Diamination of Olefins: Synthesis, Structures and Reactivity of Osmaimidazolidines

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Dedicated to Professor K. H. Dötz on the occasion of his 60th birthday

Abstract: The diamination of certain olefins bearing electron-withdrawing substituents proceeds with well-defined bisimido and trisimido complexes of osmium. The products are obtained as osmaimidazolidines which are of unprecedented stability with regards to olefin functionalisation. Osmium complexes from related dihydroxylation or aminohydroxylation are significantly less stable and thereby promote catalytic reactions. This difference in reaction profile has been investigated and chiral osmium heterocycles obtained from olefin difunctionalisation were characterised by X-ray analysis for the first time. Kinetic studies on the reaction profile have also been carried out. An asymmetric version of this reaction is based on chiral nonracemic auxiliaries and leads to diastereomerically enriched osmaimidazolidines with up to 90% *de*. This sequence represents the first asymmetric diamination of olefins. Attempts on the use of chiral ligands for direct asymmetric diamination as well as the consequences of osmaimidazolidine properties for a catalytic reaction are discussed.

Keywords: diamination · osmium · stereoselective synthesis · transition-metal complexes

Introduction

Vicinal diamines represent an important class of organic compounds which are of upmost importance in various areas of today's chemistry including medicinal and biological chemistry,[1] asymmetric synthesis[2–6] and chiral oligomers.[2, 3, 7] The synthesis of diastereomerically and enantiomerically pure derivatives of the 1,2-diamino group is therefore of high importance. To achieve this purpose, a variety of approaches have been devised.[2, 8] Apart from routine resolution procedures,[2, 9] these include the asymmetric C–C bond formation employing reductive homo- or hetero-coupling of imines[2, 10] and 1,2- or 1,4-addition to imines, hydrazones or nitro olefins, respectively.[2, 8, 11] Concepts in the area of C–X bond formation rely on substitution reactions on carbon sp^3 centres with appropriate nitrogen nucleophiles. Substrates include aziridines[2, 12] or 1,2-diols and 1,2-amino alcohols upon hydroxyl group activation.[2, 13] A sequence using the double Overman rearrangement has recently been reported.[14] Alternatively, synthesis of 1,2-diamines from asymmetric reduction of bisimines or α-amino imines has been described.[2, 15] Finally, a complementary biochemical approach consists of a lipase-catalysed resolution of racemic vicinal diamines.[16]

On the other hand, oxidative transformation of C–C double bonds represents a powerful approach towards vicinal difunctionalisation. Within this area, asymmetric catalytic Sharpless dihydroxylation (AD)[17] and aminohydroxylation (AA)[18] are the most important achievements which have developed into broad applicability. Nevertheless, the closely related reaction of direct asymmetric diamination (ADA) has remained unknown so far and even investigations into stereochemically unselective reactions of this type have remained particularly scarce. In 1974 Barluenga and Aznar discovered the suitability of thallium(III) salts to promote addition of anilines to unfunctionalised C–C double bonds.[19] This reaction apparently proceeds via aminothallation of the olefin followed by subsequent reductive dethallation by a second amine [Scheme 1, Eq. (1)]. A related reaction sequence by Bäckvall employed palladium(II) and lead(IV) to promote addition of aliphatic amines to simple olefins [Eq. (2)].[20] Sharpless' use of preformed bis- and trisimidoosmium complexes allowed reaction with fumaric esters and both aromatic (styrene) and aliphatic olefins [Eq. (3a)].[21] Later, Schrock described the application of a related compound bearing a sterically hindered aromatic imido substituent that reacted with ethyl-

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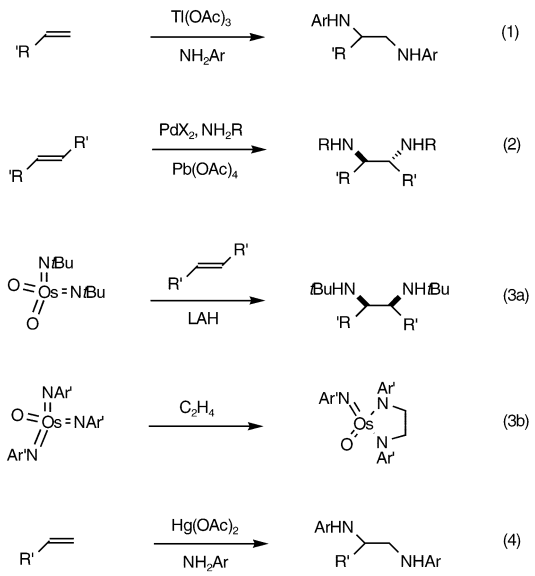
ene, norbornene and cyclopentene to give diamine derivatives as the sole products.[22] Moreover, the shown compound derived from reaction with ethylene has been the only one of these derivatives that had been characterised by X-ray analysis [Eq. (3b)].[22c] Finally, Barluenga devised the use of mercury(II) salts for a diamination reaction similar in nature to the thallium mediated one [Eq. (4)].[23]



Scheme 1. Metal-mediated diamination of olefins.

Ever since, no further investigation into the area of metal-mediated diamination of olefins has been undertaken and a related catalytic diamination of olefins has yet to be developed. So far, there have been disparate reports on reactions from which diamines have been isolated either as by-products in aziridinations[24] or as the result of solvent incorporation in reactions with Ritter-type termination.[25, 26]

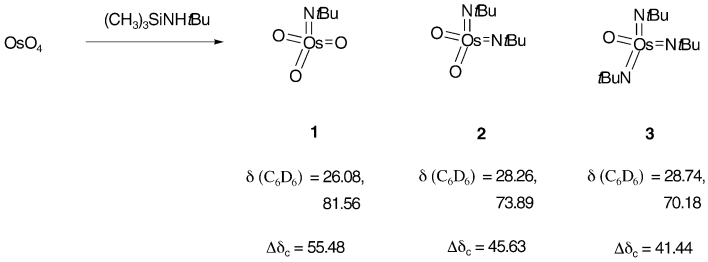
We have recently reported on a first stoichiometric asymmetric diamination of fumaric and acrylic esters[27] as well as on the synthesis of an osmaimidazolidine as ligand for asymmetric catalysis[28]and here wish to present a full account of this work as well as a detailed analysis on the reaction profile of this diamination and of the structural properties of osmaimidazolidines.

Results and Discussion

Synthesis of Os^{VIII}-imido complexes: The conversion of osmium tetroxide into bis- and trisimido species had first been investigated by Sharpless who favoured a two-step procedure involving the synthesis of the mono-imido complex **1** from aqueous *tert*-butyl amine followed by subsequent further imination with the aid of phosphane iminates.[21] Later reports by Nugent[29] and Wilkinson[30] on the direct synthesis of **2** and **3** relied on the use of *N*-trimethylsilyl *tert*-butyl amine.

In our hands, it turned out most convenient to directly treat an *n*-hexane solution of osmium tetroxide with a 20- to 25-fold excess of *N*-trimethylsilyl *tert*-butyl amine to obtain a mixture of the three imido compounds **1**, **2** and **3**. This crude mixture can be separated on silica gel chromatography to yield the desired complexes **2** and **3** in yields of around 40 and 15%, respectively. The monoimido complex **1**, which is isolated in 40% yield, can be re-submitted to reaction with *N*-trimethylsilyl *tert*-butyl amine to yield a further amount of **2** and **3** (28 and 53% yield, respectively, on a 5 mmol scale).

Within this approach, the different imido complexes can be conveniently distinguished from their respective NMR spectra. As had been described for **1** and **2** by Nugent and Haymore,[31] the relative difference in shift $\Delta\delta_C$ as observed from the respective ^{13}C NMR can be correlated to the relative electron density at Os^{VIII}. Thus, it can be related directly to the number of amino moieties present in the complex, a trend that is apparently maintained in going from **2** to **3**. The respective shifts for the signals of the methyl and the quaternary carbon atoms and the corresponding shift differences are given in Scheme 2.

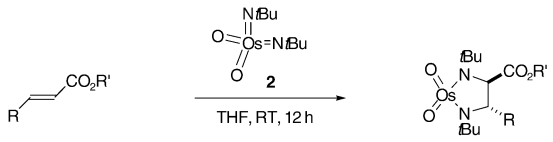


Scheme 2. Synthesis of osmium imido complexes.

Reactions of bisimido osmium(VIII) complex 2: As expected, the reaction of **2** with simple olefins is rather slow resulting in relatively low chemical yields. Certainly, the use of electron-poor olefins as substrates is of greater interest since the respective reaction rates are higher; there had been a previous report that the products from reactions with fumarates are characterised by a more enhanced stability.[21] Thus, it was decided to investigate the scope of the diamination of olefins bearing electron-withdrawing substituents.

Acrylic esters: The reaction between **2** and methyl cinnamate **4** was chosen for elucidation of optimum reaction conditions. The reaction was relatively unaffected by changes in the conditions. It proceeds with over 75% chemical yield in various solvents ranging from dichloromethane or THF and dioxane to benzene and toluene. Concentrations between 0.1 and 2 molar in olefin have no influence on the yield. In solvents such as benzene and THF the reaction even proceeds under ambient atmosphere. If not stated otherwise, all reactions described in this article were carried out in THF and under Ar. Moreover, it was found that for a ratio of **4**:**2** in the range of 1.0 to 2.0, the reaction outcome is independent of the amounts of olefin present. Thus, 1.2 equivalents of olefin were generally used (given yields are based on the amount of **2**).

Under these conditions, various olefins were converted into osmaimidazolidines with excellent yields (Scheme 3, Table 1). Within this series of reactions the use of methyl, benzyl and *tert*-butyl cinnamate gave the corresponding diamination



Scheme 3. Diamination of acrylic esters with bisimido complex **2**.

Table 1. Diamination of acrylic esters.

	Substrate	R	R′	Yield [%][a]	Product
1	**4**	C_6H_5	CH_3	94	**12**
2	**5**	C_6H_5	$C(CH_3)_3$	96	**13**
3	**6**	C_6H_5	$CH_2C_6H_5$	89	**14**
4	**7**	CH_3	CH_3	91	**15**
5	**8**	CH_3	C_2H_5	92	**16**
6	**9**	H	CH_3	98	**17**
7	**10**	CO_2CH_3	CH_3	90	**18**
8	**11**	3-pyridinyl	CH_3	78	**19**

[a] Isolated yield after column chromatography.

products **12**–**14** with the three orthogonally protected esters. In similar reactions, crotonates **7**, **8** and acrylate **9** gave clean reactions to furnish the respective diamination products in high yields. Another of the results from Scheme 3 is of particular interest. Diamination of 3-pyridyl methyl acrylate **11** gave the corresponding osmaimidazolidine **19** in 78% isolated yield after column chromatography. In related osmium-mediated or catalysed dihydroxylation or amino-hydroxylation reactions,[32] compounds displaying a free pyridine nitrogen constitute a problematic class of substrates either since they undergo coordination to the osmium reagent[33] or because they suffer from oxidation of the pyridine nitrogen under catalytic conditions. However, in the present case, no competitive products could be isolated indicating that the pyridinyl moiety does not exercise any deleterious effect.

In all these examples and for the related examples discussed below, the diamination reaction turned out to be both highly stereospecific and highly chemoselective. All spectroscopic investigations on the crude reaction mixtures displayed only *trans*-configured osmaimidazolidine products **12**–**19** proving that the original geometry of the olefin was preserved. Identically, the formation of diol or amino alcohol products originating from the competitive addition of oxo ligands was never observed indicating that the bisimido complex **2** exclusively transfers its two amino groups to the olefinic substrate. Given the high stability of the resulting osmaimidazolidines it was possible to obtain X-ray quality crystals for several of the products. Two examples, the solid-state structures of complexes **12** and **13**, are depicted in Figures 1 and 2 (data on these structures are given in Table 5) and represent the first structural elucidations of chiral osmaimidazolidines.

For the diamination of electron-deficient olefins there is no major electronic influence on reaction rate as could be determined from a competition experiment. When a C_6D_6 solution containing equal amounts of dimethyl fumarate (**10**) and methyl cinnamate (**4**) was added to reaction with one equivalent of **2**, NMR analysis showed that both products **12** and **18** were formed in about equal amounts at every stage of the reaction between 17 and 92% conversion. This result

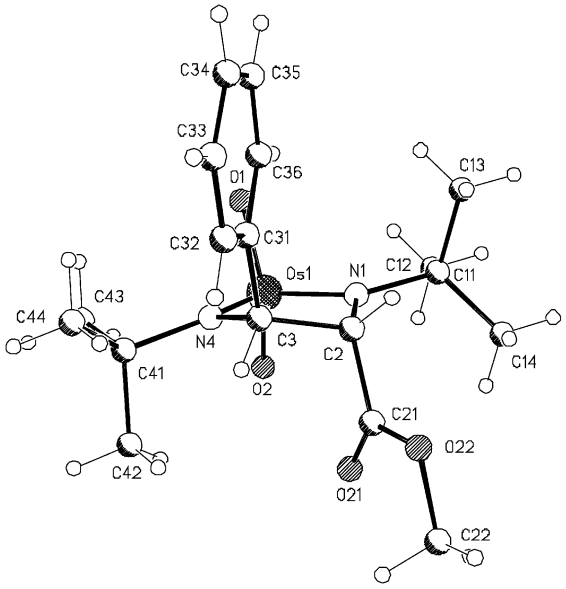


Figure 1. Solid-state structure of osmaimidazolidine **12**. Selected bond lengths [Å] and angles [°]: Os1–O1 1.731(2), Os1–O2 1.722(2), Os1–N1 1.881(2), Os1–N4 1.881(2), N1-Os1-N4 82.40(10), O1-Os1-N1 112.50 (10), O2-Os1-N1 111.85(10), O2-Os1-N4 113.13(9).

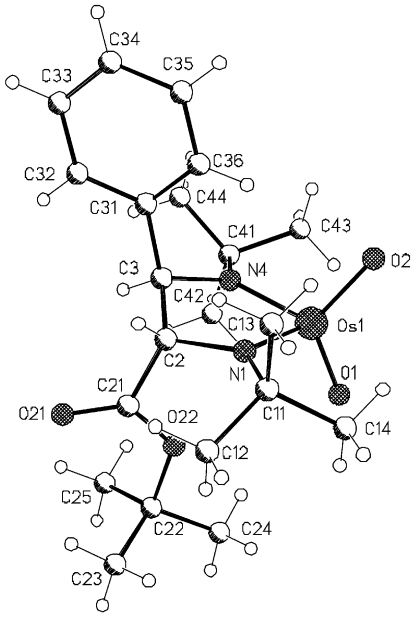
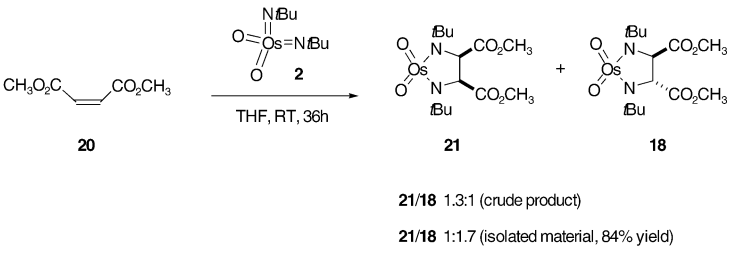


Figure 2. Solid-state structure of osmaimidazolidine **13**. Selected bond lengths [Å] and angles [°]: Os1–O1 1.721(3), Os1–O2 1.731(3), Os1–N1 1.881(4), Os1–N4 1.884(4), N1-Os1-N4 82.27(15), O1-Os1-N1 111.64(16), O2-Os1-N1 111.86(16), O2-Os1-N4 110.90(16).

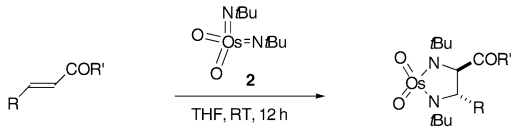
proves that evidently one carbonyl group is sufficient in order to achieve maximum reaction rate for the diamination. Dimethyl maleinic ester **20** underwent diamination in the presence of **2** (Scheme 4). However, this reaction proceeded at very low rate and appeared to be solvent dependent since product formation was only detected for a reaction in THF. Moreover, a mixture of the expected *syn*-configured compound **21** and its corresponding *trans*-isomer **18** was isolated. The latter one was identified from its characteristic set of signals which were identical to the ones from the authentical



Scheme 4. Diamination of maleic ester **20**.

sample derived from diamination of dimethyl fumarate **10** with **2**. Importantly, the original ratio of 1.3:1 in favour of **21** (determined by proton NMR from the crude reaction mixture) was found to have been reversed to 1:1.7 after column chromatography. Apparently, under the reaction conditions, equilibration of the primarily formed product **21** takes place, which is enhanced further during purification on silica gel. Isolation of a pure sample of compound **21** was therefore not possible and its ^{1}H NMR characterisation was carried out by subtractions of the signals of the known compound **18**. Finally, treatment of the 1:1.7 mixture of **21**:**18** with triethylammonium chloride resulted in complete equilibration and complex **18** was isolated as sole compound. This indicates that conversion of **21** to the thermodynamically stable *trans*-configured complex **18** is indeed the decisive process.[34]

Further carbonyl derivatives: After the synthesis of osmaimidazolidines by diamination of acrylic esters had been established, we turned our attention towards the related electron-deficient olefins. In particular, the functional groups of amides, ketones and aldehydes were studied. In all these cases, the respective osmaimidazolidines were obtained as sole products and in high chemical yields (Scheme 5, Table 2). This is a noteworthy feature of this chemistry since related



Scheme 5. Diamination of electron-deficient olefins.

Table 2. Diamination of electron-deficient olefins.

	Substrate	R	R′	Yield [%][a]	Product
1	**22**	C_6H_5	$NHC(CH_3)_3$	89	**28**
2	**23**	CH_3	$NHC(CH_3)_3$	86	**29**
3	**24**	H	$NHC(CH_3)_3$	89	**30**
4	**25**	C_6H_5	$NCH_3(OCH_3)$	84	**31**
5	**26**	C_6H_5	C_6H_5	91	**32**
6	**27**	C_6H_5	H	92	**33**

[a] Isolated yield after column chromatography.

osmium-mediated or catalysed reactions do not tolerate many of these functional groups.[17, 18] As an important result, bisimido osmium reagent **2** selectively oxidises the C–C double bond in **27** leaving the aldehyde function intact. In contrast to the configurational stability of α-amino aldehydes which are generally of notorious sensitivity,[35] complex **33** does not suffer any stereochemical changes upon exposure to base or weak acids and the *trans*-configuration is maintained at all time. This again confirms that the *trans*-arrangement represents the thermodynamically preferred configuration for osmaimidazolidines.

In an otherwise identical diamination reaction, acrylonitrile (**34**) was transformed into the corresponding 4-cyano-substituted osmaimidazolidine **35** which was isolated in 76% yield.

Again, all products described were of high stability and two of them, complexes **28** (Figure 3) and **32** (Figure 4), were characterised in the solid state. Their overall stereochemical features coincide well with the ones of **12** and **13** depicted

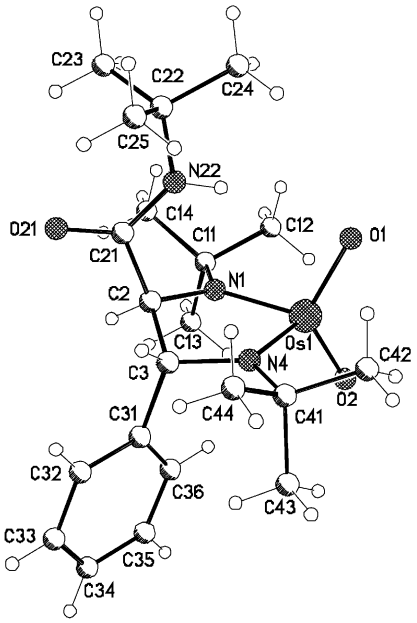


Figure 3. Solid-state structure of osmaimidazolidine **28**. Selected bond lengths [Å] and angles [°]: Os1–O1 1.729(3), Os1–O2 1.725(3), Os1–N1 1.881(3), Os1–N4 1.878(3), N4-Os1-N1 82.49(14), O1-Os1-N1 108.56(14), O2-Os1-N1 113.03(14), O2-Os1-N4 110.95(15).

above. Their most important characteristics are the pseudo-tetrahedral coordination at the central Os atom and the relatively small difference in Os–O double bond and Os–N bond. For the former, values in the usual range of 1.7 Å were determined while the latter showed bond lengths of about 1.88 Å. This indicates significant π-character for the Os–N bonds and points to an increased stability of the osmium diamino chelate structure.

From a structural point of view, the stability of all these products is amazing. First, their monomeric character is unprecedented. As it had already been observed by Criegee,[33] that related glycolate complexes of Os^{VI} resulting from dihydroxylation reactions are lacking electronic stabilisation and thus convert into more stable bisglycolate derivatives.[36] Monoglycolates can only be stabilised by additional coordi-

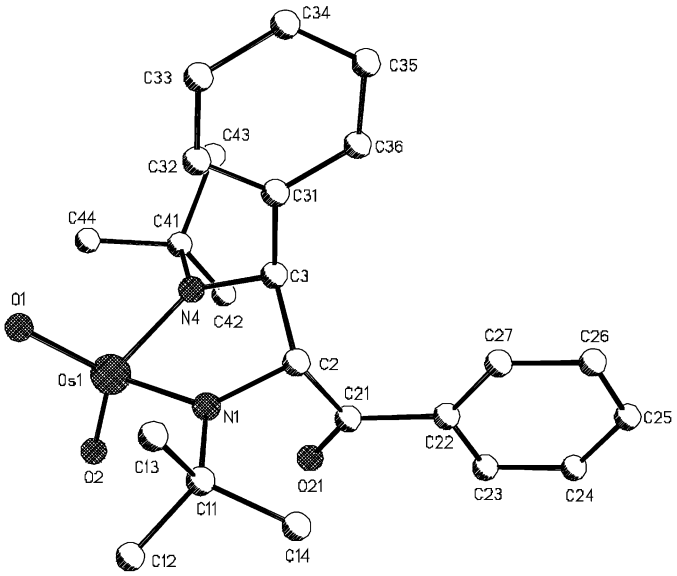
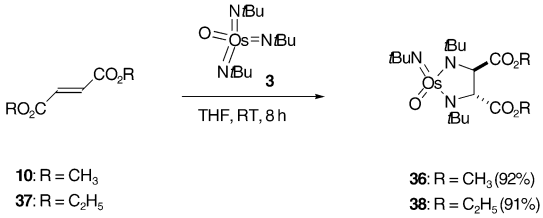


Figure 4. Solid-state structure of osmaimidazolidine **32** (hydrogen atoms are omitted). Selected bond lengths [Å] and angles [°]: Os1–O1 1.716(3), Os1–O2 1.715(4), Os1–N1 1.880(4), Os1–N4 1.886(4), N1-Os1-N4 81.45(15), O1-Os1-N1 111.79(17), O2-Os1-N1 111.80(18), O2-Os1-N4 114.23(15).

Reactions of trisimido osmium(VIII) complex 3 with olefins: Within the reaction of the related trisimido complex **3** investigation has been limited to fumaric esters. Diamination of dimethyl fumarate (**10**) had already been described by Sharpless in 1977.[21] Under the present reaction conditions, this substrate and the related diethyl ester gave excellent product formation (Scheme 6). However, unlike the case with the bisimido reagent **2**, complex **3** did not give any detectable product from reaction with maleic ester **20**. Again, the *tert*-butylimido-oxoosma(VI)imidazolidine products **36** and **38** are stable, deep red solids that cannot be re-oxidised to Os^{VIII} with common homogeneous oxidants such as hydrogen peroxide, chloramine-T or *N*-methyl morpholine *N*-oxide.



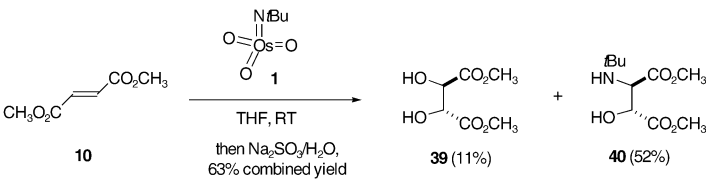
Scheme 6. Diamination of fumarates with trisimido complex **3**.

nation of σ-donors such as pyridines,[37] *Cinchona* alkaloids,[38] and diamines[4a, 39] or by dimerisation.[40] These results also apply for the corresponding azaglycolates as products from aminohydroxylation of olefins.[41]

The observed stability of monomeric osmaimidazolidines is the direct consequence of the electron-rich Os–N bonds and their inherent double-bond character which accounts for a formal 16 to 18 electron Os centre. Moreover, some of these osmaimidazolidines were of particular interest for comparison with the related glycolate and azaglycolate osmium complexes. For example, the amides **28**–**31** were stable even under prolonged exposure to aqueous oxidative solutions. Thus, when a 2 M solution of **28** in tetrahydrofuran was treated with amine *N*-oxides or an aqueous solution of chloramine-T and heated for 24 h, the osmaimidazolidine was recovered unchanged and in nearly quantitative yield. Under otherwise identical conditions, related azaglycolate osmium complexes bearing residual amido moieties are known to undergo spontaneous reoxidation, olefin functionalisation and subsequent hydrolysis.[42] This chemistry has been the basis for recent development of secondary cycle osmium catalysis.[43] Apparently, the inherent stability of osmaimidazolidines of **28**–**31** in general owes to the electronic saturation of the Os^{VI} centre that prevents reoxidation to Os^{VIII}. Any type of diamine hydrolysis would only result after osmium reoxidation, however, it is the strength of the diamine–osmium chelate and the additional Os–N double bond character that prevents this prerequisite step. Moreover, various other attempts to cleave the osmium–nitrogen bonds remained unsuccessful. These included use of reducing agents such as sodium sulfite or sodium thiosulfate. Removal of the osmium centre was found to be possible only by interaction with strong hydride reducing agents such as lithium aluminium hydride or sodium borohydride.[27, 44]

In contrast to the data for related dioxo complex **18**, careful examination of the NMR spectra revealed a pronounced non-symmetry for the signals both of the hydrogen atoms and the carbon atoms of the heterocyclic part of the osmaimidazolidine. This is not surprising since the arrangement at Os locates the oxo and the imido ligand on different sides of the osmaimidazolidine and thus enforces non-equivalency of the incorporated atoms and functional groups.

In order to get a further insight into the relative behaviour of **1**–**3** towards electron-deficient olefins, the oxidation of dimethyl fumarate (**10**) was investigated. First, the thus far unknown reaction of **1** with this olefin gave a complicated product mixture.[45] Since glycolate osmate esters and their monoaza derivatives are generally known to display only limited stability,[17, 18, 33] the reaction was worked up with an aqueous Na_2SO_3 solution. From this, dimethyl tartrate **39** and its monoaza analogue **40** were identified and were present in a ratio of 1:6 which shows that **1** does not oxidise **10** in a chemoselective fashion (Scheme 7). It is widely accepted that the chemoselectivity of monoimido osmium(VIII) compounds can be correlated to the electron density at Os. For example, for **1** the aminoalcohol/diol ratios can be greatly increased upon coordination of tertiary amine ligands to the osmium reagent.[18, 46] This effect is maintained for moderate electron acceptor imido-substituents such as tosylate, carbamates and amides, but is reversed for stronger electron acceptors, either



Scheme 7. Competitive oxidative functionalisation of **10** with **1**.

due to loss of reactivity of the imido-ligand transfer itself or to its direct hydrolysis. In these cases, diol by-product is formed in significant amounts and can dominate the reaction as a whole. For example, in the presence of haloamine salts derived from trifluoroacetamide dihydroxylation becomes the exclusive pathway.[47] In accord with this, the increase in electron density at osmium in going from **1** to **3** as already deduced from the relative difference in $\Delta^{13}C$ NMR shifts results in a dramatic increase in chemoselectivity and contrarily to **1**, compounds **2** and **3** give diamination products exclusively.[21, 27]

The overall reaction profile was investigated in a competition experiment in THF with 3 mmol dimethyl fumarate (**10**) and 1 mmol each of the respective oxidants **1**–**3**. The reaction proceeding was monitored with samples being taken every hour, worked-up and analysed by ^1H NMR. Given the low conversion of **1**, tartrate amounts were below the detection level. The relative amino alcohol formation originating from **1** turned out to be relatively slow (27% conversion of **1** after 3 h). Osmaimidazolidine formation with **2** and **3** occurred at higher, albeit different rates (Figure 5).

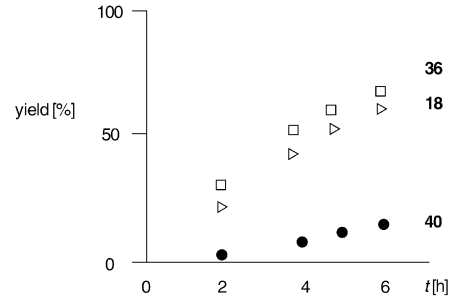
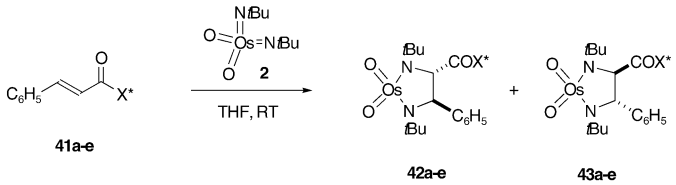


Figure 5. Competition experiments for oxidation of dimethyl fumarate (**10**) with osmium reagents **1**–**3**. Formation of **39** was below detection level.

The relative rates were investigated within a second experiment. Here, diamination in the presence of an excess amount of **10** (10 mmol) was carried out with 1 mmol each of **2** and **3**. Interestingly, diamination with **3** appears to proceed with higher rate than the related reaction with **2**, despite the potentially disadvantageous bulk from the additional *tert*-butyl imido substituent of the former reagent. Therefore, most probably, the relative increase of reactivity from **1** to **3** has its basis in the increased electron density at the respective Os centres. Currently, this conclusion remains limited to the present case of electron-deficient olefins since the behaviour of the respective ratios regarding aminohydroxylation and diamination, and competitive diamination appear to be substrate-depending.[47] Within this context, one should also note the general importance of substrate geometry: while OsO_4 in AD reactions shows a high preference for electron rich or neutral (*Z*)-olefins, monoimido–osmium derivatives for AA reaction tend to prefer electron-demanding (*E*)-olefins. This is further pronounced for the present stoichiometric diamination reaction which strongly favours electron-deficient (*E*)-olefins.[21, 27] Consequently, dimethyl maleic ester reacts extremely slowly with **2** and is unreactive with **3**. Noteworthy, for the purpose of olefin diamination with imido reagents, imido osmium(VIII) reagents **1**–**3** appear to be unique since attempts to react acceptor-substituted olefins such as **4** and **10** with methyl tris(*tert*-butylimido)rhenium(VII) and related compounds[48, 49] gave no detectable diamination at all.[47]

Diastereoselective transformations: Given the successful diamination of acrylic esters and related compounds, chiral enantiopure derivatives should serve as suitable substrates for diastereoselective diamination reactions of this type.[50] Such an appproach which would be an example of chiral auxiliary directed asymmetric synthesis between a non-racemic olefin and an achiral diaminating reagent was investigated for the case of enantiopure alcohols. It had already been used for the parent dihydroxylation to convert chiral olefins to diastereomerically enriched or pure diol derivatives.[51, 52] Interestingly, there is only one example regarding a stereoselective olefin functionalization that employs the monoimido compound **2** or related in situ generated imido complexes and naturally occurring terpenes as chiral non-racemic starting material.[53] A chiral cinnamate had been investigated already in 1989 within a stoichiometric aminohydroxylation of 13-cinnamoyl baccatin III. However, the reaction was unselective and yielded all four diastereoisomers.[54]

For the present purpose, incorporation of a chiral non-racemic auxiliary into the ester functionality could devise a route towards stereoselective diamination via differentiation of the diastereotopic sides of the C–C double bond. For example, (−)-menthol, 1-phenyl ethanol, (+)-fenchol and the Oppolzer sultam all gave the osmaimidazolidine complexes **42** and **43** with moderate diastereomeric ratios ranging from 1:1 to 2.6: 1 (Scheme 8).



Scheme 8. Auxiliary screening for asymmetric osmaimidazolidine formation.

Table 3. Diastereomeric ratios for diamination with selected chiral auxiliaries. The absolute configuration in products **42a**–**c**,**e** and **43a**–**c**,**e** are undetermined.

	Substrate	X*H	Ratio **42**:**43**[a]
1	**41a**	1-phenyl ethanol	1:1
2	**41b**	campher sultame	2.6:1
3	**41c**	(−)-menthol	1.5:1
4	**41d**	(−)-8-phenyl menthol	3.2:1
5	**41e**	fenchol	1.4:1

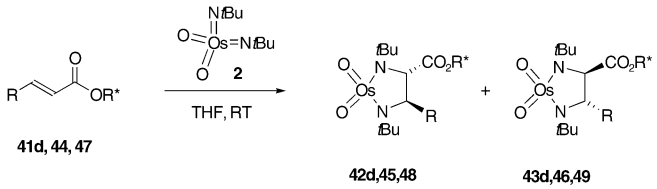
[a] Determined from ^1H NMR spectra of the crude reaction mixture.

From this auxiliary screening, 8-phenyl menthol was found to give the best results as summarized in Table 3. While this reagent induced only a moderate 78:22 diastereomeric ratio for **42d**:**43d** at 30°C, this value could be significantly improved to up to 94:6 when the reaction was carried out at

Table 4. Diastereomeric ratios for diamination with (−)-8-phenyl menthol as chiral auxiliary.

	Substrate	R	Yield [%][a]	Product ratio[b]
1	**41a**	C_6H_5	68	78:22 (**42d**/**43d**)
2[c]	**41a**	C_6H_5	56	94:6 (**42d**/**43d**)
3	**44**	CH_3	81	72:28 (**45**/**46**)
4	**47**	H	96	88:12 (**48**/**49**)
5[c]	**47**	H	88	95:5 (**48**/**49**)

[a] Diastereomeric mixture after column chromatography. [b] Determined by analytical HPLC. [c] The reaction was run at −15 °C.

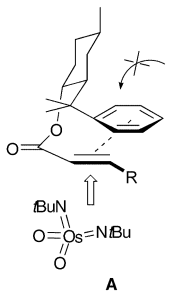


Scheme 9. Asymmetric diamination with (−)-8-phenyl menthol as chiral auxiliary [R*OH = (−)-8-phenyl menthol].

−15 °C (Table 4, Scheme 9). However, this increase in *dr* was accomplished by a significantly lower reaction rate and a period of 36 h was required to reach a combined yield of 56%. As observed for the related achiral substrates discussed above, no solvent dependence was observed and diaminations in dichloromethane and benzene gave nearly identical ratios for **42d**:**43d**. Attempted column chromatographic separation of the two diastereomers proved difficult and semipreparative HPLC was preferential for their complete separation.

At room temperature, the crotyl derivative **44** gave a comparable diastereomeric ratio of 72:28 for **45**:**46**. Interestingly, the mono-substituted acrylic ester **47** yielded an improved ratio of 88:12 for **48**:**49** and proceeded at higher rate. Again, lowering the temperature to −15 °C had a beneficial effect on diastereoselectivity and the two diamination products **48**/**49** were obtained with 95:5 *dr*. The X-ray structure of the major diastereoisomer **42d** has been reported.[27] An ORTEP plot is depicted in Figure 6.

The observed configuration for this major isomer is in agreement with a stereochemical transition state in which the diastereotopic *Si* face of the reactive C–C double bond is selectively shielded by the adjacent phenyl moiety of the chiral terpene auxiliary. Thus, diamination occurs preferentially from the more accessible *Re* face of the olefin furnishing the observed 4*R*,5*S*-configuration for the major diastereomer, a reaction outcome that is reminiscent of an AD reaction on methylacrylates.[51b] Such a stereochemical model **A** of a π-stacking interaction had first been suggested by several groups for diastereoselective reactions of 8-phenyl menthyl acrylates,[55] among which the most pronounced example is on Fischer carbene complexes as chiral Michael acceptors.[56]



A

Chiral, non-racemic diamino alcohols could be obtained in both enantiomeric forms from

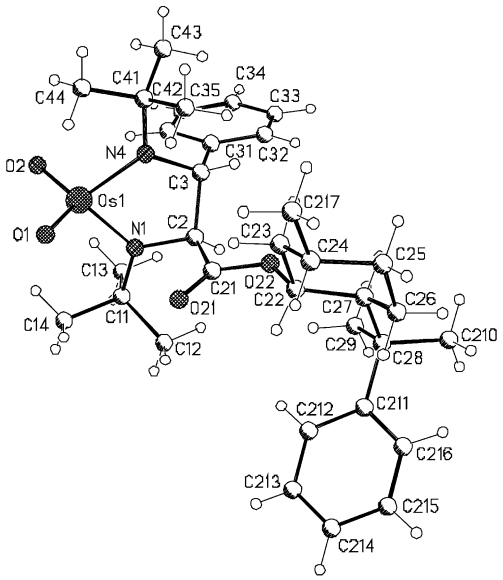
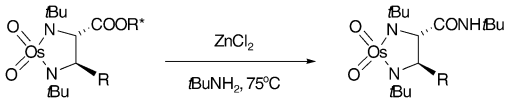


Figure 6. Solid-state structure of major diastereoisomer **42d**.[27] Selected bond lengths [Å] and angles [°]: Os1–O1 1.726(4), Os1–O2 1.727(3), Os1–N1 1.884(4), Os1–N4 1.896(4), N1-Os1-N4 81.14(18), O1-Os1-N1 110.96(18), O2-Os1-N1 113.64(18), O2-Os1-N4 110.03(19).

LAH reduction of the diastereomerically pure complexes **42d** and **43d**, repectively.[27] In order to obtain enantiomerically pure metal-free diamino amides from $NaBH_4$ reduction, it turned out necessary to convert the osmaimidazolidine ester groups into their corresponding amides. This transformation was achieved by using a substoichiometric amount of zinc(II) chloride (25 mol%) and the amine as solvent (Scheme 10).



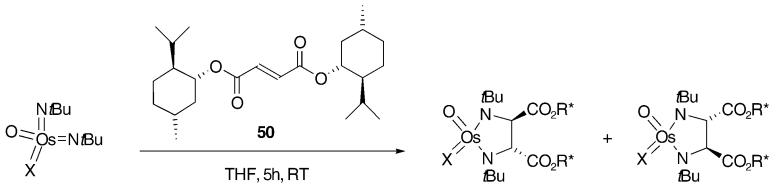
42d: R = C_6H_5 **28** (67%)
45: R = CH_3 **29** (72%)

Scheme 10. Functional group transformation of osmaimidazolidines.

After 36 hours at 75 °C, the desired amides **28** and **29** were isolated in good yields (67 and 72%, respectively, together with unreacted starting material). Analysis by analytical HPLC confirmed that the new compounds had not undergone racemisation.[57] However, when related *N*-alkylated α-amino acids were added under the same conditions, significantly lower reaction rates for amide formation were observed.[47] Certainly, in case of epimerization at the C–H acidic centre in α-position to the carbonyl moiety the resulting *syn*-configured osmaimidazolidine re-isomerises to the thermodynamically stable *trans*-isomer as it had already been observed in case of the complexes **18** and **21** (see above). However, since the second stereogenic centre is not prone to epimerisation, its absolute configuration determines the regeneration of the overall *trans*-arrangement and thus the original absolute configuration as originating from the starting material is preserved. In accord with this observation, a related transformation on the mono-substituted, diastereomerically pure

osmaimidazolidine **17** led to a sample **30** which displayed only a low enantiomeric excess of 67%. Thus, enantiomerically pure samples of **28** and **29** are available that can be converted to enantiopure diamino carbamides as described previously.[27]

In view of the excellent reactivity of the imido complexes **2** and **3** towards alkyl fumarates their reaction with a chiral nonracemic analogue, the commercially available bis[(−)menthyl] fumarate (**50**), was investigated as well (Scheme 11).



Scheme 11. Diastereoselective diamination of bis[(−)-menthyl] fumarate (**50**) [R*OH = (−)-menthol].

Thus, its reaction with **2** led to diastereomers **51** and **52** in a ratio of 81:19. This ratio could be significantly increased when complex **2** was changed for the trisimido derivative **3** and products **53** and **54** were isolated in $>95:<5$ *dr*.[27] The absolute configuration of the products was unambigously determined from an X-ray analysis of the major diastereomer **53** (Figure 7) as *R*,*R*. Understanding that there should be no

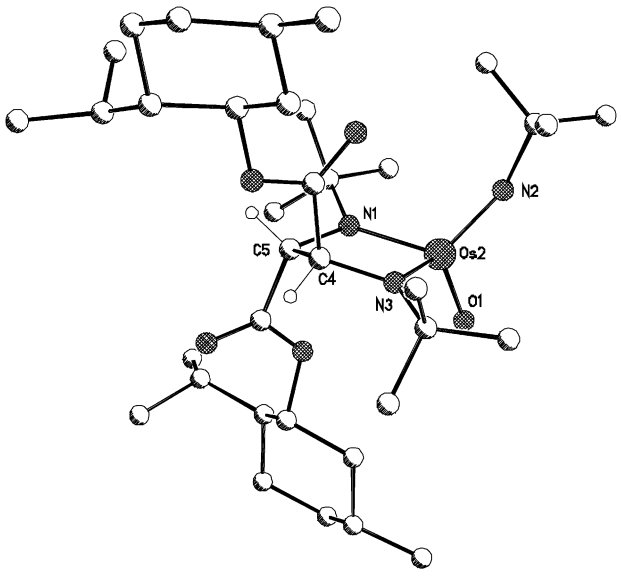


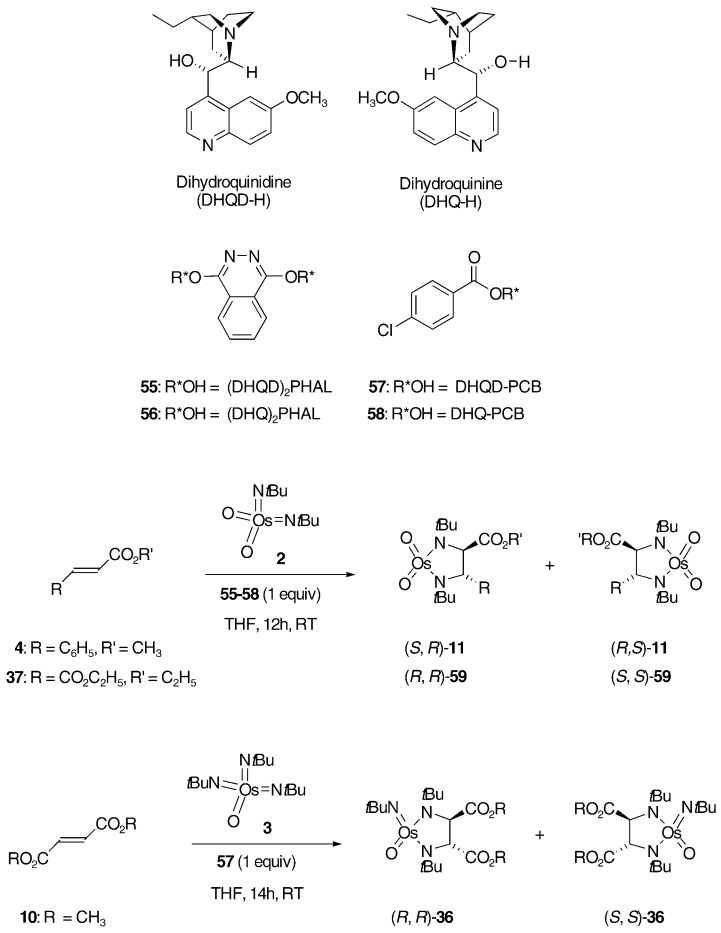
Figure 7. Solid-state structure of major diastereoisomer **53** (except for the stereogenic centres at C4 and C5, hydrogen atoms are omitted). Selected bond lengths [Å] and angles [°]: Os2−O1 1.707(6), Os2−N2 1.727(7), Os2−N3 1.887(8), N1−Os2 1.893(7), N2-Os2-N3 112.5(3), O1-Os2-N1 110.6(3), O1-Os2-N2 115.5(3), N3-Os2-N1 81.9 (3), C36-N2-Os2 157.4(6).

severe difference in the course of diamination reactions with **2** and **3**, respectively, an identical absolute configuration is assumed for the dioxo derivative **51**. It is important to note that the (*R*,*R*)-configuration results from *Si* face addition, an approach that is opposite to the one in the related case employing the 8-phenyl-menthyl auxiliary. This latter auxiliary dominates the stereoselective diamination via an active π-stacking conformation that apparently overrides the given preference in stereodiscrimination with the (−)-menthyl moiety. The oxidative conversion of chiral fumarate **50** has been previously described to occur with oxidants such as osmiumtetroxide[58] and potassium permanganate[59, 60] yielding mixtures of diastereomers with an analogous preference for the (*R*,*R*)-diastereomer,[59] albeit with lower *dr*. Regarding the structure of **53** itself, it is important to note that the remaining imido ligand coordinates in a bent fashion of an 157° angle. This indicates that the ring nitrogen atoms contribute most of the electronic stabilisation to the Os centre and the imido ligand is involved only to a much lower extend. In contrast, Schrock's arylimido osmaimidazolidine structure[22b] displays a nearly linear imido ligand with an N−Os−C angle of 178° indicative of a reversed electron donation via the imido lone pair.

A chiral catalyst obtained from **53** was described recently and represents the first successful application of an osmaimidazolidine based chiral ligand in asymmetric catalysis.[28] It also showed that removal of the *tert*-butyl entities might not be necessary in order to transform the diamination product into useful compounds for further asymmetric synthesis.

Enantioselective transformations: The successful use of *Cinchona* alkaloid derivatives of dihydroquinine and dihydroquinidine in related reactions of dihydroxylation[17] and aminohydroxylation[18] is well-documented and prompted use of these compounds as ligands in the present diamination reaction. The resulting osmacycles were submitted directly to HPLC analysis since the required manipulation for release of the diamino moiety was considered inappropriate. For 2,2-diooxo osmaimidazolidines **11** and **59**, and for *tert*-butylimido osmaimidazolidine **36** enantiomers could be separated on analytical chiral HPLC. However, regardless whether DHQD or DHQ derivatives were used as chiral ligands for diamination with **2** or **3**, no asymmetric induction could be obtained and all products isolated from these runs in the presence of potential ligands **55**–**58** were essentially racemic (Scheme 12).

Careful ^{1}H NMR titration studies for different ratios of **2** and the standard first-generation PCB ligand of DHQD (**57**) did not suggest any complexation at all. Apparently, even in the presence of a 20-fold excess of DHQD-CLB **57** there was no change in the NMR shifts of the respective set of signals for the two compounds. This is a pronounced difference to the related situation for both osmiumtetroxide and the monoimido complex **1** which form *Cinchona* alkaloid complexes that can be detected spectroscopically. For these two Os compounds, an equilibrium between the free complex and the ligated derivative has been established.[46, 61] Such a behaviour



Scheme 12. Attempts towards an asymmetric diamination employing *Cinchona* alkaloid ligands.

which is indispensable for ligand-accelerated catalysis[62] can prove rather problematic in asymmetric stoichiometric transformations. In such case, tight binding between ligand and metal centre is preferable. The inability of bis- and trisimido-complexes **2** and **3**, respectively, to undergo complexation to *Cinchona* alkaloids results from the *tert*-butylimido ligands at osmium. Since these entities contain a basic lone pair at each nitrogen of the imido ligand, donation of electron density to the formally 16e-osmium centre is enhanced and results in a significantly diminished Lewis acidity at the metal centre, if any. As a consequence, no σ-coordination of external ligands is feasible. This result also explains the apparent ease of diamination of pyridyl acrylate **11** since a potentially competing coordination of the pyridino group to the Os^{VIII} reagent cannot take place.

In view of the difficulties that have been encountered in the stoichiometric diamination reaction, a potential catalytic diamination will require the involvement of more labile osmaimidazolidine complexes. This might be achieved from use of a bistosylimido compound or related complexes, however, removal of the product diamine from the osmium centre will then require anhydrous conditions and use of an amino or amido compound as a discrete precursor to an imido moiety at osmium. The elaboration of such catalytic cycles depends crucially on an equilibrated potential energy level surface for all reactive intermediates.[63] The drastic increase in stability of osmaimidazolidines as primary products of the diamination prevents such a scenario. Given the current stability of *N*,*N*′-dialkyl osmaimidazolidines the development of catalytic reactions proceeding at efficient rates remains challenging. Thus, the search for bistosylimido derivatives of osmium(VIII) and for defined osmaimidazolidine complexes of similar lability as their glycolate and azaglycolate osmate esters, respectively, constitutes the present focus of ongoing research.

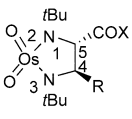
Conclusion

A detailed investigation on the diamination of electron-poor olefins by means of preformed bis- and trisimido osmium reagents has been described. The products were obtained as osmaimidazolidines with a pronounced stability. The latter fact has been correlated to an enhanced electronic saturation at the osmium centre due to donation from the basic free lone pair at the ring nitrogen atoms. This electronic effect renders the chemistry of osmaimazolidines different from the one of its glycolate and azaglycolate osmate ester counterparts. The most significant consequences are the stability of the resulting Os^{VI} centre towards reoxidation and the inherent stability towards hydrolytical cleavage of the monomeric Os–diamine entity. At present, the development of catalytic versions on the basis of the described chemistry appears problematic. A first asymmetric diamination of olefins has been developed by using chiral non-racemic auxiliaries that led to the isolation of diastereomerically enriched osmaimidazolidines that can be transformed by defined chemical transformations.

Experimental Section

General: Osmium(VIII) oxide was purchased from Strem. *tert*-Butylamine, *N*-trimethylsilyl *tert*-butylamine, methyl cinnamate, benzyl cinnamate, metyl acrylate, chalcone, bis[(−)-menthyl] fumarate, $(DHQD)_2PHAL$ and $(DHQ)_2PHAL$ were purchased from Fluka. Cinnamoyl chloride, 3-pyridine acrylic acid, cinnamic aldehyde, methyl crotonate, ethyl crotonate, dimethyl fumarate, diethyl fumarate, dimethyl maleic ester, zinc chloride, (−)-8-phenyl menthyl and phenyl magnesium chloride (2.0 M solution in THF) were purchased from Aldrich. The following compounds were synthesised following literature procedures: *tert*-butyl cinnamate,[64] *N*-*tert*-butyl cinnamide,[65] *N*-*tert*-butyl crotonamide,[66] *N*-*tert*-butyl acrylamide,[67] *N*-methoxy, *N*-methyl cinnamide,[68] 1-phenylethyl cinnamate,[69] DHQ-PCB[17a, 61] and DHQD-PCB.[17a, 61]

THF, *n*-hexane and toluene were distilled from sodium/benzophenone under argon and saturated with argon. Dichloromethane and triethylamine were distilled from CaH_2 under argon. All other solvents were reagent grade and used as received. If not stated otherwise, "standard work-up" refers to evaporation of the solvent under reduced pressure. Column chromatography was performed with silica gel (Merck, type 60, 0.063–0.2 mm and Machery Nagel, type 60, 0.015–0.025 mm). The numbering on the osmaimidazolidines was carried out as depicted at the right in agreement with a prior publication.[27]



Optical rotations were measured on a Perkin–Elmer 341 polarimeter. Concentrations are given in g per 100 mL as dichloromethane solutions. NMR spectra were recorded on a Bruker DPX 300 MHz and Bruker DRX

500 MHz spectrometer. All chemical shifts in NMR experiments are reported as ppm downfield from TMS. The following calibrations were used: $CDCl_3$ $\delta = 7.26$ and 77.00 ppm, C_6D_6 $\delta = 7.16$ and 128.00 ppm. IR spectra were recorded on a Nicolet Magna 550 FT-IR spectrometer. MS and HRMS experiments, and elemental analysis were performed on a Kratos MS 50 and a Elementar Analysensystem Vario EL, respectively, within the service centres at the Kekulé-Department, Bonn. HPLC determinations were carried out on a Knauer Wellchrome (injection valve A0258, pump K – 100, solvent organizer K-1500, UV-detector K-2600). Data for crystal structure analysis were measured on a Nonius Kappa CCD diffractometer.

Synthesis of imido osmium(VIII) complexes from osmium tetroxide: *N*-Trimethylsilyl-*tert*-butylamine (9.0 mL, 47 mmol) was added via syringe to a solution of (1.00 g, 3.9 mmol) of OsO_4 in freshly distilled *n*-hexane. The mixture was stirred for 14 h at 30 °C after which all volatile materials were removed under reduced pressure and the remaining dark brown residue was purified by column chromatography (silica gel, CH_2Cl_2) to yield, after a small first fraction of starting material, a broad yellow band that contained the monoimido complex. Changing the eluent to CH_2Cl_2/EtOAc (80:20) gave an orange band containing the bisimido complex **2**. The trisimido complex **3** was eluted as a dark red band by changing to EtOAc. Removal of the solvents under reduced pressure left the respective imido complexes that were stored under Ar at 2 °C.

Synthesis of bisimido osmium complex 2 and trisimido osmium complex 3 from monoimido osmium complex 1: A solution of **1** (1.6 g, 5.16 mmol) in freshly distilled THF (10 mL) was treated with *N*-trimethylsilyl *tert*-butylamine (9.0 mL, 47 mmol) and stirred under Ar at overnight. Standard work-up and column chromatography as described above yielded **2** (530 mg, 28 %) and **3** (1.15 g, 53 %).

Trioxo(*N*-*tert*-butylimido)osmium(VIII) (1):[21, 29, 30] Yellow solid; ^{1}H NMR (300 MHz, C_6D_6): $\delta = 0.87$ (s, 9H); ^{13}C NMR (75 MHz, C_6D_6): $\delta = 27.42$, 82.65.

Dioxobis(*N*-*tert*-butylimido)osmium(VIII) (2):[21, 29, 30] Orange solid; ^{1}H NMR (300 MHz, C_6D_6): $\delta = 1.12$ (s, 9H); ^{13}C NMR (75 MHz, C_6D_6): $\delta = 29.60$, 75.23.

Oxotris(*N*-*tert*-butylimido)osmium(VIII) (3):[21, 29] Orange to red solid; ^{1}H NMR (300 MHz, C_6D_6): $\delta = 1.24$ (s, 9H); ^{13}C NMR (75 MHz, C_6D_6): $\delta = 30.06$, 71.50.

Methyl 3-(3′-pyridinyl) acrylate (11): A solution of thionyl chloride (2.0 mL, 27 mmol) in freshly destilled absolute methanol (15 mL) was stirred under Ar at 0 °C. 3-(3′-Pyridinyl) acrylic acid (2.0 g, 13.4 mmol) was added in small portions and the resulting reaction mixture was stirred overnight at room temperature. It was evaporated under reduced pressure to a volume of about 3 mL, diluted with dichloromethane and washed with a saturated solution of ammonium chloride. The organic phase was separated, dried over $MgSO_4$ and evaporated to leave the title compound as a colourless solid (2.14 g, 98 %). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 3.74$ (s, 3H), 6.44(d, $J = 16.0$ Hz, 1H), 7.27 (dd, $J = 4.7$, 8.1 Hz, 1H), 7.60 (d, $J = 16.0$ Hz, 1H), 7.77 (dt_{ps}, $J = 1.7$, 8.1 Hz, 1H), 8.53 (dd, $J = 1.2$, 4.7 Hz, 1H), 8.67 (d, $J = 1.3$ Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 51.71$, 120.09, 123.69, 130.17, 134.35, 140.78, 149.21, 150.50, 166.46.

General procedure for diamination of achiral olefins with osmium bisimido complex 2: Solid bisimido osmium complex **2** was added in one portion to a solution of the appropriate olefin (1.2 mmol) in freshly distilled THF and the resulting solution was stirred at room temperature overnight (approx. 12 h). The solvent was evaporated under reduced pressure and the remaining crude oily residue was analysed by NMR. The pure product was obtained by column chromatography as indicated for the individual compound.

***trans*-1,3-Bis(*tert*-butyl)-2,2-dioxo-4-phenyl-5-(methyloxycarbonyl)-2-osma(VI)imidazolidine (12)**: Obtained as described above from reaction between methyl cinnamate (194 mg, 1.2 mmol) and complex **2** (346 mg, 1.0 mmol) in THF (3 mL). Evaporation of the solvent under reduced pressure followed by column chromatography (silica gel, dichloromethane/*n*-hexane 1:1) gave the title compound as an orange-to-red solid (496 mg, 0.94 mmol, 94 %). ^{1}H NMR (500 MHz, C_6D_6): $\delta = 1.06$ (s, 9H), 1.17 (s, 9H), 3.36 (s, 3H), 4.35 (s, 1H), 4.97 (s, 1H), 6.97 – 7.01 (m, 1H), 7.05 – 7.10 (m, 2H), 7.28 – 7.32 (m, 2H); ^{13}C NMR (125 MHz, C_6D_6): $\delta = 29.77$, 30.60, 51.67, 66.79, 67.66, 82.32, 85.24, 126.71, 128.29, 128.85, 146.08, 173.26; IR (KBr): $\tilde{\nu} = 2980$, 1749, 1468, 1454, 1369, 1196, 1169, 999, 904, 887 cm^{-1}; MS (EI): *m*/*z* (%): 528 (22) $[M]^+$, 513 (28), 469 (100), 413 (90), 357 (41); HRMS: calcd for $C_{18}H_{28}N_2O_4{}^{188}Os$: 524.1608, found: 524.1606.

***trans*-1,3-Bis(*tert*-butyl)-2,2-dioxo-4-phenyl-5-(*tert*-butyloxycarbonyl)-2-osma(VI)imidazolidine (13)**: Obtained as described above from reaction between *tert*-butyl cinnamate (1.14 g, 5.59 mmol) and complex **2** (1.7 g, 4.66 mmol) in THF (10 mL). Evaporation of the solvent under reduced pressure followed by column chromatography (silica gel, dichloromethane/diethyl ether 10:1) gave the title compound as a red solid (2.55 g, 4.47 mmol, 96 %). ^{1}H NMR (300 MHz, C_6D_6): $\delta = 1.12$ (s, 9H), 1.19 (s, 9H), 1.39 (s, 9H), 4.15 (s, 1H), 4.98 (s, 1H), 7.12 – 7.24 (m, 5H); ^{1}H NMR (300 MHz, CD_2Cl_2): $\delta = 1.14$ (s, 9H), 1.21 (s, 9H), 1.41 (s, 9H), 4.18 (s, 1H), 5.00 (s, 1H), 7.16 – 7.22 (m, 5H); ^{13}C NMR (75 MHz, C_6D_6): $\delta = 27.96$, 29.94, 30.84, 66.79, 67.49, 81.99, 82.61, 86.26, 126.77, 127.68, 128.85, 146.43, 172.00; ^{13}C NMR (75 MHz, CD_2Cl_2): $\delta = 26.95$, 28.95, 29.77, 66.34, 67.06, 81.38, 81.48, 84.75, 125.62, 126.95, 127.77, 144.91, 170.82; IR (KBr): $\tilde{\nu} = 2978$, 1714, 1365, 1298, 1184, 1155, 904, 891 cm^{-1}; MS (EI): *m*/*z* (%): 570 (8) $[M]^+$, 469 (100), 413 (79), 357 (38); HRMS: calcd for $C_{21}H_{34}N_2O_4{}^{188}Os$: 566.2077, found: 566.2085.

***trans*-1,3-Bis(*tert*-butyl)-2,2-dioxo-4-phenyl-5-(benzyloxycarbonyl)-2-osma(VI)imidazolidine (14)**: Obtained as described above from reaction between benzyl cinnamate (286 mg, 1.2 mmol) and complex **2** (364 mg, 1.0 mmol) in THF (5 mL). Evaporation of the solvent under reduced pressure followed by column chromatography (silica gel, dichloromethane/diethyl ether 2:1) gave the title compound as a dark red solid (538 mg, 0.89 mmol, 89 %). ^{1}H NMR (300 MHz, C_6D_6): $\delta = 1.13$ (s, 9H), 1.20 (s, 9H), 4.46 (s, 1H), 5.06 (d, $J = 12.1$ Hz, 1H), 5.10 (s, 1H), 5.17 (d, $J = 12.1$ Hz, 1H), 7.05 – 7.27 (m, 6H), 7.34 – 7.41 (m, 2H), 7.46 – 7.51 (m, 2H); ^{13}C NMR (75 MHz, C_6D_6): $\delta = 29.83$, 30.60, 66.84, 67.14, 67.62, 82.42, 85.39, 126.73, 128.06, 128.68, 128.75, 128.89, 129.35, 135.75, 146.06, 172.49; IR (KBr): $\tilde{\nu} =$ 2972, 2362, 2337, 1751, 1734, 1456, 1367, 1190, 1159, 908, 895 cm^{-1}; MS (EI): *m*/*z* (%): 604 (9) $[M]^+$, 469 (100), 413 (63), 357 (36); HRMS: calcd for $C_{24}H_{32}N_2O_4{}^{188}Os$: 600.1920, found: 600.1914; elemental analysis calcd (%) for $C_{24}H_{32}N_2O_4Os$: C 47.82, H 5.35, N 4.65; found: C 48.09, H 5.61, N 4.91.

***trans*-1,3-Bis(*tert*-butyl)-2,2-dioxo-4-methyl-5-(methyloxycarbonyl)-2-osma(VI)imidazolidine (15)**: Obtained as described above from reaction between methyl crotonate (120 mg, 1.2 mmol) and complex **2** (364 mg, 1.0 mmol) in THF (2 mL). Evaporation of the solvent under reduced pressure followed by column chromatography (silica gel, dichloromethane/diethyl ether 10:1) gave the title compound as a dark purple solid (424 mg, 0.91 mmol, 91 %). ^{1}H NMR (300 MHz, C_6D_6): $\delta = 0.90$ (d, $J = 6.2$ Hz, 3H), 1.14 (s, 9H), 1.19 (s, 9H), 3.29 (s, 3H), 3.86 (q, $J = 6.2$ Hz, 1H), 3.87 (s, 1H); ^{13}C NMR (75 MHz, C_6D_6): $\delta = 24.44$, 29.93, 30.54, 51.48, 66.46, 66.64, 74.56, 81.99, 173.28; IR (KBr): $\tilde{\nu} = 2976$, 2362, 2337, 1751, 1365, 1196, 1176, 909, 887 cm^{-1}; MS (EI): *m*/*z* (%): 466 (16) $[M]^+$, 451 (24), 407 (33), 351 (55), 295 (36), 84 (37), 57 (100); HRMS: calcd for $C_{13}H_{26}N_2O_4{}^{188}Os$: 462.1452; found: 462.1456.

***trans*-1,3-Bis(*tert*-butyl)-2,2-dioxo-4-methyl-5-(ethyloxycarbonyl)-2-osma(VI)imidazolidine (16)**: Obtained as described above from reaction between ethyl crotonate (137 mg, 1.2 mmol) and complex **2** (364 mg, 1.0 mmol) in THF (2 mL). Evaporation of the solvent under reduced pressure followed by column chromatography (silica gel, dichloromethane/diethyl ether 10:1) gave the title compound as a deep red to purple solid (442 mg, 0.92 mmol, 92 %). ^{1}H NMR (300 MHz, C_6D_6): $\delta = 0.91$ (d, $J = 6.0$ Hz, 3H), 0.99 (t, $J = 7.1$ Hz, 3H), 1.16 (s, 9H), 1.22 (s, 9H), 3.85 (q, $J = 7.1$ Hz, 2H), 3.87 (s, 1H), 3.91 (q, $J = 6.0$ Hz, 1H); ^{13}C NMR (75 MHz, C_6D_6): $\delta = 14.04$, 24.46, 29.99, 30.57, 61.08, 66.45, 66.53, 74.57, 82.07, 172.88; IR (KBr): $\tilde{\nu} = 2966$, 2362, 2330, 1748, 1349, 1190, 1119, 910, 885 cm^{-1}; MS (EI): *m*/*z* (%): 480 (8) $[M]^+$, 465 (9), 407 (28), 351 (41), 295 (22), 84 (42), 57 (100); HRMS: calcd for $C_{14}H_{28}N_2O_4{}^{188}Os$: 476.1608, found: 476.1603.

***trans*-1,3-Bis(*tert*-butyl)-2,2-dioxo-5-(methyloxycarbonyl)-2-osma(VI)imidazolidine (17)**: Obtained as described above from reaction between methyl acrylate (50 μL, 0.58 mmol) and complex **2** (177 mg, 0.48 mmol) in THF (1.5 mL). Evaporation of the solvent under reduced pressure followed by column chromatography (silica gel, dichloromethane/*n*-hexane 1:1) gave the title compound as a red solid (213 mg, 0.47 mmol, 98 %). ^{1}H NMR (300 MHz, C_6D_6): $\delta = 1.14$ (s, 9H), 1.24 (s, 9H), 3.27 (s, 3H), 3.35 (dd, $J = 0.75$ Hz, $J = 12.4$ Hz, 1H), 3.46 (dd, $J = 6.6$ Hz, $J = 12.4$ Hz, 1H), 4.14 (dd, $J = 0.75$ Hz, $J = 6.6$ Hz, 1H); ^{13}C NMR (75 MHz, C_6D_6): $\delta = 29.34$, 29.82, 51.60, 66.63, 66.79, 68.80, 75.19, 173.64; IR (KBr): $\tilde{\nu} =$ 2970, 1751, 1734, 1466, 1367, 1188, 1169, 1111, 1038, 1014, 1001, 891 cm^{-1}; MS (EI): *m*/*z* (%):

450 (27) $[M]^+$, 437 (28), 393 (100), 337 (42), 281 (53); HRMS: calcd for $C_{12}H_{24}N_2O_4{}^{188}Os$: 448.1295, found: 448.1303.

***trans*-1,3-Bis(*tert*-butyl)-2,2-dioxo-4,5-bis(methyloxycarbonyl)-2-osma-(VI)imidazolidine (18)**:[21] Obtained as described above from reaction between dimethyl fumarate (173 mg, 1.2 mmol) and complex **2** (364 mg, 1.0 mmol) in THF (4 mL). Evaporation of the solvent under reduced pressure followed by column chromatography (silica gel, dichloromethane/*n*-hexane 4:1) gave the title compound as a red solid (457 mg, 0.9 mmol, 90%). ^{1}H NMR (300 MHz, C_6D_6): $\delta = 1.16$ (s, 18H), 3.30 (s, 6H), 4.50 (s, 2H); ^{13}C NMR (75 MHz, C_6D_6): $\delta = 29.85$, 52.02, 66.70, 80.55, 172.20; IR (KBr): $\tilde{\nu} = 2960$, 1743, 1432, 1365, 1207, 1117, 937, 922 cm^{-1}; MS (EI): *m*/*z* (%): 510 (9) $[M]^+$, 495 (28), 451 (100), 395 (33), 339 (66).

***trans*-1,3-Bis(*tert*-butyl)-2,2-dioxo-4-(3′-pyridinyl)-5-(methyloxycarbonyl)-2-osma(VI)imidazolidine (19)**: Obtained as described above from reaction between methyl 3-(3′-pyridinyl)acrylate (106 mg, 0.65 mmol) and complex **2** (200 mg, 0.54 mmol) in freshly distilled THF (3 mL). Evaporation of the solvent under reduced pressure followed by column chromatography (silica gel, dichloromethane/diethyl ether 10:1) gave the title compound as a bright red solid (222 mg, 0.42 mmol, 78%). ^{1}H NMR (300 MHz, C_6D_6): $\delta =$ 1.01 (s, 9H), 1.08 (s, 9H), 3.32 (s, 3H), 4.19 (s, 1H), 4.87 (s, 1H), 6.68 (dd, $J = 4.7$, 8.0 Hz, 1H), 7.59 (dt_{ps}, $J = 1.7$, 8.0 Hz, 1H), 8.41 (dd, $J = 1.9$, 4.7 Hz, 1H), 8.66 (d, $J = 2.0$ Hz, 1H); ^{13}C NMR (75 MHz, C_6D_6): $\delta = 29.73$, 30.56, 51.84, 66.75, 67.58, 79.72, 84.79, 123.37, 133.10, 141.26, 149.24, 149.81, 172.72; IR (KBr): $\tilde{\nu} = 3003$, 2972, 2968, 2355, 2339, 1755, 1463, 1366, 1194, 902, 891 cm^{-1}; MS (EI): *m*/*z* (%): 528 (4) $[M]^+$, 478 (22), 414 (24), 358 (14), 147 (28), 105 (61), 57 (100); HRMS: calcd for $C_{17}H_{27}N_3O_4{}^{188}Os$: 525.1558, found: 525.1553.

Competition experiment for diamination with bisimido complex 2: A solution of methyl cinnamate (162 mg, 1 mmol) and dimethyl fumarate (144 mg, 1 mmol) in C_6D_6 (3 mL) under Ar was treated with complex **2** (364 mg, 1 mmol) and stirred at RT. The reaction was monitored by ^{1}H NMR with samples being taken every 60 min and the reaction outcome was determined by comparison of the integrals of the respective signals in the ^{1}H NMR spectra.

***cis*-1,3-Bis(*tert*-butyl)-2,2-dioxo-4,5-bis(methyloxycarbonyl)-2-osma(VI)-imidazolidine (21)**: A solution of dimethyl maleic ester (72 mg, 0.5 mmol) in THF (5 mL) was treated with complex **2** (91 mg, 0.25 mmol) and stirred for 14 h at RT. The solvent was removed under reduced pressure. Analysis by ^{1}H NMR showed a ratio of 1.3:1 for the title compound and **18**. Column chromatography (silica gel, *n*-hexane/ethyl acetate 4:1) gave a red solid material (136 mg, 0.21 mmol, 84%) which was analysed by ^{1}H NMR to consist of a 1:1.7 mixture of the title compound and **18**. Data for **21**: ^{1}H NMR (300 MHz, C_6D_6): $\delta = 0{,}97$ (s, 18H), 3.07 (s, 6H), 4.42 (s, 2H).

***trans*-1,3-Bis(*tert*-butyl)-2,2-dioxo-4-phenyl-5-(*N*-*tert*-butylaminocarbonyl)-2-osma(VI)imidazolidine (28)**: Obtained as described above from reaction between *N*-*tert*-butyl cinnamoyl amide (244 mg, 1.2 mmol) and complex **2** (364 mg, 1.0 mmol) in THF (3 mL). Evaporation of the solvent under reduced pressure followed by column chromatography (silica gel *n*-hexane/ethyl acetate 4:1) gave the title compound as a bright red solid (506 mg, 0.89 mmol, 89%). ^{1}H NMR (300 MHz, C_6D_6): $\delta = 1.02$ (s, 9H), 1.15 (s, 9H), 1.37 (s, 9H), 4.31 (s, 1H), 5.25 (s, 1H), 5.77 (br s, 1H), 6.92–7.01 (m, 1H), 7.02–7.10 (m, 2H), 7.31–7.40 (m, 2H); ^{13}C NMR (75 MHz, C_6D_6): $\delta = 28.70$, 29.77, 30.40, 51.48, 67.45, 67.96, 83.23, 87.66, 127.87, 128.17, 128.82, 146.28, 171.82; IR (KBr): $\tilde{\nu} = 2976$, 1674, 1515, 1456, 1394, 1369, 1311, 1242, 1184, 995, 983, 901, 891 cm^{-1}; MS (EI): *m*/*z* (%): 569 (4) $[M]^+$, 469 (94), 413 (100), 357 (46), 310 (19); HRMS: calcd for $C_{21}H_{35}N_3O_3{}^{188}Os$: 565.2237, found: 565.2242.

***trans*-1,3-Bis(*tert*-butyl)-2,2-dioxo-4-methyl-5-(*N*-*tert*-butylaminocarbonyl)-2-osma(VI)imidazolidine (29)**: Obtained as described above from reaction between *N*-*tert*-butyl crotyl amide (141 mg, 1.0 mmol) and complex **2** (303 mg, 0.83 mmol) in THF (2 mL). Evaporation of the solvent under reduced pressure followed by column chromatography (silica gel *n*-hexane/ethyl acetate 4:1) gave the title compound as a bright red solid (362 mg, 0.72 mmol, 86%). ^{1}H NMR (300 MHz, C_6D_6): $\delta = 0.90$ (d, $J =$ 6.2 Hz, 3H), 1.11 (s, 9H), 1.16 (s, 9H), 1.31 (s, 9H), 3.85 (s, 1H), 4.12 (q, $J =$ 6.2 Hz, 3H), 4.59–4.65 (br s, 1H); ^{13}C NMR (75 MHz, C_6D_6): $\delta = 14.16$, 28.64, 29.92, 30.30, 50.66, 51.28, 67.09, 164.53; IR (KBr): $\tilde{\nu} = 2970$, 2927, 2362, 2333, 1674, 1653, 1456, 1367, 1190, 906, 885 cm^{-1}; MS (EI): *m*/*z* (%): 507 (9) $[M]^+$, 451 (45), 352 (61), 296 (22), 57 (100); elemental analysis calcd (%) for $C_{16}H_{33}N_3O_3Os$: C 38.00, H 6.58, N 8.31; found: C 37.68, H 6.65, N 8.22.

***trans*-1,3-Bis(*tert*-butyl)-2,2-dioxo-5-(*N*-*tert*-butylaminocarbonyl)-2-osma(VI)imidazolidine (30)**: Obtained as described above from reaction between *N*-*tert*-butyl acrylamide (120 mg, 0.94 mmol) and complex **2** (287 mg, 0.79 mmol) in THF (1 mL). Evaporation of the solvent under reduced pressure followed by column chromatography (silica gel, *n*-hexane/ethyl acetate 4:1) gave the title compound as a bright red solid (345 mg, 0.70 mmol, 89%). ^{1}H NMR (300 MHz, C_6D_6): $\delta = 0.82$ (s, 9H), 0.95 (s, 9H), 1.04 (s, 9H), 3.19–3.26 (m, 2H), 3.34 (dd, $J = 0.8$, 12.2 Hz, 1H), 3.85 (dd, $J = 0.8$, 6.4 Hz, 1H); ^{13}C NMR (75 MHz, C_6D_6): $\delta = 28.68$, 29.18, 29.81, 50.82, 51.21, 53.26, 66.86, 67.48, 169.98; IR (KBr): $\tilde{\nu} = 3388$, 3265, 3068, 2970, 2362, 2337, 1670, 1625, 1551, 1458, 1363, 1220, 982, 908, 887 cm^{-1}; MS (EI): *m*/*z* (%): 493 (2) $[M]^+$, 394 (54), 337 (40), 57 (100); HRMS: calcd for $C_{15}H_{31}N_3O_3{}^{188}Os$: 489.1924, found: 489.1931; elemental analysis calcd (%) for $C_{15}H_{31}N_3O_3Os$: C 36.64, H 6.36, N 8.55; found: C 36.33, H 6.61, N 8.44.

***trans*-1,3-Bis(*tert*-butyl)-2,2-dioxo-4-phenyl-5-(*N*-methoxy,*N*-methyl-aminocarbonyl)-2-osma(VI)imidazolidine (31)**: Obtained as described above from reaction between *N*-methoxy,*N*-methyl-cinnamoylamide (100 mg, 0.52 mmol) and complex **2** (159 mg, 0.44 mmol) in THF (3 mL). Evaporation of the solvent under reduced pressure followed by column chromatography (silica gel, *n*-hexanes/ethyl acetate 2:1) gave the title compound as a red oily solid (203 mg, 0.37 mmol, 84%). ^{1}H NMR (300 MHz, C_6D_6): $\delta = 1.24$ (s, 9H), 1.25 (s, 9H), 2.81 (s, 3H), 3.05 (s, 3H), 4.71 (s, 1H), 4.96 (S, 1H), 7.01–7.17 (m, 3H), 7.43–7.48 (m, 2H); ^{13}C NMR (75 MHz, C_6D_6): $\delta = 30.30$, 30.90, 33.11, 60.67, 66.80, 67.72, 81.35, 82.21, 126.86, 127.79, 128.11, 128.76, 146.99, 174.10; IR (KBr): $\tilde{\nu} = 2972$, 2933, 2362, 2337, 1676, 1464, 1367, 1190, 909, 903 cm^{-1}; MS (EI): *m*/*z* (%): 557 (3) $[M]^+$, 469 (40), 413 (62), 357 (44), 146 (33), 105 (31), 57 (100); HRMS: calcd for $C_{19}H_{31}N_3O_4{}^{188}Os$: 553.1872, found: 553.1883; elemental analysis calcd (%) for $C_{19}H_{31}N_3O_4Os$: C 41.07, H 5.62, N 7.56; found: C 41.00, H 5.79, N 7.22.

***trans*-1,3-Bis(*tert*-butyl)-2,2-dioxo-4-phenyl-5-(phenylcarbonyl)-2-osma-(VI)imidazolidine (32)**: Obtained as described above from reaction between chalcone (125 mg, 0.6 mmol) and complex **2** (183 mg, 0.5 mmol) in THF (4 mL). Evaporation of the solvent under reduced pressure followed by column chromatography (silica gel, dichloromethane/*n*-hexane 4:1) gave the title compound as a bright red solid (260 mg, 0.45 mmol, 91%). ^{1}H NMR (300 MHz, C_6D_6): $\delta = 1.00$ (s, 9H), 1.03 (s, 9H), 4.68 (s, 1H), 5.26 (s, 1H), 6.90–7.11 (m, 6H), 7.18–7.25 (m, 2H), 7.80–7.85 (m, 2H); ^{13}C NMR (75 MHz, C_6D_6): $\delta = 30.39$, 30.80, 88.78, 67.56, 81.20, 85.89, 126.75, 128.20, 128.59, 129,13, 129.37, 133.61, 136.00, 146.43, 196.76; IR (KBr): $\tilde{\nu} = 2972$, 1689, 1450, 1369, 1212, 1184, 970, 901, 894 cm^{-1}; MS (EI): *m*/*z* (%): 573 $[M]^+$, 496 (53), 393 (47), 146 (29), 195 (25), 57 (100); elemental analysis calcd (%) for $C_{23}H_{30}N_2O_3Os$: C 48.23, H 5.28, N 4.89; found: C 48.08, H 5.33, N 4.77.

***trans*-1,3-Bis(*tert*-butyl)-2,2-dioxo-4-phenyl-5-formyl-2-osma(VI)imidazolidine (33)**: Obtained as described above from reaction between cinnamic aldehyde (146 mg, 1.2 mmol) and complex **2** (364 mg, 1.0 mmol) in THF (5 mL). Evaporation of the solvent under reduced pressure followed by column chromatography (silica gel, dichloromethane/diethyl ether 10:1) gave the title compound as a dark red solid (527 mg, 0.92 mmol, 92%). ^{1}H NMR (300 MHz, C_6D_6): $\delta = 0.94$ (s, 9H), 1.09 (s, 9H), 3.86 (d, $J =$ 3.0 Hz, 1H), 4.89 (s, 1H), 6.94–7.07 (m, 5H), 9.26 (d, $J = 3.0$ Hz, 1H); ^{13}C NMR (75 MHz, C_6D_6): $\delta = 30.12$, 30.46, 66.89, 67.88, 80.57, 89.20, 126.85, 128.08, 128.86, 144.82, 201.47; IR (KBr): $\tilde{\nu} = 2976$, 1731, 1464, 1366, 1184, 897 cm^{-1}; MS (EI): *m*/*z* (%): 469 (51) $[M - CHO]^+$, 413 (72), 357 (64), 146 (43), 57 (100); HRMS: calcd for $C_{17}H_{26}N_2O_3{}^{188}Os$: 494.1499, found: 494.1495; elemental analysis calcd (%) for $C_{17}H_{26}N_2O_3Os$: C 41.11, H 5.28, N 5.64; found: C 41.00, H 5.71, N 5.67.

***trans*-1,3-Bis(*tert*-butyl)-2,2-dioxo-5-cyano-2-osma(VI)imidazolidine (35)**: Obtained as described above from reaction between acrylonitrile (50 μL, 0.75 mmol) and complex **2** (92 mg, 0.25 mmol) in THF (1 mL). Evaporation of the solvent under reduced pressure followed by column chromatography (silica gel *n*-hexane/ethyl acetate 4:1) gave the title compound as a bright red, air-sensitive solid (79 mg, 0.19 mmol, 76%). ^{1}H NMR (300 MHz, C_6D_6): $\delta = 1.17$ (s, 9H), 1.22 (s, 9H), 3.30 (dd, $J = 0.78$ Hz, $J = 11.9$ Hz, 1H), 3.46 (dd, $J = 6.7$ Hz, $J = 11.9$ Hz, 1H), 4.14 (dd, $J = 0.78$ Hz, $J = 6.7$ Hz, 1H); ^{13}C NMR (75 MHz, C_6D_6): $\delta = 29.03$, 29.58, 52.53, 64.30, 65.81, 67.78,

169.68; IR (KBr): $\tilde{\nu}$ = 3021, 2965, 1751, 1442, 1295, 1182, 894, 704 cm^{-1}; MS (EI): *m*/*z* (%): 418 (8) $[M]^+$, 393 (100), 337 (32), 281 (45); HRMS: calcd for $C_{11}H_{21}N_3O_2{}^{188}Os$: 415.1191, found: 415.1189.

***trans*-1,3-Bis(*tert*-butyl)-2-oxo-2-*tert*-butylimido-4,5-bis(methyloxycarbonyl)-2-osma(VI)imidazolidine (36)**:[21] Obtained as described above from reaction between dimethyl fumarate (86 mg, 0.6 mmol) and complex **3** (210 mg, 0.5 mmol) in THF (2 mL). Evaporation of the solvent under reduced pressure followed by column chromatography (silica gel, dichloromethane/ethyl acetate 10:1) gave the title compound as deep red solid (260 mg, 0.46 mmol, 92%). ^{1}H NMR (300 MHz, C_6D_6): δ = 1.27 (s, 9H), 1.28 (s, 9H), 1.49 (s, 9H), 3.22 (s, 3H), 3.41 s, 3H), 4.56 (s, 3H), 4.58 (s, 3H); ^{13}C NMR (75 MHz, C_6D_6): δ = 30.31, 31.35, 31.69, 51.64, 51.68, 63.66, 64.17, 69.33, 80.56, 81.96, 173.39, 173.97; MS (EI): *m*/*z* (%): 565 (22) $[M]^+$, 550 (22), 506 (100), 394 (20); HRMS: calcd for $C_{18}H_{35}N_3O_5{}^{188}Os$: 561.2135, found: 561.2132; analytical HPLC: Daicel Chiralpak AS, 254 nm, *n*-hexane/2-propanol 98:2, 0.5 mL min^{-1}; t_R = 13.4 min [(+)-**36**], 15.4 min [(−)-**36**].

***trans*-1,3-Bis(*tert*-butyl)-2-oxo-2-*tert*-butylimido-4,5-bis(ethyloxycarbonyl)-2-osma(VI)imidazolidine (38)**: Obtained as described above from reaction between diethyl fumarate (103 mg, 0.6 mmol) and complex **3** (210 mg, 0.5 mmol) in THF (2 mL). Evaporation of the solvent under reduced pressure followed by column chromatography (silica gel, dichloromethane/ethyl acetate 10:1) gave the title compound as deep red solid (270 mg, 0.46 mmol, 91%). ^{1}H NMR (300 MHz, C_6D_6): δ = 0.90 (t, *J* = 7.2 Hz, 3H), 1.08 (t, *J* = 7.2 Hz, 3H), 1.31 (s, 9H), 1.34 (s, 9H), 1.51 (s, 9H), 3.84 (q, *J* = 7.2 Hz, 2H), 4.01 (q, *J* = 7.2 Hz, 2H), 4.59 (d, *J* = 0.6 Hz, 1H), 4.63 (d, *J* = 0.6 Hz, 1H); ^{13}C NMR (75 MHz, C_6D_6): δ = 14.48, 14.50, 30.68, 31.81, 32.16, 61.29, 61.55, 63.97, 64.47, 69.59, 80.93, 82.41, 173.30, 173.90; IR (KBr): $\tilde{\nu}$ = 2972, 2935, 2904, 2870, 1751, 1464, 1365, 1234, 1200, 1108, 962, 893 cm^{-1}; MS (EI): *m*/*z* (%): 593 (17) $[M]^+$, 520 (100), 464 (39), 408 (36), 72 (28), 57 (67); HRMS: calcd for $C_{20}H_{39}N_3O_5{}^{188}Os$: 589.2448, found: 589.2450.

Dihydroxylation/aminohydroxylation of dimethyl fumarate (10) with monoimido complex 1: Solid monoimido complex **1** (309 mg, 1 mmol) was added in one portion to a solution of dimethyl fumarate (290 mg, 2 mmol) in freshly distilled THF (5 mL) and the resulting solution was stirred at room temperature overnight and then treated with a saturated solution of sodium bisulfite. The aqueous layer was extracted with dichloromethane, dried over $MgSO_4$ and evaporated under reduced pressure. The crude product as analysed by NMR to indicate unreacted starting material, dimethyl tartrate **39** and the monoaza analogue **40**. Purification by column chromatography (dichloromethane/ethyl acetate 4:1) gave **39** as first, and **40** as second fraction.

Dimethyl tartrate (39): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.85 (s, 6H), 4.55 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 53.08, 72.00, 171.89.

Dimethyl 2-hydroxy-3-(*N*-*tert*-butyl)amino succinate (40): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.04 (s, 9H), 3.28–3.42 (br s, 2H), 3.77 (s, 3H), 3.78 (s, 3H), 3.84 (d, *J* = 3.4 Hz, 1H), 4.42 (d, *J* = 3.4 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 28.71, 51.73, 52.44, 52.75, 57.58, 72.38, 172.13, 173.11; IR (KBr): $\tilde{\nu}$ = 3012, 2976, 2970, 1783, 1764, 1127, 1008, 989 cm^{-1}; MS (EI): *m*/*z* (%): 234 (21) $[M]^+$, 178 (100), 162 (35), 122 (41); HRMS: calcd for $C_{10}H_{19}NO_5$: 233.1263, found: 233.1261; elemental analysis calcd (%) for $C_{10}H_{19}NO_5$: C 51.49, H 8.21, N 6.00; found: C 51.33, H 8.59, N 6.23.

Competitive bisfunctionalisation of dimethyl fumarate (Figure 5): To a solution of dimethyl fumarate (722 mg, 5 mmol) in freshly distilled THF (5 mL) were added subsequentely monoimido complex **1** (155 mg, 0.5 mmol), bisimido complex **2** (182 mg, 0.5 mmol) and trisimido complex **3** (210 mg, 0.5 mmol) and the resulting solution was stirred at room temperature. Every 120 min, samples were taken from this solution and treated with a saturated solution of sodium bisulfite. Extraction with dichloromethane, drying over $MgSO_4$ and evaporation of the organic solvent under reduced pressure gave a crude product. This was analysed by ^{1}H NMR to determine the ratio of unreacted starting material, **12**, **18** and **39**. Formation of **40** was below detection level.

Screening of chiral auxiliaries for diastereoselective diamination with complex 2: In these cases, diamination was carried out as described above for the achiral substrates and the diastereomeric ratio of the crude product mixture was estimated from a comparison of the hydrogen signals at C-4 and C-5 of the osmaimidazolidines. Generally, these reactions were not worked-up and purified any further, and a representative example is given below for the diamination of (−)-8-phenyl menthyl cinnamate.

Synthesis of 8-phenyl menthyl cinnamate (41d):[74] DMAP (672 mg, 5.5 mmol) was added in one portion at 0 °C to a solution of cinnamoyl chloride (830 mg, 5 mmol) in freshly distilled THF (30 mL). An immediate precipitate was observed and the resulting inhomogeneous solution was stirred for 15 min before a solution of 8-phenyl menthol (1.16 g, 5 mmol) in dichloromethane (5 mL) was added. The resulting solution was allowed to warm to room temperature and stirred overnight. The solvent was removed under reduced pressure and the crude product was purified by column chromatograpy (silica gel, hexanes/ethyl acetate 15:1) to give the title compound as a white solid (1.1 g, 61%). ^{1}H NMR (300 MHz, C_6D_6): δ = 0.74–1.10 (m, 3H), 0.80 (d, *J* = 6.6 Hz, 3H), 1.15 (s, 3H), 1.25 (s, 3H), 1.35–1.75 (m, 3H), 1.80–1.93 (m, 1H), 1.96–2.10 (m, 1H), 4.83 (dt, *J* = 4.4, 10.8 Hz, 1H), 5.69 (d, *J* = 16.0, 1H), 6.96–7.33 (m, 11H); ^{13}C NMR (75 MHz, C_6D_6): δ = 21.77, 24.28, 26.50, 28.42, 31.28, 34.63, 39.58, 50.68, 74.28, 118.77, 124.73, 125.41, 127.92, 127.96, 128.68, 129.86, 134.57, 143.54, 151.79, 166.00.

Asymmetric diamination of 8-phenyl menthyl cinnamate 41d: (−)-8-Phenyl menthyl cinnamate (181 mg, 0.5 mmol) was added to a solution of bis(*N*-*tert*-butylimido)dioxoosmium(VIII) (**2**) (183 mg, 0.5 mmol) in freshly distilled THF (5 mL). The resulting orange solution was stirred at RT for 8 h during which it turned dark red. The solvent was removed under reduced pressure to leave a red-brown oil which was passed through a small pad of silica gel (hexanes/ethyl acetate 4:1). After evaporation of the solvents under reduced pressure, the pure mixture of the two diastereomers (248 mg, 0.34 mmol, 68% yield) was separated by semipreparative HPLC (Knauer Eurospher 100CN, *t*BuOCH$_3$/*n*-hexane 15:85, 14 mL min^{-1}, 254 nm). t_R = 12.9 min for **43d** and 15.6 min for **42d**; analytical HPLC: Knauer Eurospher 100CN, *t*BuOCH$_3$/*n*-hexane 20:80, 1.0 mL min^{-1}, 254 nm, t_R = 7.4 min [(+)-**43d**], 8.8 min [(−)-**42d**].

(4*R*,5*S*)-*trans*-1,3-Bis(*tert*-butyl)-2,2-dioxo-4-phenyl-5-[(−)-(8-phenylmenthyloxy)carbonyl]-2-osma(VI)imidazolidine (42d): Obtained as a purple solid; $[\alpha]_D^{28}$ = −1922 (*c* = 0.15); ^{1}H NMR (300 MHz, C_6D_6): δ = 0.47–1.39 (m, 6H), 0.71 (d, *J* = 6.6 Hz, 3H), 1.16 (s, 9H), 1.29 (s, 3H), 1.34 (s, 9H), 1.58 (s, 3H), 1.85–1.99 (m, 1H), 2.01–2.12 (m, 1H), 4.32 (s, 1H), 5.02 (dt, *J* = 4.3, 10.5 Hz, 1H), 5.21 (s, 1H), 7.00–7.28 (m, 9H), 7.40–7.46 (m, 1H); ^{13}C NMR (75 MHz, C_6D_6): δ = 21.81, 23.97, 27.75, 30.23, 30.95, 31.37, 31.39, 34.56, 40.71, 41.55, 50.59, 66.84, 67.83, 76.72, 81.73, 85.03, 125.99, 127.02, 128.17, 128.52, 128.91, 146, 08, 150.42, 171.73; IR (KBr): $\tilde{\nu}$ = 2972, 2950, 2868, 1730, 1367, 1194, 912, 885, 768, 700 cm^{-1}; MS (EI): *m*/*z* (%): 728 (2) $[M]^+$, 469 (17), 413 (8), 279 (15), 146 (100); HRMS: calcd for $C_{33}H_{48}N_2O_4{}^{188}Os$: 724.3172, found: 724.3161.

(4*S*,5*R*)-*trans*-1,3-Bis(*tert*-butyl)-2,2-dioxo-4-phenyl-5-[(−)-(8-phenylmenthyloxy)carbonyl]-2-osma(VI)imidazolidine (43d): Obtained as a purple solid. $[\alpha]_D^{28}$ = +1110 (*c* = 0.12); ^{1}H NMR (300 MHz, C_6D_6): δ = 0.79 (d, *J* = 6.4 Hz, 3H), 0.80–0.95 (m, 4H), 1.08 (s, 3H), 1.18 (s, 9H), 1.19 (s, 9H), 1.22 (s, 3H), 1.43–1.55 (m, 1H), 1.60–1.71 (m, 1H), 2.05–2.20 (m, 2H), 3.64 (s, 1H), 4.77 (dt, *J* = 4.1, 10.7 Hz, 1H), 4.90 (s, 1H), 6.85–6.93 (m, 1H), 7.01–7.28 (m, 9H); ^{13}C NMR (75 MHz, C_6D_6): δ = 21.85, 23.77, 26.74, 29.44, 30.23, 30.93, 31.28, 34.81, 39.49, 41.80, 50.19, 66.81, 67.44, 76.35, 81.31, 84.11, 125.41, 125.69, 127.18, 127.67, 127.90, 128.31, 128.63, 171.23; IR (KBr): $\tilde{\nu}$ = 2970, 2927, 2870, 1741, 1367, 1192, 1169, 913, 901, 700 cm^{-1}; MS (EI): *m*/*z* (%): 728 (2) $[M]^+$, 469 (17), 413 (11), 279 (39), 146 (100); HRMS: calcd for $C_{33}H_{48}N_2O_4{}^{188}Os$: 724.3172, found: 724.3166.

Synthesis of 8-phenyl menthyl crotylate (44): To a solution of crotyl chloride (462 mg, 3 mmol) in freshly distilled THF (30 mL) at 0 °C was added DMAP (403 mg, 3.3 mmol) in one portion. An immediate precipitate was observed and the resulting inhomogeneous solution was stirred for 15 min before a solution of 8-phenyl menthol (697 mg, 3 mmol) in dichloromethane (5 mL) was added. The resulting solution was allowed to warm to room temperature and stirred overnight. The solvent was removed under reduced pressure and the crude product was purified by column chromatograpy (silica gel, hexanes/ethyl acetate 12:1) to give the title compound as a white solid (0.488 g, 54%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.71–1.17 (m, 3H), 0.76 (d, *J* = 6.6 Hz, 3H), 1.12 (s, 3H), 1.21 (s, 3H), 1.32–1.41 (m, 1H), 1.61 (dd, *J* = 1.7, 7.0 Hz, 3H), 1.79–1.86 (m, 1H), 1.90–1.98 (m, 1H), 4.83 (dt, *J* = 4.4, 10.6 Hz, 1H), 5.24 (dd, *J* = 1.7, 15.5 Hz, 1H), 6.35 (ddd, *J* = 1.7, 7.0, 15.5 Hz, 1H), 6.98–7.03 (m, 2H), 7.11–7.19 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 17.61, 21.70, 25.25, 26.57, 27.52, 31.19, 34.56,

39.62, 41.68, 50.52, 73.92, 123.09, 124.64, 125.34, 127.82, 143.54, 151.54, 165.48.

Asymmetric diamination of 8-phenyl menthyl crotylate (44): (−)-8-Phenyl menthyl crotylate (301 mg, 1.0 mmol) was added to a solution of **2** (182 mg, 0.5 mmol) in freshly distilled THF (5 mL). The resulting orange solution was stirred at RT for 8 h during which it turned dark red. The solvent was removed under reduced pressure to leave a crude red product which was analysed by ^{1}H NMR and then purified by column chromatography on silica gel (hexanes/ethyl acetate 5:1). After evaporation of the solvents under reduced pressure, the pure mixture of the two diastereomers (270 mg, 0.41 mmol, 81 % yield) was separated by semipreparative HPLC (Knauer Eurospher 100CN, *t*BuOCH$_3$/*n*-hexane 15:85, 14 mL min^{-1}, 254 nm). $t_R = 17.5$ min for **46** and 19.0 min for **45**; analytical HPLC: Knauer Eurospher 100CN, *t*BuOCH$_3$/*n*-hexane 20:80, 1.0 mL min^{-1}, 254 nm, t_R 9.9 min [(+)-**46**], 10.4 min [(−)-**45**].

(4*R*,5*S*)-*trans*-1,3-Bis(*tert*-butyl)-2,2-dioxo-4-methyl-5-[(−)-(8-phenyl-menthyloxy)carbonyl]-2-osma(VI)imidazolidine (45): Obtained as a purple solid. $[\alpha]_D^{28} = -1676$ ($c = 0.08$); ^{1}H NMR (300 MHz, C_6D_6): $\delta = 0.69-0.96$ (m, 3H), 0.75 (d, $J = 6.4$ Hz, 3H), 0.90 (d, $J = 6.2$ Hz, 3H), 1.02 (s, 3H), 1.15–1.30 (m, 1H), 1.16 (s, 9H), 1.18 (s, 3H), 1.34 (s, 9H), 1.43–1.49 (m, 1H), 1.57–1.65 (m, 1H), 1.99–2.08 m, 2H), 3.12 (s, 1H), 3.78 (q, $J = 6.2$ Hz, 1H), 4.64 (dt, $J = 4.1$, 10.7 Hz, 1H), 6.98–7.04 (m, 1H), 7.18–7.26 (m, 4H); ^{13}C NMR (75 MHz, C_6D_6): $\delta = 21.85$, 23.02, 24.41, 26.49, 29.89, 30.30, 30.74, 31.22, 34.84, 39.39, 41.84, 50.03, 66.27, 66.50, 73.53, 75.92, 80.86, 125.32, 125.53, 128.25, 152.84, 171.10. IR (KBr): $\tilde{\nu} = 2968$, 2941, 1734, 1365, 1203, 912, 897, 700 cm^{-1}; MS (EI): *m*/*z* (%): 666 (9) $[M]^+$, 647 (19), 407 (100), 351 (52), 295 (23), 119 (20); HRMS: calcd for $C_{28}H_{46}N_2O_4{}^{188}Os$: 662.3016, found: 662.3010.

(4*S*,5*R*)-*trans*-1,3-Bis(*tert*-butyl)-2,2-dioxo-4-methyl-5-[(−)-8-(phenyl-menthyloxy)carbonyl]-2-osma(VI)imidazolidine (46): Obtained as a red/purple solid. $[\alpha]_D^{28} = +1375$ ($c = 0.06$); ^{1}H NMR (300 MHz, C_6D_6): $\delta =$ 0.65–0.93 (m, 3H), 0.74 (d, $J = 6.4$ Hz, 3H), 0.91 (d, $J = 6.2$ Hz, 3H), 1.07 (s, 3H), 1.19 (s, 9H), 1.21–1.52 (m, 3H), 1.30 (s, 3H), 1.35 (s, 9H), 1.99–2.10 (m, 2H), 3.49 (s, 1H), 3.76 (q, $J = 6.2$ Hz, 1H), 4.82 (dt, $J = 4.1$, 10.6 Hz, 1H), 7.00–7.09 (m, 1H), 7.14–7.28 (m, 4H); ^{13}C NMR (75 MHz, C_6D_6): $\delta =$ 21.86, 22.98, 24.55, 25.87, 28.26, 30.23, 30.85, 31.89, 34.74, 39.87, 41.34, 49.46, 66.42, 66.72, 74.04, 75.91, 81.69, 125.60, 125.62, 128.11, 151.81, 171.51; IR (KBr): $\tilde{\nu} = 2972$, 2926, 2868, 2362, 1337, 1738, 1367, 1196, 1174, 912, 894, 700 cm^{-1}; MS (EI): *m*/*z* (%): 666 (11) $[M]^+$, 407 (100), 351 (44), 295 (21), 119 (17); HRMS: calcd for $C_{28}H_{46}N_2O_4{}^{188}Os$: 662.3016, found: 662.3012.

Synthesis of 8-phenyl menthyl acrylate (47): DMAP (672 mg, 5.5 mmol) was added in one portion to a solution of acrylic chloride (452 mg, 5 mmol) in freshly distilled THF (30 mL) at 0 °C. An immediate precipitate was observed and the resulting inhomogeneous solution was stirred for 15 min before a solution of 8-phenyl menthol (1.16 g, 5 mmol) in dichloromethane (5 mL) was added. The resulting solution was allowed to warm to room temperature and stirred overnight. The solvent was removed under reduced pressure and the crude product was purified by column chromatograpy (silica gel, hexanes/ethyl acetate 14:1) to give the title compound as a white solid (0.673 g, 43 %). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.78$ (d, $J =$ 6.6 Hz, 3H), 0.81–1.05 (m, 3H), 1.14 (s, 3H), 1.23 (s, 3H), 1.35–1.45 (m, 1H), 1.52–1.62 (m, 2H), 1.82–1.87 (m, 1H), 1.92–2.01 (m, 1H), 4.79 (dt, $J = 4.3$, 10.7 Hz, 1H), 5.45–5.55 (m, 2H), 5.91 (ddd, $J = 4.7$, 9.4, 14.1 Hz, 1H), 7.00–7.02 (m, 2H), 7.12–7.19 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 21.70$, 25.35, 26.58, 27.46, 31.22, 34.53, 39.64, 41.59, 50.48, 74.44, 124.90, 125.31, 127.89, 128.86, 129.70, 151.40, 165.25.

Asymmetric diamination of 8-phenyl menthyl acrylate (47): (−)-8-Phenyl menthyl acrylate (286 mg, 1.0 mmol) was added to a solution of **2** (183 mg, 0.5 mmol) in freshly distilled THF (5 mL). The resulting orange solution was stirred at RT for 4 h during which it turned dark red. The solvent was removed under reduced pressure to leave a red-brown oil which was analysed by ^{1}H NMR and then purified by column chromatography on silica gel (hexanes/ethyl acetate 6:1). After evaporation of the solvents under reduced pressure, the pure mixture of the two diastereomers (313 mg, 0.48 mmol, 96 % yield) was separated by semipreparative HPLC (Knauer Eurospher 100CN, *t*BuOCH$_3$/*n*-hexane 20:80, 14 mL min^{-1}, 254 nm); $t_R = 13.4$ min for **49** and 15.0 min for **48**; analytical HPLC: Knauer Eurospher 100 CN, 254 nm, *n*-hexane/*t*BuOCH$_3$ 80:20, 1.0 mL min^{-1}, $t_R = 10.0$ min [(−)-**48**], 11.4 min [(+)-**49**].

(5*S*)-*trans*-1,3-Bis(*tert*-butyl)-2,2-dioxo-5-[(−)-(8-phenyl-menthyloxy)carbonyl]-2-osma(VI)imidazolidine (48): Obtained as a red to purple solid; $[\alpha]_D^{28} = -956$ ($c = 0.13$); ^{1}H NMR (300 MHz, C_6D_6): $\delta = 0.60-0.93$ (m, 3H), 0.72 (d, $J = 6.4$ Hz, 3H), 1.03–1.58 (m, 3H), 1.09 (s, 3H), 1.13 (s, 9H), 1.27 (s, 3H), 1.36 (s, 9H), 1.91–2.05 (m, 2H), 3.35 (dd, $J = 1.3$, 12.0 Hz, 1H), 3.41 (dd, $J = 6.0$, 12.0 Hz, 1H), 3.60 (dd, $J = 1.3$, 6.0 Hz, 1H), 4.74 (dt, $J = 4.1$, 10.6 Hz, 1H), 7.03–7.08 (m, 1H), 7.21–7.28 (m, 4H); ^{13}C NMR (75 MHz, C_6D_6): $\delta = 21.79$, 25.13, 26.78, 28.20, 29.37, 30.16, 31.23, 34.75, 39.74, 41.82, 50.31, 66.46, 66.72, 67.85, 74.23, 76.04, 125.42, 125.69, 128.31, 152.34, 171.64; IR (KBr): $\tilde{\nu} = 2964$, 2929, 2872, 1741, 1458, 1365, 1198, 1180, 908, 897, 706 cm^{-1}; MS (EI): *m*/*z* (%): 652 (56) $[M]^+$, 393 (100), 337 (14), 281 (20), 119 (18); HRMS: calcd for $C_{27}H_{44}N_2O_4{}^{188}Os$: 648.2859, found: 648.2857.

(5*R*)-*trans*-1,3-Bis(*tert*-butyl)-2,2-dioxo-5-[(−)-(8-phenyl-menthyloxy)carbonyl]-2-osma(VI)imidazolidine (49): Obtained as a deep red solid; $[\alpha]_D^{28} = +710$ ($c = 0.04$); ^{1}H NMR (300 MHz, C_6D_6): $\delta = 0.59-0.75$ (m, 2H), 0.73 (d, $J = 6.6$ Hz, 3H), 0.80–0.91 (m, 2H), 1.08 (s, 3H), 1.10–1.18 (m, 2H), 1.23 (s, 9H), 1.26 (s, 3H), 1.30 (s, 9H), 1.30–1.41 (m, 1H), 1.44–1.52 (m, 1H), 1.99–2.07 (m, 2H), 3.35–3.46 (m, 2H), 3.59 (dd, $J = 1.7$, 5.5 Hz, 1H), 4.76 (dt, $J = 4.2$, 10.7 Hz, 1H), 7.01–7.07 (m, 1H), 7.13–7.26 (m, 4H); ^{13}C NMR (75 MHz, C_6D_6): $\delta = 21.86$, 25.45, 26.86, 28.32, 29.62, 30.12, 31.28, 34.70, 39.77, 41.22, 49.80, 66.79, 66. 81, 69.01, 74.76, 75.98, 125.49, 125.68, 128.25, 151.96, 172.06; IR (KBr): $\tilde{\nu} = 2968$, 2929, 2870, 2362, 2337, 1738, 1367, 1194, 1174, 912, 897, 768, 702 cm^{-1}; MS (EI): *m*/*z* (%): 652 (4) $[M]^+$, 393 (100), 337 (11), 281 (17), 119 (10); HRMS: calcd for $C_{27}H_{44}N_2O_4{}^{188}Os$: 648.2859, found: 648.2860.

Representative procedure for aminolysis of 5-alkyloxycarbonyl osmaimidazolidines with *N*-*tert*-butyl amine: A solution of complex **42 d** (365 mg, 0.5 mmol) in *N*-*tert*-butyl amine (20 mL) was treated with zinc chloride (0.13 mmol) under Ar. The Schlenk apparatus was sealed and heated to 70 °C for 24 h. After cooling to room temperature and standard work-up, the remaining pink residue was purified by column chromatography (silica gel, *n*-hexanes/ethyl acetate 4:1) to eluate remaining starting material. Changing the eluents to *n*-hexanes/ethyl acetate 2:1) gave the desired amide (4*R*,5*S*)-**28** (191 mg, 0.34 mmol, 67 %) that eluated as a red band. NMR spectroscopic data for the obtained osmaimidazolidines were in complete agreement with those of authentic samples from direct diamination.

Asymmetric diamination of bis[(−)-menthyl] fumarate (50) with osmium complex 2: Bis[(−)-menthyl] fumarate (235 mg, 0.6 mmol) was added to a solution of bis (*N*-*tert*-butylimido)dioxoosmium(VIII) (183 mg, 0.5 mmol) in freshly distilled THF (5 mL). The resulting orange solution was stirred at RT for 5 h during which it turned dark red. The solvent was removed under reduced pressure to leave a red-brown oil which was analysed by ^{1}H NMR and the purified by column chromatography on silica gel (hexanes/ethyl acetate 4:1). After evaporation of the solvents under reduced pressure, the pure mixture of the two diastereomers (334 mg, 0.44 mmol, 88 %) was separated by semipreparative HPLC (Knauer Eurospher 100CN, *t*BuOCH$_3$/*n*-hexane 10:90, 14 mL min^{-1}, 254 nm). $t_R = 11.1$ min for **52** and 11.8 min for **51**; analytical HPLC: Knauer Eurospher 100 CN, 254 nm, *n*-hexane/*t*BuOCH$_3$ 90:10, 1.0 mL min^{-1}; $t_R = 7.7$ min [(−)-**52**], 8.6 min [(+)-**51**].

(4*R*,5*R*)-*trans*-1,3-Bis(*tert*-butyl)-2,2-dioxo-4,5-bis[(−)-menthyloxycarbonyl]-2-osma(VI)imidazolidine (51): Obtained as a dark orange solid; $[\alpha]_D^{28} = +663$ ($c = 0.15$); ^{1}H NMR (300 MHz, C_6D_6): $\delta = 0.54-0.92$ (m, 6H), 0.76 (d, $J = 9.0$ Hz, 6H), 0.79 (d, $J = 9.6$ Hz, 6H), 0.94–1.20 (m, 4H), 1.32–1.49 (m, 6H), 1.35 (s, 18H), 1.96–2.15 (m, 4H), 4.82 (s, 2H), 4.85 (dt, $J =$ 4.5, 10.7 Hz, 2H); ^{13}C NMR (75 MHz, C_6D_6): $\delta = 15.98$, 20.96, 22.04, 23.14, 26.05, 30.12, 31.47, 34.11, 40.92, 46.93, 66.49, 76.10, 80.89, 171.81. IR (KBr): $\tilde{\nu} = 2981$, 2935, 2317, 2303, 1736, 1326, 1149, 932, 704 cm^{-1}; MS (EI): *m*/*z* (%): 758 (7) $[M]^+$, 575 (100), 437 (14), 393 (31), 337 (10), 281 (10); elemental analysis calcd (%) for $C_{32}H_{58}N_2O_6Os$: C 50.77, H 7.72, N 3.70; found: C 50.42, H 7.61, N 3.88.

(4*S*,5*S*)-*trans*-1,3-Bis(*tert*-butyl)-2,2-dioxo-4,5-bis[(−)-menthyloxycarbonyl]-2-osma(VI)imidazolidine (52): Obtained as an orange solid; $[\alpha]_D^{28} =$ −1308 ($c = 0.1$); ^{1}H NMR (300 MHz, C_6D_6): $\delta = 0.55-1.03$ (m, 6H), 0.77(d, $J = 6.7$ Hz, 6H), 0.80 (d, $J = 6.8$ Hz,6H), 0.96 (d, $J = 7.0$ Hz, 6H), 1.08–1.56 (m, 8H), 1.35 (s, 18H), 2.03–2.11 (m, 2H), 2.14–2.24 (m, 2H), 4.68 (s, 2H), 4.74 (dt, $J = 4.3$, 10.7 H, 2H); ^{13}C NMR (75 MHz, C_6D_6): $\delta =$ 16.21, 20.98, 22.07, 23.24, 26.26, 30.17, 31.43, 34.29, 40.76, 47.16, 66.88, 76.16, 81.91, 171.62; IR (KBr): $\tilde{\nu} = 2965$, 2941, 2316, 1739, 1361, 1159, 911,

701 cm^{-1}; MS (EI): *m*/*z* (%): 758 (7) $[M]^+$, 575 (100), 437 (12), 393 (34), 337 (13), 281 (9); elemental analysis calcd (%) for $C_{32}H_{58}N_2O_6Os$: C 50.77, H 7.72, N 3.70; found: C 50.98, H 7.31, N 3.96.

Asymmetric diamination of bis[(−)-menthyl] fumarate (50) with osmium complex 3: Bis[(−)-menthyl] fumarate (295 mg, 0.75 mmol) was added to a solution of tris(*N*-*tert*-butylimido)oxoosmium(VIII) (**3**) (210 mg, 0.5 mmol) in freshly distilled THF (5 mL). The resulting brown solution was stirred at RT for 5 h during which it turned dark red. The solvent was removed under reduced pressure to leave a red-brown oil which was analysed by ^1H NMR and the purified by column chromatography on silica gel (hexanes/ethyl acetate 4:1). After evaporation of the solvents under reduced pressure, the pure mixture of the two diastereomers (378 mg, 0.47 mmol, 93% yield) was separated by semipreparative HPLC (Knauer Eurospher 100 CN, *t*BuOCH$_3$/*n*-hexane 20:80, 14 mL min^{-1}, 366 nm); $t_R = 10.6$ min for 55 and 11.7 min for 54; analytical HPLC: Knauer Eurospher 100 CN, 254 nm, *n*-hexane/*t*BuOCH$_3$ 80:20, 1.0 mL min^{-1}; $t_R = 9.7$ min [(−)-**54**], 8.1 min [(+)-**53**].

(4*R*,5*R*)-*trans*-1,3-Bis(*tert*-butyl)-2-oxo-2-*tert*-butylimido-4,5-bis[(−)-menthyloxycarbonyl]-2-osma(VI)imidazolidine (53): Obtained as an orange to brown solid; $[\alpha]_D^{28} = +595$ ($c = 0.15$); ^1H NMR (300 MHz, C_6D_6): $\delta = 0.56$–1.11 (m, 8H), 0.74 (d, $J = 6.2$ Hz, 3H), 0.77 (d, $J = 6.4$ Hz, 3H), 0.79 (d, $J = 7.2$ Hz, 3H), 0.82 (d, $J = 7.0$ Hz, 3H), 0.87 (d, $J = 7.0$ Hz, 3H), 0.97 (d, $J = 7.0$ Hz, 3H), 1.22–1.65 (m, 8H), 1.46 (s, 9H), 1.47 (s, 9H), 1.57 (s, 9H), 1.94–2.16 (m, 3H), 2.26–2.32 (m, 1H), 4.65 (d, $J = 0.6$ Hz, 1H), 4.76 (dt, $J = 4.3$, 10.3 Hz, 1H), 4.90 (d, $J = 0.6$ Hz, 1H),4.95 (dt, $J = 4.4$, 10.4 Hz); ^{13}C NMR (75 MHz, C_6D_6): $\delta = 14.27$, 16.26, 16.34, 20.69, 21.05, 22.07, 22.13, 23.32, 23.59, 26.07, 26.69, 30.49, 31.35, 31.52, 31.85, 32.8, 34.21, 34.26, 41.00, 41.10, 46.95, 63.50, 64.09, 74.91, 75.61, 80.83, 82.04, 172.84, 173.16; IR (KBr): $\tilde{\nu} = 2944$, 2919, 2341, 2327, 1747, 1354, 1165, 907, 702 cm^{-1}; MS (EI): *m*/*z* (%): 813 (3) $[M]^+$, 575 (100), 437 (21), 393 (30), 337 (16), 281 (11); elemental analysis calcd (%) for $C_{36}H_{67}N_3O_5Os$: C 53.24, H 8.32, N 5.17; found: C 53.03, H 8.49, N 5.42.

(4*S*,5*S*)-*trans*-1,3-Bis(*tert*-butyl)-2-oxo-2-*tert*-butylimido-4,5-bis[(−)-menthyloxycarbonyl]-2-osma(VI)imidazolidine (54): Obtained as a brownish solid; $[\alpha]_D^{28} = -976$ ($c = 0.02$); ^1H NMR (300 MHz, C_6D_6): $\delta = 0.69$–1.11 (m, 10H), 0.72 (d, $J = 6.4$ Hz, 3H), 0.79 (d, $J = 6.4$ Hz, 3H), 0.86 (d, $J = 7.0$ Hz, 3H), 0.87 (d, $J = 7.0$ Hz, 3H), 0.93 (d, $J = 7.0$ Hz, 3H), 0.97 (d, $J = 7.0$ Hz, 3H), 1.20–1.61 (m, 6H), 1.45 (s, 9H), 1.48 (s, 9H), 1.56 (s, 9H), 1.98–2.07 (m, 1H), 2.16–2.27 (m, 2H), 2.32–2.44 (m, 1H), 4.64 (d, $J = 0.8$ Hz, 1H), 4.67–4.82 (m, 2H), 4.68 (d, $J = 0.8$ Hz, 1H); ^{13}C NMR (75 MHz, C_6D_6): $\delta = 16.43$, 16.54, 20.95, 21.17, 22.01, 22.13, 23.38, 23.50, 26.26, 26.66, 30.54, 31.37, 31.44, 31.77, 32.11, 34.37, 34.45, 40.75, 40.81, 47.34, 47.43, 63.96, 64.34, 69.29, 74.80, 75.48, 82.09, 83.31, 172.81, 172.94; IR (KBr): $\tilde{\nu} = 2937$, 2902, 2344, 2335, 1740, 1348, 1160, 911, 705 cm^{-1}; MS (EI): *m*/*z* (%): 813 (4) $[M]^+$, 575 (100), 437 (17), 393 (22), 337 (15), 281 (16); elemental analysis calcd (%) for $C_{36}H_{67}N_3O_5Os$: C 53.24, H 8.32, N 5.17; found: C 53.37, H 8.22, N 5.55.

Attempted enantioselective diamination in the presence of cinchona alkaloid ligands: A representative experiment was performed as follows: A solution of the appropriate chiral cinchona alkaloid ligand (1.2 mmol) and the osmium reagent **2** (364 mg, 1 mmol) in THF (5 mL) was stirred at RT under Ar. The respective olefin (2 mmol) was added in one portion at RT against a positive stream of Ar and the resulting reaction mixture was stirred at RT overnight. Standard work-up and column chromatography gave the corresponding osmaimidazolidine that was purified by column chromatography as described above for the individual compound and analysed by chiral HPLC.

Osmaimidazolidine **11**: Daicel Chiralpak AS, 254 nm, *n*-hexane/2-propanol 98:2, 0.5 mL min^{-1}; $t_R = 13.5$ min [(+)-**11**], 15.6 min [(−)-**11**].

Osmaimidazolidine **36**: Daicel Chiralpak AS, 254 nm, *n*-hexane/2-propanol 98:2, 0.5 mL min^{-1}; $t_R = 13.5$ min [(+)-**36**], 15.6 min [(−)-**36**]. No full baseline separation was achieved.

***trans*-1,3-Bis(*tert*-butyl)-2,2-dioxo-4,5-bis(ethyloxycarbonyl)-2-osma(VI)-imidazolidine (59)**:[21] Obtained from a diamination as described above (88% chemical yield on a 1 mmol scale) as racemic material. ^1H NMR (300 MHz, C_6D_6): $\delta = 0.96$ (t, $J = 7.2$ Hz, 6H), 1.19 (s, 18H), 3.87 (q, $J = 7.2$ Hz, 4H), 4.54 (s, 2H); ^{13}C NMR (75 MHz, C_6D_6): $\delta = 12.68$, 28.62, 60.32, 65.33, 79.41, 170.53; IR (KBr): $\tilde{\nu} = 2974$, 1738, 1367, 1288, 1230, 1186, 1028, 904, 895 cm^{-1}; MS (EI): *m*/*z* (%): 538 (5) $[M]^+$, 465 (47), 409 (19), 353 (23), 57 (100); HRMS: calcd for $C_{16}H_{30}N_2O_6{}^{188}Os$: 534.1661, found: 534.1656; analytical HPLC: Daicel Chiralpak AS, 254 nm, *n*-hexane/2-propanol 98:2, 0.5 mL min^{-1}, $t_R = 18.7$ min [(+)-**59**], 24.4 min [(−)-**59**].

Table 5. Crystallographic data, structure solution and refinement of **12**, **13**, **28**, **32** and **53**.

	12	**13**	**28**	**32**	**53**
formula	$C_{18}H_{28}N_2O_4Os$	$C_{21}H_{34}N_2O_4Os$	$C_{21}H_{35}N_3O_3Os$	$C_{23}H_{30}N_2O_3Os$	$C_{36}H_{67}N_3O_5Os$
M_r	526.62	568.70	567.72	572.69	812.13
dimensions [mm]	0.25 × 0.10 × 0.05	0.50 × 0.25 × 0.10	0.30 × 0.20 × 0.10	0.40 × 0.20 × 0.10	0.30 × 0.05 × 0.05
crystal system	orthorhombic	monoclinic	triclinic	monoclinic	monoclinic
space group	*Pbca* (no.61)	$P2_1/c$ (no.14)	$P\bar{1}$ (no.2)	$P2_1)/c$ (no.14)	$P2_1$ (no.4)
a [Å]	13.6907(2)	11.4893(3)	10.3714(2)	17.6484(4)	9.2730(1)
b [Å]	15.2685(2)	14.6163(4)	10.7095(3)	8.4448(2)	40.2510(6)
c [Å]	18.8178(2)	14.2195(4)	10.9049(3)	15.3884(3)	10.4253(2)
α [°]			94.173(1)		
β [°]		105.631(1)	108.464(1)	100.608(1)	94.291(1)
γ [°]			92.358(1)		
V [Å^3]	3933.61(9)	2299.58(11)	1143.20(5)	2254.25(9)	3880.31(10)
Z	8	4	2	4	4
ρ [g cm^{-3}]	1.778	1.643	1.649	1.687	1.390
μ [mm^{-1}]	6.507	5.572	5.602	5.682	3.327
F(000)	2064	1128	564	1128	1680
T [K]	123(2)	123(2)	123(2)	123(2)	123(2)
$2\theta_{max}$ [°]	50.0	50.0	50.0	50.0	50.0
	$-16 \geq h \geq 16$	$-13 \geq h \geq 13$	$-12 \geq h \geq 12$	$-20 \geq h \geq 20$	$-11 \geq h \geq 11$
	$-18 \geq k \geq 18$	$-17 \geq k \geq 17$	$-12 \geq k \geq 12$	$-9 \geq k \geq 10$	$-47 \geq k \geq 47$
	$-22 \geq l \geq 22$	$-16 \geq l \geq 16$	$-12 \geq l \geq 12$	$-18 \geq l \geq 18$	$-12 \geq l \geq 12$
no. measured data	30158	23304	20431	19923	25325
no. unique data	3459	4050	4013	3955	13097
R_{int}	0.0702	0.0701	0.0798	0.0712	0.0924
refinement on	F^2	F^2	F^2	F^2	F^2
no. parameters/restraints	226/0	253/0	251/67	262/0	371/1
R[for $I > 2\sigma(I)$]	0.0193	0.0315	0.0239	0.0328	0.0497
*wR*2 (all data)	0.0428	0.0776	0.0601	0.0883	0.0941
max./min. difference peak [e Å^{-3}]	−0.618/0.905	−2.651/2.213	−1.356/1.051	−2.600/2.437	−1.749/1.573

Crystal structure determination of osmaimidazolidine complexes 12, 13, 28, 32 and 53: The data were collected on a Nonius KappaCCD diffractometer at −150 °C with $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). The structures of **28** and **53** were solved by direct methods and those of **12**, **13** and **32** were solved by Patterson methods (SHELXS-97[71]). The non-hydrogen atoms were refined anisotropically, H atoms were refined by using a riding model (full-matrix least-square refinement on F^2(SHELXS-97[72]). Details of data collection and refinement are given in Table 5. Empirical absorption collections from multiple reflections were applied for all **12**, **13**, **28**, **32** and **53**. The absolute configuration of **53** was determined by using the Flack parameter [$x = -0.07(1)$].[73] Due to the low quality of the crystals ib **54** only the Os atoms were refined anisotropically.

CCDC-206066 (**12**), -206067 (**13**), -206068 (**28**), -206069 (**32**) and -206070 (**53**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; (fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk).

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