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Journal of Organometallic Chemistry 690 (2005) 5672–5695
Journal of Organometallic Chemistry
www.elsevier.com/locate/jorganchem

Enantioselective copper catalysed 1,4-conjugate addition reactions using chiral *N*-heterocyclic carbenes

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Received 29 April 2005; accepted 4 July 2005
Available online 24 August 2005

Abstract

The preparation of a variety of chiral *N*-heterocyclic carbene (NHC) precursors is described. The relative merits of imidazolinium salts and silver carbenes as NHC precursors are discussed with respect to their synthesis, stability and performance in the copper catalysed conjugate addition of dialkyl zinc reagents to a variety of Michael acceptors. Enantioselectivities of up to 93% were achieved using as little as 4% of chiral ligand.

Keywords: Imidazolinium salts; Silver(I); Chiral *N*-heterocyclic carbenes; Enantioselective; Copper catalysed; Conjugate addition

1. Introduction

During the early 1970s, Lappert et al. [1] reported that there was a striking similarity between the metal coordination chemistry of *N*-heterocyclic carbenes and electron rich organophosphanes. Initially, their use as ligands was limited, due to their relatively difficult preparation. The first applications involved the use of free carbenes, obtained by deprotonation of the corresponding imidazolinium salt, but these compounds are extremely air and moisture sensitive. More recent investigations have shown that it is possible to deprotonate and trap the carbenes in situ [2–7]. Since this time, much work has been carried out using *N*-heterocyclic carbenes as ligands; both chiral and achiral carbenes have been prepared and tested in a variety of reactions [8]. In some cases, excellent enantiomeric excesses have been achieved [9,10].

One such reaction in which *N*-heterocyclic carbenes have been applied is the copper catalysed 1,4-addition of a dialkyl zinc reagent to an α, β-unsaturated ketone [11–16]. More recently, the copper catalysed γ-selective allylic substitution using Grignard or dialkyl zinc reagents has been reported using *N*-heterocyclic carbenes as ligands [17,18]. Early work by Alexakis et al. [19] demonstrated that a trivalent phosphorus ligand could have a strong accelerating effect on the 1,4-conjugate addition reaction, and in 2001 Woodward showed [11] that the addition of diethyl zinc to cyclohexenone could also be accelerated using the achiral Arduengo diaminocarbene [20]. Chiral phosphorous-based ligands have been shown to induce a high degree of enantiomeric excess in the 1,4-adduct [21,22] and, bearing in mind the similarity between phosphorous- and heterocyclic carbene-based ligands, we hoped to induce enantioselectivity using chiral heterocyclic carbenes (Scheme 1).

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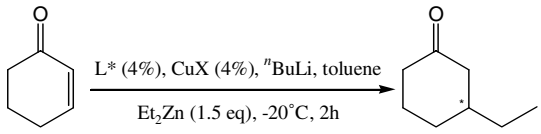
doi:10.1016/j.jorganchem.2005.07.024



Scheme 1. General method for 1,4-conjugate addition.

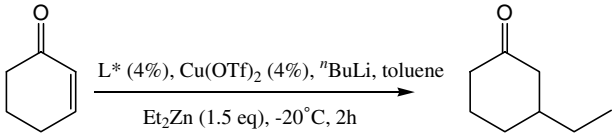
2. Results

Using conditions based upon those reported by Woodward [11], preliminary studies showed that it was possible to achieve an enantiomeric excess of 22% for the addition of diethyl zinc to cyclohexenone in the presence of $Cu(OTf)_2$ using the diaminocarbene derived from the Simpkins' diamine [23,24]. Deprotonation of imidazolinium salt **1** was carried out in situ using ^{n}BuLi at −20 °C in toluene. In order to investigate the influence of several ligand parameters, such as the steric bulk of the nitrogen substituents, the presence of a chiral backbone, of chiral substituents on the nitrogen atoms, and ring size; a range of novel imidazolinium salts (**1**–**6**) were synthesised in good yields by a reported procedure [25] from the readily available chiral diamines (Scheme 2) [26–29]. Although the presence of a bulky alkyl or aryl substituent on each nitrogen was thought to be necessary to stabilise the free diaminocarbene [30,31], it was proposed that the in situ trapping of the carbene derived from imidazolinium salt **2** should also give access to the desired copper-carbene complex.

Firstly, each of the imidazolinium salts was tested under the original conditions (Scheme 1, Table 1). Investigations were also made into pre-deprotonation of the diaminocarbene (Entry 2), but this led to a decrease in enantiomeric excess. The use of 2 equivalents of the ligand, which usually leads to an improvement in selectivity when using phosphorus based ligands [32], caused a dramatic decrease in reactivity; the addition product was obtained in only 15% yield after 14 h (Entry 3). This could be due to the formation of an inactive Cu complex in which there is a 2:1 ratio of carbene to metal, and suggests that the active species for the carbenes is different from that when using the phosphorus based ligands.

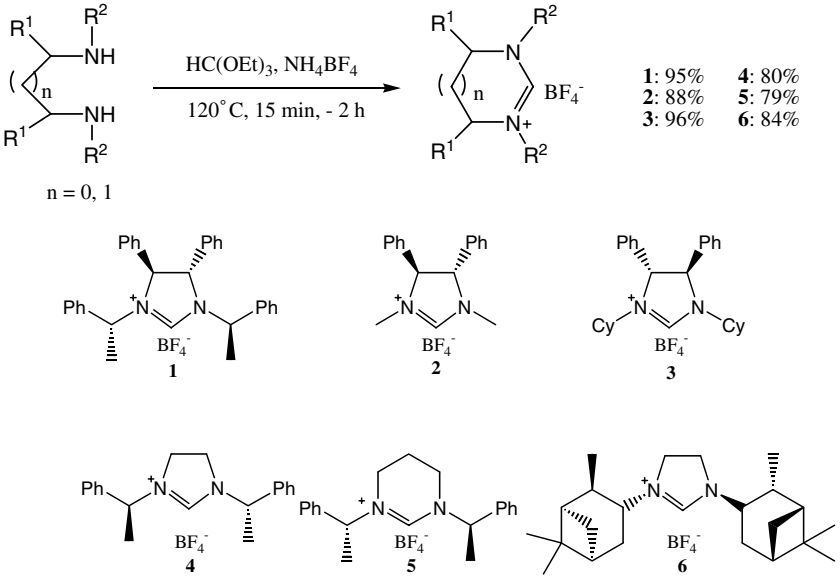
It was observed that ligand **1** gave the best results (22% enantiomeric excess) under these conditions. Ligands **2** and **3** give particularly low levels of asymmetric induction (Entries 4 and 5), presumably because

Table 1
Conjugate addition of Et_2Zn on cyclohexenone using $Cu(OTf)_2$ and a variety of novel ligands in toluene for 2 h at −20 °C



Entry	Imidazolinium salt	Yield[a] (%)	ee[b] (%)
1	**1**	92	22 (*S*)
2[c]	**1**	99	14 (*S*)
3[d]	**1**	15	20 (*S*)
4	**2**	99	4 (*S*)
5	**3**	97	7 (*S*)
6	**4**	99	13 (*S*)
7	**5**	99	13 (*R*)
8	**6**	41	14 (*S*)

For representative procedure, see experimental details.
[a] Determined by GC/MS.
[b] Determined by chiral GC (Lipodex E).
[c] Preformed ligand.
[d] Two equivalents of imidazolinium salt were used.



Scheme 2. Synthesis of imidazolinium salts.

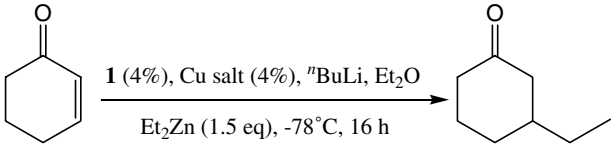
the chiral centres are relatively distant from the reacting centre. The diastereomeric pair of ligands **4** and **5** gave equal but opposite levels of stereochemical induction (Entries 6 and 7) as anticipated, despite the change in ring size which presumably does not effect the conformation of the chiral centres in the ligand. Compound **6** however, which had been reported by Hartwig to give high levels of enantiomeric excess when used as a ligand for an aryl amination reactions [28], gave disappointingly low levels of stereochemical induction (14%, Entry 8). It would appear that this species is a more effective ligand for Pd-catalysed reactions that for Cu. The low yield observed can be attributed to the hygroscopic nature of the imidazolinium salt.

In order to optimise the conditions, several Cu(I) mineral salts were tested; CuI, CuCN, $CuBF_4 \cdot 4CH_3CN$ and $CuPF_6 \cdot 4CH_3CN$ were used but on the whole, the yields were moderate and the enantioselectivities were poor (maximum ee = 11%) [12]. A range of solvents was also screened, and a significant rate increase was observed when the reaction was carried out in diethyl ether (Table 2). The reaction took only 15 min to reach completion at −20 °C, as opposed to 2 h in toluene. This allowed us to reduce the temperature of the reaction; at −50 °C, the reaction took 2 h to reach completion, but there was no real increase in enantiomeric excess. However, on decreasing the temperature to −78 °C, the enantioselectivity improved to 50% using ligand **1**.

Under these low temperature conditions, a range of cyclic and acyclic enones was tested to probe the versatility of the reaction (Table 3). Comparable results were obtained for the acyclic substrate decenone (**11**, Entry 5), but in all other cases, the enantiomeric excess of the 1,4-adduct did not exceed 26% [12]. Indeed, under these conditions, 5-methyl-3-hexen-2-one (**9**) and benzylacetone (**10**) did not react at all.

Under these new, low temperature conditions, further copper salts were also screened (Table 4). The choice of salts was based on related work in the group (conjugate addition reactions using phosphorus-based ligands), which had shown that enantioselectivities could be enhanced by the use of both copper(I) and copper(II) carboxylates [33]. Although copper(II) salts are usually cheaper and easier to handle, it has been proposed that the mechanism involves reduction of the Cu(II) species by Et_2Zn to give the true catalytic entity; Cu(I). In this work, CuTC (copper thiophene carboxylate; a Cu(I) salt) [34] and anhydrous $Cu(OAc)_2$ were tested. However, for this particular ligand, no improvements in enantiomeric excess were observed.

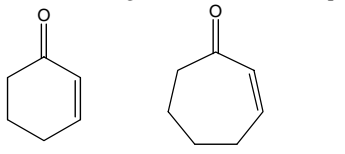
Table 2
Influence of the reaction temperature in diethyl ether using ligand **1**2



Entry	Temperature (°C)	Time (h)	Yield[a] (%)	ee[b] (%)
1	−20	0.25	97	19 (*S*)
2	−50	2	97	20 (*S*)
3	−78	16	91	50 (*S*)

[a] Determined by GC/MS.
[b] Determined by chiral GC (Lipodex E).

Table 3
Reaction using variety of substrates with ligand **1** under low temperature conditions



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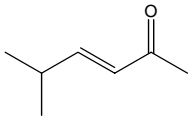

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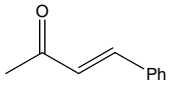

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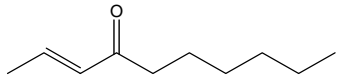

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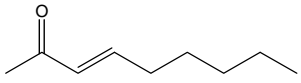

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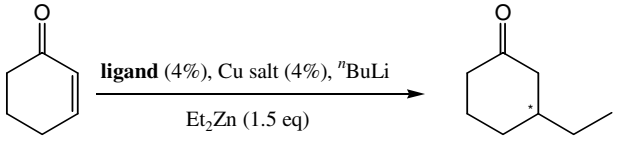
Entry	Substrate	Yield[a] (%)	ee[b] (%)
1	**7**	91	50 (*S*)
2	**8**	66	12 (*S*)
3	**9**	0	–
4	**10**	0	–
5	**11**	99	51 (+)
6	**12**	99	26 (*R*)

[a] Determined by GC/MS.
[b] Determined by chiral GC (Lipodex E).

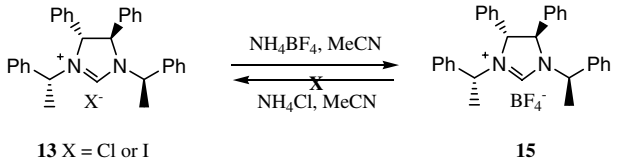
Table 4
Influence of Cu salt using ligand **1** under low temperature conditions



Entry	Cu salt (4 mol%)	Yield[a] (%)	ee[b] (%)
1	$Cu(OTf)_2$	91	50 (*S*)
2	$Cu(OAc)_2$	78	42 (*S*)
3	CuTC	88	29 (*S*)

[a] Determined by GC/MS.
[b] Determined by chiral GC (Lipodex E).

In each case, it was noted that the absolute stereochemistry of the product was related to the chiral centres of the ligand employed. For example, when ligand **4** was used, with chiral centre of *S* configuration adjacent to the nitrogen atom, the absolute stereochemistry of the product was also *S*, while the diastereomeric ligand with *R* stereocentres (ligand **5**) gave the product with the opposite but equal degree of enantioselectivity. Likewise for ligands **2** and **3**, an *S* configuration in the ligand induced an *S* configuration in the product. It was surprising to observe, therefore, that for ligand **1**, it was not the stereogenic centres adjacent to the nitrogen ((*R*) configuration), which dictated the absolute stereochemistry of the product, but the stereocentres in the backbone of the ligand (which were of (*S*) configuration). This led us to believe that, despite achieving promising levels of enantioselectivity under these conditions, ligand **1** was actually the mismatched case of a diastereomeric pair of ligands. With this in mind, the diastereomeric compound, **15**; derived from the *anti* Simpkins' diamine, was prepared. A by-product of its formation was isomer **16**, which had *meso* stereochemistry in the backbone, and this was also tested.



13 X = Cl or I **15**

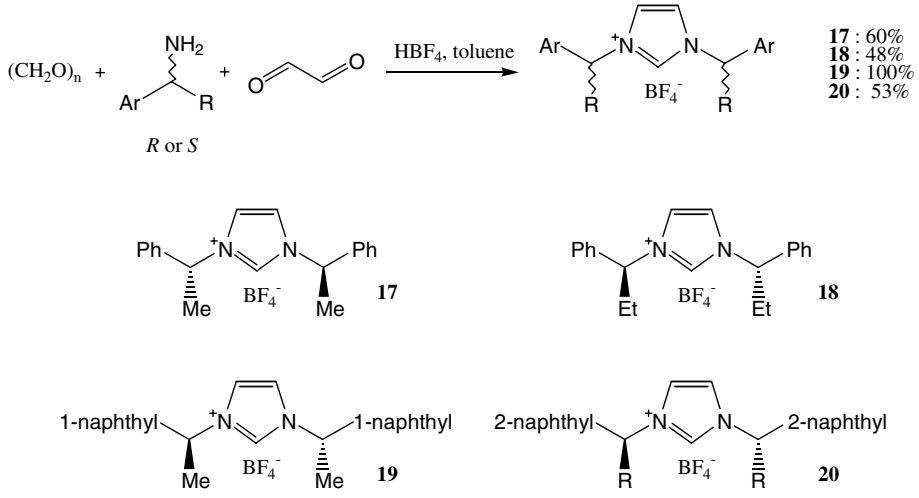
Scheme 3. Anion exchange.

Initially, the iodo-imidazolinium salts were synthesised [35], and the corresponding tetraflouroborate compounds **15** and **16** were prepared by anion exchange (Scheme 3) using NH_4BF_4 in acetonitrile overnight [36,37]. The results of 1,4-addition experiments (see Table 5) showed that in fact the "*anti*-Simpkins" ligand, **15**, yielded a 1,4-adduct with an enantiomeric excess of only 8% (although this time the product had an *R* configuration, which corresponded to all 4 stereogenic centres in the ligand), and therefore was, itself, the mismatched ligand (with respect to ligand **1**). The *meso* ligand performed slightly better, inducing an enantioselectivity of 21% with an *R* configuration (which in this case correlates with the configuration of the chiral substituents on the nitrogen atoms).

Based on the results in hand, a new range of imidazolinium salts were synthesised as carbene precursors in an attempt to probe the electronic as well as the steric effects of the ligand on the selectivity of the reaction.

Following the work of Herrmann et al. [38,39], the unsaturated ligands **17**–**20** were prepared in a one pot reaction starting from 2 equivalents of the corresponding chiral amine (Scheme 4). It should be noted that despite the unsaturation, the ligands show little π aromaticity In bonding terms, they can be better described as diaza-allyl systems [8].

Initial tests with ligand **17**, derived from (*R*)-phenylethylamine, showed promising results; under the low temperature conditions it was possible to achieve enantiomeric excesses of up to 54% using anhydrous



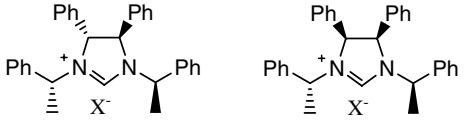
Scheme 4. Synthesis of unsaturated imidazolinium salts.

$Cu(OAc)_2$ (Entry 5). In order to observe the effect of unsaturation in the ring, the reaction was also carried out using ligand **17** in toluene at −20 °C with $Cu(OTf)_2$. An increase in selectivity from 13% to 39% was observed (Entries 1 and 2, ligands **4** and **17**, respectively, Table 6) and there was also a decrease in yield. This was probably due to the increased hygroscopicity of the unsaturated imidazolinium salt **17** with respect to its saturated counterpart **4**; ^{n}BuLi deprotonation to form the reactive carbene species may have been incomplete for ligand **17** (see Table 6).

From screening the initial set of ligands, it appeared to be important to have chiral substituents on the N-atom (which would be closer to the metal centre than any stereocentres present in the backbone of the ligand), and efforts were made to vary the steric bulk of the nitrogen substituents. It was interesting to observe that on replacing the methyl group with an ethyl (leaving the phenyl in place), exactly the same degree of enantioselectivity was observed for each of Cu salts tested (compare Entries 3–5 with Entries 6–8). The difference in absolute stereochemistry of the product was due to the configuration of the starting amine, but again, it was possible to predict the stereochemical outcome of the reaction; starting with chiral amine of *S* configuration, it was possible to obtain the 1,4-adduct with an *S* configuration, and vice versa.

On changing the size of the aromatic group on the *N*-substituent from a phenyl to a naphthyl (both the 1- and 2-naphthyl analogues were synthesised in order to probe the steric effects/requirements of each), there was no increase in the enantiomeric excess observed in the 1,4-adduct. In fact, when the 1-naphthyl substituted ligand **19** was employed (Entries 9–11) there was a considerable decrease in enantiomeric induction. The difference in the results obtained when the two different ligands (**19** and **20**) were used can be explained by their different steric requirements. This effect had previously been reported by Seebach who had investigated the 1- and 2-naphthyl derivatives of the TADDOL auxiliary [40]. In some cases, it was observed that even the stereochemical course of a reaction could be reversed by the use of the other naphthyl isomer [41]. Evidence for this was also found in crystal structures of the two TADDOL compounds which showed that the 2-naphthyl is orientated in the same direction as a simple phenyl ring, whereas the 1-naphthyl is more sterically demanding. In some cases this was responsible for reducing the catalytic activity of the ligand during a reaction [42].

Table 5
Influence of ligand counter-anion under low temperature conditions



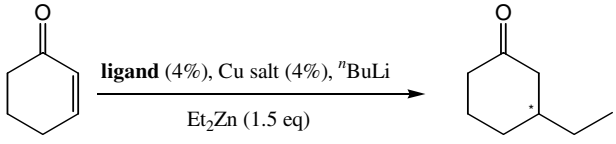
13 X = I
15 X = BF_4

14 X = I
16 X = BF_4

Entry	Ligand	Cu salt	Yield[a] (%)	ee[b] (%)
1	**1**	$Cu(OTf)_2$	91	50 (*S*)
2	**15**	$Cu(OTf)_2$	100	8 (*R*)
3	**16**	$Cu(OTf)_2$	55	21 (*R*)

[a] Determined by GC/MS.
[b] Determined by chiral GC (Lipodex E).

Table 6
1,4-addition using a range of unsaturated ligands with different Cu salts



Entry	Ligand	Cu salt	Tempertaure (°C)	Solvent	Time (h)	Yield[a] (%)	ee[b] (%)
1	**4**	$Cu(OTf)_2$	−20	Toluene	2	99	13 (*S*)
2	**17**	$Cu(OTf)_2$	−20	Toluene	2	60	39 (*R*)
3	**17**	$Cu(OTf)_2$	−78	Et_2O	16	80	42 (*R*)
4	**17**	CuTC	−78	Et_2O	16	88	52 (*R*)
5	**17**	$Cu(OAc)_2$	−78	Et_2O	16	75	54 (*R*)
6	**18**	$Cu(OTf)_2$	−78	Et_2O	16	38	42 (*S*)
7	**18**	CuTC	−78	Et_2O	16	46	52 (*S*)
8	**18**	$Cu(OAc)_2$	−78	Et_2O	16	51	54 (*S*)
9	**19**	$Cu(OTf)_2$	−78	Et_2O	16	44	27 (*S*)
10	**19**	CuTC	−78	Et_2O	16	76	38 (*S*)
11	**19**	$Cu(OAc)_2$	−78	Et_2O	16	57	2 (*S*)
12	**20**	$Cu(OTf)_2$	−78	Et_2O	16	87	37 (*S*)
13	**20**	CuTC	−78	Et_2O	16	81	51 (*S*)
14	**20**	$Cu(OAc)_2$	−78	Et_2O	16	94	46 (*S*)

[a] Determined by GC/MS.
[b] Determined by chiral GC (Lipodex E).

Although no crystal structures were obtained of the imidazolinium salts (in each case, the salt was isolated as a fine granular powder), the results obtained in the conjugate addition reactions suggest that it is the aromatic group which is closer to the reacting metal centre than the alkyl, R, group (changing from Me to Et has no effect on the reactions selectivity, whereas changing to the more sterically bulky naphthyl group we see a change, albeit a reduction in enantiomeric excess).

Roland et al. [14], have shown that it is possible to carry out the same reaction with low levels of asymmetric induction using a chiral silver(I) diaminocarbene **21** as the carbene precursor (Scheme 5).

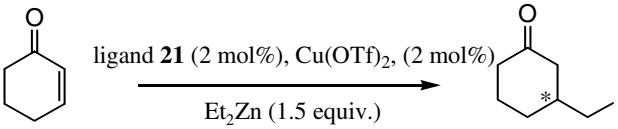
The original investigation by Roland focused on the influence of the reaction temperature and solvent effects. In each case, the substrate employed was cyclohexenone and the ligand was compound **21**. In contrast to the work carried out by Alexakis et al. [12], in which 4 mol% of ligand and Cu salt were used, these results were obtained using only 2 mol% of each.

It was observed that the rate of reaction using a silver carbene at 0 °C was vastly increased with respect to the analogous reactions using the imidazolinium salts at −20 °C (Table 7, entries 10–13). Using imidazolinium salt **1** as a ligand, the reaction in toluene took 2 h to reach completion at −20 °C (Entry 10), and it is thought that if the reaction temperature had been decreased to −78 °C, the reaction may have taken several days! We observed another difference for the reaction in dichloromethane. When the imidazolinium salt was employed, the deprotonation step was carried out in a small volume of toluene (to prevent solvent deprotonation), and then the mixture was diluted with dichloromethane (to the extent that it was the major solvent). The reaction rate appeared to be very similar to that observed in toluene, and the reactions were both complete in 2 h with a comparable degree of enantioselectivity (Entry 10 and Entry 12). However, for the silver carbenes, we can see that the rate of reaction is slower in dichloromethane than for toluene, and there is a complete loss of selectivity (Entry 5). The results in THF are comparable however; using imidazolinium salt **1**, the reaction proceeds with a low yield and negligible enantioselectivity (Entry 13). For silver carbene **21**, the same effect is observed; the reaction rate is much lower than for the other solvents, and again, the product obtained is racemic (Entry 6).

It was surprising to observe that as the reaction temperature was decreased to −78 °C, the enantioselectivity also decreased (Entries 7–9), but this effect could not be tested for imidazolinium salts due to their low rate of reaction in toluene. Another interesting observation was that the use of 2 equivalents of the silver carbene with respect to the copper salt (Entry 2, 4 mol% in total) led to very similar results as had been observed with the usual 1:1 ratio of carbene to copper salt; the yield was almost quantitative after 15 min and there was only a small decrease in enantioselectivity. This is in stark contrast with the results obtained for the chiral imidazolinium salts in which there was a large decrease in reactivity of the system when two equivalents of ligand were used (Table 1, Entry 3).

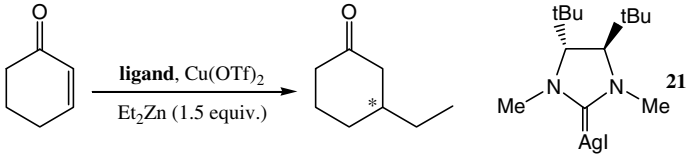
The first silver carbene complexes in the literature were prepared in 1993 by Arduengo et al. [43], and involved reaction of the free carbene with silver triflate. In this case however, the silver carbene **21** was prepared by an alternative method, described by Wang and Lin [44], in which the imidazolinium salt was treated with Ag_2O [45]. Silver carbene species are known to act as effective carbene transfer agents for the synthesis of pal-

Table 7
Influence of solvent and temperature on 1,4-addition reaction using silver carbene **21** as ligand



Entry	Solvent	Temperature (°C)	Time (h)	Yield[a] (%)	ee[b] (%)
1	Toluene	0	0.25	98	23 (*S*)
2[c]	Toluene	0	0.25	98	20 (*S*)
3	Hexane	0	0.25	99	16 (*S*)
4	Et_2O	0	0.25	95	15 (*S*)
5	DCM	0	1	62	0
6	THF	0	1	28	0
7	Toluene	−20	1	99	16 (*S*)
8	Toluene	−40	1	98	10 (*S*)
9	Toluene	−78	1	78	4 (*S*)
10[d]	Toluene	−20	2	92	22 (*S*)
11[d]	Et_2O	−20	0.25	97	19 (*S*)
12[d]	Toluene/DCM	−20	2	90	27 (*S*)
13[d]	THF	−20	2	24	3 (*S*)

[a] Determined by GC/MS.
[b] Determined by chiral GC (Lipodex E).
[c] Reaction carried out using 2 equivalents of copper salt with respect to the carbene (i.e., 4 mol% copper species, 2 mol% ligand).
[d] Reaction carried out with 4 mol% ligand **1** and 4 mol% copper species.



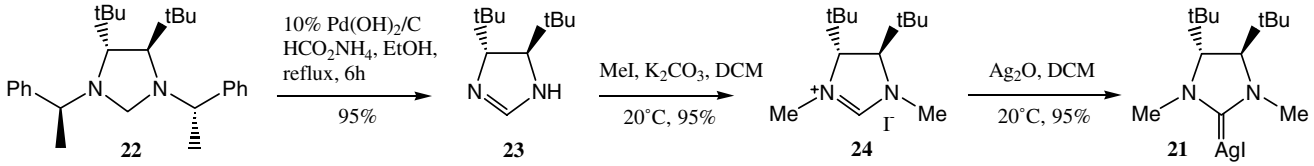
Scheme 5. 1,4-Conjugte addition using silver carbenes as ligands.

ladium or gold carbene complexes, and this has recently been applied to the synthesis of palladium–carbene complexes which have been used successfully as catalysts for C–C coupling reactions [46]. There are several advantages to using the diaminocarbene in this form, despite the synthetic route being one step longer than that for the corresponding imidazolinium salts. The silver diaminocarbene has been shown to act as an efficient transfer agent to copper(II) triflate, and the catalytic species could be easily prepared at room temperature in various solvent systems. Unlike the imidazolinium salts, the silver carbenes do not require in situ deprotonation, therefore, the use of strong bases and polar solvents is avoided, and perhaps more importantly, in terms of reaction yield, and in contrast to the imidazolinium salts, the silver carbenes are not generally hygroscopic.

The imidazolinium salt precursor to the silver carbene **21** was prepared from the known (*R*,*R*)-4,5-di-*tert*-butylimidazolidine (**23**), which itself was prepared from the aminal **22** [47], by a one-pot palladium-mediated hydrogenolysis and oxidation procedure [48]. Compound **23** was readily alkylated at 20 °C in dichloromethane using MeI to yield imidazolinium salt **24**. The desired product was isolated by precipitation with Et_2O and pentane in 95% yield. Using the Wang and Lin procedure [44], the silver(I) diaminocarbene was prepared in excellent yield by treatment with 0.5 equivalents of Ag_2O in dichloromethane (Scheme 6).

A crystal structure of the silver carbene **21** was obtained (displayed in Fig. 1 as an ORTEP diagram) which clearly shows that the compound exists in the solid state as a dimeric species in which the silver atoms are bridged by two iodine atoms.

Our attention then turned to the synthesis and application of a wider range of silver carbenes, initially this involved a comparison of the enantiomeric excesses obtained using the unsaturated imidazolinium salts as ligands with the corresponding silver carbenes. In order to prepare the desired, unsaturated, silver carbenes, it was necessary to prepare the chloro-imidazolinium analogues of the tetra-fluoroborate salts (**17**–**20**) described above. Unfortunately, it was not possible to transform the BF_4 salts directly into silver carbenes and it was only possible to prepare the chloro-imidazolinium salts in very low yield by the same one-pot procedure (17% for



Scheme 6. Synthesis of silver carbene **21**.

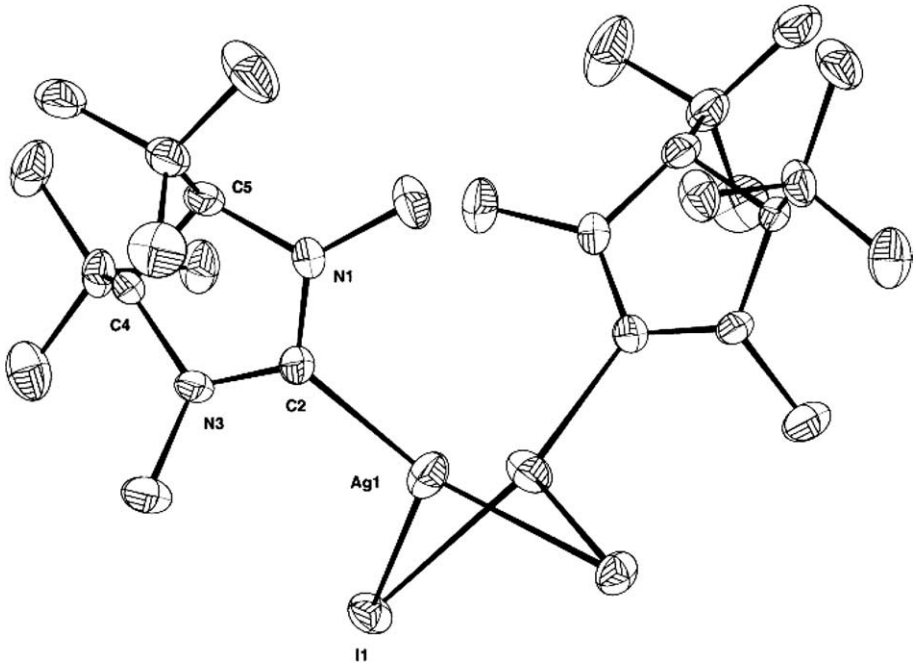


Fig. 1. ORTEP diagram of ligand **21**.

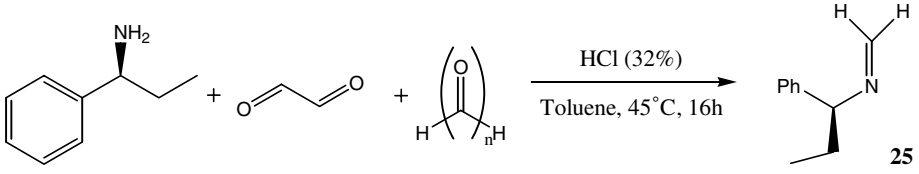
compound **26**) [38,39]. The main by-product of the reaction was the imine, **25** formed by addition of *para*-formaldehyde onto the chiral amine (Scheme 7). In addition, attempts to carry out counter anion exchange from BF_4^- to Cl^- proved to be fruitless; it appears that this reaction can only be carried out in the opposite direction.

It was, however, possible to prepare the compounds using a modified, two step procedure via the intermediate bis-imines (**27** and **28**) which were formed in excellent yield from the reaction between 2 equivalents of a chiral amine with glyoxal under acid mediated conditions (Scheme 8) [49].

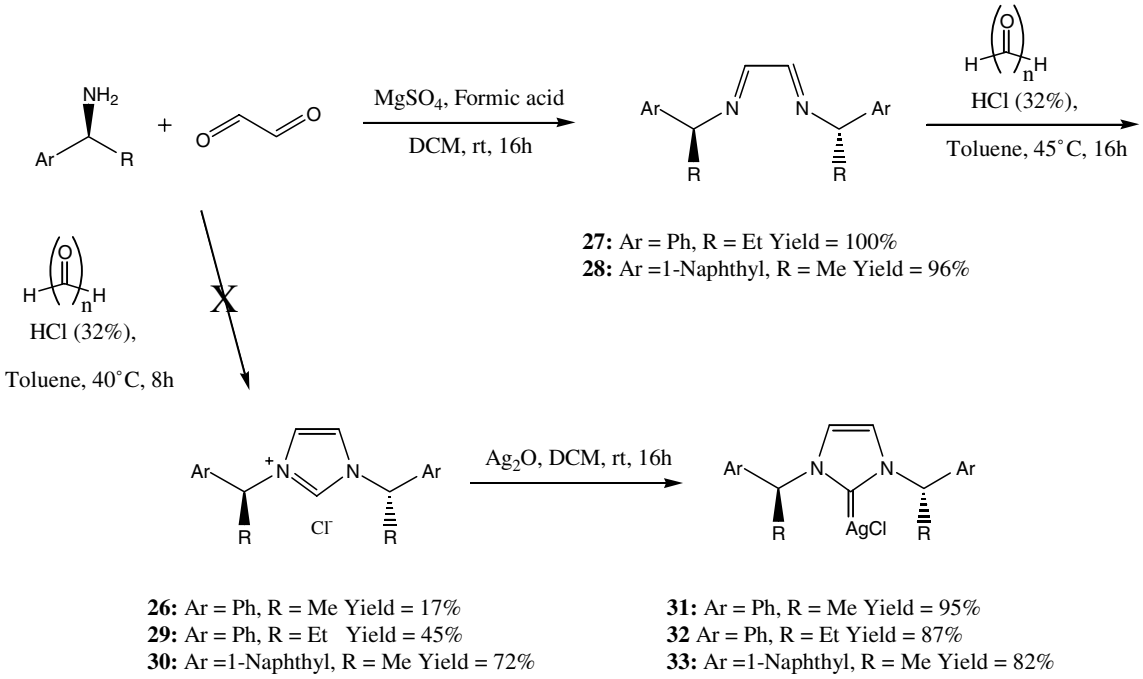
The bisimines (**27** and **28**) required no purification and were taken straight through to the corresponding chloro-imidazolinium salts by reaction with *para*-formaldehyde and HCl (32% aqueous solution) in toluene. In some cases, trituration with diethyl ether was required to purify the product, which was then transformed into the unsaturated silver carbene (**31**–**33**) by stirring overnight in anhydrous dichloromethane in the presence of 0.5 equivalents of silver(I) oxide. The silver carbenes were isolated in good yield and with a high level of purity after filtration through celite. No further purification was required.

Using silver carbene **31** as a ligand for the 1,4-addition of diethyl zinc onto cyclohexenone under the conditions previously described by Roland and co-workers [14], an enantiomeric excess of 25% was observed (Entry 1, Table 8). However, using the modified, low-temperature conditions for the same ligand, ee's of up to 62% could be achieved (Entry 3). The highest excess was obtained using CuTC as the Cu source, although $Cu(OAc)_2$ also led to an excess of 59% (Entry 4). In contrast to the results obtained with the hygroscopic BF_4 imidazolinium salts, the conversion was always quantitative.

Even more pleasing, was the observation that the reaction appeared to be applicable to other substrates, and particularly high enantiomeric excesses were achieved when cycloheptenone was employed. Using both CuTC and $Cu(OAc)_2$, the product obtained had an enantiomeric excess greater than 85% (Entries 6 and 7). As for the six-membered cyclic enone however, $Cu(OTf)_2$ gave lower results (43 and 47% for the 6 and

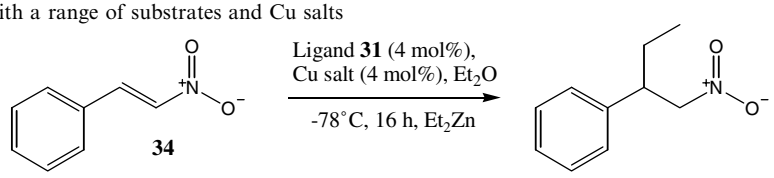


Scheme 7. Formation of imine.



Scheme 8. Synthesis of unsaturated silver carbenes.

Table 8
1,4-addition using ligand **31** with a range of substrates and Cu salts



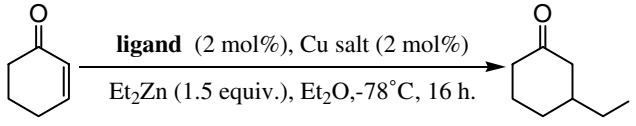
Entry	Substrate	Cu salt	Yield[a] (%)	ee[b] (%)
1[c]	**7**	$Cu(OTf)_2$	92	25 (*R*)
2	**7**	$Cu(OTf)_2$	100	37 (*R*)
3	**7**	CuTC	99	62 (*R*)
4	**7**	$Cu(OAc)_2$	100	59 (*R*)
5	**8**	$Cu(OTf)_2$	71	47 (*R*)
6	**8**	CuTC	100	86 (*R*)
7	**8**	$Cu(OAc)_2$	99	88 (*R*)
8	**34**	$Cu(OTf)_2$	92	70 (*R*)
9	**34**	CuTC	100	72 (*R*)
10	**34**	$Cu(OAc)_2$	100	75 (*R*)
11	**9**	CuTC	44	49
12	**10**	CuTC	60	42 (*S*)
13	**12**	CuTC	67	42 (*S*)

7 = cyclohexenone, 8 = cycloheptenone, 9 = nitrostyrene.
[a] Determined by GC/MS.
[b] Determined by chiral GC (Lipodex E).
[c] Using original Roland conditions [14]; 2 mol% ligand and Cu salt, toluene, rt, 1 h.

7 membered rings respectively, Entries 2 and 5). High selectivities had also been observed using phosphorus based ligands with nitrostyrene **34** [50], and with ligand **31**, good results were observed for addition to this substrate, even with $Cu(OTf)_2$ which appeared to be as efficient as the other Cu salts in this case. All three different copper salts gave enantiomeric excesses over 70% (Entries 8–10). With the acyclic enones (tested only with CuTC, Entries 11–13), enantiomeric excesses were considerably higher than those achieved with the imidazolinium salt, **1**, although for each substrate, it was observed that the reaction did not go to completion at −78 °C, even after 16h of reaction. Presumably, this is due to the lower reactivity of these substrates with respect to their cyclic counterparts. However, it should be noted that all the product yields were much higher than those obtained with the saturated ligands (compare with results in Table 3) and this is assumed to be due to the electronic rich nature of the ligands, which renders the ligand–Cu system more reactive.

As with the imidazolinium salts, investigations were made into changing the size of the substituents at the stereogenic centre adjacent to the nitrogen (Table 9). Firstly, the methyl group was substituted for an ethyl moiety and the resulting ligand (**32**) was tested in the reaction with cyclohexenone, cycloheptenone and nitrostyrene (Entries 1–9). Unlike the corresponding imidazolinium salt (**18**) which gave exactly the same results for the addition to cyclohexenone (see Table 6), the results obtained in this case were slightly improved for addition in the presence of $Cu(OTf)_2$ (but only for the cyclic enones, Entries 1 and 4) and decreased in all other cases. The 1-naphthyl derivative (**33**) was also prepared and in contrast to the results observed with the corresponding tetraflouroborate-imidazolinium salt for the addition to cyclohexenone, the enantioselectivities were

Table 9
1,4-addition using unsaturated silver carbene ligands **32** and **33** with range of substrates and Cu salts



Entry	Ligand	Substrate	Cu salt	Yield[a] (%)	ee[b] (%)
1	**32**	**7**	$Cu(OTf)_2$	85	51 (*S*)
2	**32**	**7**	CuTC	94	52 (*S*)
3	**32**	**7**	$Cu(OAc)_2$	92	55 (*S*)
4	**32**	**8**	$Cu(OTf)_2$	84	69 (*S*)
5	**32**	**8**	CuTC	90	73 (*S*)
6	**32**	**8**	$Cu(OAc)_2$	97	76 (*S*)
7	**32**	**34**	$Cu(OTf)_2$	91	38 (*S*)
8	**32**	**34**	CuTC	80	52 (*S*)
9	**32**	**34**	$Cu(OAc)_2$	98	55 (*S*)
10	**33**	**7**	$Cu(OTf)_2$	58	48 (*S*)
11	**33**	**7**	CuTC	79	54 (*S*)
12	**33**	**7**	$Cu(OAc)_2$	87	59 (*S*)
13	**33**	**8**	$Cu(OTf)_2$	60	75 (*S*)
14	**33**	**8**	CuTC	95	89 (*S*)
15	**33**	**8**	$Cu(OAc)_2$	95	93 (*S*)
16	**33**	**34**	$Cu(OTf)_2$	25	11 (*S*)
17	**33**	**34**	CuTC	98	69 (*S*)
18	**33**	**34**	$Cu(OAc)_2$	96	67 (*S*)

[a] Determined by GC/MS.
[b] Determined by chiral GC (Lipodex E).

approximately equivalent. For the addition to cycloheptenone (Entries 13–15), the results were in excess of those achieved for the six-membered ring, and also in excess of those obtained with the phenyl-derived ligand. Again, $Cu(OAc)_2$ proved to be the copper salt of choice, yielding a product with an enantiomeric excess of 93%. For almost every substrate-ligand combination, $Cu(OAc)_2$ gave the best enantiomeric excess (Entries 3, 6, 9, 12 and 15).

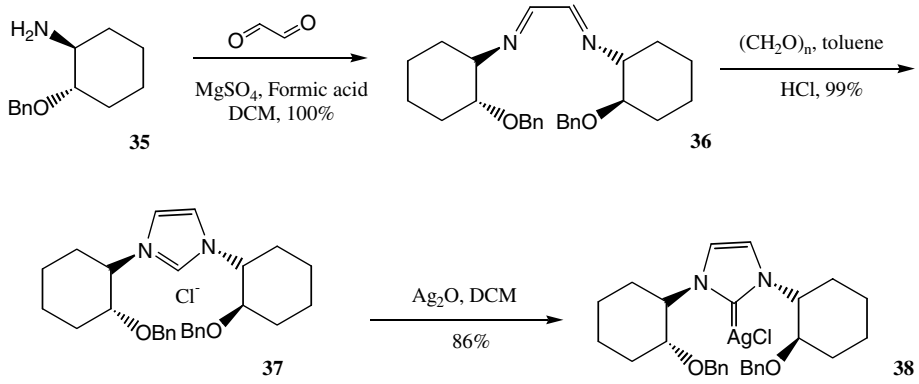
After probing the steric effects of the groups at the chiral centres adjacent to the nitrogen, investigations were made into the effect of having a chiral chelating group adjacent to the nitrogen. To investigate chelation effects, the *O*-protected enantiopure amino-alcohol **35** derived from 2-hydroxy-cyclohexylamine was employed as the starting material for the synthesis of ligand **38** (Scheme 9).

Again, a two-step procedure via the bisimine **36** [45] was employed to prepare the chloro-imidazolinium salt **37**, which was converted to the silver carbene **38** in good yield. In this particular case, some problems were encountered due to the highly hygroscopic nature of the chloro-imidazolinium salt. Exposure, even briefly, to the air resulted in absorption of H_2O, which caused the product to become sticky and very difficult to handle. Fortunately, the silver carbene was much easier to manipulate and could be tested as a ligand under the usual conditions (Table 10).

Surprisingly, the results obtained with cyclohexenone were very poor, less than 10% enantiomeric excess was measured in each case, and quite astonishingly, with this in mind, up to 73% enantiomeric excess was observed for cycloheptenone using CuTC. These results are currently inexplicable and the varying yields are also somewhat surprising. It may be that this particular silver carbene is hygroscopic and the $Cu(OTf)_2$ contained a higher percentage of moisture that either the $Cu(OAc)_2$ or CuTC, thus quenching the carbene as it formed and resulting in a lower yield.

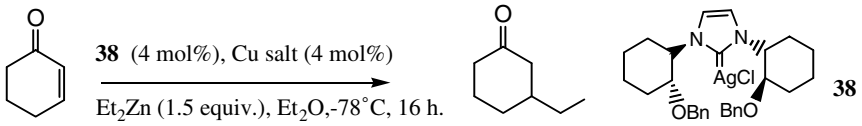
In order to probe the effect of having a sterically bulky chiral group adjacent to the nitrogen, the unsaturated analogue of Hartwigs' imidiazolinium salt (**42**) derived from α-pinene **39** was prepared (Scheme 10) [29].

In this case, attempted synthesis of the bisimine **40** by the acid catalysed route described above (Conditions A) [49] was unsuccessful and led to a complex mixture of



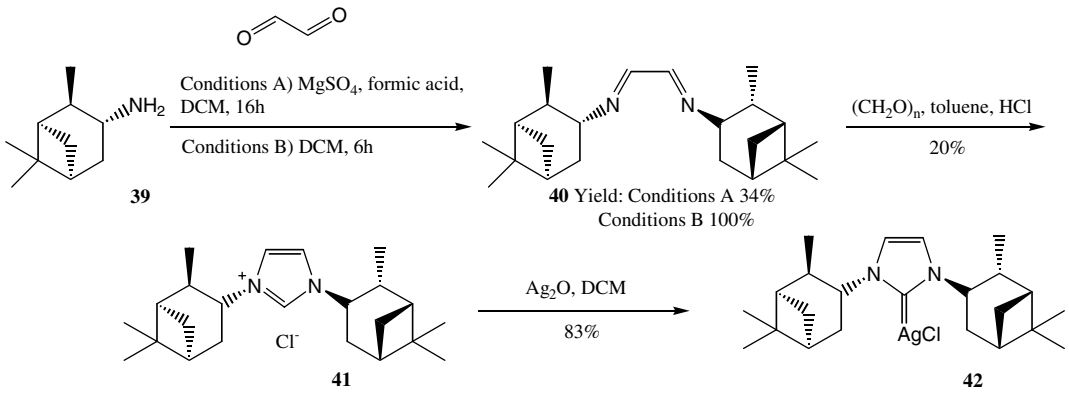
Scheme 9. Synthesis of chelating ligand **38**.

Table 10
1,4-addition reaction using ligand **38** with a range of Cu salts and substrates



Entry	Substrate	Cu salt	Yield[a] (%)	ee[b] (%)
1	**7**	$Cu(OTf)_2$	55	5 (*S*)
2	**7**	CuTC	89	5 (*S*)
3	**7**	$Cu(OAc)_2$	60	9 (*S*)
4	**8**	$Cu(OTf)_2$	15	54 (*S*)
5	**8**	CuTC	64	64 (*S*)
6	**8**	$Cu(OAc)_2$	60	73 (*S*)
7	**34**	$Cu(OTf)_2$	22	6 (*S*)
8	**34**	CuTC	70	53 (*S*)
9	**34**	$Cu(OAc)_2$	75	31 (*S*)

[a] Determined by GC/MS.
[b] Determined by chiral GC (Lipodex E).



Scheme 10. Synthesis of sterically bulky ligand **42**.

products, from which the desired bisimine could not be separated. Instead, it was possible to form compound **40** in high yield by simply mixing the chiral amine and glyoxal in dichloromethane for 5 h (Conditions B) [29]. After this time, the product was isolated by extraction and used without further purification.

Formation of the silver carbene **42** via the chloro-imidazolinium salt **41** proceeded in a satisfactory yield over the two steps, and the product was then tested in a 1,4-conjugate addition reaction using CuTC as the catalyst (Table 11); employing both cyclohexenone (Entry 1) and cycloheptenone (Entry 2) as the substrate. Unfortunately, in this case, although the reaction yield was high, the levels of stereochemical induction observed were very low, only 5% for cyclohexenone and 15% for cycloheptenone. We may conclude from these results that the ligand is too sterically hindered to induce high levels of enantiomeric excess. These enantiomeric excesses are the only ones that are lower than for the corresponding BF_4 imidazolinium salt although these results are not obtained under the same conditions. It is thought that under the low temperature conditions, the enantiomeric excess would be even higher for the BF_4 salt, although silver carbenes were much more efficient (95% yield as opposed to 22%).

Another ligand, **48**, in which the imidazolinium backbone was a phenyl ring, was synthesised according to the method described by Diver et al. [36]. The diamine **45** was prepared in a stepwise manner by coupling the homochiral amine onto dibromobenzene **43** using Pd_2dba_3 in the presence of (±) BINAP and NaO*t*-Bu. The amine-coupled product was obtained in moderate yield to give the desired diamine, which could be cyclized to form the chloro-imidazolinium salt **47** using triethylorthoformate under acidic conditions. The resulting imidazolinium salt was very hygroscopic but could be dried over P_2O_5 before forming the silver carbene **48**, which was isolated in excellent yield (Scheme 11).

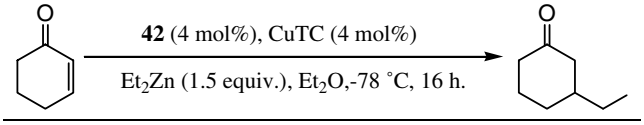
Unfortunately, the enantiomeric excesses observed when using this ligand in 1,4-addition reactions with cyclohexenone and cycloheptenone, were very low (Table 12), but it was interesting to see that for the first time, the excess achieved for cyclohexenone was superior to that for the seven membered cyclic substrate, and, perhaps more surprisingly, the absolute configuration of the cyclohexenone 1,4-adduct (*S*) was opposite to the configuration of the starting amine (*R*). This may be due to strong intramolecular π-stacking interactions between the aromatic backbone and the phenyl groups present in the nitrogen substituents, which twist the ligand into an unusual conformation.

Moving away from the unsaturated ligands, diaminocarbenes related to ligand **21**, containing chiral tertiary butyl groups in the backbone were synthesised and tested (Fig. 2), both under the conditions originally described by Roland [14] and the low temperature, ethereal conditions described above [12].

Compounds **49**, **51**, **52**, and **54**, were prepared from the chiral aminal **22** via compound **23**, and the alkylated imidazolinium salts **55**–**58** (see Scheme 12).

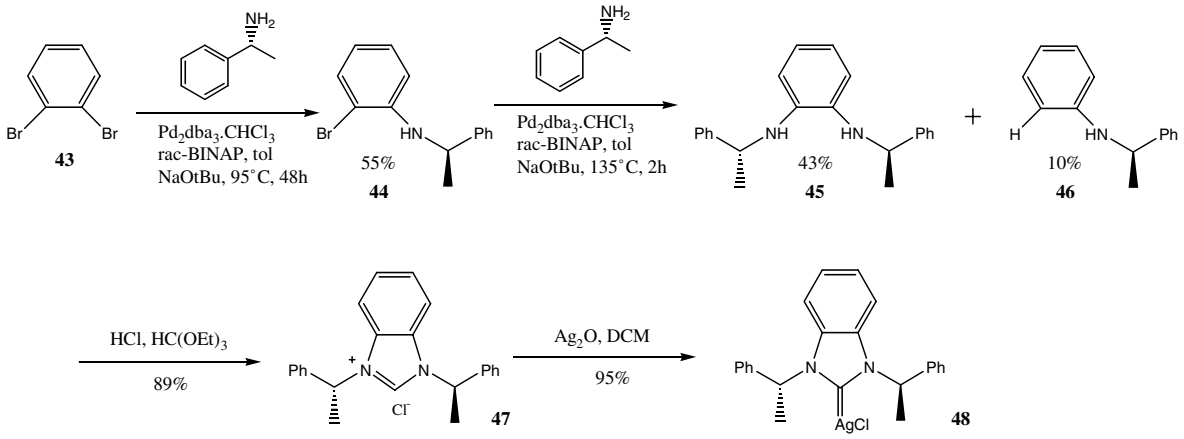
In order to preserve the chiral moieties on the nitrogen atoms, a different approach was used to prepare ligand **53** [51]. Using iodine and $NaHCO_3$ in dichloromethane, it was possible to oxidise compound **23** to give the imidazolinium salt **55** (Scheme 13) [48]. This reaction proceeded quantitatively (by TLC) but the yield of the pure product was somewhat reduced (58%) due to difficulties in isolation. Due to the low

Table 11
1,4-addition reaction using ligand **42**



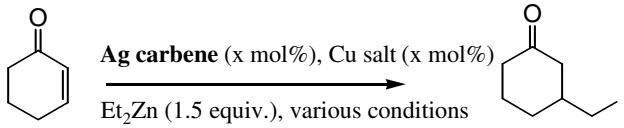
Entry	Substrate	Cu salt	Yield[a] (%)	ee[b] (%)
1	**7**	CuTC	95	4 (*S*)
2	**8**	CuTC	85	15 (*S*)

[a] Determined by GC/MS.
[b] Determined by chiral GC (Lipodex E).



Scheme 11. Synthesis of ligand **48**.

Table 12
1,4-addition reaction using ligand **48**



Entry	Substrate	Cu salt	Yield[a] (%)	ee[b] (%)
1	7	CuTC	100	21 (*S*)
2	8	CuTC	95	7 (*S*)

[a] Determined by GC/MS.
[b] Determined by chiral GC (Lipodex E).

solubility of this compound and its very high melting point (m.p. > 290 °C), although ^{1}H NMR data was obtained, complementary analysis could not be performed [52]. It was however, possible to prepare the corresponding silver carbene in reasonable yield.

From the results in Table 13, many conclusions can be drawn. Firstly, for a specific ligand, low temperature conditions using diethyl ether and CuTC yield products with higher enantiomeric excesses than the toluene/$Cu(OTf)_2$ conditions (compare Entries 1 and 2 using ligand **21**, or Entries 3 and 4 using ligand **49** where the greatest difference is observed, or Entries 6 and 7 using ligand **51**).

Contrary to expectation (since there were no chiral substituents on the nitrogen atom), the silver carbene **49** with *N*-benzyl substituents gave 58% ee for cyclohexenone (Entry 3 using CuTC as the copper source), and 76% ee for the cycloheptenone adduct (Entry 14). The high degree of stereochemical induction in this case may be rationalised with the aid of the crystal structures shown in Figs. 1 and 3 [45]. The *t*-Bu groups in the back-bone are *anti* to one another and although in Fig. 1, we see that the arrangement of substituents around each nitrogen atom is planar, the methyl groups themselves are not large enough to be affected by the back-bone substituents, so also lie in a planar arrangement. However, when a proton is replaced by a phenyl group (see Fig. 3), which is much larger than the proton, the phenyl group is displaced by the *t*-Bu groups in an *anti* fashion (one up, one down with respect to the plane), and it is this conformation which leads to increased enantiodifferentiation.

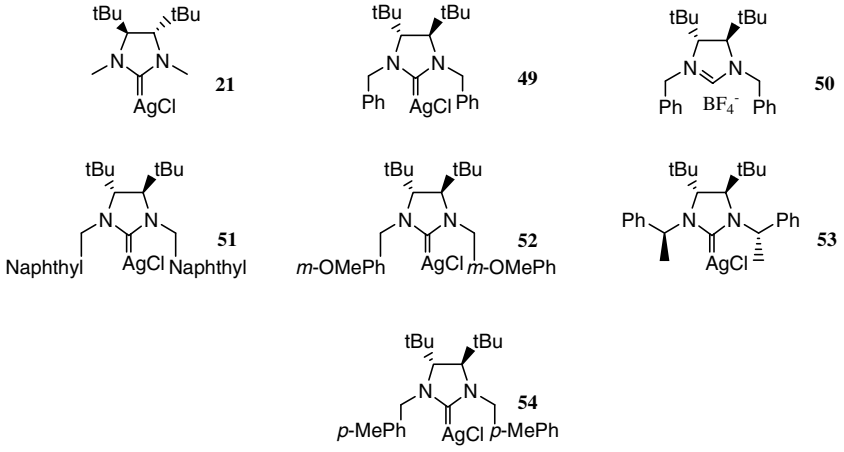
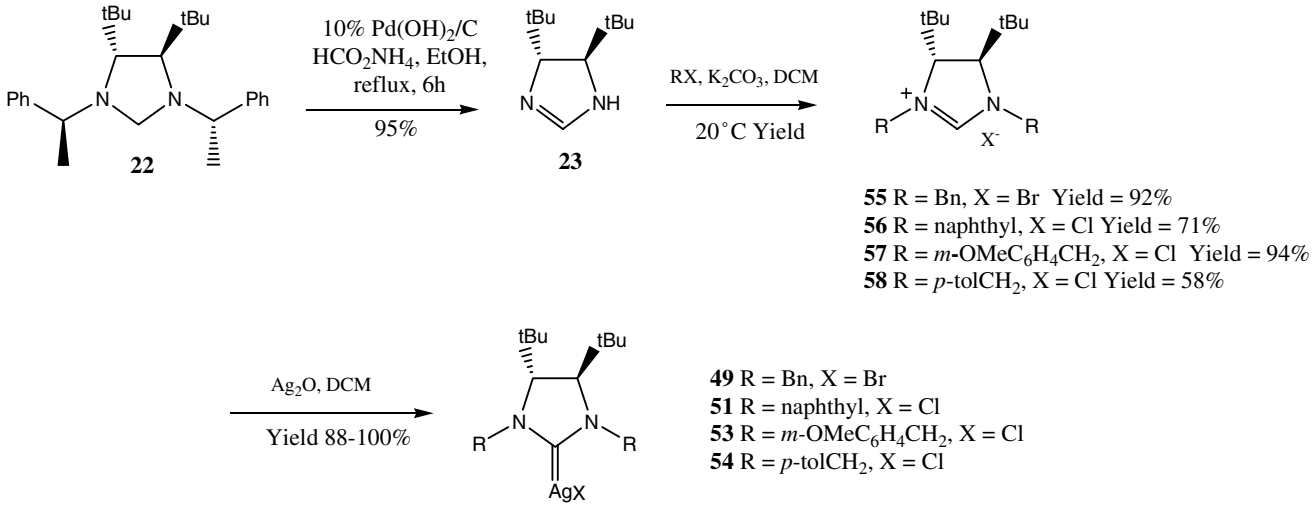


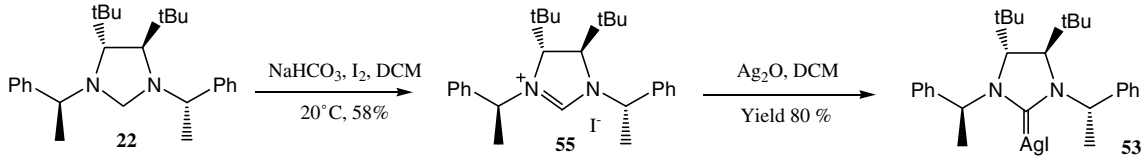
Fig. 2. Silver carbenes tested in 1,4-conjugate addition.



Scheme 12. Synthesis of silver carbenes **49**, **51**, **53**, and **54**.

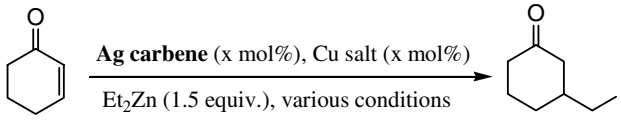
In contrast to compound **21**, ligand **49** crystallised as a monomer, but shows the same carbene-Ag-X unit. The *anti* arrangement of the benzyl groups with respect to the *t*-Bu groups is shown clearly, and it is assumed (as described above) that in this case, the N atoms are no longer planar.

For this particular ligand, it was possible to make a direct comparison between the silver carbene **49** and the corresponding imidazolinium salt **50** which had also been tested (Table 13, entry 5). Under exactly the same experimental conditions, a slight decrease in selectivity was observed for the imidazolinium salt; 52% enantio-



Scheme 13. Synthesis of silver carbene **53**.

Table 13
1,4-additions with a range of *t*-Bu substituted ligands under various conditions



Entry	Ligand (mol%)	Cu salt (mol%)	Substrate	Solvent	Tempertaure (°C)	Time (h)	Yield[a] (%)	ee[b] (%)
1	**21** (4)	CuTC (4)	7	Et_2O	−78	16	99	30 (*S*)
2	**21** (2)	$Cu(OTf)_2$ (2)	7	Toluene	0	1	98	23 (*S*)
3	**49** (4)	CuTC (4)	7	Et_2O	−78	16	100	58 (*S*)
4	**49** (2)	$Cu(OTf)_2$ (2)	7	Toluene	rt	1	100	31 (*S*)
5	**50** (4)	CuTC (4)	7	Et_2O	−78	16	95	52 (*S*)
6	**51** (4)	CuTC (4)	7	Et_2O	−78	16	99	14 (*R*)
7	**51** (2)	$Cu(OTf)_2$ (2)	7	Toluene	rt	1	98	0
8	**52** (4)	CuTC (4)	7	Et_2O	−78	16	99	69 (*S*)
9	**53** (4)	CuTC (4)	7	Et_2O	−78	16	98	29 (*S*)
10	**54** (2)	$Cu(OTf)_2$ (2)	7	Toluene	rt	1	95	23 (*S*)
11	**49** (4)	CuTC (4)	8	Et_2O	−78	16	99	76 (*S*)
12	**52** (4)	CuTC (4)	8	Et_2O	−78	16	100	88 (*S*)

[a] Determined by GC/MS.
[b] Determined by chiral GC (Lipodex E).

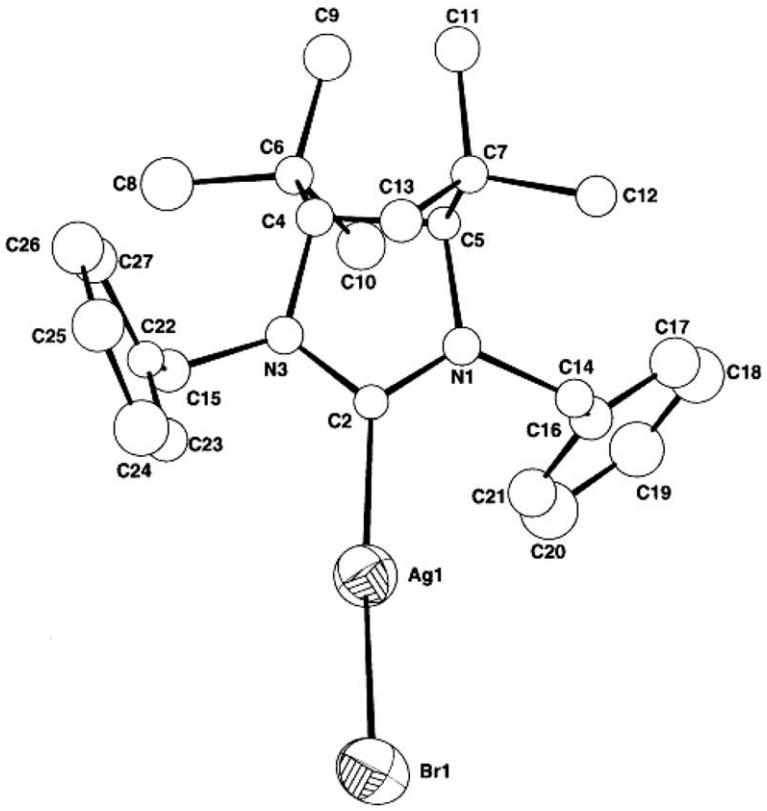


Fig. 3. ORTEP diagram of ligand **49**.

meric excess was measured (compared to 58% for the silver carbene). A difference in yield can be explained by the stability of the silver carbene with respect to the imidazolinium salt, but to explain the difference in enantiomeric excess between what should be exactly the same reactive species (the free carbene), perhaps we need to examine more closely the effects of the counteranions and/or the presence of other salts in the reaction mixture (Ag^+ for the silver carbene compared to Li^+ from the BuLi which is used to deprotonated the imidazolinium salt).

The analogous 1-naphthyl substituted silver carbene **51** gave a much lower enantiomeric excess for the addition to cyclohexenone under both sets of conditions, with a racemic product being observed in toluene with $Cu(OTf)_2$ at room temperature (Entry 7), and only 14% under the low temperature conditions (Entry 6). Presumably in this case, the *N*-substituents were too sterically demanding to induce high selectivity. The difference in sterical requirements of a simple phenyl and 1-naphthyl group may also account for the change in absolute configuration of the product which was observed in this case.

Employment of the *m*-OMe substituted analogue **52** led to a further increase in the enantiomeric excess. For the addition of Et_2Zn to cyclohexenone, the adduct could be obtained in a 95% yield with an enantiomeric excess of 69% (Entry 8), while for addition to cycloheptenone, the product was found to have an enantiomeric excess of 85% (Entry 15). At present, it is unclear whether the increased enantioselectivity is due to the chelating nature of the OMe groups, or whether it is due to their electron donating capacity. Conversely, when the *p*-Me analogue **54** was tested, there was a slight decrease in enantioselectivity with respect to the parent, Bn substituted, compound (**49**) under comparable conditions (compare Entries 4 and 10).

Perhaps more surprisingly, the ligand containing chiral substituents α to the nitrogen (**53**), also gave a relatively poor enantiomeric excess for the addition to cyclohexenone; only 29% using CuTC (Entry 9), lower even that for the simple *N*-Me analogue, **21**. It would seem that the chiral *N*-substituents are, in fact, detrimental to the level of enantioselective induction, especially when comparing this result with the *N*-benzyl ligand **49**. Interestingly for ligand **53**, as for the imidazolinium salt derived from the Simpkins' diamine (**1**), it was observed that the absolute stereochemistry of the adduct was of an *S* configuration which again, appears to be controlled from the stereocentres in the backbone of the carbene rather than the chiral groups adjacent to the nitrogen (which would be expected to give rise to a product with *R* stereochemistry).

Although the experimental conditions were not always comparable, it was observed that the enantioselectivities obtained using ligands with *t*-Bu groups in the backbone were greater than for their Ph analogues. For example, if we compare ligand **1** with ligand **50**, under comparable experimental conditions i.e., using CuTC in Et_2O at −78 °C for 16 h, the 1,4-adduct of diethyl zinc to cyclohexenone has an enantiomeric excess of 29% when ligand **1** is used (ligand **1** has 4 chiral centres including chiral substituents on the nitrogen atoms), but ligand **50** (containing only 2 stereogenic centres in the backbone) yields a product with 52% ee. This is thought to be due to the steric bulk of the *t*-Bu groups, which displace the *N*-substituents to a greater, and more favourable extent (in terms of increased levels of enantioselectivity), than the Ph groups.

3. Conclusions

Optimisation of conditions and ligand modification has led to good to excellent levels of enantiomeric excesses in the enantioselective copper catalysed 1,4-conjugate addition reaction using chiral diaminocarbenes as ligands. They allowed us to achieve some of the highest enantioselectivities (up to 93%) reported to date for this type of ligand. It should be pointed out that the synthesis of these chiral NHC is very easy and that they are less sensitive and much cheaper than phosphorus-based ligands. Further work will concentrate on studying the effects of different aryl substitution patterns with various electron-donating/withdrawing, chelating or sterically bulky nitrogen substituents in an attempt to develop an understanding of the mechanism and therefore be able to rationally design ligands which will lead to improved selectivities for a broad range of Michael acceptors.

4. Experimental

4.1. General remarks

^1H and proton-decoupled ^{13}C NMR spectra were recorded with Brucker DRX-400, Brucker AV-300 and Varian Gemini 200 spectrometers at ambient temperature. Chemical shifts are quoted in ppm relative to tetramethylsilane ($\delta = 0$) and were referenced to the residual protons in the solvent indicated. Chemical shifts are quoted relative to tetramethyl silane ($\delta = 0$). Mass spectra were recorded at the University of Geneva, using electrospray techniques with DCM as the carrier solvent, or at the Université Pierre et Marie Curie, Paris VI, using chemical ionisation (CI) techniques with NH_3 as the carrier gas. Microanalyses were carried out by the staff of the Université Pierre et Marie Curie Microanalytical department. Optical rotations were measured with a Perkin–Elmer 241 polarimeter, using a cell of 1 dm path length. The concentration *c* is expressed in g/100 mL. Melting points (m.p.) were determined using a Reichert hot plate melting point apparatus and are uncorrected. Solvents were purified by standard techniques [53], and reactions in non-aqueous media were carried out under dry nitrogen or dry argon unless otherwise stated. All other reagents were used as received.

4.2. Typical procedure for conjugate addition using imidazolinium salt in toluene at −20 °C

A dry Schlenk tube was charged with $Cu(OTf)_2$ (0.04 mmol) and imidazolinium salt (0.04 mmol) and toluene (3 mL) was added. The resulting solution was cooled to −78 °C, upon which *n*-BuLi (0.05 mmol as a 2M solution in hexanes) was added. After stirring for 30 min at low temperature, the reaction mixture was warmed up to room temperature and stirred for a further 15 min to ensure complete deprotonation. After this time, the solution was cooled back to −20 °C and diethyl zinc was added (1.5 mmol as a 1M solution in hexane). The mixture was stirred for 15 min before addition of the substrate (1 mmol, either neat, or as a solution in toluene). After stirring at −20 °C for 2 h, the reaction was quenched at low temperature by the addition of HCl (2 mL of a 1M aqueous solution). The resulting mixture was stirred until clear and the enantiomeric excesses could be measured directly using chiral GC (capillary column – Lipodex E, 0.2 λm, 50 m, 0.25 mm). The organic phases could be isolated, dried over $MgSO_4$ and the solvent concentrated in vacuo to yield the crude product, which could be purified by flash column chromatography to provide the pure product.

4.3. Typical procedure for conjugate addition using silver carbene in Et_2O at −78 °C

A dry Schlenk tube was charged with copper salt (0.04 mmol) and imidazolinium salt (0.04 mmol) and Et_2O (3 mL) was added. After stirring for 15 min at room temperature, the solution was cooled to −20 °C and diethyl zinc was added (1.5 mmol as a 1M solution in hexane). The mixture was stirred for 15 min the reaction mixture was cooled to −78 °C for addition of the substrate (1 mmol, either neat, or as a solution in toluene). After stirring at −78 °C for 16 h, the reaction was quenched at low temperature by the addition of HCl (2 mL of a 1M aqueous solution). The resulting mixture was stirred until clear and the enantiomeric excesses could be measured directly using chiral GC (capillary column – Lipodex E, 0.2

λm, 50 m, 0.25 mm). The organic phases could be isolated, dried over $MgSO_4$ and the solvent concentrated in vacuo to yield the crude product, which could be purified by flash column chromatography to provide the pure product.

4.4. Synthesis of imidazolines **1**–**6** from diamines

Into a flask equipped with a magnetic stirrer, was introduced the diamine (1 equiv.), and ammonium tetrafluoroborate (1 equiv.). A distillation cooling head was fitted with a collection head for the second stage of the reaction and the system purged with nitrogen. Triethylorthoformate (2 equiv.) was then added via syringe and the resulting mixture was heated at 120 °C for up to 2 h. After this time, the system was placed under high vacuum and the volatile by-products and excess starting materials were collected. The resulting products were purified as described below.

4.4.1. (4S,5S)-Diphenyl-1,3-bis-(1(R)-phenyl-ethyl)-4,5-dihydro-3H-imidazolinium tetraflouroborate (**1**)

The crude product was purified by recrystallisation with an ethanol-ethyl acetate mixture to give the desired compound in 95% yield as a white crystalline product.

^{1}H NMR (400 MHz, $CDCl_3$): 9.18 (s, 1H, NC*H*N), 7.40–7.11 (m, 16H, Ar*H*), 7.00–6.90 (m, 4H, Ar*H*), 4.45 (s, 2H, PhC*H*N), 4.39 (q, $J = 6.9$ Hz, 2H, PhC*H*MeN), 2.01 (d, $J = 6.9$ Hz, 6H, CH_3).

^{13}C NMR (100.6 MHz, $CDCl_3$): 153.0 (N*C*NH), 137.4, 135.4, 130.3, 129.8, 129.4, 129.0, 127.0, 126.9, 72.6, 57.9, 20.1.

$[\alpha]_D^{20} - 174$ (*c* 0.54, $CHCl_3$).

4.4.2. 1,3-Dimethyl-(4S,5S)-diphenyl-4,5-dihydro-3H-imidazol-1-ium tetrafluoroborate (**2**)

The pale yellow crude product was recrystallised with an ethyl acetate-chloroform mixture to give the desired product in 88% yield as a white crystalline product with melting point = 223–224 °C.

^{1}H NMR (200 MHz, $CDCl_3$): 8.16 (s, 1H, NC*H*N), 7.55–7.45 (m, 6H, Ar*H*), 7.40–7.30 (m, 4H, Ar*H*), 5.00 (s, 2H, NC*H*Ph), 2.97 (s, 6H, CH_3).

^{13}C NMR (50 MHz, $CDCl_3$): 159.6 (N*C*NH), 135.8, 131.0, 130.6, 128.8, 75.8, 33.8.

$[\alpha]_D^{20} + 253$ (*c* 0.59, $CHCl_3$).

4.4.3. 1,3-Dicyclohexyl-(4S,5S)-diphenyl-4,5-dihydro-3H-imidazol-1-ium tetrafluoroborate (**3**)

The pale yellow crude product was recrystallised with ethyl acetate to give the desired compound as a white crystalline solid in 96% yield.

^{1}H NMR (400 MHz, $CDCl_3$): 8.78 (s, 1H, NC*H*N), 7.55–7.45 (m, 6H, Ar*H*), 7.30–7.20 (m, 4H, Ar*H*), 4.89 (m, 8H, NC*H*Ph), 3.41 (tt, $J = 11.7$ Hz, $J = 3.5$ Hz, 2H, NC*H*), 2.10–2.00 (m, 2H, Cy*H*), 1.95–1.75 (m, 8H, Cy*H*), 1.65–1.55 (m, 2H, Cy*H*), 1.35–1.10 (m, 8H, Cy*H*).

^{13}C NMR (100.6 MHz, $CDCl_3$): 155.0 (N*C*NH), 136.7, 130.0, 126.3, 72.2, 57.7, 32.0, 30.9, 25.0, 24.9, 24.5.

$[\alpha]_D^{20} - 319$ (*c* 0.50, $CHCl_3$).

4.4.4. 1,3-Bis-(1(S)-phenyl-ethyl)-4,5-dihydro-3H-imidazol-1-ium tetraflouroborate (**4**)

The resulting oil was triturated with ethyl acetate and the resulting white solid collected by filtration. After recrystallisation with an ethanol-water mixture, the desired product was obtained in 80% yield as a white crystalline solid with melting point = 118 °C.

^{1}H NMR (200 MHz, $CDCl_3$): 8.13 (s, 1H, NC*H*N), 7.50–7.30 (m, 10H, Ar*H*), 4.80 (q, $J = 7.0$ Hz, 2H, NC*H*Me), 3.70–3.55 (m, 4H, NCH_2CH_2N), 1.67 (d, $J = 7.0$ Hz, 6H, CH_3).

^{13}C NMR (50 MHz, $CDCl_3$): 155.6 (N*C*NH), 139.2, 130.1, 129.8, 128.0, 59.0, 47.7, 19.9.

$[\alpha]_D^{20} + 23$ (*c* 0.51, $CHCl_3$).

4.4.5. 1,3-Bis-(1(R)-phenyl-ethyl)-3,4,5,6-tetrahydro-pyrimidin-1-ium tetraflouroborate (**5**)

The resulting orange oil was triturated with dichloromethane and the resulting solid collected by filtration. After recrystallisation with ethyl acetate, the desired product was obtained in 79% yield as a white crystalline solid.

^{1}H NMR (400 MHz, $CDCl_3$): 8.50 (s, 1H, NC*H*N), 7.43–7.34 (m, 10H, Ar*H*), 5.09 (q, $J = 6.8$ Hz, 2H, NC*H*Me), 3.16 (m, 4H, NCH_2), 1.87 (t, $J = 5.8$ Hz, 2H, CH_2), 1.75 (d, $J = 6.9$ Hz, 6H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$): 151.0 (N*C*NH), 136.9, 129.2, 128.9, 127.0, 63.4, 40.0, 18.9, 17.5.

$[\alpha]_D^{20} + 40$ (*c* 0.48, $CHCl_3$).

4.4.6. N,N′-Diisopinocamphenylimidazolinium tetrafluoroborate (**6**) [12]

The crude product was recrystallised from ethanol to give the desired product as a white crystalline solid in 84% yield. All spectroscopic data was in agreement with published data.

^{1}H NMR (400 MHz, $CDCl_3$): 8.40 (s, 1H, NC*H*N), 4.40 (m, 2H), 4.03 (m, 4H), 2.50 (m, 4H), 2.05 (m, 4H), 1.90 (m, 4H), 1.28 (s, 6H, $C(CH_3)_2$), 1.17 (d, $J = 7.1$ Hz, 6H, CH_3), 1.10 (s, 6H, $C(CH_3)_2$), 0.8 (d, $J = 9.6$ Hz, 2H).

4.4.7. (4R,5R)-Diphenyl-1,3-bis-(1(R)-phenyl-ethyl)-4,5-dihydro-3H-imidazolinium iodide (**13**)

^{1}H NMR (400 MHz, $CDCl_3$): 10.64 (s, 1H, NC*H*N), 7.44–7.28 (m, 16H, Ar*H*), 6.92–6.90 (m, 4H, Ar*H*), 5.55 (q, $J = 7.2$ Hz, 2H, $NCH(CH_3)$Ph), 4.47 (s, 2H, NC*H*Ph), 1.45 (d, $J = 7.2$ Hz, 6H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$): 157.6, 137.3, 136.9, 130.0, 129.7, 129.3, 129.2, 127.7, 126.8, 72.1, 58.5, 19.0.

$[\alpha]_D^{20}$ + 207.7 (*c* 0.32, $CDCl_3$).

4.4.8. (4S,5R)-Diphenyl-1,3-bis-(1(R)-phenyl-ethyl)-4,5-dihydro-3H-imidazolinium iodide (**14**)

^{1}H NMR (400 MHz, $CDCl_3$): 10.21 (s, 1H, NC*H*N), 7.55–6.79 (m, 20H, Ar*H*), 5.93 (q, $J = 6.8$ Hz, 1H, NC*H*(CH_3)Ph), 5.30 (d, $J = 11.6$ Hz, 1H, NC*H*Ph), 5.08 (d, $J = 12.0$ Hz, 1H, NC*H*Ph), 4.47 (q, $J = 6.8$ Hz, 1H, NC*H*(CH_3)Ph), 2.07 (d, $J = 6.8$ Hz, 3H, C*H*$_3$), 1.53 (d, $J = 7.2$ Hz, 3H, C*H*$_3$).

^{13}C NMR (100 MHz, $CDCl_3$): 129.5, 129.4, 129.2, 129.1, 128.7, 128.5, 128.0, 127.0, 77.2, 69.6, 58.5. Carbene carbon not observed.

$[\alpha]_D^{20}$ + 72.4 (*c* 0.21, $CDCl_3$).

4.5. General method for anion exchange (ligands **15** and **16**) [18]

In a round-bottomed flask equipped with a magnetic stirrer bar and rubber septum, were placed iodo-imidazolinium salt (1 equiv., 0.15 mmol) and MeCN (5 mL). To the resulting suspension was added ammonium tetrafluoroborate (1 equiv., 0.15 mmol). The resulting mixture was stirred at room temperature for 16 h before concentrating under reduced pressure. The crude product was triturated with chloroform, from which the yellow mother liquor was recovered. Further concentration under reduced pressure gave the desired compounds without need for further purification.

4.5.1. (4R,5R)-Diphenyl-1,3-bis-(1(R)-phenyl-ethyl)-4,5-dihydro-3H-imidazolinium tetraflouroborate (**15**)

Isolated as a pale yellow solid in 87% yield.

^{1}H NMR (400 MHz, $CDCl_3$): 10.37 (s, 1H, NC*H*N), 7.39–7.25 (m, 16H, Ar*H*), 6.91–6.89 (m, 4H, Ar*H*), 5.48 (q, $J = 7.0$ Hz, 2H, NC*H*(CH_3)Ph), 4.48 (s, 2H, NC*H*Ph), 1.43 (d, $J = 7.1$ Hz, 6H, C*H*$_3$).

^{13}C NMR (100 MHz, $CDCl_3$): 157.0, 137.2, 136.6, 129.9, 129.6, 129.3, 129.2, 127.7, 126.8, 58.4, 19.0.

$[\alpha]_D^{20}$ + 210.9 (*c* 1.11, $CDCl_3$).

4.5.2. (4S,5R)-Diphenyl-1,3-bis-(1(R)-phenyl-ethyl)-4,5-dihydro-3H-imidazolinium tetraflouroborate (**16**)

Isolated as a white solid in 100% yield.

^{1}H NMR (400 MHz, $CDCl_3$): 9.83 (s, 1H, NC*H*N), 8.00–6.80 (m, 20H, Ar*H*), 5.69 (q, $J = 7.0$ Hz, 1H, NC*H*(CH_3)Ph), 5.43 (d, $J = 12.1$ Hz, 1H, NC*H*Ph), 5.15 (d, $J = 12.1$ Hz, 1H, NC*H*Ph), 4.49 (q, $J = 7.0$ Hz, 1H, NC*H*(CH_3)Ph), 2.04 (d, $J = 7.0$ Hz, 3H, C*H*$_3$) 1.58 (d, $J = 7.1$ Hz, 3H, C*H*$_3$).

^{13}C NMR (100 MHz, $CDCl_3$): 156.9, 137.3, 130.2, 129.5, 129.4, 129.3, 129.2, 128.7, 128.5, 128.0, 126.9, 69.5, 67.9, 58.4, 58.2, 21.1, 19.2.

$[\alpha]_D^{20}$ + 49.4 (*c* 2.63, $CDCl_3$).

4.6. General method for preparation of unsaturated tetrafluoroborate-imidazolinium salts (ligands **17**–**20**) [19]

A 50 mL flask was charged with (*R*)- or (*S*)-chiral amine (10 mmol) in toluene. Under vigorous stirring and slight cooling, was added paraformaldehyde (10 mmol). After 30 min, a second equivalent of the amine was added at 0 °C. Under constant cooling, HBF_4 (10 mmol as a 32% aqueous solution) was added dropwise. After stirring for 15 min, the ice bath was removed and glyoxal was slowly added (10 mmol as a 40% aqueous solution). The resulting mixture was stirred for 30 min at room temperature, then for 12 h at 35–40 °C. After this time, the mixture was cooled to room temperature diluted with diethyl ether (10 mL) and a saturated solution of Na_2CO_3 (5 mL). The phases were then separated and the aqueous layer washed with dichloromethane (2×10 mL). The combined organic layers were washed with brine (25 mL), dried over $MgSO_4$ then concentrated under reduced pressure. The crude product in each case was isolated as a viscous brown/orange oil which could be purified by trituration using diethyl ether.

4.6.1. 1,3-Bis-(1(R)-phenyl-ethyl)-imidazolium tetraflouroborate (**17**)

The desired product was obtained as a hygroscopic yellow powder in 60% yield.

^{1}H NMR (400 MHz, $CDCl_3$): 9.26 (s, 1H, NC*H*N), 7.39–7.37 (m, 10H, Ar*H*), 7.13 (s, 2H, NC*H*=C), 5.75 (q, $J = 7.0$ Hz, 2H, NC*H*(CH_3)Ph), 1.96 (d, $J = 7.0$ Hz, 6H, C*H*$_3$).

^{13}C NMR (100 MHz, $CDCl_3$): 137.8, 133.7, 129.0, 126.9, 121.1, 60.1, 20.6.

$[\alpha]_D^{20}$ + 18.5 (*c* 0.96, $CHCl_3$).

MS (Electrospray/DCM) calculated for $C_{19}H_{21}N_2$ 277.1704, found 277.3.

4.6.2. 1,3-Bis-(1(S)-phenyl-propyl)-imidazolium tetraflouroborate (**18**)

The desired product was obtained as a hygroscopic pale yellow powder in 48% yield.

^{1}H NMR (400 MHz, $CDCl_3$): 9.54 (s, 1H, NC*H*N), 7.45–7.38 (m, 10H, Ar*H*), 7.17 (s, 2H, NC*H*=C), 5.51 (t, $J = 7.9$ Hz, 2H, NC*H*(CH_2CH_3)Ph), 2.35 (qd, $J = 13.6$ Hz, $J = 7.4$ Hz, 4H, C*H*$_2$CH$_3$), 0.94 (t, $J = 7.3$ Hz, 6H, C*H*$_3$).

^{13}C NMR (100 MHz, $CDCl_3$): 136.4, 134.9, 129.5, 127.5, 120.6, 66.3, 27.5, 10.6.

$[\alpha]_D^{20}$ − 34.2 (*c* 1.13, $CHCl_3$).

MS (Electrospray/DCM) calculated for $C_{21}H_{25}N_2$ 305.2018, found 305.3.

4.6.3. 1,3-Bis-(1(S)-1-naphthyl-ethyl)-imidazolium tetraflouroborate (**19**)

The desired product was obtained as a hygroscopic pale orange powder in 100% yield.

^{1}H NMR (400 MHz, $CDCl_3$): 9.42 (s, 1H, NC*H*N), 8.15–7.19 (m, 14H, Ar*H*), 6.89 (s, 2H, NC*H*=C), 6.56 (q, $J = 6.9$ Hz, 2H, NC*H*(CH_3)Naphth), 2.12 (d, $J = 6.9$ Hz, 6H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$): 139.4, 133.9, 132.6, 130.4, 129.2, 128.2, 127.8, 126.5, 126.1, 125.5, 124.5, 123.3.

$[\alpha]_D^{20} + 91.7$ (*c* 0.98, $CHCl_3$).

MS (Electrospray/DCM) calculated for $C_{27}H_{25}N_2$ 377.2018, found 377.3.

4.6.4. 1,3-Bis-(1(S)-2-naphthyl-ethyl)-imidazolium tetraflouroborate (**20**)

The desired product was obtained as a hygroscopic yellow powder in 53% yield.

^{1}H NMR (400 MHz, $CDCl_3$): 9.47 (s, 1H, NC*H*N), 7.92–42 (m, 14H, Ar*H*), 7.10 (s, 2H, NC*H*=C), 5.94 (q, $J = 6.9$ Hz, 2H, NC*H*(CH_3)Naphth), 2.07 (d, $J = 7.0$ Hz, 6H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$): 135.0, 134.7, 133.4, 133.1, 129.7, 128.3, 127.7, 127.2, 127.0, 126.7, 123.9, 120.6, 60.5, 20.7.

$[\alpha]_D^{20} + 6.9$ (*c* 1.02, $CHCl_3$).

MS (Electrospray/DCM) calculated for $C_{27}H_{25}N_2$ 377.2018, found 377.3.

4.6.5. (4R,5R)-1,3-Dimethyl-4,5-di-tert-butyl-imidazolin-2-ylidene silver(I) iodide (**21**)

To a solution of imidazolinium salt **24** (1 mmol) in DCM (15 mL) was added Ag_2O (0.5 mmol). The mixture was stirred at 20 °C until complete consumption of the precipitate, filtered through celite and concentrated under reduced pressure to yield the desired compound as a crystalline solid in quantitative yield. The product could be recrystallised from a mixture of pentane, DCM and Et_2O to obtain a crystal suitable for X-ray diffraction analysis.

^{1}H NMR (400 MHz, DMSO-D_6): 3.34 (s, 2H, C*Ht*-Bu), 3.21 (s, 6H, NCH_3), 0.87 (s, 18H, C(CH_3)$_3$).

^{13}C NMR (100 MHz, $CDCl_3$): 213.7, 80.5, 45.8, 41.7, 32.9.

$[\alpha]_D^{20} - 93.0$ (*c* 1.0, $CHCl_3$). *Anal.* Calc. for $C_{13}H_2IAgN_2$ (MW = 445.1): C, 35.08; H, 5.89; N, 6.29. Found C, 36.89; H, 6.60; N, 6.37%.

4.6.6. (R,R)-4,5-di-tert-butylimidazolidine (**23**)

To a solution of imidazolidine **22** [28] (1 mmol) in EtOH (20 mL), were added $Pd(OH)_2$/C (0.1 mmol) and ammonium formate (10 mmol). The resulting mixture was refluxed for 6 h, filtered and then concentrated under reduced pressure. To the residue were added Et_2O (15 mL) and K_2CO_3 (0.5 g). The resulting suspension was stirred for 1 h, filtered and then concentrated under reduced pressure to obtain the desired product as a white solid in 95% yield.

^{1}H NMR (400 MHz, $CDCl_3$): 7.05 (s, 1H, NC*H*N), 4.80 (s, 1H, N*H*), 3.27 (s, 2H, C*Ht*-Bu), 0.86 (s, 18H, C(CH_3)$_3$).

^{13}C NMR (100 MHz, $CDCl_3$): 150.7, 69.1, 33.2, 24.5.

4.6.7. (4R,5R)-1,3-Dimethyl-4,5-di-tert-butyl-imidazolinium iodide (**24**)

To a solution of imidazolidine **23** (1 mmol) in DCM (5 mL) were added K_2CO_3 (0.5 g) and MeI (2.1 mol). The resulting solution was stirred for 12 h at 20 °C then filtered through celite and concentrated under reduced pressure. The residue was dissolved in Et_2O (15 mL) and the precipitate, which formed on standing, was filtered, washed several times with pentane and dried under vacuum to afford the desired product as a white solid in 95% yield.

^{1}H NMR (400 MHz, $CDCl_3$): 10.07 (s, 1H, NC*H*N), 3.45 (s, 6H, NCH_3), 3.38 (s, 2H, C*Ht*-Bu), 1.02 (s, 18H, C(CH_3)$_3$).

^{13}C NMR (100 MHz, $CDCl_3$): 160.6, 75.5, 38.7, 37.2, 27.5.

M.p. 270–271 °C. $[\alpha]_D^{20} - 54.4$ (*c* 2.02, $CHCl_3$). *Anal.* Calc. for $C_{13}H_{27}IN_2$ (MW = 338.27): C, 46.16; H, 8.05; N, 8.28. Found C, 45.47; H, 8.36; N, 7.98%.

4.6.8. 1,3-Bis-(1(R)-phenyl-ethyl)-imidazolium chloride (**26**)

To a stirred solution of amine (6.05 g, 50 mmol) in toluene (50 mL), was added paraformaldehyde (1.5 g, 50 mmol). After stirring for 30 min at room temperature, the mixture was cooled to 0 °C and a further equivalent of amine (6.05 g, 50 mmol) was added. After stirring for 15 min, HCl (15 mL of a 3.3 M aqueous solution, 50 mmol) was added. The mixture was warmed up to room temperature before adding glyoxal (7.0 g of a 40% aqueous solution, 50 mmol). The heterogeneous mixture was stirred at 40 °C for 8 h, after which it was cooled to room temperature, diluted with Et_2O (50 mL) and quenched by addition of Na_2CO_3 (25 mL of a saturated solution). The organic phase was separated and the remaining aqueous layer was washed with DCM (6×50 mL). The combined organic layers were concentrated under reduced pressure to afford the desired product in 17% yield.

^{1}H NMR (400 MHz, $CDCl_3$): 11.51 (s, 1H, NC*H*N), 7.50–7.40 (m, 4H, Ar*H*), 7.40–7.30 (m, 6H, Ar*H*), 7.09 (d, $J = 1.5$ Hz, 2H, NC*H*=C), 6.05 (q, $J = 7.1$ Hz, 2H, NC*H*(CH_3)Ph), 2.03 (d, $J = 7.1$ Hz, 6H, CH_3).

4.7. General method for formation of diimines (compounds **27** and **28**)

To a stirred solution of amine (15 mmol) in dichloromethane (30 mL), was added $MgSO_4$ (30 mmol) and formic acid (50 mL). After stirring for 15 min at room temperature, glyoxal was added (7.5 mmol of a 40%

aqueous solution) and the resulting mixture stirred at room temperature for 16 h before filtering through celite and concentrating under reduced pressure.

*4.7.1. N,N-bis[(S)-1-phenyl-propyl]ethanediimine (**27**)*

The product was isolated in quantitative yield as a yellow oil and required no further purification.

^{1}H NMR (400 MHz, $CDCl_3$): 8.01 (s, 2H, *H*C═N), 7.31–7.20 (m, 10H, Ar*H*), 4.10 (t, $J = 9.3$ Hz, 2H, NC*H*(CH_2CH_3)Ph), 1.95 (m, 4H, CH_2CH$_3$), 0.85 (t, $J = 6.1$ Hz, 6H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$): 161.0, 142.9, 128.5, 127.2, 127.1, 53.4, 30.9, 11.0.

$[\alpha]_D^{20} - 5.8$ (*c* 1.17, $CHCl_3$).

*4.7.2. N,N-bis[(S)-1-naphthyl-ethyl]ethanediimine (**28**)*

The crude product was a viscous orange, which could be purified by washing with Et_2O. The desired product was isolated as a pale orange powder in 96% yield.

^{1}H NMR (400 MHz, $CDCl_3$): 8.17 (s, 2H, *H*C═N), 8.13 (d, $J = 9.0$ Hz, 2H, Ar*H*), 7.88 (d, $J = 8.5$ Hz, 2H, Ar*H*), 7.78 (d, $J = 8.2$ Hz, 2H, Ar*H*), 7.68 (d, $J = 7.1$ Hz, 2H, Ar*H*), 7.56–7.46 (m, 6H, Ar*H*), 5.41 (q, $J = 6.6$ Hz, 2H, NC*H*(CH_3)Ar), 1.75 (d, $J = 6.7$ Hz, 6H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$): 161.2, 139.4, 134.0, 130.7, 129.0, 127.8, 126.1, 125.6, 125.5, 124.0, 123.3, 64.8, 23.7.

$[\alpha]_D^{20} = -54.4$ (*c* 2.02, $CHCl_3$). M/S (Electrospray/DCM) calculated for $C_{26}H_{24}N_2$ 364.1939, found 365.2 (MH^+).

*4.8. General method for preparation of chloro-imidazolinium salts from diimines (compounds **29** and **30**)*

To a solution of the starting diimine (5 mmol) in toluene (25 mL) were added, paraformldehyde (5 mmol) and HCl (5 mmol of a 32% aqueous solution). The resulting mixture was heated to 45 °C for 16 h, after which it was cooled to room temperature, diluted with Et_2O (10 mL) and quenched by addition of Na_2CO_3 (5 mL of a saturated solution). The organic phase was separated and the remaining aqueous layer was washed with DCM (3×10 mL). The combined organic layers were dried over $MgSO_4$ and concentrated under reduced pressure to afford the crude product.

*4.8.1. 1,3-Bis-(1(S)-phenyl-propyl)-imidazolium chloride (**29**)*

The crude product was purified by washing with Et_2O. The precipitate was collected by filtration and dried to afford the desired product as a pale yellow solid in 45% yield.

^{1}H NMR (400 MHz, $CDCl_3$): 11.79 (s, 1H, NC*H*N), 7.53 (d, $J = 1.5$ Hz, 2H, Ar*H*), 7.51–7.35 (m, 6H, Ar*H*), 7.11 (d, $J = 7.9$ Hz, 2H, NC*H*═C), 5.76 (t, $J = 7.9$ Hz, 2H, NC*H*(CH_2CH_3)Ph), 2.49–2.39 (m, 4H, CH_2CH$_3$), 0.96 (t, $J = 7.2$ Hz, 6H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$): 159.0, 137.8, 136.6, 129.5, 127.6, 119.7, 65.9, 27.6, 10.8.

*4.8.2. 1,3-Bis-(1(S)-1-naphthyl-ethyl)-imidazolium chloride (**30**)*

The crude product was washed with Et_2O to purify. The precipitate was collected by filtration and dried to afford the desired product as a pale brown solid in 72% yield.

^{1}H NMR (400 MHz, $CDCl_3$): 11.67 (s, 1H, NC*H*N), 8.16 (d, $J = 8.4$ Hz, 2H, Ar*H*), 7.87 (d, $J = 7.9$ Hz, 4H, Ar*H*), 7.61–7.45 (m, 8H, Ar*H*), 6.86 (q, $J = 6.6$ Hz, 2H, NC*H*(CH_3)Ar), 6.79 (s, 2H, NC*H*═C), 2.19 (d, $J = 6.6$ Hz, 6H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$): 130.4, 129.2, 127.9, 126.6, 125.2, 124.4, 122.4, 120.1, 56.3, 21.6. $[\alpha]_D^{20} + 32.2$ (*c* 1.08, $CHCl_3$).

*4.9. General procedure for synthesis of silver carbene from chloro-imidazolinium salt (compounds **31**–**33**)*

To a solution of chloro-imidazolinium salt (1 mmol) in DCM (15 mL), was added Ag_2O (0.5 mmol). The mixture was stirred at room temperature for 16 h then filtered through celite and concentrated under reduced pressure to yield the desired compound as a crystalline solid.

*4.9.1. 1,3-Bis-(1(S)-1-phenyl-ethyl)-imidazolin-2-ylidene silver(I) chloride (**31**)*

The desired product was isolated in quantitative yield and required no further purification.

^{1}H NMR (400 MHz, $CDCl_3$): 7.40–7.30 (m, 6H, Ar*H*), 7.30–7.20 (m, 4H, Ar*H*), 6.95 (s, 2H, NC*H*═C), 5.76 (q, $J = 7.1$ Hz, 2H, NC*H*(CH_3)Ph), 1.84 (d, $J = 7.1$ Hz, 6H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$): 139.7, 129.1, 128.6, 126.6, 61.0, 21.4.

$[\alpha]_D^{20} + 32.7$ (*c* 1.09, $CHCl_3$).

*4.9.2. 1,3-Bis-(1(S)-phenyl-propyl)-imidazolin-2-ylidene silver(I) chloride (**32**)*

The desired product was isolated in quantitative yield and required no further purification.

^{1}H NMR (400 MHz, $CDCl_3$): 7.40–7.33 (m, 10H, Ar*H*), 7.01 (s, 2H, NC*H*═C), 5.45 (m, 2H, NC*H*(CH_2CH_3)Ph), 2.31–2.14 (m, 4H, CH_2CH$_3$), 0.89 (t, $J = 7.3$ Hz, 6H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$): 139.1, 129.1, 128.5, 126.8, 118.9, 67.4, 27.8, 11.1.

$[\alpha]_D^{20} + 48.1$ (*c* 0.75, $CHCl_3$).

*4.9.3. 1,3-Bis-(1(S)-1-naphthyl-ethyl)-imidazolin-2-ylidene silver(I) chloride (**33**)*

The desired product was isolated in 82% yield and required no further purification.

^{1}H NMR (400 MHz, $CDCl_3$): 8.15–7.42 (m, 14H, Ar*H*), 6.55 (s, 2H, NC*H*=C), 6.42 (q, $J = 6.2$ Hz, 2H, NC*H*(CH_3)Ar), 2.0 (d, $J = 6.9$ Hz, 6H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$): 134.0, 131.0, 130.0, 129.1, 127.3, 126.2, 125.1, 124.4, 122.8, 119.0, 57.4, 22.4. $[\alpha]_D^{20} + 49.8$ (*c* 0.72, $CHCl_3$).

4.9.4. N,N′-bis[(1R,2R)-2-benzyloxy-cyclohexyl]ethanediimine (**36**)

The diimine was prepared according to the general procedure described above for compounds 27–28, and was isolated in quantitative yield as a brown crystalline product, which required no further purification.

^{1}H NMR (400 MHz, $CDCl_3$): 8.06 (s, 2H, *H*C=N), 7.34–7.16 (m, 10H, Ar*H*), 4.47 (dd, $J = 22.9$ Hz, 10.9 Hz, 4H, CH_2 Ph), 3.49 (dt, $J = 3.5$, 8.9 Hz, 2H, C*H*N), 3.21 (dt, $J = 4.6$ Hz, 6.3 Hz, 2H, C*H*O), 2.16–2.13 (m, 2H, Cy*H*), 1.81–1.65 (m, 8H, Cy*H*), 1.38–1.32 (m, 6H, Cy*H*).

^{13}C NMR (100 MHz, $CDCl_3$): 161.9, 138.9, 128.2, 127.5, 127.3, 80.4, 74.9, 71.4, 32.8, 30.6, 24.4, 23.9. $[\alpha]_D^{20} = +8.4$ (*c* 0.89, $CHCl_3$). M/S (Electrospray/DCM) calculated for $C_{28}H_{36}N_2O_2$ 432.2777, found 433.3 (MH^+) and 218.5 (M − 2Bn).

4.9.5. N,N′-bis (1R,2R)-2-benzyloxy-cyclohexyl imidazolium chloride (**37**)

The chloro-imidazolinium salt was prepared according to the general procedure described above for compounds 29–30, and was isolated in 99% yield as a very hygroscopic brown crystalline product, which was dried twice over $MgSO_4$ but required no further purification.

^{1}H NMR (400 MHz, $CDCl_3$): 10.56 (s, 1H, NC*H*N), 7.97–6.98 (m, 10H, Ar*H*), 6.96 (d, $J = 1.3$ Hz, 2H, NC*H*=C), 4.40 (d, $J = 16$ Hz, 4H, CH_2 Ph), 4.13 (d, $J = 3.5$, 8.9 Hz, 2H, C*H*N), 3.21 (m, 2H, C*H*O), 1.80–1.20 (m, 16H, Cy*H*).

^{13}C NMR (100 MHz, $CDCl_3$): 153.0, 137.9, 128.9, 128.1, 127.5, 125.2, 79.4, 71.3, 64.8, 31.7, 30.8, 24.3, 23.9. $[\alpha]_D^{20} + 351.9$ (*c* 0.67, $CHCl_3$).

4.9.6. N,N′-bis (1R,2R)-2-benzyloxy-cyclohexyl-imidazolin-2-ylidene silver(I) chloride (**38**)

The silver carbene was prepared according to the general procedure described above and was isolated in 44% yield a brown crystalline product after purification by trituration with Et_2O.

^{1}H NMR (400 MHz, $CDCl_3$): 7.26–6.98 (m, 10H, Ar*H*), 6.85 (s, 2H, NC*H*=C), 4.42 (d, $J = 12$ Hz, 2H, CH_2 Ph), 4.26–4.19 (m, 2H, C*H*O), 4.17 (d, $J = 12$ Hz, 2H, CH_2 Ph), 3.67–3.62 (m, 2H, C*H*N), 2.31–1.33 (m, 16H, Cy*H*).

^{13}C NMR (100 MHz, $CDCl_3$): 137.99, 128.2, 127.5, 127.4, 118.8, 79.5, 70.3, 66.3, 33.8, 30.9, 24.9, 23.9. $[\alpha]_D^{20} = -0.89$ (*c* 1.01, $CHCl_3$). M/S (Electrospray/DCM) calculated for $C_{29}H_{36}N_2O_2AgCl$ 587.1165, found 445 (M − AgCl) and 997 ($C_{58}H_{72}N_4O_4AgCl_2$: dimeric species).

4.9.7. N,N′-bis[isopinocampheyl]ethanediimine (**40**) (method B)

To a solution of isopinene derived amine **39** (2 mmol) in DCM (6 mL), was added glyoxal (1 mmol as a 40% aqueous solution). The resulting mixture was stirred for 6 h at room temperature before diluting with Et_2O (10 mL) and washing with H_2O (15 mL). The organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was isolated as an orange solid in quantitative yield and was spectroscopically identical to the literature product.

^{1}H NMR (400 MHz, $CDCl_3$): 7.81 (s, 2H, *H*C=N), 3.40 (m, 2H, C*H*N), 2.34 (q, $J = 5.7$ Hz, 2H, C*H*), 2.22 (t, $J = 1.6$ Hz, 2H, C*H*), 2.02 (t, $J = 7.3$ Hz, 2H, C*H*), 1.93 (q, $J = 2.5$ Hz, 2H, C*H*), 1.84 (q, $J = 4.7$ Hz, 4H, C*H*), 1.19 (s, 6H, CH_3), 1.14 (d, $J = 9.7$ Hz, 2H, C*H*), 0.99 (s, 6H, CH_3), 0.95 (d, $J = 7.4$ Hz, 6H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$): 159.3, 69.9, 47.4, 43.3, 41.5, 38.8, 35.6, 33.8, 27.9, 23.5, 19.8.

4.9.8. N,N′-diisopinocampheylimidazolium chloride (**41**)

The chloro-imidazolinium salt was prepared according to the general procedure described above and was isolated in 20% yield as a pale yellow crystalline solid after trituration with Et_2O.

^{1}H NMR (400 MHz, $CDCl_3$): 11.13 (s, 1H, NC*H*N), 7.55 (s, 2H, NC*H*=C), 5.19 (dt, $J = 7.4$ Hz, $J = 10$ Hz, 2H, C*H*N), 2.55 (t, $J = 4.2$ Hz, 2H, C*H*), 2.25 (m, 2H, C*H*), 2.08 (t, $J = 2.5$ Hz, C*H*), 1.96–1.92 (m, 6H, C*H*), 1.26–1.10 (m, 18H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$): 138.1, 120.5, 59.8, 47.3, 45.2, 41.3, 38.9, 36.5, 35.2, 27.9, 23.5, 20.2.

4.9.9. N,N′-diisopinocampheyl-imidazolin-2-ylidene silver(I) chloride (**42**)

The silver carbene was prepared according to the general procedure described above and was isolated in 83% yield, after drying over $MgSO_4$, as a pale yellow crystalline solid.

^{1}H NMR (400 MHz, $CDCl_3$): 7.21 (s, 2H, NC*H*=C), 4.85–4.78 (m, 2H, C*H*N), 2.67–2.58 (m, 4H, C*H*), 2.20–1.93 (m, 10H, C*H*), 1.29–1.11 (m, 18H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): 119.2, 62.4, 47.5, 45.5, 41.5, 39.1, 37.1, 35.2, 27.9, 23.7, 20.4.

$[\alpha]_D^{20} + 431.9$ (*c* 0.44, $CHCl_3$).

4.9.10. (2-Bromophenyl)-(R)-α-methylbenzylamine (**44**)

In a resealable Schlenk tube, which had been dried under vacuum then backfilled with nitrogen, were

placed $Pd_2dba_3.CHCl_3$ (26 mg, 0.025 mmol), racemic BINAP (31 mg, 0.05 mmol) and NaO*t*-Bu (0.31 g, 3.2 mmol) and toluene (3.5 mL). This was followed by (*R*)-α-methylbenzyl-amine (0.38 mL, 2.95 mmol) and dibromobenzene (0.3 mL, 2.5 mmol). The resulting mixture was degassed, backfilled with nitrogen, sealed, and then heated to 95 °C for 45 h. After this time, the starting material had been completely consumed (by tlc) and the mixture was allowed to cool to room temperature then diluted with Et_2O, filtered through celite and concentrated under reduced pressure. The crude product was obtained as a dark brown oil which could be purified by flash column chromatography (SiO_2, cyclohexane: EtOAc, 98:2). The desired product was isolated as an orange/yellow oil in 55% yield and was spectroscopically identical to the literature compound.

^{1}H NMR (400 MHz, $CDCl_3$): 7.47 (d, $J = 1.4$ Hz, 1H, Ar*H*), 7.46–7.28 (m, 5H, Ar*H*), 7.03 (t, $J = 7.5$ Hz, 1H, Ar*H*), 6.55 (dd, $J = 8.8$ Hz, $J = 1.5$ Hz, 1H, Ar*H*), 6.44 (dd, $J = 8.2$ Hz, $J = 1.2$ Hz, 1H, Ar*H*), 4.77 (br s, 1H, N*H*), 4.56 (q, $J = 6.3$ Hz, 1H, NC*H*(CH_3)Ph), 1.63 (d, $J = 6.7$ Hz, 3H, CH_3).

4.9.11. N,N′-Bis (R)-α-methylbenzyl-1,2-diaminobenzene (45)

In a resealable Schlenk tube, which had been dried under vacuum then backfilled with nitrogen, were placed $Pd_2dba_3.CHCl_3$ (49 mg, 0.047 mmol), racemic BINAP (58 mg, 0.093 mmol) and toluene (4 mL). The mixture was degassed and backfilled with nitrogen before heating to 130 °C for 20 min. After cooling to room temperature, NaO*t*-Bu (0.24 g, 2.5 mmol) was added, followed by (*R*)-α-methylbenzyl-amine (0.38 mL, 2.95 mmol), amine **44** (0.32 g, 1.2 mmol) and toluene (5 mL). The resulting mixture was degassed, backfilled with nitrogen, sealed, and then heated to 130 °C for 2 h. After cooling to room temperature, the mixture was diluted with Et_2O, filtered through celite and concentrated under reduced pressure. The crude product was obtained as a brown oil which could be purified by flash column chromatography (SiO_2, cyclohexane:DCM, 80:20). The desired product was isolated as a dark orange oil in 43% yield and was spectroscopically identical to the literature compound.

^{1}H NMR (400 MHz, $CDCl_3$): 7.47–7.27 (m, 10H, Ar*H*), 6.65–6.50 (m, 4H, Ar*H*), 4.54 (q, $J = 6.6$ Hz, 2H, NC*H*(CH_3)Ph), 3.80 (br s, 2H, N*H*), 1.64 (d, $J = 6.7$ Hz, 6H, CH_3).

Compound **46** was also isolated from this reaction as a pale yellow solid in 12% yield.

^{1}H NMR (400 MHz, $CDCl_3$): 7.41–7.15 (m, 5H, Ar*H*), 7.12 (t, $J = 1.04$ Hz, 2H, Ar*H*), 6.69 (t $J = 7.3$ Hz, 1H, Ar*H*), 6.55 (d, $J = 7.7$ Hz, 2H, Ar*H*), 4.52 (q, $J = 6.7$ Hz, 1H, NC*H*(CH_3)Ph), 4.20 (br s, 1H, N*H*), 1.55 (d, $J = 6.7$ Hz, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$): 147.1, 145.1, 129.1, 128.7, 126.9, 125.9, 117.4, 113.5, 53.6, 25.0.

4.9.12. N,N′-Bis (R)-α-methylbenzyl-benzimidazolium chloride (47)

To a solution of diamine **45** (0.12 g, 0.36 mmol) in $(EtO)_3CH$ (7 mL) under nitrogen, was added HCl (35 mL of a 32% aqueous solution, 0.36 mmol). After stirring for 1 h at room temperature, the mixture was heated to 80 °C. When condensation was observed on the neck of the flask, the septum was removed and heating was continued for 2 h with the flask contents open to the air. After this time, the mixture was cooled to room temperature and diluted with Et_2O (15 mL). After allowing the solid to settle out, the supernatant was removed by decantation. The remaining white solid was washed 5 times with diethyl ether and the 3 times with hot toluene. The residual solvents were removed under high vacuum and then the product was dried under vacuum at 40 °C over P_2O_5 to provide the title compound as a white solid in 89% yield, which was spectroscopically identical to the literature compound.

^{1}H NMR (400 MHz, $CDCl_3$): 12.51 (s, 1H, NC*H*N), 7.55–7.33 (m, 14H, Ar*H*), 6.29 (q, $J = 6.8$ Hz, 2H, NC*H*(CH_3)Ph), 2.35 (d, $J = 6.7$ Hz, 6H, CH_3).

4.9.13. N,N′-Bis-(R)-α-methylbenzyl-benzimidazolin-2-ylidene silver(I) chloride (48)

was prepared according to the general procedure described above and was isolated in 95% yield as a fluffy off-white solid which was purified by triturating with Et_2O.

^{1}H NMR (400 MHz, $CDCl_3$): 7.41–7.13 (m, 14H, Ar*H*), 6.20 (q, $J = 7.1$ Hz, 2H, NC*H*(CH_3)Ph), 2.10 (d, $J = 7.2$ Hz, 6H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$): 138.3, 129.4, 129.1, 128.5, 126.7, 126.6, 123.9, 113.2, 59.9, 19.5.

$[\alpha]_D^{20} + 48.6$ (*c* 2.71, $CHCl_3$).

4.9.14. (4R,5R)-1,3-Dibenzyl-4,5-di-tert-butylimidazolinium tetrafluoroborate (50)

Imidazolinium bromide **58** (482 mg, 1.09 mmol) and ammonium tetrafluoroborate (114 mg, 1.09 mmol) in a mixture of acetone and Et_2O (1/1, 20 mL) were stirred overnight at ambient temperature. After filtration and evaporation of the solvents, the pure imidazolinium tetrafluoroborate **50** (490 mg, 100% yield) was obtained as an off-white solid with melting point = 125 °C.

^{1}H NMR (400 MHz, $CDCl_3$): 8.85 (s, 1H, NC*H*N), 7.44–7.34 (m, 10H, Ar*H*), 5.09 (d, $J = 14.4$ Hz, 2H, NC(*H*′)HPh), 4.52 (d, $J = 14.4$ Hz, 2H, NC(H′)*H*Ph), 3.47 (s, 2H, NC*H*t-Bu), 0.73 (s, 18H, C(CH_3)$_3$).

^{13}C NMR (100 MHz, $CDCl_3$): 158.9, 132.0, 130.2, 129.7, 70.6, 54.2, 36.1, 26.7.

$[\alpha]_D^{20} - 139.3$ (*c* 0.38, CH_2Cl_2).

4.9.15. (4R,5R)-1,3-Di-[4-methyl-benzyl]-4,5-di-tert-butylimidazolin-2-ylidene silver(I) chloride (**54**)

Obtained from imidazolinium bromide **61** in quantitative yield after 16 h, using the general procedure described above. Product obtained as off-white solid that decomposed at 75 °C.

^{1}H NMR (400 MHz, $CDCl_3$): 7.37 (d, 4H, $J = 7.9$ Hz, Ar*H*), 6.96 (d, 2H, $J = 7.9$ Hz, Ar*H*), 5.15 (d, 2H, $J = 14.3$ Hz, NC(H′)*H*Ph), 4.06 (d, 2H, $J = 14.3$ Hz, NC(*H*′)HPh), 2.93 (s, 2H, NC*Ht*-Bu), 2.08 (s, 6H, ArCH_3), 0.41 (s, 18H, C(CH_3)$_3$).

^{13}C NMR (100 MHz, $CDCl_3$): 137.8, 134.4, 130.1, 129.6, 70.7, 55.6, 35.2, 27.1, 21.1. Carbene carbon was not observed.

$[\alpha]_D^{20} - 89$ (*c* 0.22, CH_2Cl_2).

4.10. General procedure for alkyl substituted imidazolines

To a solution of imidazoline **24** (1 mmol) in DCM (5 mL) were added K_2CO_3 (0.5 g) and the appropriate alkyl halide (2.1 mmol). The solution was stirred for 12 h at 20 °C, filtered through celite and concentrated. The residue was taken up in Et_2O or pentane (15 mL) and the white precipitate that formed was filtered, washed several times with pentane and dried under vacuum to afford the expected salts (85–95%) as white solids.

4.10.1. (4R,5R)-1,3-Dibenzyl-4,5-di-tert-butylimidazolinium bromide (**58**)

^{1}H NMR (200 MHz, $CDCl_3$): 11.12 (s, 1H, NC*H*N), 7.56–7.54 (m, 4H, Ar*H*), 7.43–7.38 (m, 6H, Ar*H*), 5.53 (d, $J = 7.1$ Hz, 2H, NC(H)*H*′Ph), 4.47 (d, $J = 7.1$ Hz, 2H, NC(H′)*H*Ph), 3.38 (s, 2H, NC*Ht*-Bu), 0.68 (s, 18H, C(CH_3)$_3$).

^{13}C NMR (50 MHz, DMSO-D_6): 159.6, 132.9, 130.0, 129.4, 69.7, 53.5, 35.8, 26.5.

M.p. 249–250 °C. $[\alpha]_D^{20} - 114.3$ (*c* 1.6, $CHCl_3$). *Anal.* Calc. for $C_{25}H_{35}BrN_2$ (MW = 443.46): C, 67.71; H, 7.96; N, 6.32. Found: C, 66.55; H, 7.79; N, 6.15%.

4.10.2. (4R,5R)-1,3-Di-(1-naphthylmethyl)-4,5-di-tert-butylimidazolinium chloride (**59**)

To a solution of imidazoline **24** (1 mmol) in DCM (10 mL) were added K_2CO_3 (0.5 g) and 1-chloromethylnaphthalene (2.5 mmol). The solution was refluxed for 12 h, filtered through celite and concentrated. The residue was taken up in Et_2O. The white precipitate that formed was filtered, washed several times with ether and dried under vacuum to afford 357 mg of the expected salt (71%) as a pale beige solid.

^{1}H NMR (200 MHz, $CDCl_3$): 11.76 (s, 1H, NC*H*N), 8.65 (d, $J = 8.4$ Hz, 2H, Ar*H*), 7.89–7.55 (m, 12H, Ar*H*), 6.08 (d, $J = 14.7$ Hz, 2H, NC(H′)*H*Ph), 4.48 (d, $J = 14.7$ Hz, 2H, NC(H)*H*′Ph), 3.32 (s, 2H, NC*Ht*-Bu), 0.40 (s, 18H, C(CH_3)$_3$).

4.10.3. (4R,5R)-1,3-Di-(3-methoxybenzyl)-4,5-di-tert-butylimidazolinium chloride (**60**)

To a solution of imidazoline **24** (0.88 mmol) in DCM (5 mL) were added K_2CO_3 (0.5 g) and 3-methoxybenzyl chloride (2.2 mmol, 320 mL). The solution was refluxed for 12 h, filtered through celite and concentrated under reduced pressure. The residue was taken up in Et_2O then the white precipitate that formed was filtered, washed several times with ether and dried under vacuum to afford 381 mg of the expected salt (94%) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): 11.42 (s, 1H, NC*H*N), 7.34–6.88 (m, 8H, Ar*H*), 5.47 (d, *J* 14.0 Hz, 2H, NC(H′)*H*Ph), 4.43 (d, $J = 14$ Hz, 2H, NC(H)*H*′Ph), 3.89 (s, 6H, OCH_3), 3.40 (s, 2H, NC*Ht*-Bu), 0.72 (s, 18H, C(CH_3)$_3$).

4.10.4. (4R,5R)-1,3-[(S)-1-phenylethyl]-4,5-di-tert-butylimidazolinium iodide (**61**)

To a mixture of aminal **23** (1 mmol) and $NaHCO_3$ (1 mmol) in DCM (5 mL) was added dropwise a solution of iodine (1 mmol) in DCM (5 mL). The mixture was stirred for 24 h at 20 °C. Et_2O (50 mL) and sodium bisulfite (aqueous solution) were added. The suspension was stirred until decolorisation occurred and a white precipitate appeared in the organic phase. The solution was filtered and the precipitate was washed with Et_2O then dried to afford 290 mg (58%) of the expected compound as a white solid.

^{1}H NMR ($CDCl_3$): 10.21 (s, 1H, NC*H*N), 7.77–7.25 (m, 10H, Ar*H*), 4.64 (q, $J = 7.4$ Hz, 2H, NC*H*(CH$_3$)Ph), 3.35 (s, 2H, NC*Ht*-Bu), 2.28 (d, $J = 7.4$ Hz, 6H, NCH(CH_3)Ph), 0.60 (s, 18H, C(CH_3)$_3$).

4.11. Typical procedure for the synthesis of **49**–**54**

To a solution of imidazolinium salt **58**–**61** (1 mmol) in DCM (15 mL) was added Ag_2O (0.5 mmol). The mixture was stirred at 20 °C until the precipitate was completely consumed (4–20 h), it was then filtered through celite and concentrated to give the expected compounds as crystalline solids in quantitative yields.

4.11.1. (4R,5R)-1,3-Dibenzyl-4,5-di-tert-butylimidazolin-2-ylidene silver(I) bromide (**49**)

The single crystals of **53** suitable for X-ray diffraction analysis were obtained by recrystallisation from DCM and hexane mixture.

^{1}H NMR (200 MHz, $CDCl_3$): 7.42–7.3 (m, 10H, Ar*H*), 5.12 (d, $J = 14.5$ Hz, 2H, NC(H′)*H*Ph), 4.50 (d, $J = 4.5$ Hz, 2H, NC(H)*H*′Ph), 3.24 (s, 2H, NC*Ht*-Bu), 0.68 (s, 18H, C(CH_3)$_3$).

^{13}C NMR ($CDCl_3$): 135.4, 129.7, 129.2, 128.8, 71.2, 56.5, 35.7, 27.3.

$[\alpha]_D^{20} - 57$ (*c* 0.68, DCM). *Anal*. Calc. for $C_{25}H_{34}AgBrN_2$ (MW = 550.3): C, 54.56; H, 6.23; N, 5.09. Found: C, 55.24; H, 6.42; N, 4.89%.

4.11.2. (4R,5R)-1,3-Di-(1-naphthylmethyl)-4,5-di-tert-butylimidazolin-2-ylidene silver(I) chloride (**51**)

To a solution of imidazolinium salt (0.715 mmol) in DCM (15 mL) was added Ag_2O (0.55 equiv.). The mixture was refluxed for 12 h, filtered through celite and concentrated to give 432 mg (100%) of the expected compound as a beige crystalline solid.

^{1}H NMR (200 MHz, $CDCl_3$): 8.31–7.45 (m, 14H, Ar*H*), 5.52 (d, $J = 15.2$ Hz, 2H, NC(H′)*H*Ph), 5.07 (d, $J = 15.2$ Hz, 2H, NC(H)*H*′Ph), 3.32 (s, 2H, NC*H*t-Bu), 0.60 (s, 18H, C(CH_3)$_3$).

$[\alpha]_D^{20} + 196.0$ (*c* 0.66, $CHCl_3$).

4.11.3. (4R,5R)-1,3-Di-(3-methoxybenzyl)-4,5-di-tert-butylimidazolin-2-ylidene silver(I) chloride (**52**)

To a solution of imidazolinium salt (0.83 mmol) in DCM (15 mL) was added Ag_2O (0.55 equiv.). The mixture was refluxed for 12 h, filtered through celite and concentrated to give 470 mg (95%) of the expected compound as a white crystalline solid.

^{1}H NMR (400 MHz, $CDCl_3$): 7.30–6.80 (m, 8H, Ar*H*), 5.06 (d, $J = 15.2$ Hz, 2H, NC(H)*H*′Ph), 4.49 (d, $J = 15.2$ Hz, 2H, NC(H′)*H*Ph), 3.81 (s, 6H, OCH_3), 3.28 (s, 2H, NC*H*t-Bu), 0.75 (s, 18H, C(CH_3)$_3$).

$[\alpha]_D^{20} + 192.8$ (*c* 0.66, $CHCl_3$).

4.11.4. (4R,5R)-1,3-Bis-[(S)-1-phenylethyl]-4,5-di-tert-butylimidazolin-2-ylidene silver(I) iodide (**53**)

^{1}H NMR ($CDCl_3$): 7.72–7.23 (m, 10H, Ar*H*), 4.66 (q, $J = 7.4$ Hz, 2H, NC*H*(CH$_3$)Ph), 2.20 (s, 2H, NC*H*t-Bu), 2.15 (d, *J* 7.4 Hz, 6H, NCH(CH_3)Ph), 0.61 (s, 18H, C(CH_3)$_3$).

^{13}C NMR (DMSO-D_6): 141.3, 128.4, 127.9, 72.1, 58.2, 34.9, 26.0, 22.1. The carbene carbon was not observed.

$[\alpha]_D^{20} + 609.9$ (*c* 0.21, $CHCl_3$).

5. Supplementary material

Crystallographic data for the structural analysis of compounds **21** and **49** have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 160043 (compound **21**) and 160044 (compound **49**) [45]. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

The authors thanks Stephane Rosset for analytical support, BASF for the generous gift of chiral amines, the Swiss National Research Foundation No. 20-068095.02 and COST action D/24/003/01 (OFES Contract No. C02.0027) for financial support.

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