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Asymmetric Intramolecular C–H Insertion of α-Diazoacetamides in Water by Dirhodium(II) Catalysts Derived from Natural Amino Acids

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Abstract: The asymmetric dirhodium(II)-catalyzed intramolecular C–H insertion of α-diazo acetamides in water is described for the first time. The use of natural α-amino acids as chiral ligands allowed the preparation of novel dirhodium(II) homochiral complexes by a simple procedure consisting of the *in situ* ligand exchange starting from dirhodium tetraacetate. The catalytic system was further reused up to 7 cycles and β-lactams were obtained in good yields and enantiomeric excess.

Keywords: C–H insertion; α-diazo compounds; dirhodium(II); β-lactams; water

Dirhodium(II) complexes are efficient catalysts in carbenoid cyclopropanation, C–H, N–H and O–H activation reactions derived from α-diazo carbonyl compounds. Due to the presence of two rhodium atoms, these metallic complexes promote the formation as well as the stabilization of an organic carbene moiety that can consequently undergo an insertion reaction.[1] The use of homochiral catalysts in C–H insertion reactions in organic solvents is well documented in the literature (Figure 1) and good to excellent enantioselectivities have been achieved both for intramolecular[2] and intermolecular[1g,3] reactions. However, and despite the widely available homochiral dirhodium complexes, to the best of our knowledge, the dirhodium(II)-catalysed asymmetric intramolecular C–H insertion reaction has not been reported using water as the reaction medium. Due to the nature of the typical ligands used in the preparation of homochiral dirhodium complexes (proline derivatives[4], phthaloyl-protected amino acids[5] mandelic acid derivatives[6], amongst others) the catalysts are usually water insoluble and the reutilization of the catalyst became compromised due to the costs associated with purification

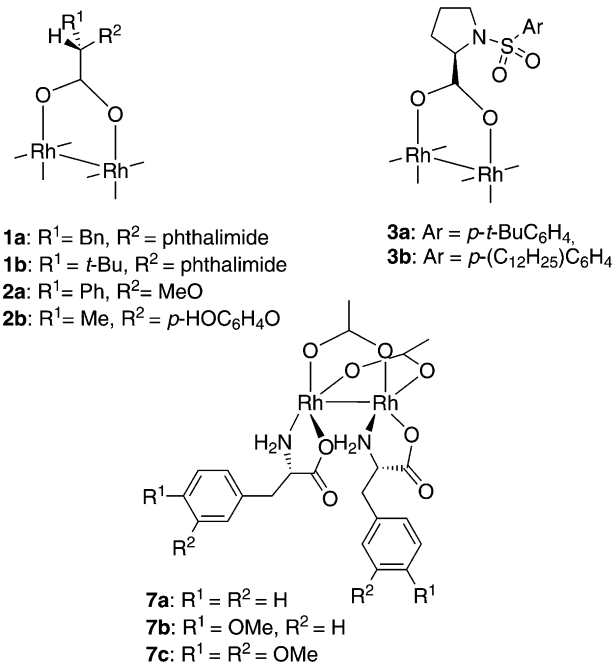
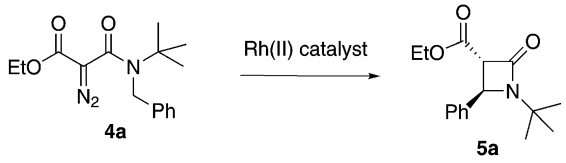


Figure 1. Some reported (**1**–**3**) homochiral dirhodium(II) catalysts and new ones (**7a**, **7b** and **7c**) derived from unprotected amino acids.

procedures. This catalyst reutilization is always desirable in a more sustainable chemistry context[7] but this becomes even more important considering the high cost of rhodium derivatives. Dirhodium catalysts were recently reported as water tolerant complexes and several examples of their use in water have been described.[8] The solubility and tolerance of some dirhodium complexes, in particular $Rh_2(OAc)_4$, allowed the reutilization of the catalytic system.[7] If a solvent is required for a reaction, water is the cheapest, most abundant solvent available and also with unique properties. Despite the widely explored use of water as solvent in organic reactions, the full potential of this solvent has not been completely brought to light and many works have been done to understand the chemical and physical properties of water and how they influence organic reactions.[9] Here we present the first asymmetric intramolecular C–H insertion in water, promoted by a dirhodium(II) catalyst obtained from reaction with natural α-amino acids. The success of intramolecular C–H insertions in water is strongly dependent on the substrate and catalyst solubility.[8g] In order to evaluate this effect on the reaction's stereoselectivity, we tested several known hydrophobic chiral dirhodium catalysts (Figure 1) on the intramolecular C–H insertion of α-diazoacetamide **4a** in dichloromethane (Scheme 1) and in water and we were glad to observe that after replacing dichloromethane by water, similar enantioselectivities could be obtained (Table 1, entries 1 and 2).



Scheme 1. Rh(II)-catalyzed intramolecular C–H insertion of α-diazoacetamide **4a**.

Despite the excellent results obtained in the α-diazoacetamide cyclization in water, namely using *N*-phthaloyl-protected amino acid dirhodium complexes derivatives (**1a** and **1b**), most of the known chiral dirhodium catalysts are poorly soluble in water. Due to the high availability of enantiomerically pure α-amino acids in nature, this type of compound can be extremely important in the preparation of enantioenriched organic molecules. Taking advantage of the chiral pool of natural products and derivatives, the use of water as the reaction medium, and the known protocol for the formation of new dirhodium(II) complexes by ligand exchange starting from dirhodium(II) tetraacetate,[10] we developed a protocol for the formation of new catalysts. Such a protocol was based on the $Rh_2(OAc)_4$ ligand exchange with an excess of α-amino acids, and after ligand exchange the complex was tested on the intramolecular C–H insertion of α-diazoacetamide **4a** for 24 h. After screening a range of α-amino acids and derivatives (see the Supporting Information for the complete table), L-phenylalanine derived complex was one of the most promising ones. $Rh_2(OAc)_4$ ligand exchange reaction was performed at 80 °C for 56 h and the catalytic activity of the newly complex formed was tested in the cyclization of diazo compound **4a** at 80 °C for 48 h. Lactam **5a** was obtained in 54% yield and 62% enantiomeric excess. Under these ligand exchange conditions, the starting $Rh_2(OAc)_4$ was completely consumed after 56 h, as determined by HPLC (Figure 2 in the Supporting Information).

By using L-phenylalanine analogues as chiral ligands in the preparation of new chiral dirhodium complexes, it was possible to determine structures of the complexes **7b** and **7c** by X-ray analysis.[11] However, the structure of the L-phenylalanine derived complex **7a** was only determined after preparative HPLC purification, due to a side product of the complex preparation that made the crystal formation difficult. The new complexes maintained two acetate bridge

Table 1. C–H insertion of α-diazoacetamide **4a**.

Entry	Rh(II) catalyst	Conditions[a]	Yield [%][b]	*cis*:*trans*[c]	*ee* [%][d]
1	**1a**	CH_2Cl_2, 25 °C, 3.5 h	93	1:0	66
2	**1a**	H_2O, 25 °C, 21 h	93	1:0	60
3	**1a**	H_2O, 80 °C, 1 h	82	1:0	56
4	**1b**	H_2O, 80 °C, 0.5 h	84	1:0	72
5	**2a**	H_2O, 80 °C, 0.5 h	75	1:0	15
6	**2b**	H_2O, 80 °C, 0.5 h	65	1:0.1	28
7	**3b**	H_2O, 80 °C, 1 h	80	1:0	0
8	**3a**	H_2O, 80 °C, 0.5 h	83	1:0	0

[a] All reactions were carried out using **4**[5c] (0.15 mmol), Rh(II) catalyst (2 mol%), solvent (1.5 mL).
[b] Isolated yield after purification by flash chromatography.
[c] Observed ratio by ^{1}H NMR of the crude reaction mixture.
[d] Determined by chiral HPLC analysis, after epimerization to *trans* diastereoisomer.

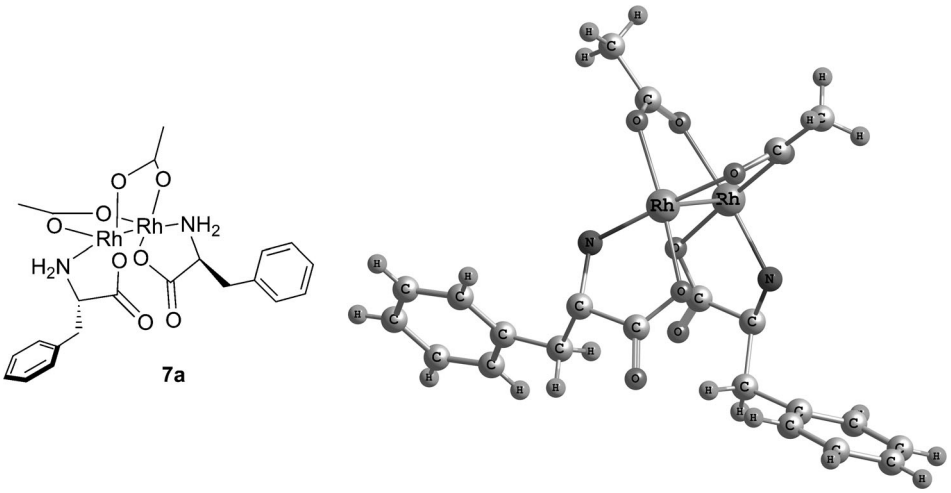
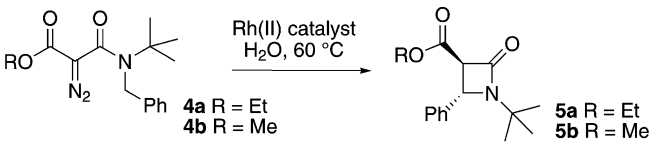


Figure 2. X-ray structure representation of **7a** (see the Supporting Information for details).

units and two amino acid units (Figure 2). However, the amino acid units do not maintain the expected bridge geometry but rather bond one of these to each rhodium atom. The amino acid unit bonds to the rhodium atom by the oxygen of the carboxylate moiety and the nitrogen atom of the amine functional group. One should also notice the different orientations of the amino acid units where the nitrogen of one amino acid unit is superimposed to the oxygen of the other amino acid unit.[12] A closed geometry has been disclosed for complexes derived from nitrogen-based chelate ligands such as phenanthroline and 2,2′-bipyridine[13] as well as for oxothioethers,[14] nevertheless to the best of our knowledge, this is the first example of such a peculiar geometry with amino acids as dirhodium ligands. In this way, three novel water soluble dirhodium complexes were prepared (**7a–c**). Recently, we observed that the complex **7a** is strongly active towards human colon adenocarcinoma cells.[11]

Such new water soluble catalysts (**7a–c**) were tested in the cyclization of α-diazoacetamide **4a** (Scheme 2) and it was possible to decrease the reaction temperature to 60 °C (Table 2, entries 1–4). A 1 mol% loading of catalyst **7a** provided the desired lactam in a lower yield and identical enantioselectivity (Table 2, entry 2), whilst a decrease to 0.5 mol% resulted in low diazo compound consumption (Table 2, entry 3). Due to the heterogeneous nature of the reaction medium, the reaction scale up to one gram of diazo compound allowed the isolation of lactam **5a** after a simple filtration of the reaction medium. However, this required longer reaction times and a slight *ee* drop to 60% (Table 4, entry 4).



Scheme 2. Rh(II)-catalyzed intramolecular C-H insertion of α-diazoacetamides **4a** and **4b** in water.

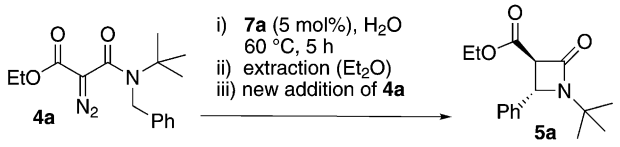
Table 2. Asymmetric C–H insertion of α-diazoacetamides **4a** and **4b** with Rh(II) catalysts **7a–c** derived from α-amino acids.

Entry	**4a**/ **4b**	Rh(II) catalyst	Reaction time [h][a]	Yield [%][b]	*cis*:*trans*[c]	*ee* [%][d]
1	**4a**	**7a**	6	85	1:0.2	66
2	**4a**	**7a**[e]	48	70	1:0.1	68
3	**4a**	**7a**[f]	48	(20)[g]	1:0	54
4	**4a**[h]	**7a**	24	77	1:0.2	60
5	**4a**	**7b**	24	80	1:0.2	53
6	**4a**	**7c**	72	67	1:4.6	32
7	**4b**	**7a**	12	81	1:0.1	46

[a] All reactions were carried out using **4**[5c] (0.15 mmol), Rh(II) catalyst (2 mol%), water (1.5 mL), except entries 2 and 3.
[b] Isolated yield after purification by flash chromatography.
[c] Observed ratio by ^{1}H NMR of the crude reaction mixture.
[d] Determined by chiral HPLC analysis, after epimerization to *trans* diastereoisomer.
[e] 1 mol% of catalyst loading.
[f] 0.5 mol% of catalyst loading.
[g] Conversion determined by ^{1}H NMR of the reaction mixture.
[h] Reaction conducted at a 3.5 mmol scale (1.06 g) of diazo compound.

Longer reaction times were needed due to the presence of the methoxy electron-donating substituent in the aryl rings of the catalyst. While the phenylalanine-derived catalyst **7a** allowed a complete reaction after 6 h (Table 2, entry 1), the introduction of electron-donating substituents lead to complexes **7b** and **7c** having decreased reactivity and 24 h were needed

Table 3. Reuse of the **7a** catalyst after cyclizations of **4a**.



Run	Yield [%][b]	*cis*:*trans*[c]	*ee* [%][d]	Run	Yield [%][b]	*cis*:*trans*[c]	*ee* [%][d]
1	81	1:0.3	58	5	85	1:0.4	74
2	82	1:0.2	68	6	82	1:0.4	74
3	79	1:0.2	70	7[e]	88	1:0.6	74
4	79	1:0.3	72				

[a] All reactions were carried out using **4**[5c] (0.15 mmol), Rh(II) catalyst (5 mol%) and water (1.5 mL) for 5 h. The reaction mixture was extracted with Et_2O (3×2 mL) and reloaded with **4a**.
[b] Isolated yield after purification by flash chromatography.
[c] Observed ratio by ^1H NMR of the crude reaction mixture.
[d] Determined by chiral HPLC analysis, after epimerization to *trans* diastereoisomer.
[e] 7 h were needed to reach complete diazo consumption.

Table 4. C–H insertion of α-diazoacetamides **4d** and **4e**.

Entry	Diazo compound	Conditions[a]	Yield [%][b]	*cis*:*trans*[c]	*ee* [%][d]
1	**4d**	$C_2H_4Cl_2$, reflux, 1.5 h	58 (80)	1:0.14	66
2	**4d**	H_2O, 80 °C, 1.5 h	45 (59)	1:1	64
3	**4e**	$C_2H_4Cl_2$, reflux, 4 h	86 (95)	1:6	62
4	**4e**	H_2O, 80 °C, 12 h	57 (82)	1:10	60

[a] All reactions were carried out using **4**[17] (0.15 mmol), **7a** catalyst (2 mol%), DCE (1.8 mL) or water (1.5 mL).
[b] Isolated yield after purification by chromatography. The observed conversion determined by ^{31}P NMR is shown in parentheses.
[c] Observed ratio by ^{31}P NMR of the crude reaction mixture.
[d] Determined by chiral HPLC analysis after epimerization to the *trans* diastereoisomer in basic alumina.

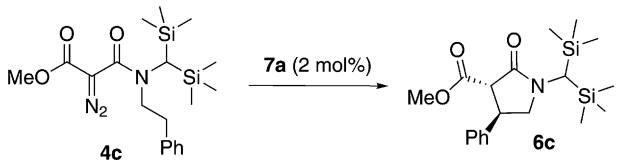
to reach complete consumption of the diazo compound (Table 2, entry 5). This aspect was more obvious when 3,4-dimethoxyphenylalanine derivative **7c** was tested whereby even after 24 h reaction the diazo compound was not completely consumed (Table 2, entry 6).

Once we observed that a side product was present after purification of **7a**, we proceeded to the preparative HPLC isolation of both complexes. From these two complexes, only **7a** was catalytically active leading to formation of **5a** in 69% *ee* and no product was observed after reaction with the unknown side product.

Several chiral dirhodium complexes were reported to perform the intramolecular C–H insertion reactions of α-diazoacetamides in excellent yields and enantioselectivities.[2b,d,6,16] For instance, the dirhodium(II) catalysts derived from *N*-phthalimide-protected amino acids have been used for the enantioselectivity preparation of lactams in up to 96% *ee*.[16b,c,d] By the use of catalyst **1b**, β-lactam **5b** can be obtained in 74% *ee* in dichloromethane after 6 h at room temperature.[5c] Typically, these catalysts have a hydrophobic character and after reaction with α-diazoacetamides the product and the catalyst have to be purified by chromatography. Since Rh_2(L-PheAla)$_2$(OAc)$_2$ (**7a**) is soluble in water and insoluble in diethyl ether, this metallic complex can be easily reused as demonstrated for substrate **4a** (Table 3).

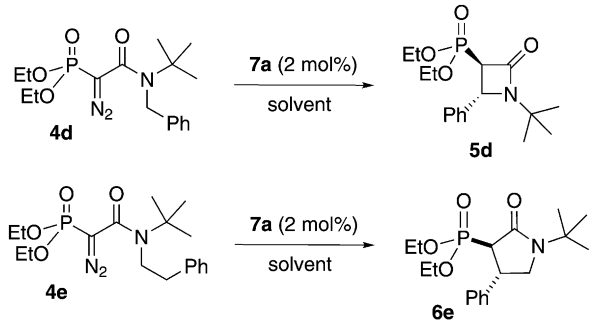
After removal of product **5a** by diethyl ether extraction, more **4a** was added and allowed to react. The catalytic system was reused six times without yield decay and a small *ee* enhancement was observed with the system reuse. This enhancement is probably attributed to the presence of vestigial diethyl ether that promotes the substrate solubilization. For a total of 7 cycles a TON of 115 was obtained.

In order to further evaluate the catalytic activity of complex **7a**, other α-diazoacetamides were submitted to our intramolecular C–H insertion conditions. Keeping the same α-alkoxycarbonyl substituent, a more sterically hindered *N*-[bis(trimethylsilyl)methyl]-substituted acetamide was evaluated (Scheme 3). Surprisingly, despite the excellent yields and regioselectivities, whereby only γ-lactam **6c** was observed, the product was obtained in very low enantioselectivity. On changing from dichloromethane to water, an opposite enantioselectivity was observed.

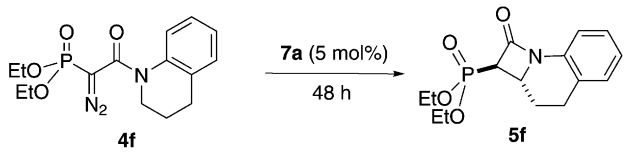


	Yield [%]	*cis:trans*	*ee* [%]
CH_2Cl_2, reflux, 40 min	81	1:1.7	17
H_2O, 80 °C, 6 h	89	1:2.8	–8

Scheme 3. 7a-catalyzed intramolecular C–H insertion of α-diazoacetamide **4c**.

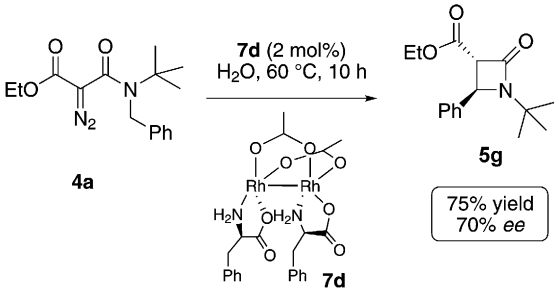


Scheme 4. 7a-catalyzed intramolecular C–H insertion of α-diazoacetamides **4d** and **4e**.



	Yield [%]	*cis:trans*	*ee* [%]
$C_2H_4Cl_2$, reflux	51 (67)	1:0.6	64
H_2O, 80 °C	33 (59)	1:0.6	52

Scheme 5. 7a-catalyzed intramolecular C–H insertion of α-diazo acetamide **4f**. All reactions were carried out using **4f**[6] (0.08 mmol), **7a** catalyst (5 mol%), DCE (0.9 mL) or water (0.8 mL).



Scheme 6. 7d-catalyzed intramolecular C–H insertion of α-diazoacetamides **4a**.

After the somewhat disappointing results obtained in the intramolecular C–H insertion of sterically hindered acetamide **4c**, we decided to explore the effect of the α-substituent. Hence, and due to our interest in finding a suitable catalyst for the enantioselective formation of α-phosphonoacetamides, we tested several of these compounds in water and dichloroethane.[18] Dirhodium complexes derived from mandelic acid were previously reported to provide α-phosphono β- and γ-lactams in moderate enantioselectivities (up to 40% *ee*).[6,17] Keeping the same acetamide substituent, compound **4d** was submitted to aqueous C–H insertion (Scheme 4) and β-lactam **5d** was obtained in 64% *ee* (Table 4, entry 2). Additionally, γ-lactam **6e** was obtained in 60% *ee* and in better yields under the same conditions (Table 4, entry 4). When using dichloroethane as the reaction solvent, similar enantioselectivities were achieved (Table 4, entries 1 and 3) and the desired lactams were obtained in up to 66% *ee*.

Envisioning that the presence of a more rigid system in the acetamide substituent would contribute to better enantioselectivities, α-diazoacetamide **4f** was submitted to the same reaction conditions (Scheme 5). However, in order to achieve over 75% consumption of the starting diazo compound, 5 mol% of the catalyst had to be used. β-Lactam **5f** was obtained in up to 64% *ee* in reasonable yields, which makes this catalyst the best one reported so far as what concerns the stereoselective intramolecular C–H insertion of α-phosphono-α-diazo acetamides. Catalysts **1–3** have been previously tested in this transformation resulting in the α-phosphono lactam formation in only 40% *ee*.[6]

Finally, in order to demonstrate the viability of this method in the preparation of enantioenriched lactams, catalyst **7d**, based on the use of enantiomer D-phenylalanine was prepared and tested in the preparation of lactam **5g**, which was achieved in 75% yield and 70% *ee* (Scheme 6).

In summary, the simple amino acid exchange on $Rh_2(OAc)_4$ in water allows the creation of a new dirhodium catalyst framework that can be used in the intramolecular C–H insertion of α-diazoacetamides in water. β-Lactams were obtained in good yields and in some cases in better enantioselectivity than the ones observed for the reaction in a usual organic solvent. These new complexes can be promising as catalysts for other dirhodium(II)-catalyzed asymmetric reactions, using water or organic solvents as the reaction medium. With the use of water as the reaction media, and due to the low solubility of the prepared catalyst in organic solvents, it was possible to recover the C–H insertion catalytic system in up to 7 runs without enantiomeric excess or yield erosion. The newly developed catalyst **7a** derived from phenylalanine allowed the preparation of α-(dialkoxyphosphoryl)-lactams in moderate enantioselectivities.

Experimental Section

General Procedure for the Intramolecular C–H Insertion

A suspension of diazo compound (0.15 mmol) and dirhodium(II) complex (2 mol%) in water (1.5 mL) was left stirring at room temperature or under heating (see Tables in the text) until complete disappearance of the yellow solid in the reaction vessel (**4a**, **4b**), or by TLC monitoring (**4c–4f**). After solvent removal the residue was purified through flash chromatography (neutral alumina or basic alumina, AcOEt/hexane) and enantiomeric excess of the product determined through HPLC.

Rh_2(S-PheAla)$_2$(OAc)$_2$ (7a)-Catalyzed Decomposition of 4a in Water and Catalyst Recycling

A suspension of **4a** (46 mg, 0.15 mmol) and the complex Rh_2(S-PheAla)$_2$(OAc)$_2$ (5.0 mg, 5 mol%) was heated at 60 °C during 5 h in water (1.5 mL). The product was extracted with Et_2O (3×2 mL) and more *N*-(benzyl)-*N*-(*tert*-butyl)-2-(ethoxycarbonyl)-2-diazoacetamide **4a** (46 mg, 0.15 mmol) was added to the aqueous layer and heated at 60 °C for another 5 h. This procedure was repeated for 7 times until the conversion started to decay. After solvent removal of each organic layer, the residue obtained was filtered over a neutral alumina pad to induce epimerization of β-lactam to the *trans* diastereoisomer. After solvent removal under reduced pressure, **5a** was obtained and the *ee* determined by chiral HPLC.

Acknowledgements

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new complexes. CCDC 864696, CCDC 765711 and CCDC 765710 contains the supplementary crystallographic data for this paper (structures of **7a**, **7b** and **7c**, respectively). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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