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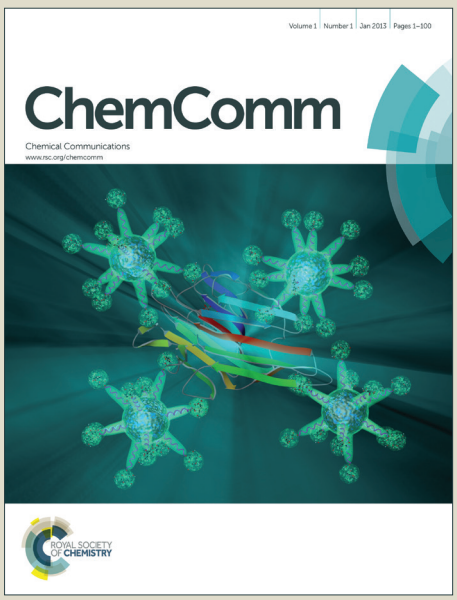

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COMMUNICATION

Methyltrioxorhenium-Catalyzed Highly Selective Dihydroxylation of 1,2-Allenylic Diphenyl Phosphine Oxides

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For the first time, methyltrioxorhenium (MTO) is applied as catalyst for the dihydroxylation of allenes in the presence of hydrogen peroxide as oxidant. The regioselectivities turn out to be well controlled, affording *β*-carbonyl-*γ*-hydroxyl diphenyl phosphine oxides as the only product. The axial chirality of optically active allenes can also be nicely transferred to the chirality center of the products. Based on chirality transfer experiments and ESI-MS studies of ^{18}O-labeled products, a possible mechanism, proceeding via regioselective epoxidation of the electron-rich carbon-carbon double bond, subsequent intermolecular nucleophilic attack of a water molecule on the *in situ* formed epoxide via neighboring group participation (NGP), and followed by rearrangement is proposed as the major reaction pathway.

Allenes[1] are a class of unique and interesting unsaturated compounds with two π-orbitals perpendicular to each other. Their electrophilic addition reactions have received much attention.[2,1h] Although controlling chemo-, regio-, and stereoselectivity is always challenging, many applications have nevertheless been found for these compounds, including halohydroxylation,[3] selenohydroxylation,[4] and hydration,[5] which provided useful synthetic methods to introduce a hydroxyl group into the allene moiety. Despite numerous reports on the transformations mentioned above, dihydroxylation[6] of allenes is still not sufficiently well developed.

The first example for allene dihydroxylation was reported by Cazes in 1996, using OsO_4 as catalyst.[6a] In this case, only low yields and/or poor regioselectivities could be achieved, showing very low synthetic potential. Later, Fleming developed an AD-mix-catalyzed asymmetric dihydroxylation reaction of simple allenes.[6b,6c] However, good enantioselectivities could only be obtained with monosubstituted aryl allenes giving rather low yields. When disubstituted allenes were applied, low conversion rates as well as low yields were observed, and over-oxidized products were formed in most cases. Moreover, the enantioselectivities were also not satisfactory. To the best of our knowledge, those are the only examples of allene dihydroxylations. Furthermore, the reaction mechanism has not been well studied so far. Considering that dihydroxylation of allenyl compounds might be a new synthetic methodology for the formation of α-hydroxy ketones[7] – their preparation is a fundamentally important subject in organic synthesis – more efficient and selective reactions are highly desirable.

Methyltrioxorhenium(VII) (MTO) has a rich history with respect to its catalytic applications since 1991,[8] its first synthesis by Beattie and Jones dating back to 1979.[8e] Due to its high efficiency for the activation of hydrogen peroxide, it has been successfully applied as a homogeneous catalyst in epoxidations, dihydroxylations, and carbon-carbon double bond cleavage of various unsaturated compounds such as alkenes, alkynes, conjugated dienes, allylic alcohols, and aromatic compounds.[8d] Although catalytic applications of MTO have been studied for more than two decades, MTO/H_2O_2-catalyzed dihydroxylations of allene derivatives remain undeveloped. Given our continuous interest in both allene chemistry[3f] and MTO chemistry,[9] we attempted to explore the reactivity of MTO-catalyzed dihydroxylation of allenes. In this work a novel catalytic protocol for the synthesis of α-hydroxyl ketones under mild conditions is reported as a result of our efforts.

To explore the reactivity of MTO-catalyzed dihydroxylation of allenes, 1,2-allenylic diphenyl phosphine oxide **1a** was chosen as model substrate. A standard reaction condition A (5 + 5 mol% of MTO, 2 equiv. of H_2O_2 (30%), CH_2Cl_2, rt) was obtained after optimization (For details see Supporting Information). Then the scope of this reaction was studied carefully (Table 1). The results show that the examined MTO/H_2O_2 catalyzed dihydroxylation reaction is applicable to various substituted allenes (with functional groups attached to different positions of the allene moiety) under condition A. It is important to note that the regioselectivities are well controlled in all examined substrates, whereas only the double bond in 2,3-position is oxidized in dihydroxylations, affording β-carbonyl-γ-hydroxyl diphenyl phosphine oxides as the only product.

In order to get to a better understanding on this dihydroxylation, the catalytic mechanism deserves a closer look. Based on literature precedents,[8c] an MTO-catalyzed epoxidation is proposed to occur in the first step, yielding a methyleneoxirane intermediate (**3**). This reaction is likely to be followed by the attack of a water molecule on **3**, resulting in the formation of the final dihydroxylation products (*vide infra*). The proposed allene epoxidation mechanism is shown in Scheme 1. It is known that MTO reacts rapidly with H_2O_2 molecules forming monoperoxo and bisperoxo complexes (denoted as mpRe and dpRe, respectively), which have been proven to be the active species in epoxidations.[8e] Similarly, two catalytic pathways for the allene epoxidation might be described based on mpRe (cycle A) and dpRe (cycle B). In the case of allene epoxidations, the oxygen transfer might be accomplished through a nucleophilic attack of the electron richer carbon-carbon double bond of the allenes to a peroxidic oxygen of mpRe or dpRe under the formation of two

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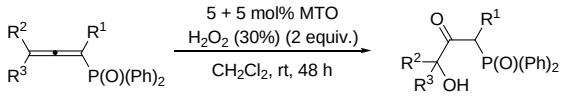
Table 1 The reaction of 1 under Condition A.[a]

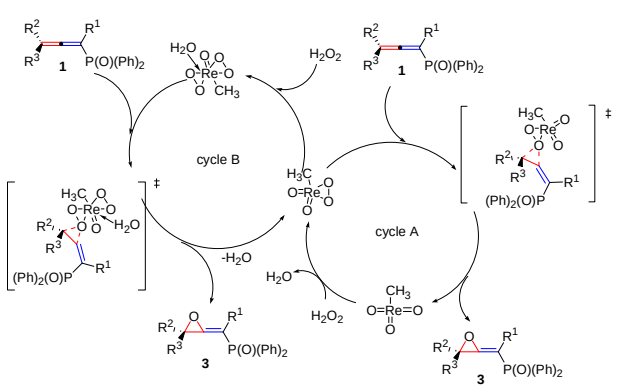


1 2

Entry	1 (R^1, R^2, R^3)	2	Isolated yield of 2 (%)
1[b]	**1b** (H, H, H)	**2b**	78
2	**1c** (Me, H, H)	**2c**	78
3	**1a** (Pr^n, H, H)	**2a**	83
4	**1d** (Bu^n, H, H)	**2d**	77
5	**1e** (H, Me, H)	**2e**	74
6	**1f** (H, Bu^n, H)	**2f**	77
7	**1g** (H, -$(CH_2)_4$-)	**2g**	70
8	**1h** (Bu^n, Me, Me)	**2h**	74
9	**1i** (Bu^n, -$(CH_2)_4$-)	**2i**	75

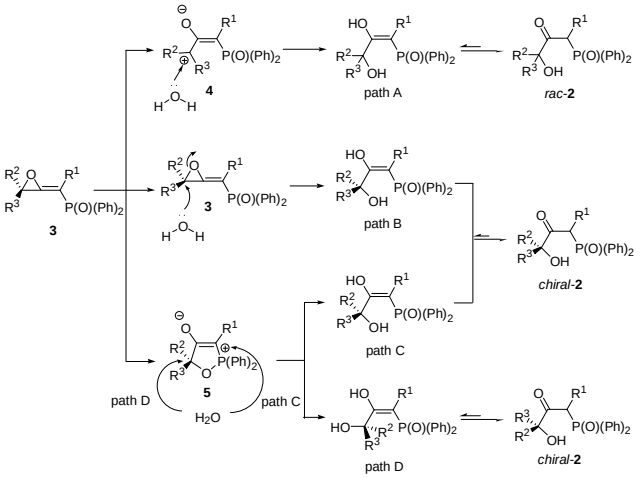
[a] The reaction was carried out using 1 (0.25 mmol), MTO (0.0125 + 0.0125 mmol), and H_2O_2 (30%) (2 equiv.) in CH_2Cl_2 (850 μL) at rt.

transition states of a "butterfly" geometry (see Scheme 1). In this step, the existence of a diphenyl phosphinyl group is crucial to control the regio- and stereoselectivities of the epoxidation reaction. Owing to the strong electron-withdrawing capability of the diphenyl phosphinyl group, the electron density of the C-C double bond in 1,2-position is lower than the density in 2,3-position. Thus, the nucleophilic attack reaction has the tendency to occur on the electron richer C-C double bond in 2,3-position. This could nicely explain the high regioselectivity of the reaction. Moreover, due to the strong steric effect of the diphenyl phosphine oxide group, the oxygen transfer process would occur on the *trans*-position to the diphenyl phosphinyl groups of the allenes, affording the intermediate **3** (Scheme 1). In this case, if a chiral allene substrate is applied, the absolute configuration of the intermediate **3** will be opposite to **1**.



Scheme 1 Proposed mechanism of MTO-catalyzed epoxidation of allenes.

Four different reaction pathways for the transformation of methyleneoxirane intermediate **3** into the final product **2** are proposed as shown in Scheme 2. In path A, high ring tension induced ring opening via a heterolytic C-O bond cleavage results in intermediate **4**, which might further react with a water molecule to form a 1,2-diol derivative. Subsequent fast rearrangement leads to the final product **2**. In path B, intermolecular nucleophilic attack of the water molecule at the sp^3-C atom of the *in situ* formed epoxide **3** affords the 1,2-diol derivative, which finally rearranges to **2**. Neighboring group participation (NGP) of the diphenylphosphinyl group[3f] should also be considered, it might generate the five-membered ring intermediate **5**. Two pathways for the ring opening process via nucleophilic attack of a water molecule at either the P-atom (path C) or C-atom (path D) might be possible. The follow-up rearrangement leads to product **2**.



Scheme 2 Four different, possible reaction pathways.

The main conclusions based on the comparison of these pathways are: If optically active substrates are applied in this reaction, path A would result in a racemic product, since a carbocation is formed at the previously chiral carbon-center. Chiral products might be generated from path B, C, or D, however, the corresponding absolute configurations of the products from path B or C would be opposite to that resulting from path D. For path B or C, the ring opening reaction of intermediate (*S*)-**3** will afford (*R*)-**2,** whereas (*R*)-**3** will afford (*S*)-**2**. However, in the case of path D, the absolute configurations of the products would remain the same as intermediate **3**. Accordingly, the whole dihydroxylation reaction of (*R*)-**1** will result in (*R*)-**2** via path B or C, and (*R*)-**1** will be transferred into (*S*)-**2** via path D.

Based on these considerations, chiral allenes (*R*)- and (*S*)-1e were synthesized and applied in this reaction under the standard conditions. The results show that the axial chirality of the allene moiety could be nicely transferred into the center chirality of the final product with only slightly decrease of the enantiopurity (Scheme 3). The absolute configuration of the chiral center was determined by X-ray diffraction study, and the result show that the dihydroxylation of (*S*)-1e affords (*R*)-2e (see Fig. S1 in Supporting Information), while (*R*)-1e is transferred to (*S*)-2e (see Fig. S2 in Supporting Information). Based on these observations, a reaction following path A should not be the major reaction pathway, since no obvious racemization was observed. The absolute configuration of the product and its high *ee* value provide solid evidence that the reaction undergoes via path D as the major reaction pathway.

As reported in our earlier work,[3f] if this reaction proceeds via NGP of the diphenylphosphinyl moiety, the reaction using $H_2{}^{18}O$ containing H_2O_2 solution might yield a product with ^{18}O atom labeled at the phosphinyl group in case of path C. However, ^{16}O atom should remain at the phosphinyl group if the reaction undergoes via path D. Therefore, ESI-MS technology was used in order to further confirm the reaction mechanism. The fragmentation of both unlabeled (**2a**) and ^{18}O labeled (**2a***) products have been carefully studied, and the spectra can be found in Figs. S3 - S17 of the Supporting Information.

The ESI-MS spectrum shows a [M+H]+ ion of **2a** at m/z = 317 with 100% relative abundance (Fig. S3). A following ESI-MS^2 measurement shows that $[2a+H]^+$ (*m/z* = 317) is fragmented into

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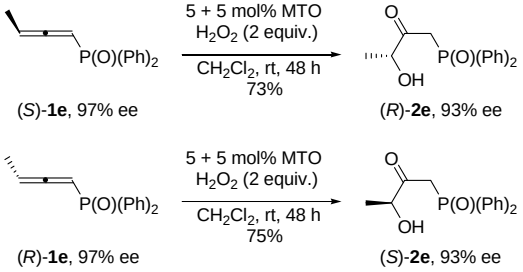
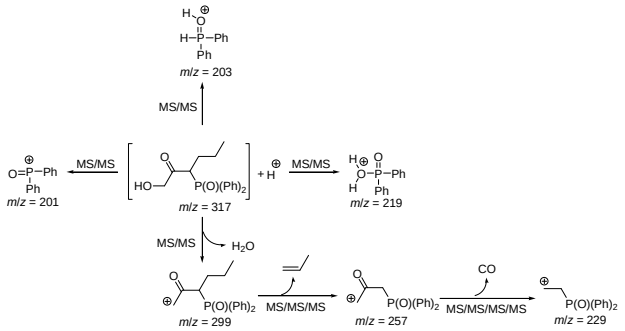
daughter ions at *m/z* = 299, 219, 203, and 201 (Fig. S4). The ESI-MS^3 spectrum shows that the ion *m/z* = 299 (dissociated from ion *m/z* = 317) could produce the fragment ion at *m/z* = 257 (Fig. S5). In the ESI-MS^4 spectrum, the ion *m/z* = 257 (dissociated from ion *m/z* = 299) produces a fragment ion at *m/z* = 229 (Fig. S6). Based on these results, a possible fragmentation way is proposed as shown in Scheme 4. In ESI-MS^2, the $[2a+H]^+$ (*m/z* = 317)



Scheme 3 Chirality transfer experiments.

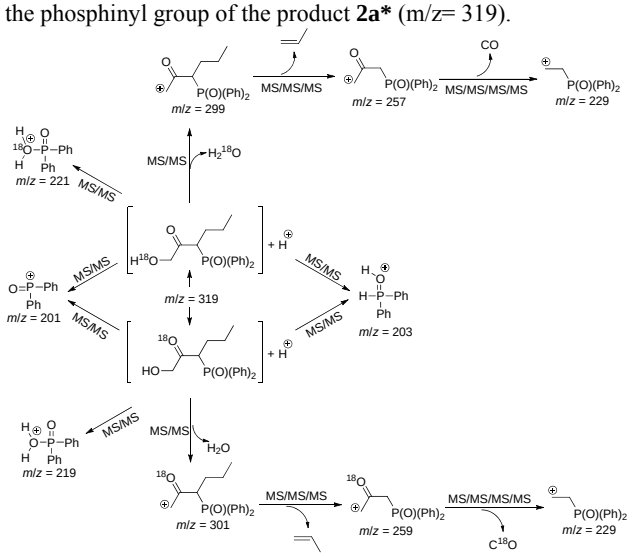
dissociates into the daughter ion at *m/z* = 299 by releasing a water molecule. The water molecule might coordinate to the ion at *m/z* = 201 to afford the ion at *m/z* = 219. In the following ESI-MS^3 study of the precursor ion at *m/z* = 299, a removal of a propylene molecule could be deduced, with the subsequent formation of the daughter ion at *m/z* = 257. In the next ESI-MS^4 measurement, a carbon monoxide molecule is lost from the precursor ion at *m/z* = 257, generating the daughter ion at *m/z* = 229. These results suggest that by examining the molecular weight (isotope pattern) of the lost water and carbon monoxide, compelling evidence based on the ^{18}O-labelling of the hydroxyl group and the carbonyl group can be obtained if the same ESI-MS measurement is executed for **2a***.



Scheme 4 The fragmentation way from the [M+H]+ ion of **2a** at m/z = 317.

Accordingly, ^{18}O-labeled **2a*** was synthesized using $H_2{}^{18}O$ solution of H_2O_2 under condition A for ESI-MS studies (For a detailed experimental procedure see Supporting Information). From the ESI-MS spectrum of **2a*** (Fig. S7), signals for unlabeled product (*m/z* = 317), one ^{18}O atom labeled product (*m/z* = 319), and two ^{18}O atoms labeled product (*m/z* = 321) are clearly observed. All the possible structures of the labeled products are shown in Fig. S7. A detailed ESI-MS^2 to ESI-MS^4 determination of the ionic peaks at *m/z* = 319 and *m/z* = 321 were carried out, respectively.

In the ESI-MS^2 spectrum of the precursor ion at *m/z* = 319, daughter ions at *m/z* = 301, 299, 221, 219, 203, and 201 are detected (Fig. S8). The daughter ions at *m/z* = 301 and 299 indicate that the loss of both H_2O and $H_2{}^{18}O$ from the precursor ion *m/z* = 319 occur. The daughter ions at *m/z* = 221 and 219, which are derived from the coordination of one H_2O or $H_2{}^{18}O$ molecule to the ion at *m/z* = 201 also confirm this interpretation. The observed ion at *m/z* = 203 can be identified as the $[HP(OH)(Ph)_2]^+$ fragment but not $[P(^{18}O)(Ph)_2]^+$ based on the high resolution MS (HRMS) measurement (Fig. S9). This result is also in accord with that observed from the ESI-MS^2 of the unlabeled product **2a** (Fig. S4). These data strongly support that both unlabeled and labeled hydroxyl groups exist in the product (*m/z* = 319). The fragment *m/z* = 299 should be derived from the product (*m/z* = 319) with one ^{18}O atom at the hydroxyl group. Thus, the carbonyl and phosphinyl groups of that molecule should be unlabeled. The next step ESI-MS^3 and ESI-MS^4 studies on its daughter ion show a similar fragmentation behavior (Figs. S10 and S11) as in the case of unlabeled product **2a** (Figs. S5 and S6). For the fragment *m/z* = 301, which should be derived from the product (*m/z* = 319) with ^{16}O at the hydroxyl group, it is important to further determine whether the ^{18}O atom is labeled on the carbonyl or on the phosphinyl group. Thus, the ion at the *m/z* = 301 was further studied by ESI-MS^3 (Fig. S12), and the spectrum shows a daughter ion at *m/z* = 259 created by the removal of propene from the fragment. The following ESI-MS^4 of the ion shows a daughter ion at *m/z* = 229, which could be derived by releasing C^{18}O from the precursor ion at *m/z* = 259 (Fig. S13). This result suggests that the ^{18}O atom should be labeled on the carbonyl group. Therefore, we can conclude that ^{18}O atom labeled product **2a*** is a mixture of ^{18}O atom labelled either on hydroxyl group or carbonyl group. Based on the above described results, a possible fragmentation way is proposed as shown in Scheme 5. Accordingly, the ^{18}O atom is not labeled at the phosphinyl group of the product **2a*** (m/z= 319).



Scheme 5 The fragmentation way from the $[M+H]^+$ ion of **2a*** at *m/z* = 319.

In the case of the ESI-MS^2 measurement of the precursor ion at *m/z* = 321, the typical daughter ions at *m/z* = 301, 221, 203, and 201 are detected (Fig. S14). The daughter ion at *m/z* = 301 shows the loss of a $H_2{}^{18}O$ molecule, indicating that the hydroxyl group of the corresponding product **2a*** is labeled by ^{18}O atom. The signal of the daughter ion at *m/z* = 221 is derived from the coordination of a $H_2{}^{18}O$ molecule to the ion at *m/z* = 201 ($[P(^{16}O)(Ph)_2]^+$). The following ESI-MS^3 of the ion *m/z* = 301 shows the signal of the ion *m/z* = 259 with a removal of a propene (Fig. S15). The next step ESI-MS^4 measurement of the ion at *m/z* = 259 shows the release of a C^{18}O and forms its daughter ion at *m/z* = 229 (Fig. S16), which proves that ^{18}O atom is labeled at the carbonyl group. Accordingly, the corresponding phosphinyl group is not labeled with ^{18}O atom for the product **2a*** (m/z = 321). Based on these results, a possible fragmentation way is proposed as shown in Scheme 6.

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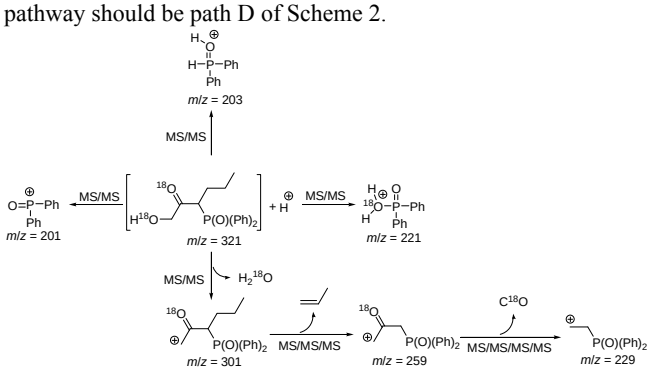
However, some weak signals at *m*/*z* = 303, 223, 219, and 205 can be also observed in the ESI-MS^2 spectrum (Fig. S14). Although these peaks are weak, they should be considered carefully. High resolution ESI-MS^2 measurement of the precursor ion at *m*/*z* = 321 was carried out in order to identify the structures of these weak signals (Fig. S17). The results indicate that these peaks are not noise signals. According to the calculated data, the weak daughter ion at *m*/*z* = 303 indicates the ion structure with ^{18}O labeled both on the carbonyl and phosphinyl groups, which also indicates the loss of a $H_2{}^{16}O$ molecule from the precursor peak at *m*/*z* = 321. Accordingly, the ion *m*/*z* = 219 is derived from the coordination of a $H_2{}^{16}O$ molecule with the ion at *m*/*z* = 201. The ion at *m*/*z* = 223 is derived from the coordination of $H^{18}O$ with $[P(^{18}O)(Ph)_2]^+$, whereas the ion at *m*/*z* = 205 originates from $[HP(^{18}OH)(Ph)_2]^+$. These results indicate that the NGP via path C might be involved. However, it is apparently a minor reaction pathway. Considering that the reaction via path C will produce the opposite enatioisomer of path D, the *ee* value of the final product should be slightly decreased, which is also consistent with the obtained results of the chirality transfer experiments. (Scheme 3).

Based on the above described ESI-MS studies, it can be deduced that in the case of ^{18}O-labeled product **2a***, only trace amounts of ^{18}O are transferred to the phosphinyl group. This means that NGP via path C indeed occurs during this reaction, but it is a minor reaction pathway. Thus, the major reaction pathway should be path D of Scheme 2.



Scheme 6 The fragmentation way from the $[M+H]^+$ ion of **2a*** at *m*/z = 321.

In conclusion, MTO-catalyzed highly chemo-, regio-, and stereo-selective dihydroxylation of 1,2-allenylic diphenyl phosphine oxides has been described. This method provides a new and effective pathway for the synthesis of *β*-carbonyl-*γ*-hydroxyl diphenyl phosphine oxides. A mechanism via NGP has been suggested and is supported by chirality transfer experiments and ESI-MS studies of ^{18}O-labeled products. To the best of our knowledge, this is the first report on the dihydroxylation of allenes using MTO as catalyst and hydrogen peroxide (30 % solution) as oxidant for the production of α-hydroxyl ketones.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Experimental procedures, ESI-MS spectra and NMR spectra. See DOI: 10.1039/b000000x/

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10 Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication Nos. CCDC-1040645 (*(S)*-2e), and CCDC-1040646 (*(R)*-2e). Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax, (+44)1223-336-033; e-mail, deposit@ccdc.cam.ac.uk.

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