagged bis(oxazolines) is generally poor, their bis[(trifluoromethyl)sulfonyl]imide-based counterparts form highly active and selective catalysts in [emim][NTf_2]

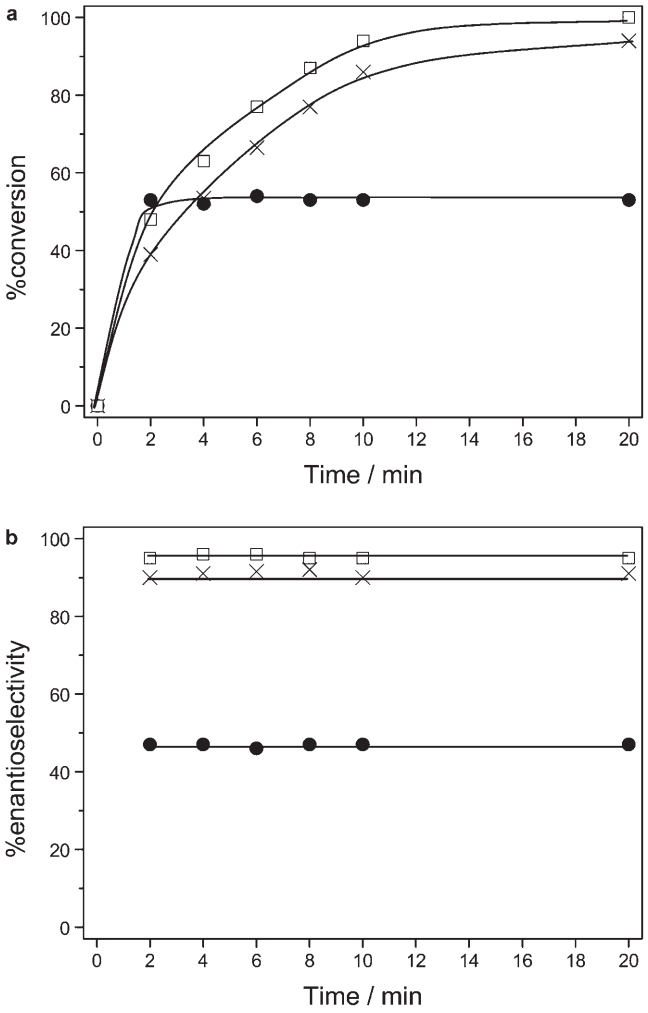


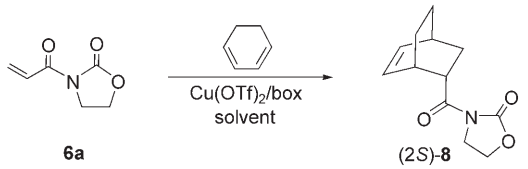
Figure 1. Variation in (**a**) percent conversion and (**b**) percent *ee* for the Diels–Alder reaction between *N*-crotonoyloxazolidinone and cyclopentadiene catalysed by Lewis acids derived from Cu(OTf)$_2$ and **3b** (×), **4b·Br** (●) and **4b·NTf_2** (□) in [emim][NTf_2] with respect to time at room temperature.

and these were therefore used for subsequent recycle experiments (*vide infra*).

A limited study of the Diels–Alder reaction between 1,3-cyclohexadiene and *N*-acryloyloxazolidinone **6a** catalysed by copper complexes generated from bis(oxazolines) **3b**, **4b·NTf_2** and **5**[35] gave good conversions (76–100%), *endo*-cycloadduct (2*S*)-**8** in excellent enantioselectivity (86–90%) and high *endo* selectivity (77–80%) in [emim][NTf_2], albeit after 36 h at room temperature (Table 3). In contrast, under similar conditions no reaction was detected in dichloromethane even after 120 h at room temperature, further highlighting the beneficial enhancement in rate for reactions conducted in ionic liquid while also maintaining good selectivities.

While ionic liquids have been investigated as a means to immobilise and recycle catalysts this ap-

Table 3. Enantioselective Diels–Alder reaction between imide **6a** and 1,3-cyclohexadiene catalyzed by 10 mol% $Cu(OTf)_2$/box in dichloromethane and [emim][NTf_2] at room temperature.



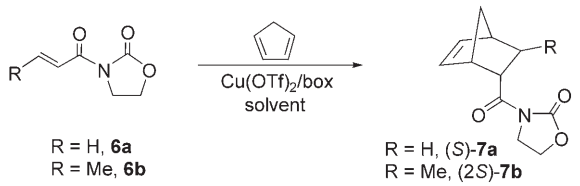
6a (2*S*)-**8**

Entry	Box	Solvent	Time [h]	Conversion [%][a,d]	*endo ee* [%][b,d]	% *endo*[c,d]
1	**3b**	[emim][NTf_2]	36	100	90	80
2	**3b**	CH_2Cl_2	120	no reaction	-	-
3	**4b·NTf$_2$**	[emim][NTf_2]	36	76	88	77
4	**4b·NTf$_2$**	CH_2Cl_2	120	no reaction	-	-
5	**5**	[emim][NTf_2]	36	80	86	79
6	**5**	CH_2Cl_2	120	no reaction	-	-

[a] Determined by ^{1}H NMR spectroscopy.
[b] Enantiomeric excess determined by HPLC (Daicel Chiralcel OD-H).
[c] The *endo*/*exo* ratio was determined by ^{1}H NMR spectroscopy.
[d] Average of three runs.

proach is not always efficient since product extraction can lead to leaching of the ligand and a gradual erosion in enantioselectivity, particularly for systems with an equilibrium between complex and free ligand.[11a–b,12] An alternative to the use of aza-bis(oxazolines), which have been shown to have an increased binding constant relative to bis(oxazolines),[12] is to covalently attach an imidazolium group to form an ionic derivative of ligand **5**. This ionic ligand type should be more effectively retained in the ionic liquid phase during the extraction process and reduce leaching. Table 4 summarises preliminary recycle experimental data for the Diels–Alder reaction of **6a** and **6b** with cyclopentadiene in [emim][NTf_2] with Lewis acid copper complexes of bis(oxazolines) **4a·Br**, **4b·Br** and **4b·NTf$_2$** showing that each catalyst recycled with no loss in enantioselectivity or reduction in conversion. In each case, the reactants formed a homogeneous phase with the ionic liquid and the product was isolated by extraction into diethyl ether. Following separation the ionic liquid/catalyst mixture was recharged with reactants and reused. A more extensive recycle

Table 4. Recycle Diels–Alder reactions of **6a** and **6b** with cyclopentadiene using 10 mol% catalyst generated from $Cu(OTf)_2$ and **4a·Br**, **4b·Br** and **4b·NTf$_2$** in [emim][NTf_2].



R = H, **6a**
R = Me, **6b**

R = H, (*S*)-**7a**
R = Me, (2*S*)-**7b**

Catalyst	Dienophile	Cycle	% Conversion[a,d]	*endo ee* [%][b,d]	% *endo*[c,d]
4a·Br	**6a**	1	95	21	87
		2	100	20	87
4b·Br	**6a**	1	36	49	88
		2	32	88	88
4b·NTf$_2$	**6a**	1	100	84	88
		2	100	86	88
4b·Br	**6b**	1	55	46	83
		2	55	45	83
4b·NTf$_2$	**6b**	1	100	95	83
		2	98	93	83

[a] Determined by ^{1}H NMR spectroscopy.
[b] Enantiomeric excess determined by HPLC (Daicel Chiralcel OD-H).
[c] The *endo*/*exo* ratio was determined by ^{1}H NMR spectroscopy.
[d] Average of three runs.

was performed using the catalyst based on **4b·NTf$_2$** to evaluate the effectiveness of introducing an imidazolium tag onto the bis(oxazoline) **5** as a means of improving retention in the ionic liquid phase during product extraction. Figure 2 clearly shows that this

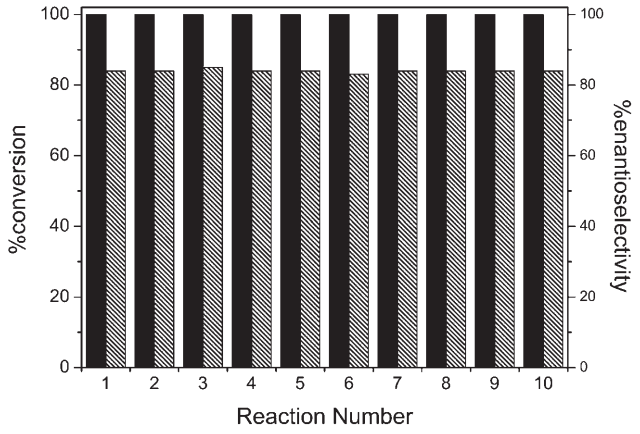


Figure 2. Variation in percentage conversion (solid) and percentage *ee* (hatched) on recycling the Diels–Alder reactions between **6a** and cyclopentadiene in [emim][NTf$_2$] using catalysts generated from **4b·NTf$_2$** and Cu(OTf)$_2$

catalyst recycled efficiently in [emim][NTf$_2$] with no significant change in enantioselectivity or conversion for at least ten successive reactions. ICP analysis of the extractant layers from initial reactions carried out in [emim][NTf$_2$] revealed that for catalysts based on **3b**, **4b·NTf$_2$** and **5** copper leaching into the organic phase was 0.03%, 0.01% and 0.015%, respectively. However, while there is little difference between the extent of copper leaching, particularly for catalysts based on **4b·NTf$_2$** and **5**, the extraction of the ligand is also important as Cu(OTf)$_2$ is not active for the present process and therefore any leaching of the ligand will eventually result in a reduction in the activity of the system. Using ion chromatography and HPLC analysis, the leaching of **4b·NTf$_2$** was examined from [emim][NTf$_2$] during the recycles and in all reactions the extraction was below the detection limit of the techniques. In contrast, for **3b**, 9.8% of the original ligand was extracted following the first reaction and further 7.9%, 6.4%, 6.2%, 6.1%, 6.1% were lost during the second to sixth reactions, respectively. Whilst leaching during the first reaction may be understandable due to the 10% excess ligand present with respect to Cu(OTf)$_2$, the extraction of over 40% of the ligand from the ionic liquid over six reactions clearly shows that attaching a charged group to the ligand markedly improves its retention in ionic liquid. Interestingly, even with this large amount of leaching, reactions using **3b** still recycle efficiently due to the very high activity of the catalyst in the ionic liquid, as shown by the complete conversion after 2 min (Table 1). This is further illustrated by the observation that even at loadings as low as 0.5 mol%, with respect to the substrate, catalyst based on **3b** gave 100% conversion and an *endo*-enantioselectivity of 95% after 2 min in [emim][NTf$_2$]. Additional studies are underway to examine the kinetics of the Diels–Alder reaction in [emim][NTf$_2$] using catalysts based on **3b** and **4b·NTf$_2$** at these much lower catalyst loadings.

Conclusions

In conclusion, it has been demonstrated that the introduction of a cationic imidazolium tag into bis(oxazolines) can be achieved in two relatively straightforward steps from readily available starting materials. Lewis acid copper complexes of these task-specific ligands catalyse the Diels–Alder reaction between dienes and oxazolidinones, with reactions in ionic liquids characterised by marked enhancements in rate and enantioselectivity compared with dichloromethane. Preliminary studies revealed that the performance of these task-specific catalysts depends on the imidazolium counterion with bis[(trifluoromethyl)sulfonyl]imide-based systems outperforming the corresponding bromide-based salts. While excellent *ee*s and high diastereoselectivity can also be obtained with [Cu((*S*,*S*)-*tert*-butyl-box)][OTf]$_2$ in CH_2Cl_2 the substantial rate enhancement obtained in ionic liquid is clearly a significant advantage, which will be particularly beneficial for more challenging, less reactive substrates. In addition, significantly shorter metal-ligand complexation times were required to achieve reproducibly high selectivities in the ionic liquid compared with dichloromethane, the former requiring a catalyst aging time of less than 5 min whereas far longer complexation times (3 h or longer) were required in dichloromethane. The introduction of an imidazolium tag into bis(oxazolines) also significantly improved the recovery and reuse of the catalyst for reactions performed in ionic liquid. In such cases the catalyst could be recycled at least ten times with no loss in activity or enantioselectivity with no leaching of the ligand observed when tagged with an imidazolium group whereas significant leaching was found for the uncharged ligand. While there are still relativity few reports of the use of task-specific ligands in asymmetric catalysis, this study has underpinned the potential benefits of this strategy which include high enantioselectivities without the need to resort to low temperatures, substantial rate enhancements compared with the corresponding reaction in organic media, the efficient recovery and reuse of the catalyst as well as the potential to develop semi-continuous processes for scale-up.

Experimental Section

General Procedures

All manipulations involving air-sensitive materials were carried out using standard Schlenk line techniques under an atmosphere of nitrogen or argon in oven-dried glassware. Diethyl ether and hexane were distilled from potassium/sodium alloy, THF from potassium/benzophenone and dichloromethane from calcium hydride. Diethyl methyl malonate, (*S*)-2-amino-3-methylbutan-1-ol, L-*tert*-leucinol, DAST and copper(II) triflate were purchased from commercial suppliers and used without further purification. 1-Ethyl-3-methyimidazolium bis[(trifluoromethyl)sulfonyl]imide ([emim][NTf_2]) was prepared following the method of Bonhôte et al. from the corresponding bromide salt.[36] The ionic liquid used in the study was found to contain 10.1 ppm bromide by suppressed ion chromatography analysis and 0.06 wt% water by Karl Fisher analysis. Oxazolidinones **6a** and **6b** were prepared according to published methods.[26,37] ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on a JEOL LAMBDA 500 or a Bruker AMX 300 instrument. Optical rotations were measured on a Optical Activity PolAAr 2001 digital polarimeter with a sodium lamp and are reported as follows: $[\alpha]_D^{20}$: (*c* g/100 mL, solvent). Thin-layer chromatography (TLC) was carried out on aluminium sheets precoated with silica gel 60F 254 and column chromatography was performed using Merck Kieselgel 60. Analytical high performance liquid chromatography (HPLC) was performed on an Agilent 110 Series HPLC equipped with a variable wavelength detector using a Daicel Chiralcel OD-H column. Enantiomeric excess was calculated from the HPLC profile.

N^1,*N*^{3}-Bi[(*S*)-1-hydroxy-3-methylbutan-2-yl]malonamide (1a)

A Schlenk flask charged with (*S*)-2-amino-3-methylbutan-1-ol (3.93 g, 38.1 mmol) and diethyl methylmalonate (3.38 g, 19.4 mmol) was heated at 120 °C for 16 h. The resulting mixture was allowed to cool to room temperature, the ethanol removed under vacuum and the resulting cream-coloured solid crystallised from chloroform-hexane to afford **1a**; yield: 3.3 g (60%); ^{1}H NMR (300.0 MHz, $CDCl_3$): δ = 7.2 (d, *J* = 8.4 Hz, 2H, N-*H*), 7.1 (d, *J* = 8.7 Hz, 2H, N-*H*), 4.10 (br s, 2H, O-*H*), 3.8 (m, 2H, CH_aH_bOH), 3.65 (m, 2H, C*H*-$CHMe_2$), 3.5 (m, 2H, CH_aH_bOH), 3.31 (q, *J* = 7.8 Hz, 1H, C*H*Me), 1.76 (sept, *J* = 6.8 Hz, 1H, C*H*Me_2), 1.72 (sept, *J* = 6.8 Hz, 1H, C*H*Me_2), 1.51 (d, *J* = 7.8 Hz, 1H, CH*Me*), 0.89 (d, *J* = 6.8 Hz, 3H, CH*Me*$_a$$Me_b$), 0.86 (d, *J* = 6.8 Hz, 3H, CH*Me*$_a$$Me_b$), 0.84 (d, *J* = 6.8 Hz, 3H, CH*Me*$_a$$Me_b$), 0.82 (d, *J* = 6.8 Hz, 3H, $CHMe_a$*Me*$_b$); ^{13}C{^{1}H} NMR (75.4 MHz, $CDCl_3$): δ = 173.1 (*C*=O), 172.9 (*C*=O), 63.9 (*C*H_2OH), 63.8 (*C*H_2OH), 57.7 (*C*H$CHMe_2$), 57.5 (*C*H$CHMe_2$), 49.4 [C(O)*C*HMe], 29.7 (*C*HMe_2), 29.6 (*C*HMe_2), 19.8 (CH*Me*$_a$$Me_b$), 19.7 (CH*Me*$_a$$Me_b$), 19.0 ($CHMe_a$*Me*$_b$), 18.8 ($CHMe_a$*Me*$_b$), 16.9 (CH*Me*); LR-MS (EI): *m*/*z* = 271 [M−OH]$^+$; HR-MS (EI): *m*/*z* = 271.202225, calcd. for $C_{14}H_{28}N_2O_3$ [M−OH]$^+$: 271.202168; anal. calcd. for $C_{14}H_{28}N_2O_4$: C 58.31, H 9.79, N 9.71; found: C 58.79, H 10.11, N 9.98; $[\alpha]_D$: −40.9 (*c* 0.088, ethanol).

N^1,*N*^{3}-Bis[(*S*)-1-hydroxy-3,3-dimethylbutan-2-yl]malonamide (1b)

Compound **1b** was prepared according to the procedure described above for **1a** and isolated in 82% yield by slow diffusion of a chloroform solution layered with hexane at room temperature. ^{1}H NMR (300.0 MHz, $CDCl_3$): δ = 7.47 (d, *J* = 8.8 Hz, 2H, N-*H*), 4.20 (br, 2H, OH), 3.61–3.83 (m, 4H, CH_aH_bOH), 3.49 (appt t, *J* = 10.9 Hz, 2H, C*H*Bu-*t*), 3.41 (q, *J* = 6.8 Hz, 1H, C*H*Me), 1.45 (d, *J* = 6.8 Hz, 1H, CH*Me*), 1.00 (s, 9H, CMe_3), 0.95 (s, 9H, CMe_3); ^{13}C{^{1}H} NMR (75.4 MHz, $CDCl_3$): δ = 173.8 (*C*=O), 62.4 (*C*H_2OH), 60.1 (*C*HCMe_3), 49.5 [C(O)*C*HMe], 33.8 (*C*Me_3), 27.1 (CMe_3), 17.2 (CH*Me*); LR-MS (EI): *m*/*z* = 271 [M−OH]$^+$; HR-MS (EI): *m*/*z* = 285.217682, calcd. for $C_{15}H_{29}N_2O_3$ [M−CH_2OH]$^+$: 285.217818; anal. calcd for $C_{16}H_{32}N_2O_4$: C 60.73, H 10.19, N 8.85; found: C 61.12, H 10.41, N 9.03; $[\alpha]_D$: +6.72 (*c* 0.124, ethanol).

(*S*)-4,5-Dihydro-2-{1-[(*S*)-4,5-dihydro-4-isopropyloxazol-2-yl]ethyl}-4-isopropyloxazole (2a)

A solution of bis(hydroxyamide) **1a** (2.09 g, 7.2 mmol) in dichloromethane (15 mL) was cooled to −78 °C and treated dropwise with DAST (2.61 g, 2.13 mL, 16.2 mmol) such that addition was complete in *ca.* 10 min. The resulting mixture was allowed to stir for a further 30 min after which time the reaction was quenched by addition of NH_4OH (2 mL). The organic layer was extracted with water (3 × 5 mL) dried over $MgSO_4$ and concentrated under reduced pressure to afford a thick orange oil that was purified by column chromatography (SiO_2, CH_2Cl_2/MeOH, 98/2) to afford **2a**; yield: 1.30 g (72). ^{1}H NMR (300.0 MHz, $CDCl_3$): δ = 4.28 (appt t, *J* = 6.1 Hz, 2H, oxazoline-CH_aH_bO), 3.94 (m, 4H, oxazoline-CH_aH_bO + oxazoline-C*H*N), 3.54 (q, *J* = 9.0 Hz, 1H, C*H*Me), 1.84 (sept, *J* = 6.8 Hz, 2H, C*H*Me_2), 1.50 (d, *J* = 8.9 Hz, 3H, CH*Me*), 0.93 (d, *J* = 6.8 Hz, 3H, CH*Me*$_a$$Me_b$), 0.92 (d, *J* = 6.8 Hz, 3H, $CHMe_a$*Me*$_b$), 0.86 (d, *J* = 6.8 Hz, 6H, $CHMe_a$*Me*$_b$); ^{13}C{^{1}H} NMR (75.4 MHz, $CDCl_3$): δ = 166.1 (oxazoline-*C*=N), 73.1 (oxazoline-*C*H_2O), 70.5 (oxazoline-*C*HN), 34.2 (*C*HMe), 32.5 (*C*HMe_2), 18.7 (CH*Me*$_a$$Me_b$) 17.9 ($CHMe_a$*Me*$_b$), 15.4 (CH*Me*); LR-MS (EI): *m*/*z* = 252 [M]$^+$; HR-MS (EI): *m*/*z* = 252.183778, calcd. for $C_{14}H_{24}N_2O_2$ [M]$^+$: 252.184288; anal. calcd. for $C_{14}H_{24}N_2O_2$: C 66.63, H 9.59, N 11.10; found: C 66.79, H 9.91, N 11.29; $[\alpha]_D$: −38.3 (*c* 0.064, ethanol).

(*S*)-4,5-Dihydro-2-{1-[(*S*)-4,5-dihydro-4-isopropyloxazol-2-yl]ethyl}-4-*tert*-butyloxazole (2b)

Compound **2b** was prepared according to the procedure described above for **2a** and isolated in 82% yield after purification by column chromatography. ^{1}H NMR (300.0 MHz, $CDCl_3$): δ = 4.14 (appt t, *J* = 6.1 Hz, 2H, oxazoline-CH_aH_bO), 4.04 (appt t, *J* = 6.1 Hz, 2H, oxazoline-CH_aH_bO), 4.14 (td, *J* = 6.1 Hz, 2H, oxazoline-C*H*N), 3.47 (q, *J* = 8.7 Hz, 1H, C*H*Me), 1.40 (d, *J* = 8.2 Hz, 3H, CH*Me*), 0.84 (s, 18H, CMe_3); ^{13}C{^{1}H} NMR (75.4 MHz, $CDCl_3$): δ = 165.9 (oxazoline-*C*=N), 75.8 (oxazoline-*C*H_2O), 69.3 (oxazoline-*C*HN), 34.1 (*C*HMe), 34.0 (*C*Me_3), 26.9 (CMe_3) 15.6 (CH*Me*); LR-MS (EI): *m*/*z* = 280 [M]$^+$; HR-MS (EI): *m*/*z* = 280.215675, calcd. for $C_{16}H_{28}N_2O_2$ [M]$^+$: 280.215078; anal. calcd. for

$C_{16}H_{28}N_2O_2$: C 68.53, H 10.06, N 9.99; found: C 68.13, H 10.61, N 9.87; $[\alpha]_D$: −93.2 (*c* 0.076, ethanol).

(*S*)-2-{7-Bromo-2-[(*S*)-4,5-dihydro-4-isopropyloxazol-2-yl]heptan-2-yl}-4,5-dihydro-4-isopropyloxazole (3a)

A flame-dried Schlenk flask charged with **2a** (0.20 g, 0.79 mmol), tetrahydrofuran (15 mL), TMEDA (0.184 g, 0.238 mL, 1,58 mmol) and a stir bar was cooled to −78 °C and BuLi (0.32 mL, 2.5 M in hexane, 0.80 mmol) was added dropwise *via* a syringe. The reaction mixture was allowed to warm to room temperature and stirred for a further 30 min. The resulting solution was added dropwise *via* cannula to a solution of 1,5-dibromopentane (0.88 g, 3.83 mmol) in THF (10 mL), cooled to 0 °C. After the addition was complete the ice bath was removed and the solution left to warm to room temperature and stirred for a further 16 h. After this time, the reaction mixture was quenched by addition of saturated aqueous NH_4Cl (15 mL), diluted with water (10 mL) and extracted with diethyl ether (3×15 mL). The organic fractions were combined washed with brine (1×50 mL) dried over $MgSO_4$ and the solvent removed under vacuum to afford a thick dark oily residue, which was purified by column chromatography (SiO_2, CH_2Cl_2/MeOH, 98/2) to afford **3a** as a pale yellow oil; yield: 0.22 g (68 %). ^{1}H NMR (300.0 MHz, $CDCl_3$): δ = 4.15 (m, 2H, oxazoline-CH_aH$_b$O), 3.90 (m, 4H, oxazoline-CH$_a$$H_b$O + oxazoline-C*H*N), 3.30 (t, *J* = 7.0 Hz, 2H, CH_2Br), 1.90 (sept, *J* = 6.5 Hz, 2H, C*H*Me$_2$), 1.85 (m, 8H, pentyl-CH_2), 1.38 (s, 3H, C*Me*), 0.95 (d, *J* = 6.5 Hz, 6H, CH*Me*$_a$Me$_b$), 0.85 (d, *J* = 6.5 Hz, 6H, CHMe$_a$*Me*$_b$); ^{13}C{^{1}H} NMR (75.4 MHz, $CDCl_3$): δ = 168.4 (oxazoline-C=N), 72.3 (oxazoline-CH_2O), 70.4 (oxazoline-*C*HN), 42.7 (*C*H$_2$Br), 36.8 [*C*Me(CH$_2$)$_5$Br], 33.7 (pentyl-*C*H$_2$), 32.8 (pentyl-*C*H$_2$), 28.7 (pentyl-*C*H$_2$), 23.8 (pentyl-*C*H$_2$), 21.8 [C*Me*(CH$_2$)$_5$Br], 18.9 (CH*Me*$_a$Me$_b$) 17.9 (CHMe$_a$*Me*$_b$); LR-MS (EI): *m*/*z* = 403 [M + H]$^+$; HR-MS (EI): *m*/*z* = 357.116684, calcd. for $C_{16}H_{26}N_2O_2Br$ [M−CH(CH$_3$)$_2$]$^+$: 357.117764; anal. calcd. for $C_{19}H_{33}N_2O_2Br$: C 56.85, H 8.29, N 6.98; found: C 57.02, H 3.56, N 7.22; $[\alpha]_D$: −59.3 (*c* 0.40, ethanol).

(*S*)-2-{7-Bromo-2-[(*S*)-4,5-dihydro-4-*tert*-butyloxazol-2-yl]heptan-2-yl}-4,5-dihydro-4-*tert*-butyloxazole (3b)

Compound **3b** was prepared according to the procedure described above for **3a** and isolated as a pale yellow oil in 74 % yield after purification by column chromatography. ^{1}H NMR (300.0 MHz, $CDCl_3$): δ = 3.97–4.11 (m, 4H, oxazoline-CH_aH$_b$O + oxazoline-C*H*N), 3.79 (dd, *J* = 6.7, 2.8 Hz, 2H, oxazoline-CH$_a$$H_b$O), 3.33 (t, *J* = 7.9 Hz, 2H, CH_2Br), 1.90 (m, 2H, pentyl-CH_2), 1.82 (m, 4H, pentyl-CH_2), 1.40 (s, 3H, C*Me*), 1.28 (m, 2H, pentyl-CH_2), 0.83 (s, 18H, C*Me*$_3$); ^{13}C{^{1}H} NMR (75.4 MHz, $CDCl_3$): δ = 168.3 (oxazoline-C=N), 75.9 (oxazoline-CH_2O), 69.1 (oxazoline-*C*HN), 42.8 (*C*H$_2$Br), 36.8 [*C*Me(CH$_2$)$_5$Br], 34.2 (pentyl-*C*H$_2$), 34.1 (*C*Me$_3$), 33.7 (pentyl-*C*H$_2$), 32.9 (pentyl-*C*H$_2$), 26.1 (C*Me*$_3$), 23.9 (pentyl-*C*H$_2$), 21.9 [C*Me*(CH$_2$)$_5$Br]; LR-MS (EI): *m*/*z* = 430 [M−CH$_3$]$^+$; HR-MS (EI): *m*/*z* = 371.133415, calcd. for $C_{17}H_{28}N_2O_2Br$ [M−C(CH$_3$)$_3$]$^+$: 371.131798; anal. calcd. for $C_{21}H_{37}N_2O_2Br$: C 58.73, H 8.68, N 6.62; found: C 58.64, H 8.33, N 7.07; $[\alpha]_D$: −84.9 (*c* 0.074, ethanol).

3-Methyl-1-{6,6-bis[(*S*)-4,5-dihydro-4-isopropyloxazol-2-yl]heptan-1-yl}imidazolium Bromide (4a·Br)

A solution of bis(oxazoline) **3a** (0.66 g, 1.64 mmol) and 2 equivalents of 2-methylimidazole (0.270 g, 3.28 mmol) in toluene (5 mL) was heated at 100 °C for 16 h after which time the solution was allowed to cool to room temperature and the solvent removed under vacuum. The resulting residue was washed exhaustively with hexane (5×15 mL) to remove the excess 2-methylimidazole and then purified by slow addition of hexane to a dichloromethane solution to afford **4a·Br** as spectroscopically and analytically pure colorless oil; yield: 0.62 g (94 %). ^{1}H NMR (300.0 MHz, $CDCl_3$): δ = 10.48 (br s, 1H, imidazole-C*H*), 7.4 (t br, *J* = 2.0 Hz, 1H, imidazole-C*H*), 7.29 (t br, *J* = 2.0 Hz, 1H, imidazole-C*H*), 4.28 (t, *J* = 7.2 Hz, 2H, imidazole-*N*-CH_2-pentyl), 4.13 (appt t, *J* = 7.4 Hz, 2H, oxazoline-CH_aH$_b$O), 4.08 (s, 3H, imidazole N-CH_3), 3.90 (m, 4H, oxazoline-CH$_a$$H_b$O + oxazoline-C*H*N), 1.81–2.17 (m, 6H, C*H*Me$_2$ + pentyl-CH_2), 1.43 (s, 3H, C*Me*), 1.36 (br, 4H, pentyl-CH_2), 0.85 (d, *J* = 6.5 Hz, 6H, CH*Me*$_a$Me$_b$), 0.84 (d, *J* = 6.5 Hz, 6H, CHMe$_a$*Me*$_b$), 0.79 (d, *J* = 6.5 Hz, 6H, CH*Me*$_a$Me$_b$), 0.77 (d, *J* = 6.5 Hz, 6H, CHMe$_a$*Me*$_b$); ^{13}C{^{1}H} NMR (75.4 MHz, $CDCl_3$): δ = 168.1 (oxazoline-*C*=N), 168.0 (oxazoline-*C*=N), 137.6 (imidazolium-*C*=N), 124.2 (imidazolium-*C*=C), 122.4 (imidazolium-C=*C*), 72.2 (oxazoline-*C*H$_2$O), 72.0 (oxazoline-*C*H$_2$O), 70.1 (oxazoline-*C*HN), 69.8 (oxazoline-*C*HN), 50.3 [N-*C*H$_2$(CH$_2$)$_4$], 42.5 [*C*Me(CH$_2$)$_5$N], 37.0 (N-*C*H$_3$), 36.7 (pentyl-*C*H$_2$), 32.6 (*C*HMe$_2$), 32.5 (*C*HMe$_2$), 30.3 (pentyl-*C*H$_2$), 26.7 (pentyl-*C*H$_2$), 23.9 (pentyl-*C*H$_2$), 21.8 [C*Me*(CH$_2$)$_5$N], 18.8 (CH*Me*$_a$Me$_b$), 18.7 (CHMe$_a$*Me*$_b$), 18.1 (CH*Me*$_c$Me$_d$), 17.9 (CHMe$_c$*Me*$_d$); LR-MS (EI): *m*/*z* = 403 [M−Br]$^+$; HR-MS (EI): *m*/*z* = 403.307304, calcd. for $C_{23}H_{39}N_4O_2$ [M−Br]$^+$: 403.307302; anal. calcd. for $C_{23}H_{39}N_4O_2Br$: C 57.14, H 8.13, N 11.59; found: C 57.44, H 8.37, N 11.87; $[\alpha]_D$: −34.3 (*c* 0.08, ethanol).

3-Methyl-1-{6,6-bis[(*S*)-4,5-dihydro-4-*tert*-butyloxazol-2-yl]heptan-1-yl}imidazolium Bromide (4b·Br)

Compound **4b·Br** was prepared according to the procedure described above for **4a·Br** and isolated as a pale yellow oil; yield: 87 %. ^{1}H NMR (300.0 MHz, $CDCl_3$): δ = 10.28 (br s, 1H, imidazole-CH), 7.61 (br, 1H, imidazole-CH), 7.38 (br, imidazole-CH), 4.27 (br t, *J* = 6.2 Hz, 2H, imidazole-*N*-CH_2-pentyl), 4.04 (s, 3H, imidazole N-CH_3), 4.01 (m, 4H, oxazoline-CH_aH$_b$O + oxazoline-C*H*N), 3.76 (t, *J* = 4.5 Hz, 2H, oxazoline-CH$_a$$H_b$O), 1.80 (br, 4H, pentyl-CH_2), 1.38 (s, 3H, C*Me*), 1.29 (br, 4H, pentyl-CH_2), 0.87 (s, 9H, C*Me*$_3$); ^{13}C{^{1}H} NMR (75.4 MHz, $CDCl_3$) δ = 168.2 (oxazoline-*C*=N), 168.1 (oxazoline-*C*=N), 138.6 (imidazolium-*C*=N), 123.7 (imidazolium-*C*=C), 122.0 (imidazolium-C=*C*), 76.1 (oxazoline-*C*H$_2$O), 75.9 (oxazoline-*C*H$_2$O), 69.1 (oxazoline-*C*HN), 69.0 (oxazoline-*C*HN), 50.5 (N-*C*H$_2$(CH$_2$)$_4$), 42.7 [*C*Me-(CH$_2$)$_5$N], 37.2 (N-*C*H$_3$), 36.8 (*C*Me$_3$), 34.1 (*C*Me$_3$), 34.0 (pentyl-*C*H$_2$), 30.3 (pentyl-*C*H$_2$), 27.3 (pentyl-*C*H$_2$), 26.2 (C*Me*$_3$), 26.1 (C*Me*$_3$), 24.1 (pentyl-*C*H$_2$), 21.9 [C*Me*-(CH$_2$)$_5$N]; LR-MS (EI): *m*/*z* = 416 [M−Br−CH$_3$]$^+$; HR-MS (EI): *m*/*z* = 416.315697, calcd. for $C_{24}H_{40}N_4O_2$ [M−Br]$^+$: 416.315127; anal. calcd. for $C_{25}H_{43}N_4O_2Br$: C 58.70, H 8.47, N 10.95; found: C 58.63, H 9.08, N 10.52; $[\alpha]_D$: −52.3 (*c* 0.2, ethanol).

3-Methyl-1-{6,6-bis[(*S*)-4,5-dihydro-4-*tert*-butyloxazol-2-yl]heptan-1-yl}imidazolium Bis[(trifluoromethyl)-sulfonyl]imide (4b·NTf_2)[36]

A solution of **4b·Br** (0.400 g, 0.08 mmol) in dichloromethane (10 mL) was treated with a solution of $LiNTf_2$ (0.024 g, 0.084 mmol, 1.05 equivs.) in water (5 mL). The resulting mixture was stirred vigorously for 6 h after which time the organic layer was separated and washed successively with water (5×5 mL). The solvent was removed under reduced pressure and the resulting liquid dried for 4 h at 60 °C under 0.1 mbar pressure to afford **4b·NTf_2** free of Br^- (no precipitate with $AgNO_3$); yield: 0.531 g (96 %).

General Procedure for Copper Catalyzed Diels–Alder Reaction between *N*-Acryloyloxazolidinone and Cyclopentadiene in Dichloromethane

A flame dried Schlenk flask was charged with ligand (0.0127 mmol, 11 mol %), copper(II) triflate (0.0042 g, 0.0115 mmol, 10 mol %) and dichloromethane and the resulting solution stirred at room temperature for 3 h. After this time to the resulting green solution was added 2-(2-propenoyl)-2-oxazolidinone (0.0162 g, 0.115 mmol) followed by freshly distilled cyclopentadiene (30 μL, 0.35 mmol). The reaction mixture was stirred at room temperature for the specified amount of time and then diluted with 10 mL of 1:1 ethyl acetate:hexane and filtered through a short column of silica gel to afford unpurified product which was analysed. The *endo/exo* ratio was determined from ^1H NMR spectroscopy and the enantiomeric excess was calculated from the HPLC profile (for **6a**: 1 mL min^{-1} flow rate, hexane:propan-2-ol = 90:10; for **6b**: 1.0 mL min^{-1} flow rate, 94 % hexane, 4 % ethyl acetate, 2 % propan-2-ol).

General Procedure for Copper Catalyzed Diels–Alder Reaction *N*-Acryloyloxazolidinone with Cyclopentadiene in [emim][NTf_2]

A flame-dried Schlenk flask was charged with ligand (0.0127 mmol, 11 mol %), copper(II) triflate (0.0042 g, 0.0115 mmol, 10 mol %) and dichloromethane and the resulting solution stirred at room temperature for 3 h. After this time [emim][NTf_2] (2 mL) was added and the dichloromethane removed under vacuum after which dienophile (0.0162 g, 0.115 mmol) was added followed by freshly distilled cyclopentadiene (30 μL, 0.35 mmol). The resulting mixture was stirred at the indicated temperature for the specified amount of time after which the ionic liquid was extracted with diethyl ether (5×3 mL) in air. The crude product was filtered through a short column of silica gel to afford unpurified product which was analysed as described above.

Ionic Liquid Recycle Experiments

Following extraction with diethyl ether, the ionic liquid solution was subjected to vacuum to remove traces of diethyl ether, flushed with inert gas and charged with further portions of oxazolidinone **6a** or **6b** (0.0162 g, 0.115 mmol) and cyclopentadiene (30 μL, 0.35 mmol) at room temperature.

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