Observations on the origin of phenylacetaldehyde in styrene epoxidation and the mechanism of oxidations catalysed by manganese complexes of porphyrins

António M. d'A. Rocha Gonsalves *[a] and Arménio C. Serra [b]

[a] *Departamento de Química, Universidade de Coimbra, Rua Larga, 3000 Coimbra, Portugal*
[b] *Universidade Católica Portuguesa, R. Dr. Mendes Pinheiro, 24, 3080 Figueira da Foz, Portugal*

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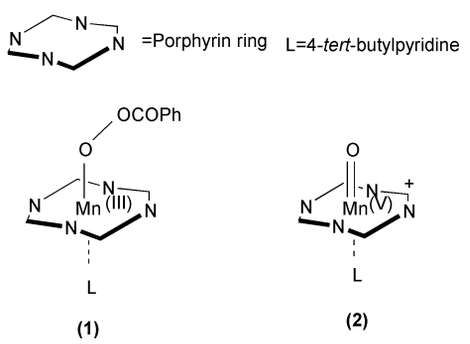
Phenylacetaldehyde (PhA) has been observed as a by-product in H_2O_2 metalloporphyrin catalytic oxidation of styrene. We have found that the mechanism of these oxidations depends on the relative amount of the carboxylic acid that is used as co-catalyst. With an excess of the organic acid less PhA is formed due to the intervention of metalloacylperoxo species (**1**) instead of a metallo-oxo species (**2**). Whatever the conditions used, the PhA which is formed comes chiefly from styrene oxide (SO) isomerization. This process seems to be due to the presence of oxygen centered radicals formed through metalloporphyrin reaction with hydrogen peroxide.

Introduction

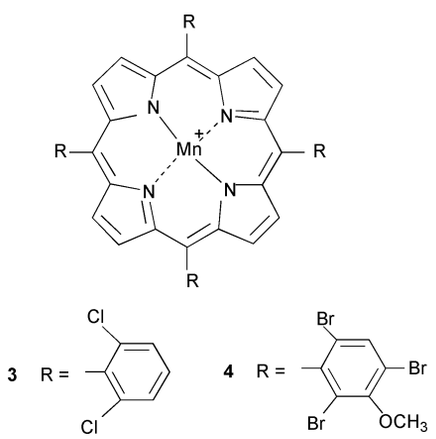
The use of hydrogen peroxide as an oxidant is still a desired objective, despite the extensive efforts dedicated to this subject. Recent proposals include the activation by rhenium compounds,[1] the formation of carbodiimide adducts[2] or activation with sodium bicarbonate.[3] However, hydrogen peroxide activation by metallic complexes of porphyrins has been shown to be promising and worth exploiting.[4]

Recently we disclosed some studies where the role of a lipophilic acid on hydrogen peroxide activation in a two-phase system is discussed.[4d,5] When in the presence of an excess of lipophilic acid metalloacylperoxo **1** is apparently the species directly involved in the oxidation of substrates instead of the more commonly reckoned intermediate, the metallo-oxo species **2**.[6] However we believe that **2** is still the oxidant species in a system where the concentration of the lipophilic acid is low.



Attempting to give extended support to our hypothesis, we decided to study the metalloporphyrin catalysed epoxidation of styrene under the conditions that favour the formation of **1** or **2** and monitored the formation of products under the two sets of conditions.

We performed this study using the manganese complexes of 5,10,15,20-tetrakis(2,6-dichlorophenyl)porphyrin (**3**) and also of the new brominated porphyrin, 5,10,15,20-tetrakis(2,4,6-tribromo-3-methoxyphenyl)porphyrin (**4**), Scheme 1.



Scheme 1 Manganese complexes of porphyrins used as catalysts.

Results and discussion

Synthesis of metalloporphyrins

Metalloporphyrin **3** had already been prepared by a known route.[7] Porphyrins having bromine atoms at positions 2 and 6 of *meso*-phenyl groups have been less studied.[8] The aldehyde required for the preparation of porphyrin **4** was synthesized by bromination of 3-hydroxybenzaldehyde followed by methylation.[9] The porphyrin was prepared by reaction of the aldehyde with pyrrole by the Lindsey procedure[10a] following our original two step methodology.[10b] The metallation of the porphyrin was carried out by the manganese acetate–acetic acid method[11] since DMF leads to some demethylation.[12]

Styrene epoxidation

It was previously reported that the metalloporphyrin catalysed epoxidation of styrene using several oxidants gives styrene oxide (SO) as the main product but that some phenylacetaldehyde (PhA) is also produced.[13] It has been claimed that the aldehyde is formed in a side route of the reaction.[13b,c,14] We expected that reaction conditions which favour the formation

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Table 1 Relative yield of styrene oxide (SO) and phenylacetaldehyde (PhA) obtained in the oxidation of styrene using catalysts **3** and **4**

Catalyst	Conditions[a]	SO%	PhA%
3	A	83	17
3	B	77	23
4	A	89	11
4	B	86	14

[a] Conditions A: molar ratio of catalyst–4-*tert*-butylpyridine–benzoic acid–styrene–H_2O_2 (5%); 1 : 1 : 20 : 200 : 1300. Conditions B: molar ratio of catalyst–4-*tert*-butylpyridine–benzoic acid–styrene–H_2O_2 (5%); 1 : 1 : 1 : 200 : 1300.

of species **1** or species **2** would have a different product distribution and so be indicative of the contribution of the two species in this catalytic system.

Considering the vagaries of previous results and the possibility of the conversion of the original oxidation products due to work-up and analytical procedures, we began by studying the analytical conditions in order to avoid epoxide isomerization into phenylacetaldehyde. While some reports were contradictory in this respect[13c,15] the majority of the works do not seem to have taken this problem into consideration. We found that with the analytical conditions ordinarily used with these substrates (t_{inj} = 200 °C, t_{det} = 220 °C and capilary column 30 m), a sample of standard epoxide showed some isomerization to PhA. The relative percentage of the PhA varied from one injection to another. Even with a low injector temperature (130 °C) some isomerization was observed. Due to these results we changed to HPLC to study the products so that the analytical values would correspond to real reaction product distributions. In some of the reported works it is said that benzaldehyde, which appears in small quantities, is one of the products from styrene epoxidation.[13a,16] HPLC analytical conditions can not distinguish between PhA and benzaldeyde but the GC/MS analysis of reaction products gave no evidence of the presence of benzaldehyde.

After establishing adequate analytical conditions, we performed catalytic experiments promoting the oxidation of different amounts of styrene in the presence of manganese complex (**3** and **4**), H_2O_2 (5%), 4-*tert*-butylpyridine and benzoic acid in a dichloromethane–water two-phase system. Two sets of experimental conditions were used, differing only in the relative amount of benzoic acid that was present. Conditions A correspond to 20 : 1 molar equivalents of benzoic acid relative to catalyst and conditions B to a 1 : 1 molar ratio. All the results reported in this work correspond to the average of two assays and to complete conversion of styrene, unless otherwise stated. If the difference of the two results was higher than 10%, a third experiment was carried out. Table 1.

It was observed that in all cases a higher amount of PhA is produced when conditions B rather than conditions A are used. In both conditions A and B catalyst **4** with bulkier bromine atoms is more selective than catalyst **3** for SO. The selectivity for SO is dependent on the amount of initial styrene as can be seen in Table 2.

For all experiments the selectivity for SO is lower with conditions B. As the initial amount of styrene increases the PhA produced is higher.

The next experiments were intended to clarify whether the formation of PhA takes place concurrently with the epoxidation or is due to isomerization of the formed epoxide, despite some claims to the contrary.[13a,b,17] We substituted the styrene by the corresponding epoxide in a 200 : 1 (epoxide–catalyst) ratio and left it to stand under the conditions of Table 1. After 40 minutes with catalyst **3** 13% of PhA was obtained under conditions A and 17% under conditions B. With catalyst **4** we obtained 7% isomerization with conditions A. This shows that hydrogen peroxide oxidation reaction conditions promote the

Table 2 Relative yield of styrene oxide (SO) and phenylacetaldehyde (PhA) obtained in the oxidation of styrene using catalyst **3** and different styrene–catalyst ratios

Styrene–catalyst ratio	Conditions[a]	SO%	PhA%
200 : 1	A	83	17
	B	77	23
300 : 1	A	77	23
	B	48	52
400 : 1	A	62	38
	B	50	50

[a] Conditions A: molar ratio of catalyst–4-*tert*-butylpyridine–benzoic acid–styrene–H_2O_2 (5%); 1 : 1 : 20 : 200–400 : 1300. Conditions B: molar ratio of catalyst–4-*tert*-butylpyridine–benzoic acid–styrene–H_2O_2 (5%); 1 : 1 : 1 : 200–400 : 1300.

Table 3 Product distribution in the catalytic oxidation of styrene in the presence of different amounts of 4-*tert*-butylpyridine as axial ligand using conditions A and catalyst **3**

Styrene–catalyst	Axial ligand–catalyst	SO%	PhA%
200 : 1	0.5 : 1	69	31
	1 : 1	83	17
	2 : 1	87	13
400 : 1	1 : 1	62	38
	2 : 1	84	16

isomerization of styrene oxide to phenylacetaldehyde, and so it is demonstrated that two sources for PhA exist in these oxidations, one simultaneous with the epoxidation, another originating from isomerization of the epoxide. The amount of PhA obtained is mainly due to isomerization. In the absence of catalyst no PhA is formed from SO, confirming that the isomerization process is mediated by the metalloporphyrin. With conditions B but without hydrogen peroxide solution only 2% PhA is formed from styrene oxide, confirming that the oxidant is necessary for the isomerization process.

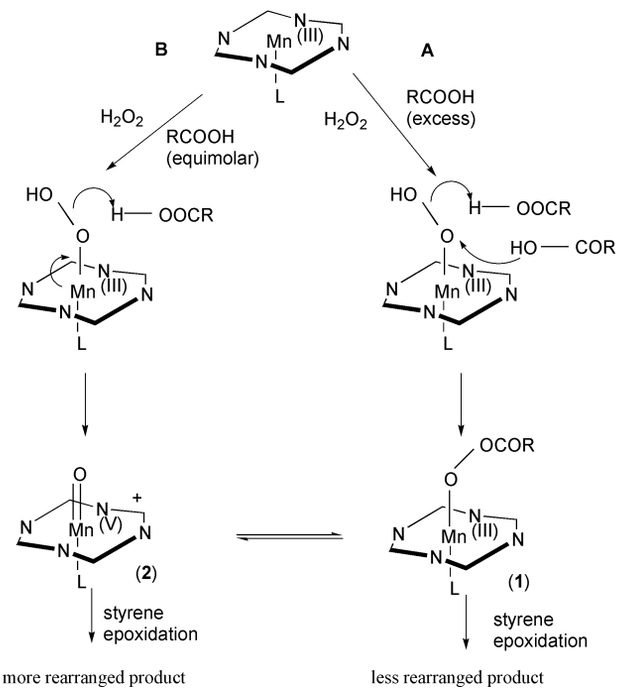
The role of the axial ligand in the selectivity of these catalysed reactions has already been studied by several workers.[13e,18] We studied how the amount of axial ligand influences the catalytic epoxidation of styrene using conditions A and catalyst **3** obtaining the results shown in Table 3.

The results show that the amount of PhA increases when the ratio axial ligand–catalyst decreases. This effect of the axial ligand is more significant in the presence of a large excess of styrene. All the experiments showed complete conversion of the substrate after 40 minutes even when that ratio was 0.5 : 1. In the absence of axial ligand we did not observe any conversion of styrene, although the same conditions produce a small isomerization of styrene oxide (7% PhA). A similar degree of isomerization (8%) is observed when SO in placed under conditions A, but in the presence of 2 equivalents of axial ligand relatively to the catalyst.

The observed results can be rationalized considering our previously proposed equilibrium between two species able to oxidize styrene,[5] Scheme 2.

In the presence of equimolar quantities of benzoic acid (conditions B) according to our mechanism the formation of the metallo-oxo intermediate **2** is favoured through pathway B. Styrene epoxidation by this species can generate phenylacetaldehyde by different proposed mechanisms.[13b,17] However in the presence of an excess of benzoic acid (conditions A) the metalloacylperoxo intermediate **1** following pathway A is favoured. This species has structural characteristics similar to a peroxoacid and may be able to epoxidize styrene by a similar oxidation mechanism while producing less PhA.[19] The amount of PhA obtained under conditions A may be due to the small amount of **2** in equilibrium with **1**.

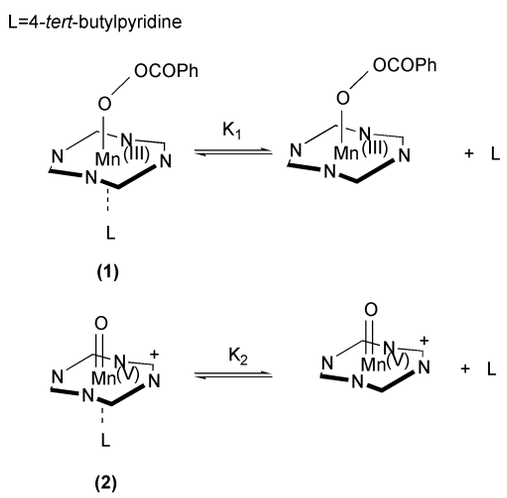
In the presence of a higher excess of styrene the number of catalytic cycles is increased and so is the amount of SO



Scheme 2 Mechanism involving the equilibrium between intermediates **1** and **2** and rearranged products therefrom.

produced. The greater amount of SO formed under these conditions increases the possibility of isomerization of SO mediated by the catalyst, producing PhA. Another source for the increased amount of PhA could be the fact that different styrene affinities for species **2** and **1** may exists. Larger excesses of styrene can in this way benefit styrene epoxidation by species **2** instead of **1** even if the conditions favour pathway A.

The effect of the axial ligand is more difficult to rationalize. Our results show that it is required for the catalytic process as well as for isomerization of the epoxide. This is reinforced by the fact that the replacement of 4-*tert*-butylpyridine by the corresponding *N*-oxide gives neither catalysis nor any isomerization. We have no data allowing us to distinguish whether the most important role of the axial ligand is in the generation of **1** or **2** or in the transfer of the oxygen atom from this species to the alkene. Certainly equilibrium exists between species **1**, **2** and their axial non-complexed forms, but only **1** and **2** are effective in catalytic processes, Scheme 3.



Scheme 3

It is likely that the corresponding equilibrium constants K_1 and K_2 have different values and that **1** and **2** have different reactivities. Accepting Scheme 2, the results obtained by us point out that larger amounts of axial ligand may favour the existence of **1**, a species leading to a small amount of rearranged product.

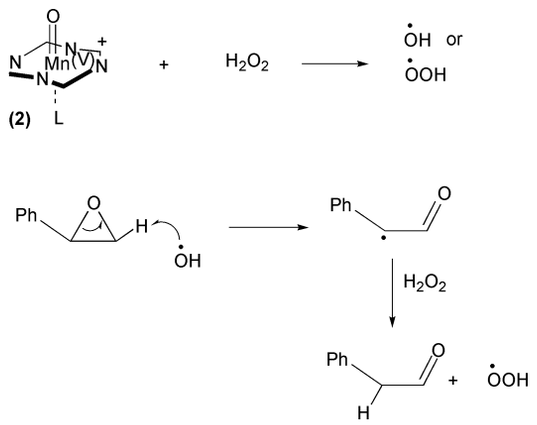
Table 4 Product distribution in the catalytic oxidation of styrene with **3** and **4** in the presence of 2,6-di-*tert*-butyl-4-methylphenol under conditions A and conditions B. Molar ratio of catalyst–2,6-di-*tert*-butyl-4-methylphenol (1 : 5)

Catalyst	Conditions	SO%	PhA%
3	A	95	5
3	B	82	18
4	A	93	7
4	B	91	9

Our proposed mechanism, outlined in Scheme 2 and the results obtained suggest that the metallo-oxo species **2** is mainly responsible for the production of PhA. For comparison proposes we changed the oxidant to sodium hypochlorite since it is well established that the oxidant species in this system is unambiguously the metallo-oxo species **2**.[13d,20,21] Surprisingly with catalyst **3** and the same axial ligand we obtained only 1% of PhA and about 10% of a new product with greater retention time. The analysis by GC/MS revealed that this new compound shows a mass peak compatible with a dichorophenylethane, a result already observed by us in similar oxidations.[7] When we tried the isomerization of SO under these conditions, no PhA was obtained. Taking into account these results, the hypothesis of the intervention of species **2** in the production of PhA in the styrene catalytic epoxidation must be rethought. If the direct interaction of metallo-oxo species **2** with styrene does not generate the amount of PhA observed in H_2O_2 epoxidations, we thought that perhaps an indirect interaction might occur. Traylor *et al.* pointed out the importance of the reaction of metallo-oxo species as **2** with the oxidants, particularly in the case of hydroperoxides.[22] These reactions, which compete with substrate oxidation, generate oxygen centred radicals that have already been pointed out by us and others as one of the explanations for the degradation of this type of catalyst in hydrogen peroxide systems.[5,23] In the case of styrene epoxidation these radicals could also be responsible for PhA formation. To check this hypothesis we carried out styrene epoxidations in the presence of 2,6-di-*tert*-butyl-4-methylphenol, a known radical scavenger. The results are shown in Table 4.

The results show a clear reduction of the amount of PhA in the two sets of conditions compared with similar reactions performed in the absence of 2,6-di-*tert*-butyl-4-methylphenol (Table 1). Again conditions B that favour the presence of metallo-oxo species **2** always give a greater amount of isomerization product than conditions A. This is more relevant to catalyst **3** than catalyst **4**. An experiment of isomerization of SO with catalyst **3** and without hydrogen peroxide gave only 2% PhA. Another experiment of isomerization with catalyst **3** in conditions A and in the presence of the radical scavenger gave 3% PhA against 13% obtained in the absence of 2,6-di-*tert*-butyl-4-methylphenol. Undoubtedly these results point to the intervention of radicals in the isomerization process possibly by an indirect process involving hydroxyl or perhydroxyl radicals generated by reaction of metallo-oxo species **2** with hydrogen peroxide, Scheme 4.

The intervention of oxygen centred radicals in the isomerization process was plainly established by putting the styrene oxide dissolved in dichloromethane in the presence of a solution of Fenton's reagent (H_2SO_4–H_2O_2–$FeSO_4$) which is known to generate hydroxyl radicals.[24] After stirring for 40 minutes we observed that 85% PhA was formed. When the styrene oxide was placed in a similar acid solution but in the absence of the iron salt only 14% PhA was formed after 40 minutes. On addition of the iron salt the amount of PhA increased to 91% after an extra 40 minutes. In a control experiment the iron salt was added to the styrene oxide solution to give only 18% of PhA after 40 minutes. On addition of the



Scheme 4

hydrogen peroxide we got complete isomerization of SO to PhA after 20 minutes. As far as we know, this isomerization process was never described in the Fenton system. This will be further exploited.

Conclusions

The phenylacetaldehyde which is formed as a product in the metalloporphyrin catalysed epoxidation of styrene is of two distinct origins. Partly due to a secondary branch of the epoxidation mechanism as generally accepted, we found that the major source is, however, the isomerization of the primary product, styrene oxide. It was demonstrated that this isomerization is promoted by the presence of oxygen centered radicals which are themselves generated from H_2O_2 interaction with the catalyst.

Experimental

Instrumental methods

^{1}H NMR spectra were recorded on a 300 MHz Bruker-AMX spectrometer. Mass spectra were obtained on a VG 7070E mass spectrometer. Elemental analysis was carried out using a Fisons Instruments EA 1108-CHNS-O apparatus. Absorption spectra were measured on a Jasco 7800 spectrophotometer. Gas chromatography was carried out on a Hewlett-Packard 5890 A with a flame ionisation detector; it was equipped with a OV1(25m × 0.3 mm, id) capillary column. HPLC analyses were carried out using a Gilson 307 pump and a Gilson UV/V 151 detector at 254 nm. A 250/4 mm Nucleosil 50-7 Macherey-Nagel column was used with a mobile phase consisting of a mixture of hexane–isopropanol (99 : 1) at 1 mL min^{-1}. GC/MS analyses were carried out on a Agilent 6890 GC system with a Hewlett Packard 5973 Mass Selective detector equipped with a capillary column HP-5 MS (25 m).

Reagents

Dichloromethane was distilled from P_2O_5 before use. Other solvents used were commercially available and used as received. Styrene was obtained from Riedel and was passed through a short column of alumina before use. Hydrogen peroxide 5% was prepared from a concentrated solution from Riedel and titrated by iodometry. The pH of this solution was set to 4.5–5 with hydrogen carbonate.

Styrene oxide and phenylacetaldehyde were purchased from Aldrich. 2,4,6-Tribromo-5-methoxybenzaldehyde was prepared by known procedures.[9]

General procedure for oxidation reactions

A 20 mL flask was charged with 2.5×10^{-3} mmol of the metalloporphyrin and volumes of dichloromethane solutions of organic acid and axial ligand that gave 2 mL total volume and the correct organic acid–axial ligand–catalyst ratio. Then the alkene and 2 mL of hydrogen peroxide (5%) were added and the mixture stirred at maximal rate. At the end of the reaction a sample of 250 μL of the organic phase was taken and put on the top of a small column of silica and eluted into a 10 mL dilution flask with 6 mL hexane–dichloromethane (3 : 1) mixture. Experiments were made to ensure that this volume of eluant was sufficient to elute all the products formed. The volume was made up to 10 mL with hexane and analysed by HPLC. The conversions were monitored by removing aliquots and examining by GC against internal standard (bromobenzene).

General procedure of Fenton isomerization of SO

About 50 mL of a solution of 0.05 M sulfuric acid and 0.2 M hydrogen peroxide was prepared and bubbled with nitrogen. After that an amount of iron(II) sulfate was added to give a 0.04 M solution; 5 mL were taken and added to 2 mL dichloromethane with 50 μl styrene oxide, and stirred.

Synthesis of porphyrins

***meso*-Tetrakis(2,6-dichlorophenyl)porphyrin (3).** Compound **3** was prepared by using the nitrobenzene–acetic acid method.[25]

***meso*-Tetrakis(2,4,6-tribromo-5-methoxyphenyl)porphyrin.** A solution of 2.2 g (6.0 mmol) of 2,4,6-tribromo-5-methoxybenzaldehyde and 0.37 mL (6.0 mmol) of pyrrole in 500 mL of distilled CH_2Cl_2 was purged with N_2 for 15 min, then 0.10 mL of a solution of $BF_3{\cdot}OEt_2$ (0.25 mL in 1 mL of CH_2Cl_2) was added at room temperature. The solution was left for 3 hours, neutralized with 25 μL of triethylamine and concentrated to 200 mL. This solution was then poured over a solution of acetic acid–acetic anhydride–H_2O_2 (35%) (100 : 5 : 3) and left for 2 hours at 40 °C. The acid was washed with water and the solution neutralized, dried and concentrated *in vacuo*. The residue was chromatographed on alumina (CH_2Cl_2–petroleum ether 40–60, 9 : 1) giving 0.450 g of the porphyrin as a red band, yield = 18%. Recrystallization in CH_2Cl_2–methanol gave an analytical sample. Found: C, 34.5; H, 1.4; N, 2.9. $C_{48}H_{26}N_4O_4Br_{12}$ requires C, 34.3; H, 1.6; N, 3.3%. V/UV λ_{max} (CH_2Cl_2/nm) 421 [log (ε/dm^3 mol^{-1}cm^{-1}) 5.5], 516 (3.4), 589 (4.0), 659 (3.6); δ_H (300 MHz; $CDCl_3$; Me_4Si): 8.7 (8H, s, β-H), 8.2 (4H, s, Ar), 4.1 (12H, m, Me), −2.5 (2H, s, NH); (M + H$^+$) (FAB) = 1671.

The manganese complex of porphyrin **3** was obtained by the DMF method.[26]

Manganese(III) complex of *meso*-(2,4,6-tribromo-5-methoxyphenyl)porphyrin (4). *meso*-Tetrakis (2,4,6-tribromo-5-methoxyphenyl)porphyrin (300 mg) was added to a solution of 400 mg of manganese(II) acetate and 500 mg of sodium acetate in 100 mL of acetic acid. The mixture was refluxed for 6 hours. After that 250 mL of CH_2Cl_2 were added and the organic phase washed with water and dried (Na_2SO_4). The solution was concentrated and the residue chromatographed on silica-gel (CH_2Cl_2, then CH_2Cl_2–ethyl ether 1 : 1). The fraction with the complex was washed with a concentrated solution of NaCl, dried and evaporated giving 195 mg of the manganese complex, yield 62%. λ_{max} (CH_2Cl_2/nm) 481 (relative height 100%), 584 (7.6), 618 (sh); M$^+$(FAB$^+$) = 1726 (18%), 1728 (30), 1730 (62), 1732 (88), 1733 (6), 1734 (100), 1735 (12), 1736 (90), 1737 (18), 1738 (58), 1739 (18), 1740 (30), 1741 (10), 1742 (16).

Acknowledgements

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