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The acid accelerated ruthenium-catalysed dihydroxylation. Scope and limitations

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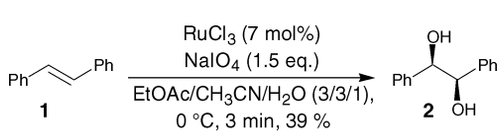
Recently, we discovered a significant rate acceleration in RuO_4-catalysed dihydroxylations of olefins by addition of Brönsted-acids resulting in a reduction of the catalyst loading to only 0.5 mol%. The present paper gives a full account on the optimisation protocol that led to the discovery of the beneficial influence of protic acids. A strong focus is set on the detailed description of the influence of different reaction parameters on both reactivity and selectivity. In the second part an intense investigation of scope and limitations will be presented. The results provided in this manuscript might lead to a deeper understanding of competing processes that influence the selectivity in RuO_4-catalysed dihydroxylations.

Introduction

The catalytic and stereoselective introduction of oxygen containing functional groups represents a challenging problem in organic synthesis.[1] Among the so far known oxidations the dihydroxylation of C,C-double bonds occupies an important place.[2] The current success in the development of new and efficient olefinations *via* metathesis further underlines the usefulness of these oxygenation processes.[3] Within the past twenty years the osmium-catalysed dihydroxylation became a benchmark reaction when it comes to generality and selectivity.[4] Due to the pericyclic character of the stereoinducing step the double bond geometry is translated into the relative stereochemistry of the two adjacent stereocentres. Thus, the question of diastereoselectivity in the oxidation can be finally reduced to a stereoselective olefination. However, some problems are connected with osmium-catalysed reactions.[4] The catalyst is very expensive, volatile and toxic. These three issues prevent a successful application on an industrial scale. Different alternative oxidants have been tried in order to circumvent the use of osmium. The isoelectronic ruthenium(VIII) oxide, prepared *in situ* from inexpensive ruthenium(III) chloride, seems to be the most promising one (Scheme 1).[5] Dihydroxylations under RuO_4-catalysis are in general very fast (Shing coined the reaction as "flash-dihydroxylation"). However, due to the high redox potential of the catalyst ($E°$ (Os(VIII)/Os(VI): 1.020 V, Ru(VIII)/Ru(VI): 1.400 V) the reactions are often not very selective and difficult to control.



Scheme 1 "Flash-dihydroxylation" of stilbene **1**.

It is for that reason, that this transformation has been rarely used in the past. The chemistry of highly oxidised transition metals is in the centre of our current research. During our investigations on ruthenium-catalysed oxidation processes we discovered a significant rate acceleration of the dihydroxylation using catalytic amounts of protic acids.[6] The present paper provides a detailed description of our investigations on factors influencing the selectivity and reactivity of the reaction. Apart from this methodological information an intense screening of scope, limitations and chemoselectivity will be provided in the second part. The results presented in this paper lead to a more practical and understandable alternative dihydroxylation method applicable to the oxidation of a variety of structural diverse olefins.

Results and discussion

Overoxidation and formation of fission products are common side reactions in ruthenium-catalysed dihydroxylations. Different scenarios could account for these unwanted transformations (Fig. 2). Apart from a classical $NaIO_4$-assisted glycol cleavage of diol **VI** RuO_4 **I** itself could react with **VI** in a sequence of condensation–electrocyclic fragmentation. These options were ruled out by two simple control experiments. A comparison of the reaction rate for the RuO_4/$NaIO_4$- and $NaIO_4$-assisted glycol cleavage of hydrobenzoin **2** indicated that RuO_4 accelerates the fission reaction, however, both of these fragmentations are slow on the time scale of the dihydroxylation (Fig. 1).[6]

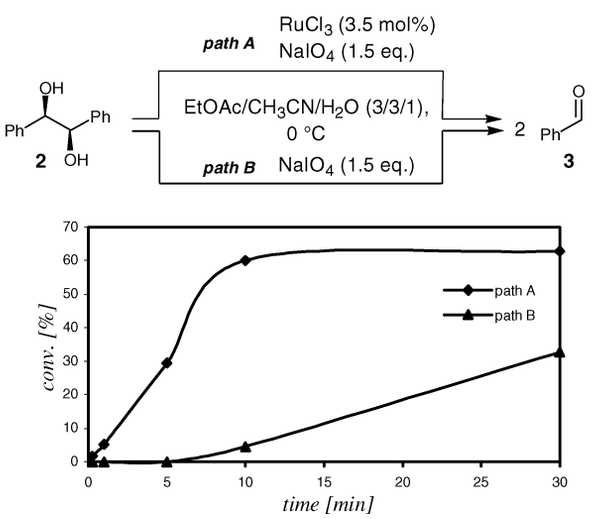


Fig. 1 Conversion–time-curve for the cleavage of hydrobenzoin **2**.

Accordingly, aldehyde **IV** has to be formed *via* a side reaction in the catalytic cycle (Fig. 2). In a proposed mechanism olefin **II** adds to RuO_4 **I** to give ester **III**, which can react in two different ways. Apart from an oxidation to ruthenium(VIII)-species **V** an

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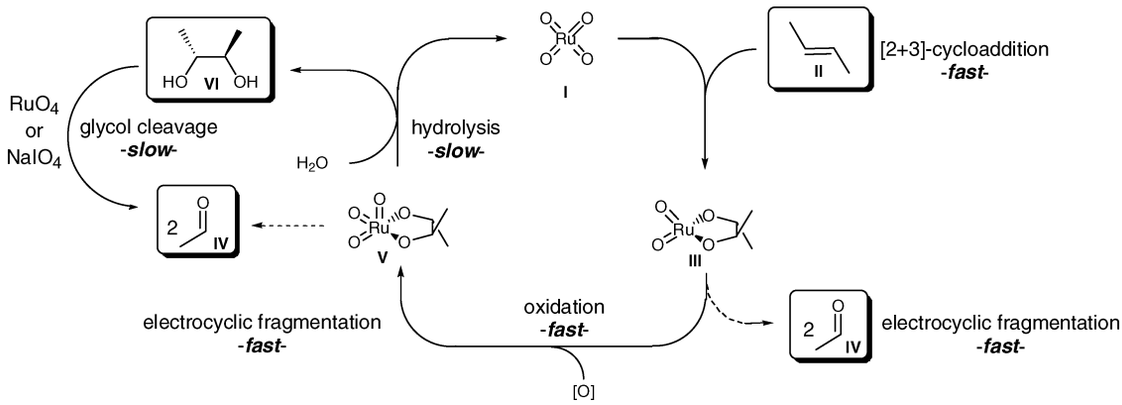


Fig. 2 Proposed mechanism for the formation of fission products.

entropically favourable electrocyclic fragmentation results in the formation of aldehyde **IV** and RuO_2. Furthermore, ruthenate **V** can react in two competing ways. A hydrolysis furnishes the desired diol **VI** while regenerating the catalytically active RuO_4 **I**, or an electrocyclic fragmentation leads to aldehyde **IV**. Based upon the results of preliminary control experiments we hypothesised the hydrolysis of ruthenate ester **V** to be the rate limiting step in the dihydroxylation. If the hydrolysis is too slow, the intermediate ruthenium species **V** reacts in the fragmentation pathway towards aldehyde **IV**. Hence, the strategy to improve the selectivity for the dihydroxylation must include an accelerated hydrolysis of ruthenate **V**.

Optimisation protocol

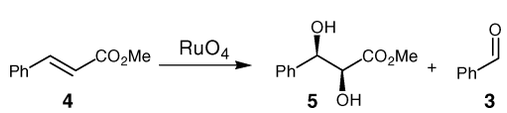
RuO_4 is isoelectronic to OsO_4, however, due to its position in the periodic table of elements the redox potential is much higher (*vide supra*). Another major difference is the stability of ruthenium(VIII) oxide at different pH-values. Whereas OsO_4 can be used in alkaline solution, RuO_4 is only stable up to pH 9. Above this pH-value it reacts with the free hydroxide to give perruthenate RuO_4^-.[7] Hence, an optimisation protocol for this dihydroxylation can only partially rely on the results of the osmylation reactions. In osmium-catalysed dihydroxylations the hydrolysis of the intermediate osmates represents the rate limiting step.[4] Sharpless and others investigated different approaches to speed up the cleavage of metallo esters. From a mechanistic point of view the hydrolysis starts with a nucleophilic addition of water towards the metal centre. One way to improve this addition is the use of an organic solvent known to be homogenous, mixable, with water. Different solvent combinations and stoichiometries were tested, however, the original solvent mixture of ethyl acetate/acetonitrile/water (3/3/1) proved to be best. Different from the related osmylations a homogenous mixture using acetone or *tert*-butanol as organic solvents did not improve the conversion. Moreover, the selectivity for the dihydroxylated product **5** dropped significantly (Table 1). This is most likely due to an acceleration of the $NaIO_4$-assisted glycol cleavage. Methyl *tert*-butyl ether showed a good selectivity, albeit the conversion stops at 50%.

These results are in line with observations reported by Yang and Zhang recently, in which replacement of ethyl acetate and acetonitrile by 1,2-dichloroethane resulted in the clean oxidative cleavage of the C,C-double bond by the $RuCl_3/NaIO_4$-system.[8] Hence, water immiscible solvents like dichloromethane stabilise the intermediate ruthenates **III** or **V** resulting in a predominant electrocyclic fragmentation, while water miscible solvents increase the activation of $NaIO_4$ resulting in an accelerated periodate-assisted glycol cleavage of product **VI**. At this point no further investigations on the solvent effect was performed. The original solvent combination[5] of ethyl acetate, acetonitrile and water in a ratio of 3 : 3 : 1 seems to be the optimum.

Subsequently, the influence of higher temperatures on the reaction course was investigated (Table 2). Thus, increasing the temperature lead to a predominant formation of fission products. Apparently, the electrocyclic fragmentation is faster at elevated temperature. Hence, an acceleration of the hydrolysis by a simple variation of these reaction parameters was not possible.

At this point we sought for additives known to speed up the hydrolysis of metallo esters. Sharpless used this strategy in order to oxidise highly substituted or electron-poor olefins.[4,9] Although the use of sulfonamides improved the hydrolysis in osmylations an influence on both selectivity and reactivity in ruthenium-catalysed dihydroxylations was not observed.[10] Akashi's work on a faster hydrolysis in the osmylation reaction by addition of tetra-*n*-alkyl ammonium acetates did not prove useful for the related ruthenium-catalysed dihydroxylations.[11] Moreover, the acetate inhibits the catalyst very efficiently. This is in line with earlier observations on the influence of carboxylates on RuO_4-catalysed oxidations.[12] We then investigated the possibility to use an accelerated hydrolysis of the ruthenate under slightly alkaline conditions. However, a further limitation for an accelerated hydrolysis is given by the instability of

Table 1 Influence of solvent



4 5 3

Entry[a]	Solvent	5 : 3[b]	Conv. [%][b]
1	CH_2Cl_2 (6 mL)/CH_3CN (6 mL)/H_2O (2 mL)	44 : 56	4
2	MTBE (6 mL)/CH_3CN (6 mL)/H_2O (2 mL)	75 : 25	49
3	acetone (6 mL)/ CH_3CN (6 mL)/H_2O (2 mL)	38 : 72	31
4	*t*-BuOH (6 mL)/ CH_3CN (6 mL)/H_2O (2 mL)	0 : 100	24
5	EtOAc (6 mL)/CH_3CN (6 mL)/H_2O (2 mL)	84 : 16	81

[a] All reactions were performed on a 1 mmol scale using 3.5 mol% $RuCl_3$ (as a 0.1 M solution in H_2O), 1.5 equiv. $NaIO_4$ at 0 °C and stopped after 5 minutes by addition of 10 mL sat. $Na_2S_2O_3$-solution. [b] Determined by GC-integration.

Table 2 Influence of temperature

Entry[a]	*T* [°C]	**5** : **3**[b]	Conv. [%][b]
1	0	84 : 16	81
2	5	79 : 21	88
3	10	71 : 29	94
4	20	39 : 61	99

[a] All reactions were performed as indicated in Table 1 in a solvent system of EtOAc (6 mL)/CH_3CN (6 mL)/H_2O (2 mL). [b] Determined by GC-integration.

Table 3 Influence of pH

Entry[a]	pH[b]	**5** : **3**[b]	Conv. [%][c]
1	1	78 : 22	93
2	2	75 : 25	88
3	3	77 : 23	79
4	4	76 : 24	74
5	5	74 : 26	68
6	6	75 : 25	69
7	7	74 : 26	67
8	8	73 : 27	61
9	9	56 : 44	46
10	10	36 : 64	12

[a] All reactions were performed as indicated in Table 2. [b] The pH was adjusted by addition of a certain amount of K_2CO_3 (pH > 7) or H_2SO_4 (pH < 7) to water. [c] Determined by GC-integration.

ruthenium(VIII) oxide under basic (pH > 9) conditions.[7] In contrast to the osmylation inorganic bases like hydroxides or organic bases like pyridine or tertiary nitrogen compounds inhibit the reaction. Different buffer solutions have been tried, however, due to the rather low solubility of $NaIO_4$ in water the reactions in the presence of buffer were usually sluggish and very slow. Furthermore, the formation of black precipitates was observed. It is for that reason, that the pH-value was adjusted manually by addition of K_2CO_3 or 1 M H_2SO_4. As can be seen from Table 3 the conversion increases with a decreasing pH.[13] The selectivity is not affected.

Because of the accelerated hydrolysis further attempts to lower the amount of catalyst while maintaining the total amount of acid were performed. At pH = 1 the amount of $RuCl_3$ was reduced stepwise. The results are visualized in Fig. 3. The addition of acid allowed a decrease in catalyst loading down to only 0.5 mol%.

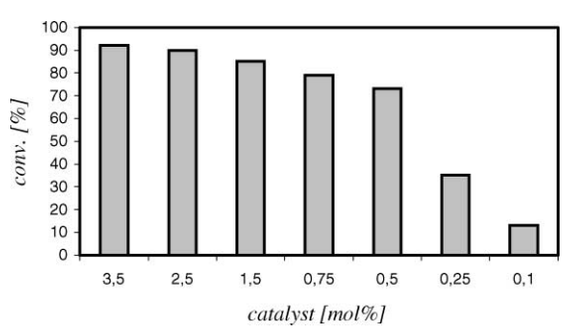


Fig. 3 Conversion at different catalyst concentrations (pH = 1).

Up to this point sulfuric acid has been used as proton source. The influence of other acid sources was investigated next (Table 4). Carboxylic acids had a minor influence on the selectivity, however, under these conditions they did not inhibit the catalytic system. Stronger Brönsted-acids showed a significant influence (Table 4).

Increasing the amount of acid resulted in a fast conversion paired with a good selectivity within 5 minutes (Fig. 4). With regard to the scope and limitations the maximum amount of added acid was chosen to be 20 mol% H_2SO_4. Higher acid

Table 4 Influence of acid

Entry[a]	Acid	**5** : **3**[b]	Conv. [%][b]
1	—	74 : 26	29
2	HOAc	70 : 30	65
3	TFA	79 : 21	66
4	Benzoic acid	69 : 31	59
5	Citric acid	66 : 34	44
6	$MeSO_3H$	78 : 22	81
7	*p*-TosOH	76 : 24	80
8	HCl	77 : 23	69
9	H_2SO_4	79 : 21	90
10	H_3PO_4	89 : 11	39
11	HNO_3	71 : 29	75

[a] All reactions were performed on a 1 mmol scale using 0.5 mol% $RuCl_3$ (as a 0.1 M solution in H_2O), 1.5 equiv. $NaIO_4$ and 5.0 mol% protic acid (as a 1 M solution in water) at 0 °C in EtOAc (6 mL)/CH_3CN (6 mL)/H_2O (2 mL) and stopped after 5 minutes by addition of 10 mL sat. $Na_2S_2O_3$-solution. [b] Determined by GC-integration.

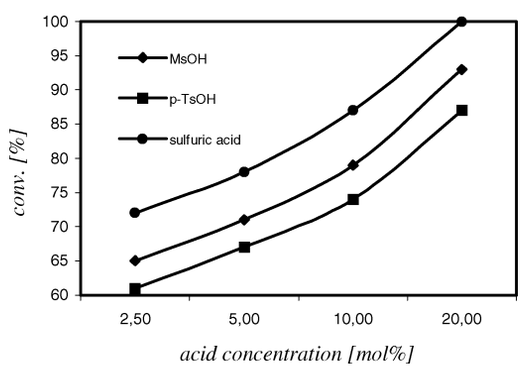
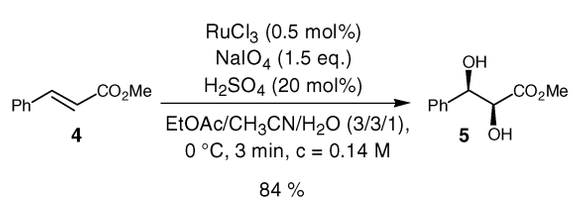


Fig. 4 Influence of acid concentration.

concentrations accelerate the reaction but lead to the formation of side products, *e.g.* aldehydes.

The acidity of the aqueous phase is dependant on the amount of water. Thus, keeping the amount of added acid constant while dividing the total amount of solvent by a factor of two increases the proton concentration. We were pleased to find, that the selectivity and conversion was quantitative within 3 minutes resulting in an isolated yield of 84% diol **4** (Scheme 2).



Scheme 2 Optimised conditions for the "flash-dihydroxylation".

The effect of acid can be rationalised in analogy to the acid catalysed cleavage of carboxylic acid esters by an activation of the intermediate ruthenate **V** (Fig. 2) *via* coordination of a proton to one of the Ru–O-bonds (Fig. 5). The resulting electron-deficient ruthenate **VII** should react fast with the incoming water to give the desired diol **VI** and catalyst **I**. The concept of an acid accelerated nucleophilic addition has recently been used in the development of a direct RuO_4-catalysed ketohydroxylation of olefins[14] and mono oxidation of *vic*-diols[15] under slightly acidic conditions. In either of these three reactions the

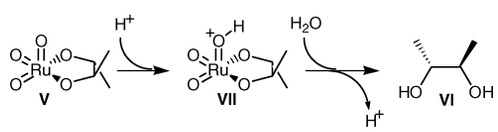
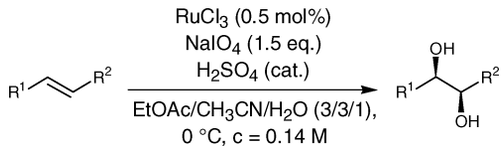


Fig. 5 Postulated activation of ruthenate **VI** by protonation.

Table 5 Dihydroxylation of mono- and 1,2-disubstituted olefins



Entry[a]	R^1	R^2	Product	H_2SO_4 [mol %]	Time [min]	Yield [%][b]
1	Ph	Ph	**2**	20	3	79
2	Ph	CO_2Me	**5**	20	5	84
3	C_6H_{13}	H	**6**	5	2	87
4	C_4H_9	C_4H_9	**7**	5	2	91
5	Ph	H	**8**	5	2	86
6		CN	**9**	20	2	85
7		CH_2Ph	**10**	10	2	68
8		CH_2Cl	**11**	20	4	79
9		CH_2SO_2Ph	**12**	20	5	94
10		CH_2N_3	**13**	20	2	65
11		CH_2NHAc	**14**	20	5	79
12		C(O)Ph	**15**	20	5	59 (81)[c]
13		CH_2OBn	**16**	10	3	73
14		CH_2OAc	**17**	20	3	78
15	Cyclohexyl		**18**	20		74
16		$CONEt_2$	**19**	20	4	71
17		CO_2Me	**20**	20	3	84
18	CO_2Et	CO_2Et	**21**	20	2	96

[a] All reactions were performed on a 2 mmol scale using 0.5 mol% $RuCl_3$ (as a 0.1 M solution in H_2O), 1.5 equiv. $NaIO_4$ at 0 °C in EtOAc (6 mL)/CH_3CN (6 mL)/H_2O (2 mL) in the presence of the given amount of sulfuric acid. [b] Isolated yield. [c] Yield in brackets refers to the yield based on recovered starting material.

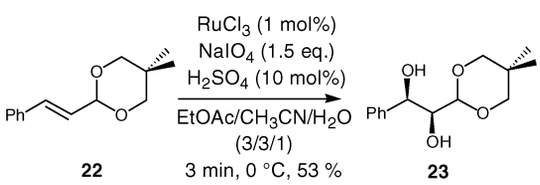
presence of protons is essential for the outcome of the reaction. However, the activation mechanism remains a postulate and further investigations along these lines have to be performed.

Having in hand the optimised conditions we turned our attention to the scope and limitations of the new acid accelerated ruthenium-catalysed dihydroxylation.

Scope and limitations

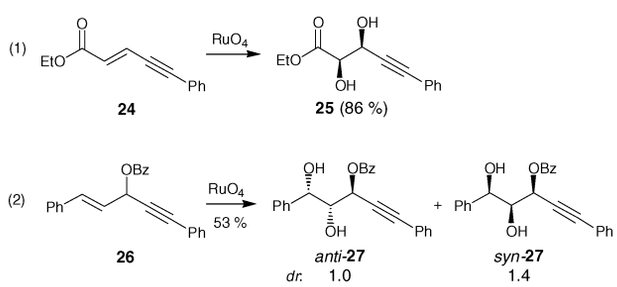
Scope. The acidic reaction media was expected to cause incompatibilities with acid labile functional groups. A wide variety of different olefins was prepared and dihydroxylated in good to excellent yields. By varying the amount of added acid a broad scope of functional groups is tolerated (Table 5). Minor amounts of fission products are standard byproducts, which can be removed conveniently *via* recrystallisation or chromatography.

Acid labile protecting groups like silyl ethers are not stable under the reaction conditions (*vide infra*). However, allylic halides (entry 8) known to be prone to hydrolysis as well as esters (entries 2, 14, 17 and 18) or amides (entries 11 and 16) are compatible with the acidic conditions. Apparently, the dihydroxylation of the double bond is too fast for any competing side reaction. Byproducts resulting from an oxidation of activated C,H-bonds (benzylic C,H-bonds, entries 7 and 13; tertiary C,H-bonds, entries 15–17) were not observed. The short reaction time and low temperature allows even the dihydroxylation of acetal **23** using 1 mol% ruthenium-catalyst (Scheme 3).



Scheme 3 Dihydroxylation of acetal **23**.

Following these lines we investigated the oxidation of substrates incorporating both an alkyne and alkene moiety. Alkynes can be efficiently converted into 1,2-diketones using RuO_4.[16] In order to get first information on the relative reactivities in the ruthenium-catalysed dihydroxylation of double *vs.* triple bonds, ester **24** (Scheme 4, eqn. (1)) and benzoate **26** (Scheme 4, eqn. (2)) were prepared and oxidised under standard conditions (Scheme 4).



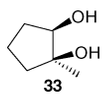
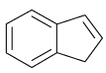
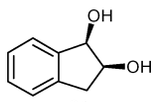
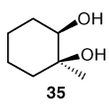
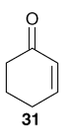
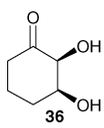
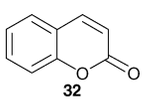
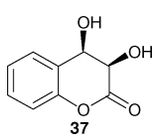
Scheme 4 Oxidation of enynes **24** and **26**.

The dihydroxylation occurred exclusively at the C,C-double bond, the alkyne moiety was kept intact. The simple diastereoselectivity of the process is modest, but comparable to the selectivities obtained in analogous osmium-catalysed oxidation reactions. The dihydroxylation of a double bond is much faster compared to the oxidation of a triple bond. Hence, apart from functional groups like esters, chlorides, azides or amides alkynes are tolerated as well.

Different cycloalkenes were oxidised under the optimised conditions. The results are outlined in Table 6.

As mentioned above the hydrolysis is the rate limiting step. Therefore, the dihydroxylation of cyclic olefins can be problematic due to a favourable fast electrocyclic fragmentation caused by the release of ring strain. Cyclic olefins are oxidised in moderate to good yields. The moderate yields in the case of cyclopentene and cyclohexene derivatives (entries 1 and 3) might be due to the polarity of the final products. Furthermore, allylic oxidation products and scission products were detected in minor amounts. The oxidation of indene **29** (entry 2) is very interesting since it clearly indicates that in this case the oxidation of the double activated allylic and benzylic proton is slow on the time scale of the oxidation reaction. Chiral cyclic alkenes

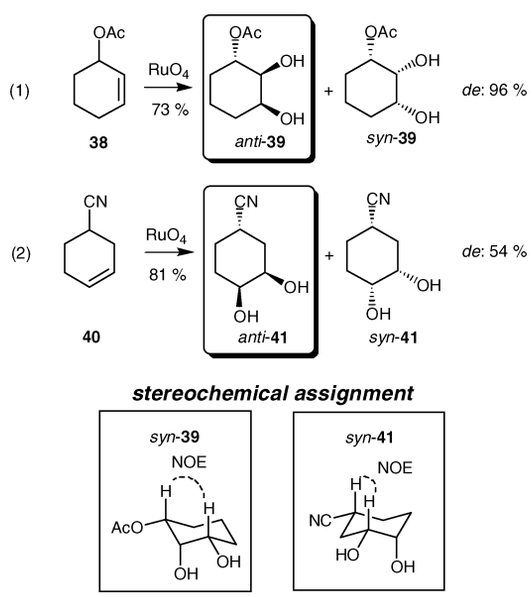
Table 6 Dihydroxylation of cycloalkenes

Entry[a]	Substrate	Product	Time [min]	Yield [%][b]
1	 28	 33	3	61
2	 29	 34	5	75
3	 30	 35	3	79
4	 31	 36	3	69
5	 32	 37	5	79

[a] All reactions were performed under the conditions listed in Table 4. [b] Isolated yield.

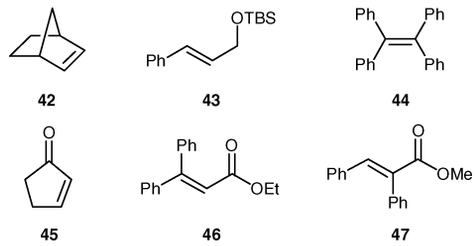
are oxidised in moderate to good stereoselectivities following the Kishi-rules.[17] Whereas the oxidation of allyl acetate **38** furnished *anti*- and *syn*-**39** with high diastereoselectivity (Scheme 5, eqn. (1)), as expected the homoallylic stereocentre in **40** had a smaller influence on the selectivity in **41** (Scheme 5, eqn. (2)). The stereochemical assignments are based upon NOE-measurements as shown below.

The results shown so far clearly underline the broad scope of the acid-accelerated dihydroxylation protocol.



Scheme 5 Dihydroxylation of chiral cyclic olefins **38** and **40**.

Limitations. Although a broad scope of different olefins can be dihydroxylated in good to excellent yields, certain limitations do exist. A survey of problematic substrates is given in Scheme 6. The mechanistic scenario shown in Fig. 2 can serve as an explanation. The acidic conditions speed up the hydrolysis,

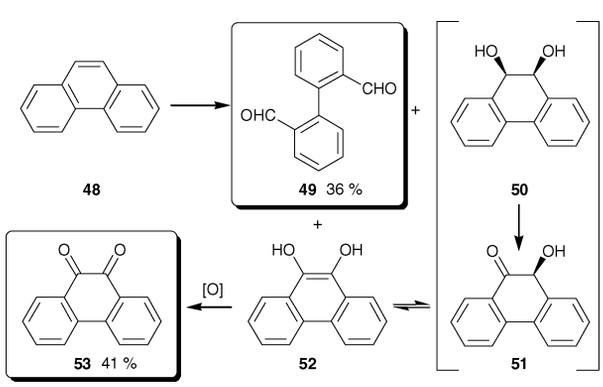


Scheme 6 Limitations of the dihydroxylation.

however, acid labile groups like silyl ethers are not stable under the reaction conditions. Apart from desilylation and concomitant oxidation of the liberated hydroxy group a silyl group migration is a competing side reaction leading to different mono-, di- and even persilylated products in varying amounts.

The most problematic side reaction still remains the electrocyclic fragmentation resulting in the formation of aldehydes. This reaction is in particular problematic, if the resulting aldehyde is stabilised by a neighbouring group (*e.g.* aryl groups), or if the scission product is thermodynamically favored due to the release of ring strain. A lower temperature might suppress these fragmentation processes, however, the presence of water does not allow temperatures lower than −5 °C. Finally, highly substituted olefins are not very reactive towards dihydroxylation reagents. Hence, stabilised tri- and tetrasubstituted olefins can not be converted to the diols most likely due to the stability of the intermediate ruthenate ester. Based upon our observations these are the only limitations observed.

Interestingly, phenanthrene **48** could not be converted to the corresponding diol **50**. Instead a mixture of fission product **49** and *o*-quinone **53** was obtained (Scheme 7). The formation of **53** might be explained by a fast overoxidation of the intermediate diol **50** to the corresponding ketol **51**, which tautomerises under the acidic reaction conditions to the *o*-hydroquinone **52**. **52** is oxidised to the stable *o*-quinone **53** under the acidic reaction conditions.



Scheme 7 Oxidation of phenanthrene **48**.

The limitations do however emphasise the need for further studies on this oxidation in order to develop protocols for the dihydroxylation of these problematic substrates.

Summary

The present paper describes our investigations on the scope and limitations of the acid accelerated RuO_4-catalysed dihydroxylation protocol. A wide range of different olefins are oxidised in good to excellent yields. The interplay of ruthenium- and acid concentration allows the dihydroxylation of acid labile alkenes. Due to the very short reaction times acid assisted side reaction are often of minor importance. Hence, the acid accelerated ruthenium-catalysed dihydroxylation is a less expensive and toxic oxidation reaction that is suitable for the preparation of a variety of racemic glycols.

Experimental

Ethyl acetate and pentane were purified by distillation over $CaCl_2$ prior to use. $RuCl_3$ was obtained from Aldrich. A stock solution was prepared calculating with $RuCl_3(H_2O)_2$ and dissolving the catalyst (2.44 g, 10 mmol) in 100 mL water (0.1 M). The deep brown solution can be stored on the bench for weeks without loss of activity. Flash-chromatography was done on silica 60 (230–400 mesh). Infrared spectra (IR) were recorded as a thin film between KBr-plates. The instrument used was a Bruker IFS 66 FT-IR spectrophotometer. Proton (^{1}H NMR, 400 MHz) and carbon (^{13}C NMR, 100.6 MHz) nuclear magnetic resonance spectra were recorded in deuteriochloroform and referenced to the solvent signal. The instrument used was a Bruker DRX 400. All signal points are listed on a δ-scale in ppm and coupling constants are in Hz. All commercially available starting materials were used without further purification.

General procedure for the dihydroxylation

In a 50 mL round-bottomed flask equipped with magnetic stirring bar and overpressure valve $NaIO_4$ (642 mg, 3 mmol) was stirred in 1.5 mL H_2O. 1 M H_2SO_4 (400 μL, 0.4 mmol) was added. After all solids were dissolved the solution was cooled to 0 °C. A 0.1 M aqueous solution of $RuCl_3$ (100 μL, 0.01 mmol) was added and the mixture was stirred until the color turned bright yellow. Ethyl acetate (6 mL) was added and stirring was continued for 5 min. Acetonitrile (6 mL) was added and stirring was continued for further 5 min. The olefin (2 mmol) was added in one portion and the resulting slurry was stirred until all starting material was consumed. The mixture was poured onto 15 mL sat. $NaHCO_3$- and 20 mL sat. $Na_2S_2O_3$-solution. Phases were separated and the aqueous layer was extracted with ethyl acetate (3 × 30 mL). After drying the combined organic layer over Na_2SO_4 and evaporation of the solvent in vacuum the crude product was purified by flash-chromatography.

(1*R,2*R**)-1,2-Diphenyl-ethane-1,2-diol (2).**[18] Following the general procedure diol **2** (338 mg, 1.58 mmol, 79%) was obtained as a colourless solid; mp 150 °C; R_f. 0.36 (3 : 1 pentane/ethyl acetate); ν_{max}(KBr)/cm^{-1} 3499 (s), 3395 (s), 2895 (m), 1452 (m), 1198 (s), 1044 (s), 777 (s), 705 (s), 696 (s), 519 (m); δ_H (400 MHz, $CDCl_3$) 7.16–7.23 (6 H, m, aryl-*H*), 7.08–7.10 (4 H, m, aryl-*H*), 4.67 (2 H, s, H-1 and H-2), 3.02 (2 H, s, OH); δ_C (100 MHz, $CDCl_3$) 139.9, 128.0, 127.9, 127.0, 79.2; *m*/*z* (EI) 214 (1%, M$^+$), 108 (92, $C_7H_8O^+$), 107 (100, $C_7H_7O^+$), 105 (72, $C_7H_5O^+$), 79 (95, $C_6H_7^+$), 77 (100, $C_6H_5^+$).

(2*S,3*R**)-2,3-Dihydroxy-3-phenyl-propionic acid methyl ester (5).**[19] Following the general procedure diol **5** (339 mg, 1.68 mmol, 84%) was obtained as a white solid; mp 79 °C. R_f 0.30 (4 : 1 pentane/ethyl acetate); ν_{max}(KBr)/cm^{-1} 3495 (s), 3378 (s), 3086 (m), 3062 (m), 3038 (m), 3007 (m), 2954 (s), 2931 (m), 1732 (s), 1493 (s), 1458 (s), 1324 (s), 1308 (s), 1104 (s), 1083 (s); δ_H (400 MHz, $CDCl_3$) 7.22–7.38 (5 H, m, aryl-*H*), 4.94 (1 H, d, *J* 3.3, H-3), 4.28 (1 H, d, *J* 3.3, H-2), 3.70 (3 H, s, C*H*$_3$), 3.49 (2 H, s, O*H*); δ_C (100 MHz, $CDCl_3$) 173.2, 140.0, 128.4, 128.2, 126.3, 75.0, 74.5, 52.7; *m*/*z* (EI) 196 (2%, M$^+$), 119 (30, $C_4H_7O_4^+$), 107 (100, $C_7H_7O^+$), 105 (54, $C_7H_5O^+$), 90 (96, $C_7H_6^+$), 79 (92, $C_6H_7^+$), 77 (85, $C_6H_5^+$).

(2*R)-Octane-1,2-diol (6).**[18] Following the general procedure diol **6** (254 mg, 1.74 mmol) was obtained as a colourless oil (yield: 87%); R_f. 0.33 (7 : 1 pentane/ethyl acetate); ν_{max}(film)/cm^{-1} 3341 (s), 2922 (s), 2858 (s), 1466 (s), 1072 (s), 1040 (s); δ_H (400 MHz, $CDCl_3$) 3.73–3.66 (1 H, m, H-2), 3.63 (1 H, dd, *J* 11.0, 2.8, C*H*$_2$OH), 3.41 (1 H, dd, *J* 11.0, 7.8, C*H*$_2$OH), 2.76 (2 H, s, O*H*), 1.51–1.20 (10 H, m, C*H*$_2$), 0.87 (3 H, t, *J* 6.9, C*H*$_3$); δ_C (100 MHz, $CDCl_3$) 72.5, 66.9, 33.3, 31.9, 29.4, 25.7, 22.7, 14.2; *m*/*z* (EI) 145 (1%, M$^+$ − H), 115 (40), 97 (95), 69 (30), 55 (100, $C_4H_7^+$).

(5*R,6*R**)-Decane-5,6-diol (7).**[18] Following the general procedure diol **7** (317 mg, 1.82 mmol, 91%) was obtained as a colourless solid; mp 50 °C; R_f. 0.56 (5 : 1 pentane/ethyl acetate); ν_{max}(KBr)/cm^{-1} 3409 (s), 2954 (s), 2932 (s), 2858 (m), 1465 (m), 1147 (m), 1073 (m); δ_H (400 MHz, $CDCl_3$) 3.37–3.39 (2 H, m, H-5 and H-6), 2.12 (2 H, s, O*H*), 1.28–1.50 (12 H, m, C*H*$_2$), 0.90 (6 H, t, *J* 7.1, C*H*$_3$); δ_C (100 MHz, $CDCl_3$) 74.5, 33.3, 27.7, 22.7, 14.1; *m*/*z* (EI) 176 (29%, M$^+$ + H$_2$), 134 (43), 115 (100, $C_7H_{15}O^+$), 105 (42), 92 (31).

(2*R)-Phenylethane-1,2-diol (8).**[18] Following the general procedure diol **8** (237 mg, 1.72 mmol, 86%) was obtained as a colourless solid; mp 67 °C; R_f 0.23 (3 : 1 pentane/ethyl acetate); ν_{max}(KBr)/cm^{-1} 3213 (s), 2933 (m), 1457 (s), 1100 (s), 1054 (s); δ_H (400 MHz, $CDCl_3$) 7.35–7.23 (5 H, m, aryl-*H*), 4.76 (1 H, dd, *J* 8.4, 3.6, H-2), 3.69 (1 H, dd, *J* 11.2, 3.6, C*H*$_2$OH), 3.60 (1 H, dd, *J* 11.2, 8.0, C*H*$_2$OH), 3.08 (2 H, s, O*H*); δ_C (100 MHz, $CDCl_3$) 140.5, 128.6, 128.1, 126.2, 74.8, 68.1; *m*/*z* (EI) 138 (11%, M$^+$), 107 (100, $C_7H_7O^+$), 91 (10), 79 (91), 77 (73).

(2*S,3*R**)-2,3-Dihydroxy-3-phenylpropanenitrile (9).**[20] Following the general procedure diol **9** (277 mg, 1.70 mmol, 85%) was obtained as a colourless oil; R_f 0.53 (1 : 1 pentane/ethyl acetate); ν_{max}(film)/cm^{-1} 3421 (s), 2904 (m), 2361 (m), 1699 (m), 1496 (s), 1455 (s), 1197 (m), 1078 (s); δ_H (400 MHz, $CDCl_3$) 7.49–7.41 (5 H, m, aryl-*H*), 4.87 (1 H, d, *J* 6.0, H-2), 4.47 (1 H, dd, *J* 6.5, 6.5, H-3), 3.40 (1 H, d, *J* 6.9, O*H*), 3.07 (1 H, s, O*H*); δ_C (100 MHz, $CDCl_3$) 137.0, 129.5, 129.0, 126.9, 118.0, 74.8, 66.4; *m*/*z* (EI) 163 (1%, M$^+$), 105 (100, $C_7H_5O^+$), 91 (6), 77 (43).

(1*R,2*R**)-1,3-Diphenylpropane-1,2-diol (10).**[21] Following the general procedure diol **10** (310 mg, 1.36 mmol, 68%) was obtained as a colourless solid; mp 83 °C; R_f 0.32 (3 : 1 pentane/ethyl acetate); ν_{max}(KBr)/cm^{-1} 3434 (s, br), 3252 (s, br), 2916 (m), 2897 (m), 1604 (w), 1495 (s), 1453 (s), 1040 (s), 1020 (s); δ_H (400 MHz, $CDCl_3$) 7.37–7.16 (10 H, m, aryl-*H*), 4.52 (1 H, d, *J* 6.3, H-1), 3.93 (1 H, ddd, *J* 9.0, 6.3, 4.0, H-2), 2.72 (1 H, dd, *J* 13.8, 4.0, C*H*$_2$), 2.63 (1 H, dd, *J* 13.8, 9.0, C*H*$_2$), 2.29 (2 H, s, O*H*); δ_C (100 MHz, $CDCl_3$) 141.0, 138.1, 129.5, 128.8, 128.73, 128.70, 128.3, 127.0, 126.7, 39.6; *m*/*z* (EI) 228 (1%, M$^+$), 121 (14), 108 (100, $C_7H_8O^+$), 91 (40), 79 (46), 77 (35).

(1*R,2*S**)-3-Chloro-1-phenyl-propane-1,2-diol (11).**[22] Following the general procedure diol **11** (295 mg, 1.58 mmol, 79%) was obtained as a colourless oil; R_f. 0.26 (3 : 1 pentane/ethyl acetate); ν_{max}(film)/cm^{-1} 3394 (s), 1454 (m), 1197 (m), 1058 (m), 764 (m), 702 (m); δ_H (400 MHz, $CDCl_3$) 7.31–7.37 (5 H, m, aryl-*H*), 4.69 (1 H, d, *J* 6.8, H-1), 3.87 (1 H, ddd, *J* 6.8, 5.6, 4.0, H-2), 3.53 (1 H, dd, *J* 11.6, 4.0, C*H*$_2$), 3.45 (1 H, dd, *J* 11.6, 5.6, C*H*$_2$); δ_C (100 MHz, $CDCl_3$) 139.9, 128.8, 128.6, 126.7, 75.5, 74.8, 46.2; *m*/*z* (EI) 150 (8%, M$^+$ − Cl), 107 (100, $C_7H_7O^+$), 91 (16), 79 (81), 51 (16).

(1*S,2*R**)-1-Phenyl-3-(phenylsulfonyl)propane-1,2-diol (12).** Following the general procedure diol **12** (549 mg, 1.88 mmol, 94%) was obtained as a colourless solid; (found: C, 61.69; H, 5.48. $C_{15}H_{16}O_4S$ requires: C, 61.62; H, 5.52%); mp 133 °C; R_f. 0.48 (3 : 2 pentane/ethyl acetate); ν_{max}(KBr)/cm^{-1} 3521 (s), 3064 (w), 3028 (w), 2976 (w), 2942 (w), 2925 (w), 1168 (s), 1147 (m), 1084 (m); δ_H (400 MHz, $CDCl_3$) 7.80–7.84 (2 H, m, aryl-*H*), 7.49–7.65 (3 H, m, aryl-*H*), 7.20–7.30 (5 H, m, aryl-*H*), 4.56 (1 H, d, *J* 6.0, H-1), 4.24 (1 H, ddd, *J* 9.4, 6.0, 2.0, H-2), 3.25 (1 H, dd, *J* 14.6, 9.4, C*H*$_2$), 3.21 (1 H, dd, *J* 14.6, 0.2, C*H*$_2$), 2.60 (2 H, s, O*H*); δ_C (100 MHz, $CDCl_3$) 139.2, 139.0, 134.2, 129.5, 128.9, 128.7, 128.0, 126.9, 70.5, 58.8, 37.1; *m*/*z* (EI) 310 (42%, M$^+$ + H_2O), 275 (100, $C_{15}H_{15}O_3S^+$), 132 (27); HRMS (FAB$^+$LR, $C_{15}H_{16}O_4S$). Calc. 292.0769, found. 292.0774.

(1*R,2*R**)-3-Azido-1-phenylpropane-1,2-diol (13).** Following the general procedure diol **13** (251 mg, 1.30 mmol, 65%) was obtained as a yellow oil; (found: C, 55.88; H, 5.78. $C_9H_{11}N_3O_2$

requires: C, 55.95; H, 5.74%); R_f 0.31 (3 : 2 pentane/ethyl acetate); ν_{max}(film)/cm^{-1} 3394 (s), 3087 (w), 3064 (w), 3032 (w), 2924 (w), 2103 (s), 1083 (m), 1043 (m); δ_H (400 MHz, $CDCl_3$) 7.18–7.43 (5 H, m, aryl-*H*), 4.72 (1 H, dd, *J* 6.7, 1.8, H-1), 3.88 (1 H, m, H-2), 3.55 (1 H, dt, *J* 11.5, 3.5, H-3), 3.38 (1 H, ddd, *J* 11.5, 5.7, 2.7, H-3), 3.08 (2 H, s, O*H*); δ_C (100 MHz, $CDCl_3$) 140.1, 128.9, 128.7, 126.7, 75.24, 75.20, 53.1; *m*/*z* (EI) 193 (44%, M^+ + H), 177 (23), 147 (15), 106 (100, $C_7H_6O^+$); HRMS (FAB$^+$LR, $C_9H_{11}N_3O_2$). Calc. 193.0851, found. 193.0832.

(1*R,3*R**)-*N*-(2,3-Dihydroxy-3-phenyl-propyl)-acetamide (14).** Following the general procedure diol **14** (331 mg, 1.58 mmol, 79%) was obtained as a colourless oil; (found: C, 63.09; H, 7.28. $C_{11}H_{15}NO_3$ requires: C, 63.14; H, 7.23%); R_f. 0.18 (ethyl acetate); ν_{max}(film)/cm^{-1} 3319 (s), 2930 (m), 1653 (s), 1558 (s), 1453 (s), 1295 (m), 1102 (s), 1047 (s); δ_H (400 MHz, $CDCl_3$) 7.26–7.33 (5 H, m, aryl-*H*), 5.29 (1 H, s, N*H*), 4.48 (1 H, d, *J* 6.0, H-3), 3.57–3.94 (2 H, s, O*H*), 3.75 (1 H, m, H-2), 3.28 (1 H, m, CH_2), 3.13 (1 H, m, CH_2), 1.90 (3 H, s, CH_3); δ_C (100 MHz, $CDCl_3$) 173.3, 141.9, 130.1, 129.6, 128.1, 76.4, 76.2, 43.9, 24.4; *m*/*z* (EI) 207 (4%, $M^+ - H_2$), 136 (69), 107 (94), 91 (18), 77 (100, $C_6H_5^+$); HRMS (FAB$^+$LR, $C_{11}H_{16}NO_3$). Calc. 210.1130, found. 210.1122.

(2*S,3*R**)-2,3-Dihydroxy-1,3-diphenyl-propan-1-one (15).**[23] Following the general procedure diol **15** (286 mg, 1.18 mmol, 59%) was obtained as a colourless solid; mp 117 °C; R_f. 0.15 (3 : 1 pentane/ethyl acetate); ν_{max}(KBr)/cm^{-1} 3434 (s), 3065 (w), 2929 (m), 2857 (w), 1694 (s), 1598 (m), 1579 (m), 1450 (m), 1284 (s), 1227 (s), 1113 (s); δ_H (400 MHz, $CDCl_3$) 7.41–7.78 (10 H, m, aryl-*H*), 6.36 (1 H, d, *J* 8.0, H-3), 5.01 (1 H, d, *J* 8.0, H-2); δ_C (100 MHz, $CDCl_3$) 189.7, 130.7, 130.6, 130.1, 129.1, 128.9, 128.7, 128.6, 128.5, 88.7, 87.8; *m*/*z* (EI) 224 (1%, $M^+ - H_2O$), 207 (100, $M^+ - C_{15}H_{13}O^+$), 179 (30), 165 (14), 131 (37), 103 (38), 77 (74).

(1*R,2*R**)-3-Benzyloxy-1-phenyl-propane-1,2-diol (16).**[5] Following the general procedure diol **16** (386 mg, 1.46 mmol, 73%) was obtained as a colourless solid; mp 61 °C; R_f. 0.28 (3 : 1 pentane/ethyl acetate); ν_{max}(KBr)/cm^{-1} 3415 (s), 3031 (w), 3030 (w), 2876 (w), 1495 (m), 1118 (s), 1026 (s), 737 (s), 700 (s); δ_H (400 MHz, $CDCl_3$) 7.31–7.36 (10 H, m, aryl-*H*), 4.72 (1 H, d, *J* 5.5, H-2), 4.54 (1 H, d, *J* 12.0, phenyl-CH_2), 4.47 (1 H, d, *J* 12.0, phenyl-CH_2), 3.83 (1 H, m, H-2), 3.50 (1 H, dd, *J* 9.5, 3.0, H-3), 3.42 (1 H, dd, *J* 9.5, 5.5 Hz, H-3), 3.11 (s, 1*H*, OH), 2.83 (s, 1*H*, OH); δ_C (100 MHz, $CDCl_3$) 141.9, 139.1, 130.0, 129.9, 129.5, 129.4, 129.3, 128.1, 76.3, 76.2, 75.1, 72.5; *m*/*z* (EI) 258 (1%, M^+), 150 (11), 121 (10), 108 (68), 91 (100, $C_7H_7^+$), 77 (81).

Acetic acid (2*R,3*R**)-2,3-dihydroxy-3-phenyl-propyl ester (17).**[5] Following the general procedure diol **17** (328 mg, 1.56 mmol, 78%) was obtained as a colourless oil; R_f. 0.38 (1 : 1 pentane/ethyl acetate); ν_{max}(film)/cm^{-1} 3418 (s), 3032 (w), 2900 (w), 1723 (s), 1381 (m), 1244 (s), 704 (s); δ_H (400 MHz, $CDCl_3$) 7.28–7.38 (5 H, m, aryl-*H*), 4.58 (1 H, d, *J* 6.4, H-3), 4.04 (1 H, m, H-2), 3.91 (2 H, m, CH_2), 2.86 (2 H, br. s., O*H*), 2.02 (3 H, s, CH_3); δ_C (100 MHz, $CDCl_3$) 140.1, 128.8, 128.5, 127.2, 126.7, 74.6, 74.1, 65.3, 20.9; *m*/*z* (EI) 212 (11%, $M^+ + H_2$), 105 (100, $C_7H_5O^+$), 91 (7), 77 (29).

(2*R,3*R**)-3-Cyclohexyl-2,3-dihydroxypropyl acetate (18).** Following the general procedure diol **18** (320 mg, 1.48 mmol, 74%) was obtained as a colourless solid; (found: C, 61.14; H, 9.36. $C_{11}H_{20}O_4$ requires: C, 61.09; H, 9.32%); mp 88 °C; R_f 0.65 (1 : 1 pentane/ethyl acetate); ν_{max}(KBr)/cm^{-1} 3358 (s), 2923 (s), 2855 (m), 1736 (s), 1449 (w), 1384 (w), 1250 (s), 1124 (m), 1042 (s); δ_H (400 MHz, $CDCl_3$) 4.19 (1 H, dd, *J* 11.5, 4.5, H-1), 4.11 (1 H, dd, *J* 11.5, 7.0, H-1), 3.95–3.85 (1 H, m, H-3), 3.21 (1 H, dd, *J* 6.9, 3.0, H-2), 2.27 (2 H, s, O*H*), 2.07 (3 H, s, CH_3), 1.91–1.83 (1 H, m, cyclohexyl-*H*), 1.78–1.61 (4 H, m, cyclohexyl-*H*), 1.53–1.43 (m, 4*H*, cyclohexyl-*H*), 1.27–0.96 (2 H, m, cyclohexyl-*H*); δ_C (100 MHz, $CDCl_3$) 171.6, 75.6, 69.4, 66.9, 40.3, 29.6, 28.5, 26.5, 26.2, 26.1, 21.0; *m*/*z* (EI) 199 (15%, $M^+ + H - H_2O$), 160 (9), 129 (29), 117 (100, $C_5H_9O_3^+$), 101 (10), 75 (17); HRMS (FAB$^+$LR, $C_{11}H_{21}O_4$). Calc. 217.1440, found. 217.1427.

(2*S,3*R**)-3-Cyclohexyl-*N*,*N*-diethyl-2,3-dihydroxypropanamide (19).** Following the general procedure diol **19** (345 mg, 1.42 mmol, 71%) was obtained as a colourless solid; (found: C, 64.11; H, 10.33. $C_{13}H_{25}NO_3$ requires: C, 64.16; H, 10.36%); mp 149 °C; R_f 0.63 (3 : 1 pentane/ethyl acetate); ν_{max}(KBr)/cm^{-1} 3290 (s), 2933 (s), 2854 (s), 1700 (s), 1683 (s), 1465 (s), 1114 (m), 1049 (m); δ_H (400 MHz, $CDCl_3$) 5.15 (1 H, s, H-2), 3.83 (4 H, m, CH_2), 3.46 (1 H, m, H-3), 2.13–2.04 (2 H, m, cyclohexyl-*H*), 1.98 (1 H, d, cyclohexyl-*H*), 1.89–1.76 (6 H, m, CH_3), 1.72–1.60 (4 H, m, cyclohexyl-*H*), 1.41–1.13 (4 H, m, cyclohexyl-*H*); δ_C (100 MHz, $CDCl_3$) 154.9, 52.5, 51.8, 32.8, 30.0, 29.6, 29.5, 29.0, 25.9, 25.9, 25.8, 25.4, 25.1; *m*/*z* (EI) 199 (100%, $M^+ - C_2H_4O$), 181 (31), 155 (19), 117 (21), 99 (23).

(2*S,3*R**)-Methyl 3-cyclohexyl-2,3-dihydroxypropanoate (20).** Following the general procedure diol **20** (340 mg, 1.68 mmol, 84%) was obtained as a colourless solid; (found: C, 59.34; H, 9.01. $C_{10}H_{18}O_4$ requires: C, 59.39; H, 8.97%); mp 82 °C; R_f 0.87 (3 : 1 pentane/ethyl acetate); ν_{max}(KBr)/cm^{-1} 3330 (s), 2927 (s), 2851 (m), 1733 (s), 1628 (s), 1576 (m), 1446 (m), 1246 (m), 1115 (m), 1039 (m); δ_H (400 MHz, $CDCl_3$) 4.30 (1 H, s, H-2), 3.82 (3 H, s, CH_3), 3.55 (1 H, d, *J* 8.7, H-3), 2.09–2.01 (1 H, m, cyclohexyl-*H*), 1.82–1.64 (2 H, m, cyclohexyl-*H*), 1.63–1.54 (2 H, m, cyclohexyl-*H*), 1.40–1.18 (4 H, m, cyclohexyl-*H*), 1.16–0.96 (2 H, m, cyclohexyl-*H*); δ_C (100 MHz, $CDCl_3$) 174.9, 71.1, 52.9, 40.5, 33.9, 29.5, 29.2, 26.4, 26.0, 25.9; *m*/*z* (EI) 200 (2%, $M^+ - H_2$), 146 (44), 90 (100, $C_7H_6^+$), 55 (17); HRMS (FAB$^+$LR, $C_{10}H_{19}O_4$). Calc. 203.1283, found. 203.1309.

(1*S,2*S**)-Diethyl 2,3-dihydroxysuccinate (21).**[24] Following the general procedure diol **21** (396 mg, 1.92 mmol, 96%) was obtained as a colourless oil; R_f 0.44 (3 : 2 pentane/ethyl acetate); ν_{max}(film)/cm^{-1} 3470 (s), 2984 (s), 2939 (m), 2910 (m), 2876 (w), 1745 (s), 1129 (s), 1089 (s); δ_H (400 MHz, $CDCl_3$) 4.49 (2*H*, s, H-2 and H-3), 4.23 (4 H, q, *J* 7.0, CH_2), 3.55 (2 H, s, O*H*), 1.25 (6 H, t, *J* 7.0, CH_3); δ_C (100 MHz, $CDCl_3$) 171.6, 72.2, 62.3, 14.0; *m*/*z* (EI) 207 (5%, $M^+ + H^+$), 134 (30), 132 (62), 104 (100, $C_4H_6O_3^+$), 87 (49), 76 (100), 59 (100, $C_2H_3O_2^+$).

(1*S,2*R**)-1-(5,5-Dimethyl-1,3-dioxan-2-yl)-2-phenylethane-1,2-diol (23).** Following the general procedure diol **23** (267 mg, 1.06 mmol, 53%) was obtained as a colourless solid; (found: C, 66.68; H, 8.02. $C_{14}H_{20}O_4$ requires: C, 66.65; H, 7.99%); mp 126 °C; R_f 0.84 (3 : 1 pentane/ethyl acetate); ν_{max}(KBr)/cm^{-1} 3447 (s, br), 3362 (s, br), 2955 (m), 2871 (m), 1495 (m), 1473 (m), 1396 (m), 1091 (s), 1030 (s); δ_H (400 MHz, $CDCl_3$) 7.41–7.24 (5 H, m, aryl-*H*), 4.99 (1 H, d, *J* 3.2, H-1), 4.46 (1 H, d, *J* 3.2, H-3), 3.68 (2 H, d, *J* 10.8, CH_2), 3.64 (1 H, dd, *J* 3.2, H-3), 3.43 (2 H, d, *J* 10.8, CH_2), 3.18 (1 H, s, O*H*), 2.60 (1 H, s, O*H*), 1.20 (3 H, s, CH_3), 0.72 (3 H, s, CH_3); δ_C (100 MHz, $CDCl_3$) 140.7, 128.5, 127.8, 126.6, 101.2, 77.3, 75.5, 72.5, 31.3, 30.6, 23.1, 21.8; *m*/*z* (EI) 252 (3%, M^+), 207 (27), 194 (13), 117 (31), 91 (100, $C_7H_7^+$); HRMS (FAB$^+$LR, $C_{14}H_{20}NaO_4$). Calc. 275.1259, found. 275.1235.

(2*S,3*R**)-2,3-Dihydroxy-5-phenylpent-4-ynoic acid ethyl ester (25).** Following the general procedure diol **25** (344 mg, 1.72 mmol, 86%) was obtained as a colourless oil; (found: C, 66.71; H, 5.97. $C_{13}H_{14}O_4$ requires: C, 66.66; H, 6.02%); R_f 0.14 (3 : 1 pentane/ethyl acetate); ν_{max}(film)/cm^{-1} 3404 (s, br), 2360 (s), 2340 (s), 1735 (s), 1276 (m), 1114 (s), 1053 (m); δ_H (400 MHz, $CDCl_3$) 7.36–7.47 (2 H, m, aryl-*H*), 7.21–7.36 (3 H, m. aryl-*H*), 4.89 (1 H, d, *J* 2.5, H-2), 4.39 (1 H, d, *J* 2.5, H-3), 4.32

(2 H, q, *J* 7.5, C*H*$_2$), 3.47 (1 H, s, O*H*), 2.98 (1 H, s, O*H*), 1.32 (3 H, t, *J* 7.5, C*H*$_3$); δ_C (100 MHz, $CDCl_3$) 173.2, 133.3, 130.2, 129.7, 123.5, 87.6, 77.6, 75.2, 65.9, 64.0, 15.6; *m*/*z* (EI) 234 (3%, M^+), 143 (9), 131 (100, $C_9H_7O^+$), 115 (35), 104 (89), 76 (63). HRMS (FAB$^+$LR, $C_{13}H_{14}O_4$). Calc. 234.0892, found. 234.0897.

Benzoic acid 1-(1,2-dihydroxy-2-phenyl-ethyl)-3-phenyl-prop-2-ynyl ester (27). Following the general procedure diol **27** was obtained as a diastereomeric mixture (*syn*-**27**/*anti*-**27**, 1.4 : 1.0 (^{1}H NMR-integration)) as a colourless oil (395 mg, 1.06 mmol, 53%), that was separated *via* flash-chromatography.

Diastereomer 1: (*1S**,2*R**,3*R**)-*benzoic acid (1,2-dihydroxy-2-phenyl-ethyl)-3-phenyl-prop-2-ynyl ester (anti*-27). (164 mg, 0.44 mmol, 22%); (found: C, 77.38; H, 5.38. $C_{24}H_{20}O_4$ requires: C, 77.40; H, 5.41%); R_f 0.21 (3 : 1 pentane/ethyl acetate); ν_{max}(film)/cm^{-1} 3421 (s), 3063 (m), 3033 (m), 2927 (m), 1726 (s), 1601 (m), 1491 (m), 1452 (m), 1267 (s), 1112 (m), 1069 (m), 1026 (m); δ_H (400 MHz, $CDCl_3$) 7.97 (2 H, d, *J* 8.0, aryl-*H*), 7.62–7.16 (13 H, m, aryl-*H*), 5.87 (1 H, d, *J* 5.5, H-3), 5.11 (1 H, d, *J* 4.8, H-1), 4.13 (1 H, dd, *J* 5.1, 5.1, H-2), 3.26 (2 H, s, O*H*); δ_C (100 MHz, $CDCl_3$) 165.6, 140.5, 133.5, 132.1, 130.0, 129.1, 128.8, 128.5,128.4, 128.3, 126.8, 121.8, 87.7, 83.8, 77.0, 73.7, 66.2.

Diastereomer 2: (*1R**,2*S**,3*R**)-*benzoic acid (1,2-dihydroxy-2-phenyl-ethyl)-3-phenyl-prop-2-ynyl ester (syn*-27). (231 mg, 0.62 mmol, 31%); (found: C, 77.41; H, 5.40. $C_{24}H_{20}O_4$ requires: C, 77.40; H, 5.41%); ν_{max}(film)/cm^{-1} 3409 (s), 3063 (m), 2033 (m), 2928 (m), 1732 (s), 1601 (m), 1491 (m), 1452 (m), 1266 (s), 1107 (m), 1069 (m), 1026 (m); δ_H (400 MHz, $CDCl_3$) 8.04 (2 H, d, *J* 7.6, aryl-*H*), 7.64–7.15 (13 H, m, aryl-*H*), 5.70 (1 H, d, *J* 4.1, H-3), 4.93 (1 H, d, *J* 6.1, H-1), 4.14 (1 H, dd, *J* 6.1, 4.1, H-2), 3.28 (2 H, s, O*H*); δ_C (100 MHz, $CDCl_3$) 165.4, 139.7, 133.6, 132.2, 130.0, 129.4, 129.2, 128.9, 128.6, 128.6, 128.4, 126.9, 121.8, 88.3, 82.9, 76.7, 74.2, 66.5.

(1*S,2*R**)-1-Methyl-cyclopentane-1,2-diol (33).**[25] Following the general procedure diol **33** (142 mg, 1.22 mmol, 61%) was obtained as a colourless solid; mp 23 °C; R_f 0.17 (3 : 1 pentane/ethyl acetate); ν_{max}(KBr)/cm^{-1} 3454 (s), 3394 (s), 3307 (s), 2970 (s), 2869 (m), 1465 (m), 1414 (m), 1373 (m), 1339 (m), 1165 (s), 1145 (s), 1122 (s); δ_H (400 MHz, $CDCl_3$) 3.56 (1 H, dd, *J* 7.0, H-2), 2.10 (2 H, s, O*H*), 1.97–1.89 (1 H, m, C*H*$_2$), 1.88 (3 H, m, C*H*$_2$), 1.62–1.46 (2 H, m, CH$_2$), 1.29 (3 H, s, C*H*$_3$); δ_C (100 MHz, $CDCl_3$) 87.1, 86.3, 37.2, 30.0, 25.9, 19.4; *m*/*z* (EI) 115 (23%, $M^+ - H$), 98 (100, $M^+ - H_2O$), 82 (68), 67 (81), 55 (35).

(1*S,2*S**)-Indane-1,2-diol (34).**[26] Following the general procedure diol **34** (225 mg, 1.50 mmol, 75%) was obtained as a colourless solid; mp 107 °C; R_f 0.32 (5 : 1 pentane/ethyl acetate); ν_{max}(KBr)/cm^{-1} 3523 (m), 3440 (s), 3334 (s, br), 2951 (w), 2924 (m), 1579 (w), 1460 (w), 1431 (w), 1319 (s), 1153 (s), 1105 (s); δ_H (400 MHz, $CDCl_3$) 7.41–7.93 (1 H, m, aryl-*H*), 7.26–7.09 (3 H, m, aryl-*H*), 4.97 (1 H, d, *J* 5.0, H-1), 4.46 (1 H, dd, *J* 9.0, 5.0, H-2), 3.08 (1 H, dd, *J* 16.3, 5.8, H-3), 2.92 (1 H, dd, *J* 16.3, 3.5, H-3), 2.65 (2 H, s, O*H*); δ_C (100 MHz, $CDCl_3$) 142.1, 140.3, 129.0, 127.4, 125.6, 125.2, 76.1, 73.6, 38.8; *m*/*z* (EI) 146 (73%, $M^+ - 2\ H_2$), 107 (83), 91 (62), 79 (81), 69 (59), 60 (100, $C_2H_4O_2^+$).

(1*S,2*R**)-1-Methyl-cyclohexane-1,2-diol (35).**[27] Following the general procedure diol **35** (195 mg, 1.58 mmol, 79%) was obtained as a colourless solid; mp 67 °C; R_f 0.78 (3 : 1 pentane/ethyl acetate); ν_{max}(KBr)/cm^{-1} 3326 (s), 2991 (m), 2938 (s), 2881 (s), 2860 (s), 1716 (m), 1458 (m), 1444 (m), 1405 (m), 1370 (m), 1151 (s), 1087 (s), 1063 (s); δ_H (400 MHz, $CDCl_3$) 3.27 (1 H, t, *J* 5.7, H-2), 2.34 (2 H, s, O*H*), 1.79–1.72 (1 H, m, C*H*$_2$), 1.68–1.54 (5 H, m, C*H*$_2$), 1.41–1.30 (2 H, m, C*H*$_2$), 1.22 (3 H, s, C*H*$_3$); δ_C (100 MHz, $CDCl_3$) 82.5, 72.2, 37.2, 37.0, 29.0, 22.0; *m*/*z* (EI) 129 (15%, $M^+ - H$), 112 (100, $M^+ - H_2O$), 96 (97), 81 (91), 71 (44), 55 (36).

(2*S,3*S**)-2,3-Dihydroxycyclohexanone (36).**[5] Following the general procedure diol **36** (179 mg, 1.38 mmol, 69%) was obtained as a colourless solid; mp 52 °C; R_f 0.25 (3 : 2 pentane/ethyl acetate); ν_{max}(KBr)/cm^{-1} 3405 (s), 2949 (m), 1718 (s), 1140 (m), 1107 (m) 1075 (m); δ_H (400 MHz, $CDCl_3$) 4.35–4.39 (1 H, m, H-2), 4.13 (1 H, dd, *J* 3.3, 1.2, H-3), 3.49 (2 H, s, O*H*), 2.49 (1 H, dq, *J* 13.6, 2.3, C*H*$_2$), 2.32 (1 H, dt, *J* 13.6, 1.2, C*H*$_2$), 2.03–2.14 (2 H, m, C*H*$_2$), 1.75–1.82 (2 H, m, C*H*$_2$); δ_C (100 MHz, $CDCl_3$) 210.2, 77.5, 72.8, 39.1, 29.0, 21.2; *m*/*z* (EI) 130 (37%, M^+), 112 (61), 86 (79), 83 (76), 73 (80), 69 (55), 58 (67), 57 (92), 55 (100, $C_3H_3O^+$).

(3*S,4*S**)-3,4-Dihydroxychroman-2-one (37).** Following the general procedure diol **37** (285 mg, 1.58 mmol, 79%) was obtained as a colourless solid; (found: C, 59.97; H, 4.52. $C_9H_8O_4$ requires: C, 60.00; H, 4.48%); mp 142 °C; R_f 0.58 (1 : 1 pentane/ethyl acetate); ν_{max}(KBr)/cm^{-1} 3431 (s), 3308 (s), 2887 (w), 1774 (s), 1487 (m), 1461 (s), 1158 (s), 1129 (s), 1113 (s), 1066 (s); δ_H (400 MHz, $(CD_3)_2CO$) 7.45–7.39 (2 H, m, aryl-*H*), 7.20 (1 H, t, *J* 7.5, aryl-*H*), 7.07 (1 H, d, *J* 8.1, aryl-H), 4.92–4.87 (2 H, m, O*H*), 4.79 (1 H, d, *J* 6.0, H-3), 4.69 (1 H, dd, *J* 6.0, 3.4, H-2); δ_C (100 MHz, $(CD_3)_2CO$) 170.1, 152.0, 131.2, 130.3, 125.3, 117.3, 71.6, 70.1; *m*/*z* (EI) 180 (15%, M^+), 123 (100, $C_7H_7O_2^+$), 105 (25), 95 (29), 77 (46); HRMS (FAB$^+$LR, $C_9H_8NaO_4$). Calc. 203.0320, found. 203.0349.

(1*S,2*S**,3*S**)-2,3-Dihydroxycyclohexyl acetate (*anti*-39).**[5] Following the general procedure diol **39** was obtained as a diastereomeric mixture (*syn*-**39**/*anti*-**39**, 1.0 : 32.3 (^{1}H NMR-integration)) as a colourless oil (254 mg, 1.46 mmol, 73%), that was separated *via* flash-chromatography (3 : 2 pentane/ethyl acetate).

Diastereomer 1: (*1S**,2*S**,3*S**)-*2,3-dihydroxycyclohexyl acetate (anti-**39**)*. (246 mg, 1.41 mmol, 71%); R_f 0.19 (3 : 2 pentane/ethyl acetate); ν_{max}(film)/cm^{-1} 3442 (s), 2942 (w), 2870 (w), 1732 (s), 1066 (m), 1042 (m); δ_H (400 MHz, $CDCl_3$) 4.95 (1 H, ddd, *J* 9.7, 4.3, H-1), 4.03 (1 H, ddd, *J* 4.3, 2.8, H-2), 3.52 (1 H, dd, *J* 8.5, 3.0, H-3), 3.30 (2 H, s, O*H*), 2.01 (3 H, s, C*H*$_3$), 1.88–1.94 (1 H, m, H-6), 1.78–1.85 (1 H, m, H-4), 1.62–1.71 (1 H, m, H-5), 1.45–1.51 (1 H, m, H-5), 1.38–1.44 (1 H, m, H-4), 1.26–1.36 (1 H, m, H-6); δ_C (100 MHz, $CDCl_3$) 172.0, 77.1, 74.4, 70.1, 30.1, 29.2, 21.5, 18.3; *m*/*z* (EI) 114 (48%, M^+-CH_4O_2), 96 (50), 70 (100, $C_4H_6O^+$), 57 (74).

Diastereomer 2: (*1S**,2*R**,3*R**)-*2,3-dihydroxycyclohexyl acetate (syn-**39**)*. (8 mg, 0.05 mmol, 2%); R_f 0.09 (3 : 2 pentane/ethyl acetate); ν_{max}(film)/cm^{-1} 3442 (s), 2942 (w), 2870 (w), 1732 (s), 1066 (m), 1042 (m); δ_H (400 MHz, $CDCl_3$) 4.70 (1 H, ddd, *J* 10.5, 4.8, 2.5, H-1), 4.02 (1 H, s, H-2), 3.60 (1 H, ddd, *J* 10.3, 4.8, 2.8, H-3), 2.88 (2 H, s, O*H*), 2.02 (3 H, s, C*H*$_3$), 1.55–1.74 (4 H, m, C*H*$_2$), 1.15–1.28 (2 H, m, C*H*$_2$); δ_C (100 MHz, $CDCl_3$) 170.6, 74.0, 71.3, 70.8, 28.1, 24.6, 21.6, 19.5; *m*/*z* (EI) 114 (68%, $M^+ - CH_4O_2$), 96 (42), 70 (100, $C_4H_6O^+$), 57 (44).

3,4-Dihydroxy-cyclohexanecarbonitrile (41). Following the general procedure diol **41** was obtained as an inseparable diastereomeric mixture (*syn*-**41**/*anti*-**41**, 1.0 : 3.3 (^{1}H NMR-integration)) as a colourless oil (254 mg, 1.46 mmol, 73%); (found: C, 59.52; H, 7.86. $C_7H_{11}NO_2$ requires: C, 59.56; H, 7.85%); R_f 0.18 (diethyl ether); ν_{max}(KBr)/cm^{-1} 3447 (s), 2954 (m), 2246 (m), 1635 (m), 1073 (m).

Diastereomer 1: (*1R**,3*S**,4*R**)-*3,4-dihydroxy-cyclohexanecarbonitrile (anti-**41**)*. δ_H (400 MHz, $CDCl_3$) 4.05 (1 H, m, H-1), 3.78 (1 H, m, H-3), 2.92 (1 H, m, H-4), 2.12–2.19 (1 H, m, C*H*$_2$), 2.05 (2 H, s, O*H*), 1.91–1.98 (1 H, m, C*H*$_2$), 1.73–1.81 (3 H, m, C*H*$_2$), 1.57–1.62 (1 H, m, C*H*$_2$); δ_C (100 MHz, $CDCl_3$) 122.3, 69.5, 67.9, 32.8, 31.4, 27.2; *m*/*z* (EI) 140 (2%, $M^+ - H$), 114 (17), 96 (35), 85 (84), 69 (100, $C_5H_9^+$), 54 (88).

Diastereomer 2: (*1S**,3*S**,4*R**)-*3,4-dihydroxy-cyclohexanecarbonitrile (syn-**41**)*. (164 mg, 0.44 mmol, 22%); δ_H (400 MHz, $CDCl_3$) 3.91 (1 H, m, H-3), 3.65 (1 H, m, H-4), 2.52 (1 H, m,

H-1), 2.06 (2 H, s, O*H*), 1.91–2.08 (2 H, m, CH_2), 1.76–1.81 (3 H, m, CH_2), 1.55 (1 H, m, CH_2); δ_C (100 MHz, $CDCl_3$) 121.9, 69.5, 68.3, 32.8, 28.6, 25.5, 23.4; *m*/*z* (EI) 140 (10%, $M^+ - H$), 114 (27), 96 (53), 84 (42), 69 (100, $C_5H_9^+$), 54 (76).

Oxidation of phenanthrene (48). Following the general procedure a mixture of **51** (yellowish solid, 151 mg, 0.72 mmol, 36%) and **53** (yellowish solid, 171 mg, 0.82 mmol, 41%) was obtained.

1,1′-Biphenyl-2,2′-dicarbaldehyde (49).[28] Mp 61 °C; R_f 0.73 (7 : 1 pentane/ethyl acetate); ν_{max}(KBr)/cm^{-1} 3445 (m), 3376 (m), 3079 (w), 3056 (w), 3029 (w), 2834 (m), 2749 (m), 2729 (m), 1693 (s), 1593 (s), 1392 (m), 1248 (m), 1195 (m), 1164 (s); δ_H (400 MHz, $CDCl_3$) 9.82 (2 H, s, C*H*O), 8.02 (2 H, d, *J* 7.6, aryl-*H*), 7.65 (2 H, td, *J* 7.5, 1.4, aryl-*H*), 7.58 (2 H, t, *J* 7.5, aryl-*H*), 7.33 (2 H, d, *J* 7.5, aryl-*H*); δ_C (100 MHz, $CDCl_3$) 236.1, 141.4, 135.8, 133.6, 131.9, 129.0, 128.7; *m*/*z* (EI) 210 (7%, M^+), 181 (100, $M^+ - CHO$), 152 (67), 126 (9), 76 (18).

Phenanthrene-9,10-dione (53).[29] Mp 148 °C; R_f 0.84 (7 : 1 pentane/ethyl acetate); ν_{max}(KBr)/cm^{-1} 3446 (m), 3065 (w), 1674 (s), 1591 (s), 1451 (m), 1294 (s), 1282 (s); δ_H (400 MHz, $CDCl_3$) 8.17 (2*H*, dd, *J* 7.9, 1.3, aryl-*H*), 8.00 (2 H, d, *J* 7.9, aryl-*H*), 7.70 (2 H, td, *J* 7.4, 1.3, aryl-*H*), 7.45 (2 H, t, *J* 7.4, aryl-*H*), 1.55 (2 H, s, O*H*); δ_C (100 MHz, $CDCl_3$) 236.1, 136.2, 131.2, 130.7, 129.7, 127.5, 124.1; *m*/*z* (EI) 208 (20%, M^+), 180 (100, $M^+ - CO$), 152 (56), 126 (12), 76 (17).

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