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Journal of Organometallic Chemistry 632 (2001) 27–40

Journal of Organometallic Chemistry

www.elsevier.com/locate/jorganchem

Synthesis of chiral (7*R*)-[η⁶-5-(*N*,*N*-dimethylamino)-7-formyl-1,3-benzodioxole]-chromium complex and its application in the synthesis of optically active *cis*-β-lactams

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Received 18 February 2001; accepted 11 March 2001

Dedicated to Professor Alberto R. Dias honouring his pioneer contribution to organometallic chemistry in Portugal.

Abstract

Prochiral imine chromium complexes derived from the racemic (5-*N*,*N*-dimetylamino-7-formyl-1,3-benzodioxole)chromium complex **4** and several amines reacted with acetoxylketene, generated from its corresponding acid chloride and triethylamine, to produce the corresponding β-lactam complexes **6a**, **6b** and **6c** with complete control of *cis*-diastereoselectivity. In a similar manner, the imine condensation of the chiral imine complexes **11a** and **11b**, derived from the chiral aldehyde complex **4I**, not only provides complete *cis*-diastereoselection of the β-lactam complexes **12a** and **12b,** but remarkable enantioselectivities as well. X-ray crystal structures of **4I** and **12a** were obtained and the mechanics implications within the context of the general mode proposed by several authors for the stereochemical outcome of the Staudinger reaction are in agreement with these results.

Keywords: Chromium; Asymmetric synthesis; Imine complexes; Cycloadditions; β-Lactams

1. Introduction

It is well known that the β-lactam skeleton is the key structural element to a variety of antibiotics and a versatile precursor of a great number of molecules of diverse structures and different biological activities [1]. For many years the efforts of the organic synthetic community have been directed towards searching for new β-lactam antibiotics to meet the challenges of bacterial resistance to the existing drugs and it is well known that the biological activity of β-lactams and β-lactamase inhibitors most often is associated with a single enantiomer [1d,2].

Ketenes are especially susceptible to [2 + 2] cycloadditions [3]; their reaction with imines, known as the Staudinger reaction [4], has been studied extensively and is now recognised as one of the most convenient approaches to β-lactams [1b,5] due to its versatility and stereochemical predictability [6]. This reaction, in contrast to the ester–enolate–imine condensation [1a,7] (subjected to the limitations of enolate basicity [8]), generally affords *cis*-β-lactams and is widely employed in the synthesis of diverse monolactam antibiotics. Some compounds of this particular class have potent biological activity [1b,1d,9].

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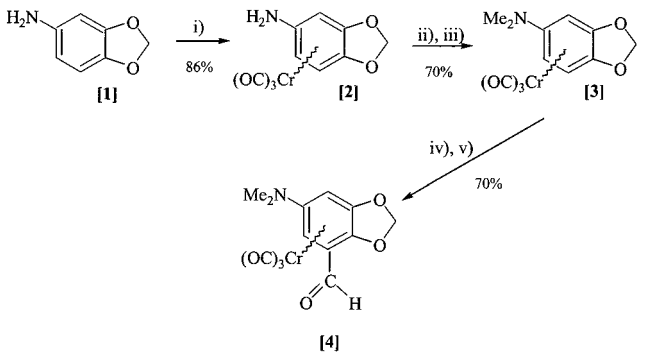
0022-328X/01/$ - see front matter
PII: S0022-328X(01)00806-3

Planar chiral transition-metal π-complexes of *ortho*- or *meta*-disubstituted arenes have emerged as useful starting materials in asymmetric organic synthesis because the metal coordination enhances arene reactivity, facilitating regio- and diastereoselective substitution of positions on or adjacent to the aromatic ring (for reviews see Ref. [10]). Therefore, planar chirality enables new stereogenic centres to be formed and some work involving the synthesis of β-lactam chromium complexes has been developed [6c,11].

The development of methodology for the preparation of monocyclic β-lactams has attracted considerable interest from both academic and industrial points of view and the concept of structural modifications at C(4) and C(3) positions of the azetidin-2-one rings is of current interest (for reviews on β-lactam antibiotics see Ref. [12]). While abundant information on the diverse substitution patterns of optically active β-lactams exists, the synthesis of these kinds of compound, in which chemical manipulation at C(4) position of the azetidin-2-one nucleus was introduced using chiral (5-amino-1,3-benzodioxole)chromium complexes, is the subject of this investigation. To check the feasibility of this reaction, we first examined the [2 + 2] cycloaddition reaction between ketenes and imine complexes derived from the aldehyde complex **4** in their racemic and optically active forms providing the exclusive *cis*-azetidin-2-one complexes. High enantioselectivities of β-lactams were observed using the chiral complex **4I** as starting material. The X-ray crystal structures of **4I** and **12a** indicated unambiguously their relative configurations as (7*R*)-[η^6-5-(*N*,*N*-dimethylamino)-7-formyl-1,3-benzodioxole]tricarbonylchromium and (7*R*,3′*R*,4′*S*)-{1′-(4″-fluorophenyl)-3′-acetoxy-4′-[η^6-5-(*N*,*N*-dimethylamino)-1,3-benzodioxole]azetidin-2′-one}tricarbonylchromium complexes, respectively.



[1] [2] [3] [4]

Scheme 1. Reagents: (i) $Cr(CO)_6$, (n-Bu)$_2$O–THF (10:1); (ii) NaH (five equivalents); (iii) MeI (five equivalents); (iv) n-BuLi (1.5 equivalents); and (v) DMF (five equivalents).

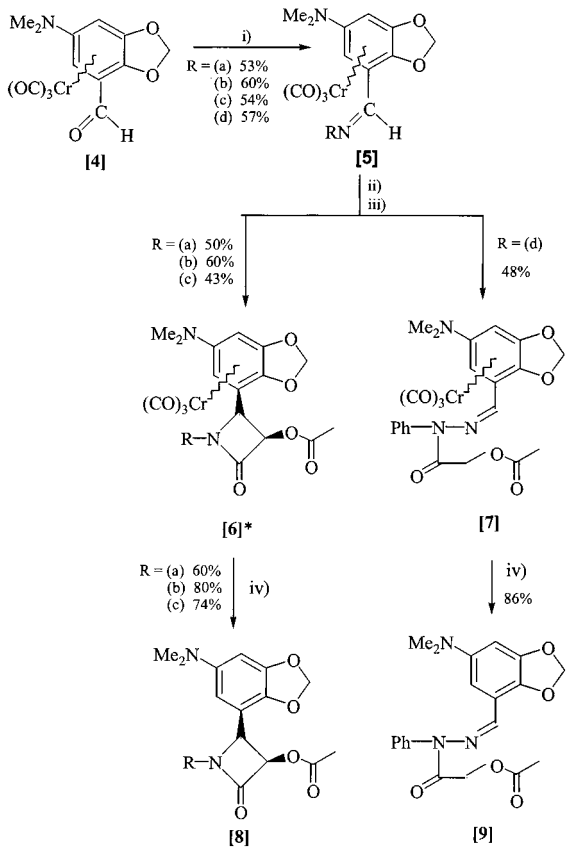
2. Results and discussion

The first outstanding contribution to the total regioselectivity and asymmetric synthesis of the (5-*N*,*N*-dimetylamino-1,3-benzodioxole)chromium complex derivative **4** (in our starting material dimethylaniline is coupled to the dioxolane ring) to afford β-lactams with high levels of enantioselectivity was based on early findings reported on dimethylaniline and *ortho*- or *meta*-disubstituted aldehyde complexes [5b,13], and on both (1,3-benzodioxole) [14] and dimethylaniline complexes [15], in which Schmalz and Simpkins, respectively, have found that the metallation of those complexes with some chiral bases gave disappointing results. Secondly, our investigation was initiated with the aim of establishing whether (5-*N*,*N*-dimetylamino-1,3-benzodioxole-7-imine)chromium complexes are suitable chiral sources for the diastereoselective synthesis of *cis*-[1′-(phenyl-substituted)-3′-acetoxy-4′-(5-*N*,*N*-dimetylamino-1,3-benzodioxole)-azetidin-2′-one]chromium complexes (*cis*-β-lactams)[1] via the Staudinger reaction. Finally, the *cis* selectivity of β-lactams always observed in our study, using acetoxyacetyl chloride as ketene source and both prochiral and chiral imine chromium complexes, can be accounted for by a two-step mechanism involving ketenes + imines that has been documented by experimental and theoretical calculations [1b,16].

5-Amino-1,3-benzodioxole was chosen for several reasons: (i) 1,3-benzodioxole is a subunit of a large number of natural products [17] and there is a large variety of its derivatives used in the pharmaceutical industry [18]; (ii) the presence of the amino group at C(5) and the OCH_2 group in the fused dioxolane ring of 1,3-benzodioxole could allow us to afford total regioselectivity on **4** with reasonable yields; and (iii) to introduce in the azetidin-2-one ring the 1,3-benzodioxole as C(4′) substituent.

Conversion of **1** into its $Cr(CO)_3$ complex was accomplished with the $Cr(CO)_6$–Bu_2O–THF reflux [19]. Facile formation of **2** was afforded in 86% yield after recrystallisation and the complex was totally characterised (Scheme 1). The amino group of complex **2** was methylated in the presence of NaH–MeI and complex **3** was obtained in 70% yield as yellow crystals after column chromatography and recrystallisation. The choice of solvents, base and temperature used in the metallation/DMF sequence has been optimised, and the best reaction conditions for the introduction of the

[1] For clarity the azetidin-2-one ring atoms were numbered as N(1′), C(2′), C(3′) and C(4′).



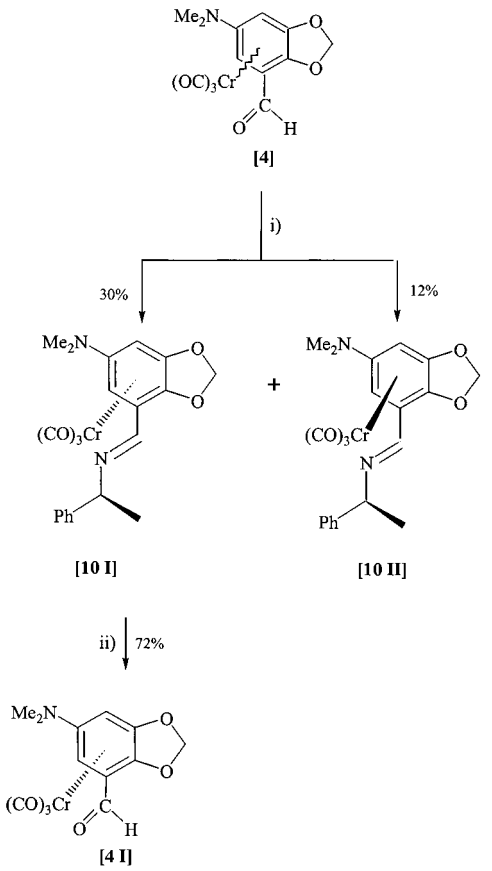
Scheme 2. Reagents: (i) RNH_2; R=4F–C_6H_4 (a), CH_2Ph (b), Ph (c), NHPh (d) and molecular sieves 4 Å; (ii) Et_3N; (iii) CH_3CO_2COCl; and (iv) $h\nu/O_2$. *Only one enantiomer is drawn.

aldehyde function in complex **3** were attained in the presence of THF–Et_2O (1:1) as solvents at -30°C, *n*-BuLi and DMF, and the expected exclusive functionalisation at C(7) was observed. The ^{1}H-NMR spectrum of the racemic complex **4** shows H(4) and H(6) at δ 4.64 and 5.47 with a *meta* coupling constant of 2.4 Hz and the two non-equivalent CH_2 proton singlets, as observed in complexes **2** and **3** (Scheme 1). Imines **5a**, **5b**, **5c** and **5d** were prepared as yellow crystals by condensation of **4** with 4-fluoroaniline, benzylamine, aniline and phenyl hydrazine in yields of 53, 60, 54 and 57%, respectively (Scheme 2). These results were obtained after several runs at different reaction conditions according to the literature [1g,6b,6c,6i]. To check the feasibility of the Staudinger reaction, the cycloaddition reactions were examined between the reactive ketenes generated in situ from acetoxyacetyl chloride and afterwards from phenylacetyl chloride. Treatment of the imine complexes **5a**, **5b** and **5c** with acetoxyacetyl chloride and triethylamine in dichloromethane as solvent at 0°C led exclusively to the *cis*-β-lactam complexes **6a**, **6b** and **6c**, respectively. Inspection of the ^{1}H-NMR spectral data of their crude mixtures indicated that only one stereoisomer had been formed and the *cis* disposition of the vicinal methine protons at C(3′) and C(4′) in each azetidin-2′-one ring of the complexes was confirmed easily on the basis of their coupling constants ($J_{3',4'} \approx$ 5.4 Hz), and is in line with what has been reported by other authors for similar reactions [2b,6b,20]. These complexes were isolated as single *cis*-diastereomers in 50, 60 and 45% yields, respectively, after column chromatography and recrystallisation. As the transformation acid chlorides → ketenes presents its own problems, the use of these kinds of base as dehydrohalogenating agents generates ammonium salts as interfering by-products and the yields obtained could result from this fact. The protocol mentioned above was extended to imine **5d** and the ^{1}H-NMR spectrum of the crude mixture did not show traces of the corresponding β-lactam complex, despite careful and repeated attempts to isolate it. After purification, complex **7** was isolated as an orange powder in 50% yield and its ^{1}H-NMR spectrum showed the presence of the CH_3COOCH_2CO group, the two *meta* protons in the complexed arene ring and the two non-equivalent CH_2 proton singlets of the dioxolane ring. The ^{13}C-NMR spectrum also confirmed the presence of the CH_3COOCH_2CO group and DEPT and the ^{1}H–^{13}C heteronuclear experiments (HMQC) allowed the structural assignment of **7**. This absence of cycloaddition [2 + 2] could be reasoned taking into account the presence of the NHPh group attached to the iminic nitrogen on **5d**. Presumably, the nucleophilicity of the nitrogen lone pair of the imine complex is strongly diminished by the electron-withdrawing effect of the NHPh group attached to it [21], which has precluded the cycloaddition reaction to the ketene. Instead, abstraction of the acidic NH proton by triethylamine could occur, allowing the reaction with the acid chloride to proceed, and this route could access complex **7**.

Once the best reaction conditions to obtain the *cis*-β-lactam complexes **6a**, **6b** and **6c** were established, phenylacetyl chloride was used to generate in situ the corresponding ketene and the imine complex **5a** was allowed to react. Despite several runs, no traces of the corresponding β-lactam complexes were detected in the ^{1}H-NMR spectral data. It is difficult to anticipate how aryl substituents such as phenyl would behave because its conformation may vary [22] and, consequently, different results can occur from the interactions between the ketene substituents and the substituents of the imine complexes.

Complexes **6a**, **6b**, **6c** and **7** were subjected to decomplexation reactions by exposing ether solutions to air and sunlight until the yellow colour of the solutions disappeared. After purification, the decomplexed *cis*-β-lactams **8a**, **8b**, **8c** and compound **9,** respectively, were afforded (Scheme 2).

On the basis of these results, we now report our results on the enantioselective synthesis of β-lactam complexes using the chiral aldehyde complex **4I** as



Scheme 3. Reagents: (i) (*S*)-(−)-(α)-methylbenzylamine, molecular sieves 4 Å; and (ii) HCl. Only complex **10I** was hydrolised to obtain **4I**.

starting material. Taking into account the literature, chiral bases were not used according to the results of Schmalz [14] and Simpkins [15] on (1,3-benzodioxole) and (dimethylaniline)chromium complexes, respectively. Therefore, the resolution of **4** was tested using three different methods in which semioxamazone derivatives [13a] and oxazolidines of valinol [23] were not successful because the separation of their diastereoisomeric forms was not achieved either by chromatography or by recrystallisation. Treatment of **4** with (*S*)-(−)-(α)-methylbenzylamine in Et_2O gave, after the usual work-up, an orange solid and the ^{1}H-NMR spectral data of the crude mixture showed two imine complexes **10I** and **10II** in a 1:1 ratio. The d.e. of these imines were higher than 95% by ^{1}H-NMR measurements. Their separation was only possible by recrystallisation and, first, complex **10I** was afforded as red crystals. With no more complex **10I** in the solution, complex **10II** recrystallised as an orange powder and the total characterisation of both the complexes was consistent with their presence. Therefore, the chiral aldehyde required for our synthesis of **4I** was accessible by hydrolysis of **10I** (Scheme 3). All the spectral data of **4I** were identical to those observed on its racemic form but the determination of its enantiomeric excess (e.e.), by both the ^{1}H-NMR method using the chiral shift reagent Eu(hfc)$_3$ [24] and HPLC analysis using a chromatographic column Chiralcel OJ [14], failed. Nevertheless, the X-ray crystal structure determination of **4I** confirmed its relative configuration as (7*R*)-(5-*N*,*N*-dimethylamino-7-formyl-1,3-benzodioxole)chromium complex and its specific rotation indicated $[\alpha]_D^{25} = -364$.

Two perspective views of **4I**, with the atomic-labelling scheme, were obtained with ORTEP [25] and are presented in Fig. 1. Interatomic distances and angles are given in Table 1.

We can see the aldehyde function *anti* to the OCH_2 group from the dioxolane ring of **4I**, which is in line with the analogous complexes [23]. The $Cr(CO)_3$ group lies in an eclipsed conformation relative to the carbocyclic ring. Also, the Cr–C (ring) distance is maximum relative to the amino substituent at C(5). The results from an out-of-plane deformation of the carbocyclic ring, with C(5) significantly displaced out of the mean plane in the opposite direction of the chromium atom, have also been observed for other (amino-substituted arene)chromium complexes [26]. A displacement of the

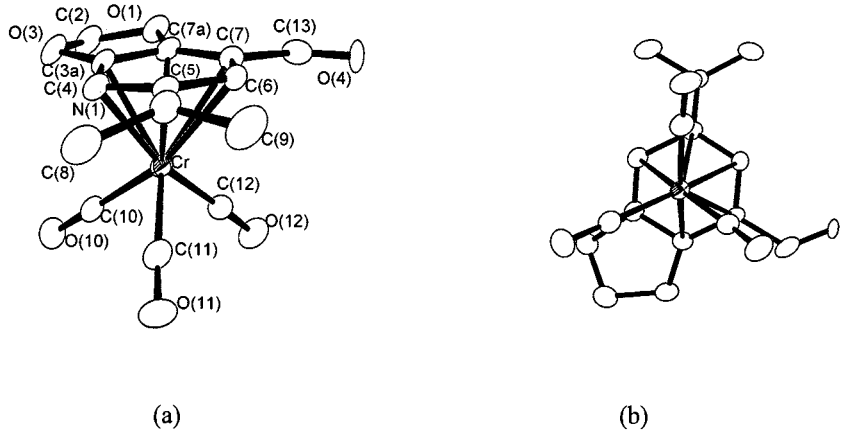


Fig. 1. (a) Molecular structure of complex **4I**. (b) View of molecule showing the relative positions of the carbonyl ligands to the carbocyclic ring.

Table 1
Selected geometric parameters for complexes **4I** and **12a**. Molecule 1 and molecule 2 of complexes **4I** and **12a** refer to the presence of two molecules in the asymmetric unit

	Complex **4I**		Complex **12a**	
	Molecule 1	Molecule 2	Molecule 1	Molecule 2
Bond lengths (Å)				
Cr–C(10)	1.732(6)	1.779(6)	1.757(6)	1.791(6)
Cr–C(11)	2.080(7)	2.094(7)	1.799(6)	1.806(6)
Cr–C(12)	1.773(7)	1.693(7)	1.797(8)	1.817(7)
Cr–C(3a)	2.039(5)	2.379(6)	2.233(5)	2.219(6)
Cr–C(4)	2.122(6)	2.525(5)	2.267(5)	2.274(6)
Cr–C(5)	2.451(6)	2.397(6)	2.328(6)	2.361(6)
Cr–C(6)	2.429(6)	2.027(6)	2.239(5)	2.247(6)
Cr–C(7)	2.211(6)	1.951(5)	2.289(5)	2.270(5)
Cr–C(7a)	2.057(5)	2.113(6)	2.285(4)	2.263(5)
C(3a)–C(4)	1.417(9)	1.403(9)	1.394(7)	1.403(8)
C(4)–C(5)	1.566(10)	1.440(9)	1.426(7)	1.413(8)
C(5)–C(6)	1.436(8)	1.524(9)	1.437(7)	1.452(7)
C(6)–C(7)	1.464(9)	1.519(10)	1.440(6)	1.427(7)
C(7)–C(7a)	1.469(9)	1.433(11)	1.369(6)	1.364(7)
C(7a)–C(3a)	1.431(9)	1.439(11)	1.407(6)	1.408(7)
C(3a)–O(3)	1.453(8)	1.420(8)	1.370(5)	1.363(7)
O(3)–C(2)	1.473(9)	1.527(10)	1.469(6)	1.452(8)
C(2)–O(1)	1.528(10)	1.474(10)	1.427(6)	1.433(7)
O(1)–C(7a)	1.407(7)	1.398(8)	1.385(5)	1.393(6)
C(7)–C(13)			1.517(6)	1.533(6)
N(2)–C(18)			1.421(6)	1.408(6)
C(14)–O(4)			1.207(6)	1.205(7)
C(15)–O(5)			1.422(6)	1.423(6)
C(13)–C(15)			1.563(7)	1.580(7)
C(15)–C(14)			1.498(7)	1.496(7)
C(14)–N(2)			1.372(7)	1.373(7)
N(2)–C(13)			1.456(6)	1.453(6)
Bond angles (°)				
C(10)–Cr–C(11)	87.8(3)	92.5(3)	86.4(3)	88.8(3)
C(11)–Cr–C(12)	95.1(3)	87.3(3)	90.1(3)	89.0(3)
C(10)–Cr–C(12)	95.5(3)	95.3(3)	84.5(3)	84.7(3)
O(5)–C(15)–C(14)			112.0(4)	113.1(5)
O(5)–C(15)–C(13)			115.9(4)	113.4(4)
C(14)–C(15)–C(13)			85.8(4)	85.7(4)
O(4)–C(14)–N(2)			131.0(5)	133.7(5)
O(4)–C(14)–C(15)			136.6(5)	133.7(5)
N(2)–C(14)–C(15)			92.4(4)	92.5(4)
C(14)–N(2)–C(18)			132.6(4)	131.7(4)
C(14)–N(2)–C(13)			94.9(4)	95.5(4)
C(18)–N(2)–C(13)			131.6(4)	131.5(4)
N(2)–C(13)–C(15)			86.7(4)	86.2(4)
N(2)–C(13)–C(7)			113.8(4)	114.8(4)
C(7)–C(13)–C(15)			114.5(4)	114.8(4)

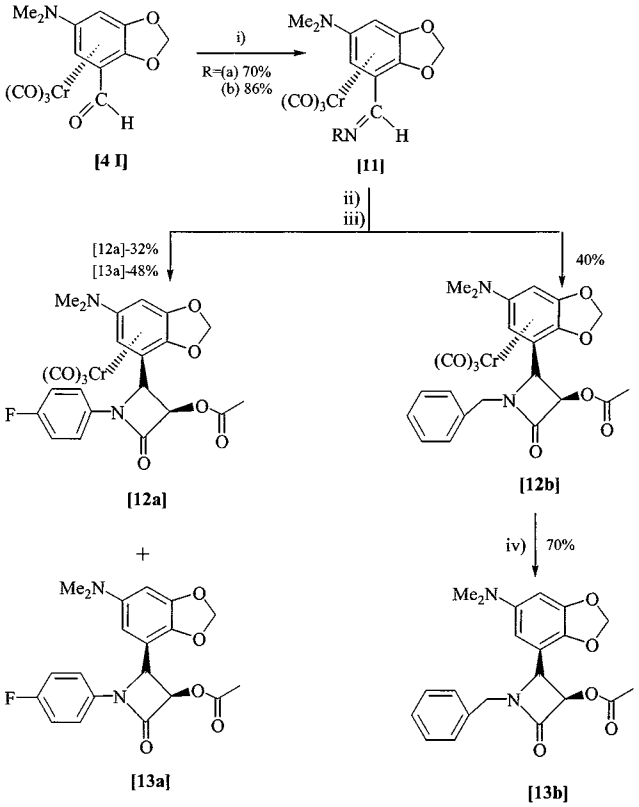
$Cr(CO)_3$ moiety with respect to the arene ring is also observed. In fact, the chromium atom projection on to the arene ring medium plan (see Fig. 1b) is shifted from the barycentric of the ring towards atom C(7a).

Following the established protocol relative to the racemic series of *cis*-β-lactam complexes, chiral imine complexes **11** were prepared and the e.e. determined by HPLC was higher than 95%. Complete *cis* diastereoselectivity in β-lactam complexes was also achieved using acetoxyacetyl chloride in the presence of triethylamine and the optically active Schiff bases **11a** and **11b**. The e.e. determination of **12a** and **12b** was not possible by HPLC because no acceptable experimental conditions were found to separate the racemic complexes **6a** and **6b**. However, X-ray crystal structure determination of **12a** confirmed its relative configuration as (7*R*,3′*R*,4′*S*)-{1′-(4″-fluorophenyl)-3′-acetoxy-4′-[η^6-5-(*N*,*N*-dimethylamino)-1,3-benzodioxole]azetidin-2′-one}tricarbonylchromium complex in which the *cis*-β-lactam complex carries three contiguous chiral centres (Scheme 4); and the e.e. of the decomplexed *cis*-β-lactams **13a** and **13b** were higher than 90 and 85%, respectively, using a Lichrocart column (*n*-hexane–2-propanol, 1:1).

Fig. 2 shows two perspective views of complex **12a** and the corresponding atomic-labelling scheme. The interatomic distances and angles are presented in Table 1. As for the aldehyde complex **4I**, the $Cr(CO)_3$ group has an eclipsed conformation relative to the carbocyclic ring and the Cr–C (ring) distance is maximum in the case of C(5). An interesting structural feature of complex **12a** is the almost coplanar pyramidal disposition of the three valences of the nitrogen atom at the 2-azetidin-2′-one ring, as reported in the literature [27]. This latter aspect adds interest to this β-lactams because it has been reported [28] that the relative pyramidalisation of the nitrogen atom in both monocyclic and bicyclic β-lactam antibiotics is directly related to their biological activity.

The *cis* selectivity always observed in the present study, using acetoxyacetyl chloride as the ketene source and chiral imine chromium complexes to yield the corresponding *cis*-azetidin-2-ones, can be accounted for by a two-step mechanism in which the first step is a nucleophilic attack of the iminic nitrogen lone pair over the sp-hybridised carbon atom of the ketene to form a zwitterionic intermediate according to the *exo* mode. The second step of the reaction is a conrotatory ring closure of the intermediate to yield the corresponding four-membered ring (Scheme 5).

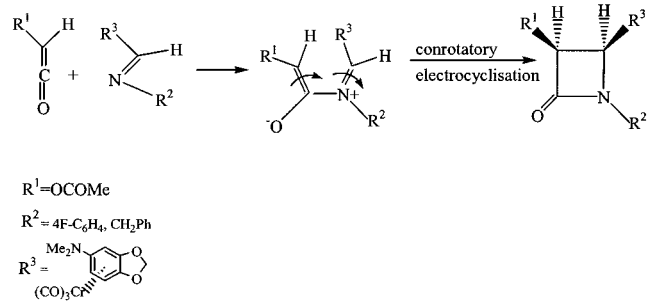
The acetoxy group in the synthesised *cis*-β-lactams is suitable for its nucleophilic substitution [12c] and can also be transformed easily into the amino function present in some mono β-lactam antibiotics [29], with complete inversion of configuration at the C(3′) position of the β-lactam ring, not directly accessible through the Staudinger reaction. Finally, earlier work [30] would indicate that the 3′-acetoxy-β-lactams might be attractive precursors of the α-amino acids and related compounds.



Scheme 4. Reagents: (i) RNH_2; R=4F–C_6H_4 (a), CH_2Ph, and (b) molecular sieves 4 Å; (ii) Et_3N; (iii) $CH_3CO_2CH_2COCl$; and (iv) $h\nu/O_2$.

3. Concluding remarks

From the results in the present study four key points deserve to be mentioned: (i) (7*R*)-[η^6-5-(*N*,*N*-dimethylamino)-7-(*N*′-imino)-1,3-benzodioxole]tricarbonylchromium complexes **11a** and **11b** are suitable chiral sources for the development of new substitution patterns of optically active β-lactams via the Staudinger reaction;



Scheme 5. Schematic representation of the possible initial approach between the imine complex **11** and the non-symmetric acetoxyketene.

(ii) it was also demonstrated that the efficiency of this process is dependent on the reactivity of both the imine complex and the ketene used; (iii) it should be possible to substitute the acetoxy group at C(3′) position and to invert the stereochemistry at the C(3′) position of the β-lactam complexes; and (iv) since methods for the synthesis of α-amino acids in their (*R*) and (*S*) forms are now abundant, the presence of the (1,3-benzodioxole) subunit in this class of β-lactams opens up new perspectives not only in the field of β-lactam antibiotics, but also in the chemistry that employs β-lactams as chiral-starting materials. Further studies of the applications of other methodologies to the chemical synthesis of β-lactams are in progress in our laboratory, including the use of a nucleophile-catalysed reaction of electron-deficient imines in order to develop a catalytic, shuttle-base route to the optically active β-lactams.

4. Experimental

4.1. General procedures

Melting points (m.p.) were determined on a Reichert Thermovar m.p. apparatus, and are uncorrected. Infrared (IR) spectra were obtained on a Perkin–Elmer

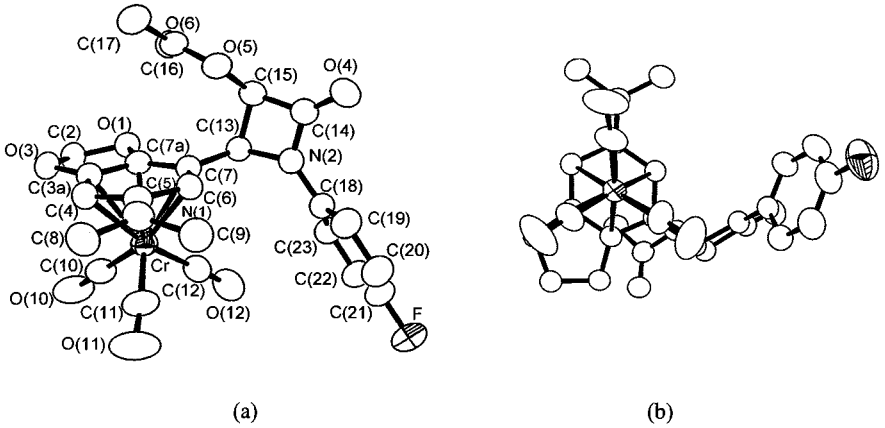


Fig. 2. (a) Molecular structure of complex **12a**. (b) View of molecule showing the relative positions of the carbonyl ligands to the carbocyclic ring.

1725X FT-IR spectrometer using neat films on NaCl plates or KBr pellets. NMR spectra were recorded in $CDCl_3$ in a General Electric QE-300 P spectrometer (operated at 300 MHz for ^1H and 75 MHz for ^{13}C spectra) or in a Bruker ARX spectrometer (operated at 400 MHz for ^1H and 100 MHz for ^{13}C spectra). Chemical shift values are given in parts per million (ppm) relative to tetramethylsilane and J values are given in Hertz. $^1H\{^{13}C\}$ heteronuclear correlation experiments (HETCORR, COLOC, HMQC or HMBC) were carried out for most of the compounds and in some cases (**5b**, **5d**, **7**, **9**, **11b** and **13b**) the experiments were performed at low temperature (5°C). Mass spectra were acquired on a Kratos MS 25 RF instrument operating at 70 eV. High-resolution mass spectra were determined on an Extrell (Waters) FTMS 2001-DT S.T.I.C.R. mass spectrometer. Elemental analyses were performed on a Carlo Erba 1106 elemental analyser. Optical rotations were recorded on a Perkin–Elmer 241 polarimeter. X-ray diffraction studies were performed at room temperature (r.t.) with a Stoe IPDS image plate equipped with Mo–K_α radiation (0.7107 Å). The structures were solved using SHELXS97 [31] and refined with SHELXL97 [32]. HPLC analyses were carried out with a Spectra-Physics apparatus using a chiral chromatographic column (0.46 cm ID × 25 cm) Chiralcel OJ. All separations were conducted at ambient temperature using an isocratic solvent system, which was composed by *n*-hexane–2-propanol (90:10, 80:20, 75:25, 70:30, 65:35, 60:40, 50:50; v/v). The complexes were detected by UV absorption at 254 nm. The flow rate for the resolution of isomers of complex **5a** was 0.7 ml min^{-1} (solvent: *n*-hexane–2-propanol, 70:30; v/v). No acceptable separation was found for the racemic mixtures **4**, **6a** and **8a** on this column. The decomplexed racemic mixtures **8a** and **8b** were resolved on a Lichrocart column (0.4 ID × 25 cm), using *n*-hexane–2-propanol, 50:50 as the mobile phase and 0.7 ml min^{-1} as the flow rate. All reactions involving the preparation or utilisation of (η^6-arene)tricarbonylchromium complexes were performed under a N_2 atmosphere. Tetrahydrofuran and Et_2O were distilled from sodium benzophenone ketyl under N_2. Dichloromethane was distilled over CaH_2 under N_2. Dibutyl ether was dried over sodium and distilled under an atmosphere of N_2 prior to use. Sodium hydride was obtained as 80% dispersion in oil, from which the oil was removed by repeated washings with *n*-hexane and drying under vacuum. All the other reagents were used as received or purified by standard methods [33]. Organic extracts were dried over anhydrous $MgSO_4$. Column chromatography was carried out using Merck silica gel 60 (230–400 mesh). The complexed β-lactams were not stable and, consequently, all the ^{13}C-NMR data could not be obtained. In contrast, the corresponding decomplexed β-lactams gave all the ^{13}C-NMR data. Due to instability of complex **7**, elemental analysis was only carried out in the decomplexed compound **9**.

4.2. (η^6-5-Amino-1,3-benzodioxole)tricarbonylchromium (2)

A mixture of 5-amino-1,3-benzodioxole (**1**) (1.25 g, 9.12 mmol) and $Cr(CO)_6$ (2.40 g, 10.91 mmol) in deoxygenated $(n\text{-}Bu)_2O$ (50 ml)–THF (5 ml) was heated under reflux for 5 days. The resulting solution was cooled, filtered through celite with Et_2O and concentrated under reduced pressure to afford complex **2**. Recrystallisation from CH_2Cl_2–*n*-hexane gave a yellow powder (2.14 g, 86%), m.p. (dec.) 133–135°C. ^1H-NMR ($CDCl_3$, 300 MHz): $\delta = 3.42$ (s, 2H, NH_2), 4.38 (dd, 1H, $J = 1.8$ and 6.6 Hz, ArH), 5.13 (d, 1H, $J = 1.8$ Hz, ArH), 5.61 (s, 1H, CH_2), 5.68 (d, 1H, $J = 6.6$ Hz, ArH), 5.91 (s, 1H, CH_2). ^{13}C-NMR (CD_3COCD_3, 75 MHz): $\delta = 65.74$ (Ar), 68.90 (Ar), 80.87 (Ar), 100.91 (CH_2), 120.81 (Ar, C_{quat}), 130.72 (Ar, C_{quat}), 134.35 (Ar, C_{quat}), 236.34 (C≡O). FABMS; m/z (%): 274 ([MH^+], 22), 273 ([M^+], 82), 217 (100), 189 (44). IR (KBr, cm^{-1}): ν_{max} 3479 (N–H), 1942, 1872, 1849, 1814 (C≡O). Anal. Found: C, 43.68; H, 2.51; N, 4.96. Calc. for $C_{10}H_7O_5NCr$ (MW 273.17): C, 43.97; H, 2.58; N, 5.13%.

4.3. [η^6-5-(N,N-Dimethylamino)-1,3-benzodioxole]-tricarbonylchromium (3)

A suspension of NaH (1.19 g, 49.45 mmol) was added to a solution of (η^6-5-amino-1,3-benzodioxole)tricarbonylchromium (**2**) (2.70 g, 9.89 mmol) in THF (20 ml). When no further gas evolved, the mixture was cooled to 0°C and methyl iodide was added (3.10 g, 49.45 mmol). After stirring the reaction for 2 h at 0°C and for about 2 h at r.t., the resulting solution was filtered with CH_2Cl_2, first through celite and then through a silica column to yield complex **3**. Recrystallisation from CH_2Cl_2–*n*-hexane gave yellow crystals (2.21 g, 70%), m.p. (dec.) 135–136°C. ^1H-NMR ($CDCl_3$, 300 MHz): $\delta = 2.83$ [s, 6H, $N(CH_3)_2$], 4.22 (dd, 1H, $J = 2.2$ and 8.0 Hz, ArH), 5.09 (d, 1H, $J = 2.2$ Hz, ArH), 5.59 (s, 1H, CH_2), 5.68 (d, 1H, $J = 8.0$ Hz, ArH), 5.88 (s, 1H, CH_2). ^{13}C-NMR ($CDCl_3$, 75 MHz): $\delta =$ 40.38 [$N(CH_3)_2$], 62.03 (Ar), 65.16 (Ar), 79.20 (Ar), 99.79 (CH_2), 119.62 (Ar, C_{quat}), 130.63 (Ar, C_{quat}), 133.04 (Ar, C_{quat}), 234.77 (C≡O). IR (KBr, cm^{-1}): ν_{max} 1943, 1850 (C≡O). EIMS; m/z (%): 301 ([M^+], 2), 245 (2), 217 (5), 165 (100). Anal. Found: C, 48.12; H, 3.77; N, 4.44. Calc. for $C_{12}H_{11}O_5NCr$ (MW 301.22): C, 47.85; H, 3.68; N, 4.65%.

4.4. [η^6-5-(*N*,*N*-Dimethylamino)-7-formyl-1,3-benzodioxole]tricarbonylchromium (**4**)

n-Butyllithium (9.0 ml, 11.0 mmol) was added dropwise to a cooled solution (−30°C) of complex **3** (2.21 g, 7.34 mmol) in THF (20 ml) and Et_2O (20 ml) with stirring for 1 h. *N*,*N*-Dimethylformamide (2.8 ml, 36.7 mmol) was added, the mixture was stirred for 1 h at −30°C and the solution was allowed to react for 1 h at r.t. The solution was washed with NH_4Cl (20 ml)–H_2O (20 ml) and dried. Removal of the solvent and the crude product washed with *n*-hexane gave complex **4**. Recrystallisation from CH_2Cl_2–*n*-hexane gave a red powder (1.67 g, 70%), m.p. (dec.) 128–130°C. ^{1}H-NMR ($CDCl_3$, 300 MHz): $\delta = 2.88$ [s, 6H, $N(CH_3)_2$], 4.64 (d, 1H, $J = 2.4$ Hz, ArH), 5.47 (d, 1H, $J = 2.4$ Hz, ArH), 5.85 (s, 1H, CH_2), 6.11 (s, 1H, CH_2), 10.01 (s, 1H, CHO). ^{13}C-NMR ($CDCl_3$, 75 MHz): $\delta = 40.56$ [$N(CH_3)_2$], 61.46 (Ar), 64.40 (Ar), 82.99 (Ar, C_{quat}), 101.50 (CH_2), 124.83 (Ar, C_{quat}), 128.14 (Ar, C_{quat}), 131.08 (Ar, C_{quat}), 185.96 (C=O), 233.37 (C≡O). EIMS; *m*/*z* (%): 329 ([M^+], 2), 273 (2), 245 (5), 193 (100). IR (KBr, cm^{-1}): ν_{max} 1946, 1891, 1847 (C≡O), 1688 (C=O). Anal. Found: C, 47.38; H, 3.63; N, 4.32. Calc. $C_{13}H_{11}O_6NCr$ (329.23): C, 47.43; H, 3.37; N, 4.25%.

4.5. General method for synthesis of imine complexes **5** and **11**

The required aniline (five equivalents) was added to a solution of complex **4** containing 4 Å molecular sieves in THF (20 ml) or CH_2Cl_2 (20 ml). The mixture was stirred for 4 h. After filtration through celite and evaporation of the solvent, the crude product washed with *n*-hexane gave a compound which was identified as the corresponding imine complex.

4.5.1. [η^6-5-(*N*,*N*-Dimethylamino)-7-(*N*′-4′-fluorophenylimino)-1,3-benzodioxole]-tricarbonylchromium (**5a**)

4-Fluoroaniline (0.70 ml, 7.16 mmol) and complex **4** (0.47 g, 1.43 mmol) in THF afforded **5a**. Recrystallisation from CH_2Cl_2–*n*-hexane gave a red powder (0.32 g, 53%), m.p. (dec.) 144–145°C. ^{1}H-NMR ($CDCl_3$, 300 MHz): $\delta = 2.94$ [s, 6H, $N(CH_3)_2$], 5.04 (d, 1H, $J = 1.2$ Hz, ArH), 5.29 (d, 1H, $J = 1.2$ Hz, ArH), 5.82 (s, 1H, CH_2), 6.06 (s, 1H, CH_2), 7.05–7.24 (m, 4H, Ar′H), 8.47 (s, 1H, CHN). ^{13}C-NMR ($CDCl_3$, 75 MHz): $\delta = 40.57$ [$N(CH_3)_2$], 61.81 (Ar), 62.56 (Ar), 87.08 (Ar, C_{quat}), 100.72 (CH_2), 115.99 (d, 2Ar′, $J = 22.6$ Hz), 122.02 (Ar, C_{quat}), 122.53 (d, 2Ar′, $J = 8.4$ Hz), 129.76 (Ar, C_{quat}), 132.42 (Ar, C_{quat}), 147.12 (Ar′, C_{quat}), 153.52 (CHN), 161.61 (d, Ar′, $J = 243.6$ Hz, C_{quat}), 234.51 (C≡O). EIMS; *m*/*z* (%): 422 ([M^+], 1), 366 (9), 338 (17), 286 (100). IR (KBr, cm^{-1}): ν_{max} 1938, 1873, 1848 (C≡O), 1629 (C=N). Found: 422.03643. Calc. for $C_{19}H_{15}O_5N_2CrF$: 422.03646.

4.5.2. [η^6-5-(*N*,*N*-Dimethylamino)-7-(*N*′-benzylimino)-1,3-benzodioxole]tricarbonylchromium (**5b**)

Benzylamine (0.28 ml, 2.59 mmol) and complex **4** (0.17 g, 0.517 mmol) in CH_2Cl_2 afforded **5b**. Recrystallisation from CH_2Cl_2–*n*-hexane gave an orange powder (0.13 g, 60%), m.p. (dec.) 121–124°C. ^{1}H-NMR ($CDCl_3$, 300 MHz): $\delta = 2.89$ [s, 6H, $N(CH_3)_2$], 4.79–4.92 (m, 3H, CH_2 and ArH), 5.22 (d, 1H, $J = 2.1$ Hz, ArH), 5.78 (s, 1H, CH_2), 6.02 (s, 1H, CH_2), 7.26–7.40 (m, 5H, Ar′H), 8.40 (s, 1H, CHN). ^{13}C-NMR ($CDCl_3$, 100 MHz): $\delta = 40.52$ [$N(CH_3)_2$], 61.92 (Ar), 62.23 (Ar), 64.99 (CH_2), 87.99 (Ar, C_{quat}), 100.47 (CH_2), 121.04 (Ar, C_{quat}), 127.39 (Ar′), 128.41 (Ar′), 128.66 (Ar′), 129.89 (Ar, C_{quat}), 132.60 (Ar, C_{quat}), 138.04 (Ar′, C_{quat}), 155.29 (CHN), 234.82 (C≡O). EIMS; *m*/*z* (%): 334 ([$M^+ - 3CO$], 1), 282 (100). IR (KBr, cm^{-1}): ν_{max} 1938, 1870, 1844 (C≡O), 1646 (C=N). Found: 418.05795. Calc. for $C_{20}H_{18}O_5N_2Cr$: 418.06153.

4.5.3. [η^6-5-(*N*,*N*-Dimethylamino)-7-(*N*′-phenylimino)-1,3-benzodioxole]tricarbonylchromium (**5c**)

Aniline (0.60 ml, 6.33 mmol) and complex **4** (0.42 g, 1.23 mmol) in THF afforded **5c**. Recrystallisation from CH_2Cl_2–*n*-hexane gave a red powder (0.28 g, 54%), m.p. (dec.) 141–143°C. ^{1}H-NMR ($CDCl_3$, 300 MHz): $\delta = 2.94$ [s, 6H, $N(CH_3)_2$], 5.03 (d, 1H, $J = 2.1$ Hz, ArH), 5.29 (d, 1H, $J = 2.1$ Hz, ArH), 5.82 (s, 1H, CH_2), 6.06 (s, 1H, CH_2), 7.21–7.40 (m, 5H, Ar′H), 8.49 (s, 1H, CHN). ^{13}C-NMR ($CDCl_3$, 75 MHz): $\delta = 40.52$ [$N(CH_3)_2$], 61.88 (Ar), 62.55 (Ar), 87.24 (Ar, C_{quat}), 100.68 (CH_2), 120.93 (Ar′), 122.01 (Ar, C_{quat}), 126.59 (Ar′), 129.19 (Ar′), 129.73 (Ar, C_{quat}), 132.41 (Ar, C_{quat}), 151.06 (Ar′, C_{quat}), 153.68 (CHN), 234.52 (C≡O). EIMS; *m*/*z* (%): 404 ([M^+], 6), 320 (13), 268 (100). IR (KBr, cm^{-1}): ν_{max} 1933, 1868, 1841 (C≡O), 1629 (C=N). Anal. Found: C, 56.39; H, 4.22; N, 6.93. Calc. for $C_{19}H_{16}O_5N_2Cr$ (MW 404.35): C, 56.43; H, 3.99; N, 6.93%.

4.5.4. [η^6-5-(*N*,*N*-Dimethylamino)-7-(*N*′-phenylamino-imino)-1,3-benzodioxole]tricarbonylchromium (**5d**)

Phenylhydrazine (0.60 ml, 5.62 mmol) and complex **4** (0.37 g, 1.13 mmol) in CH_2Cl_2 afforded **5d**. Recrystallisation from CH_2Cl_2–*n*-hexane gave red crystals (0.27 g, 57%), m.p. (dec.) 139–142°C. ^{1}H-NMR ($CDCl_3$, 300 MHz): $\delta = 2.95$ [(s, 6H, $N(CH_3)_2$], 5.02 (d, 1H, $J = 3.0$ Hz, ArH), 5.13 (d, 1H, $J = 3.0$ Hz, ArH), 5.79 (s, 1H, CH_2), 6.04 (s, 1H, CH_2), 6.93–7.35 (m, 5H, Ar′H), 7.64 (s, 1H, CHN), 8.03 (s, 1H, NH). ^{13}C-NMR ($CDCl_3$, 100 MHz): $\delta = 40.57$ [$N(CH_3)_2$], 60.97 (Ar), 61.58 (Ar), 91.07 (CHN), 100.00 (CH_2), 112.84 (Ar′), 118.23 (Ar, C_{quat}), 120.96 (Ar′), 127.80 (Ar, C_{quat}), 129.33 (Ar′), 130.11 (Ar, C_{quat}), 132.79 (Ar, C_{quat}), 143.34 (Ar′,

C_{quat}), 235.20 (C≡O). FABMS; m/z (%): 420 ([MH^+], 13), 419 ([M^+], 19), 363 (30), 335 (100), 283 (44). IR (KBr, cm^{-1}): ν_{max} 3307 (N–H), 1939, 1867, 1822 (C≡O), 1580 (C=N). Anal. Found: C, 54.79; H, 4.01; N, 9.87. Calc. for $C_{19}H_{17}O_5N_3Cr$ (MW 419.36): C, 54.42; H, 4.09; N, 10.2%.

4.6. General method for synthesis of the β-lactam complexes **6**, **12**, **13** and the imine complex **7**

To a stirred solution of the imine complex (one equivalent) in CH_2Cl_2, Et_3N (six equivalents) previously distilled and acetoxyacetyl chloride (three or six equivalents) were added at 0°C. After 1 h, the reaction mixture was allowed to warm up to r.t., and was further stirred at this temperature for several hours. When the reaction was completed (TLC), an aqueous (aq.) solution of NH_4Cl (30 ml) was added and the aq. layer was extracted with Et_2O (30 ml). The combined organic extracts were dried, filtered and concentrated to give the crude product. Column chromatography (*n*-hexane–Et_2O, 1:1) yielded the β-lactam complexes, in some reactions the complexed and decomplexed ones and the imine complex **7** were also obtained. The compounds were recrystallised from Et_2O–*n*-hexane.

4.6.1. {1′-(4″-Fluorophenyl)-3′-acetoxy-4′-[η⁶-5-(N,N-dimethylamino)-1,3-benzodioxole]-azetidin-2′-one}tricarbonylchromium (**6a**)

Imine complex **5a** (0.32 g, 0.76 mmol), Et_3N (0.64 ml, 4.56 mmol) and acetoxyacetyl chloride (0.25 ml, 2.28 mmol) after 20 h of reaction at r.t. afforded **6a**. Recrystallisation yielded yellow crystals (0.19 g, 50%), m.p. (dec.) 138–140°C. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 2.05 (s, 3H, CH_3COO), 2.72 [s, 6H, $(NCH_3)_2$], 4.37 (d, 1H, J = 1.8 Hz, ArH), 5.11 (d, 1H, J = 1.8 Hz, ArH), 5.46 (s, 1H, CH_2), 5.67 (d, 1H, J = 5.4 Hz, CH), 5.88 (s, 1H, CH_2), 6.43 (d, 1H, J = 5.4 Hz, CH), 7.13 (t, 2H, J = 9.0 Hz, Ar′H), 7.70 (m, 2H, Ar′H). EIMS; m/z (%): 386 ([$M^+ - Cr(CO)_3$], 10), 286 (29), 52 (100). IR (KBr, cm^{-1}): ν_{max} 1947, 1880, 1862 (C≡O), 1773, 1753 (C=O). Anal. Found: C, 52.96; H, 3.62; N, 5.22. Calc. for $C_{23}H_{19}O_8N_2CrF$ (MW 522.41): C, 52.88; H, 3.67; N, 5.36%.

4.6.2. {1′-Benzyl-3′-acetoxy-4′-[η⁶-5-(N,N-dimethylamino)-1,3-benzodioxole]-azetidin-2′-one}tricarbonylchromium (**6b**)

Imine complex **5b** (0.13 g, 0.31 mmol), Et_3N (0.26 ml, 1.86 mmol) and acetoxyacetyl chloride (0.10 ml, 0.93 mmol) after 4 h of reaction at r.t. afforded **6b**. Recrystallisation yielded yellow crystals (0.096 g, 60%), m.p. (dec.) 123–126°C. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 1.94 (s, 3H, CH_3COO), 2.50 [s, 6H, $(NCH_3)_2$], 3.88 (d, 1H, J = 2.1 Hz, ArH), 4.44 (d, 1H, J = 15.0 Hz, NCH_2), 4.86 (d, 1H, J = 15.0 Hz, NCH_2), 4.94 (d, 1H, J = 2.1 Hz, ArH), 5.26 (d, 1H, J = 5.1 Hz, CH), 5.44 (s, 1H, CH_2), 5.87 (s, 1H, CH_2), 6.15 (d, 1H, J = 5.1 Hz, CH), 7.28–7.57 (m, 5H, Ar′H). EIMS; m/z (%): 434 ([$M^+ - 3CO$], 1), 382 (100), 282 (46). IR (KBr, cm^{-1}): ν_{max} 1937, 1871, 1851 (C≡O), 1782, 1762 (C=O). Anal. Found: C, 55.59, H, 4.26, N, 5.26. Calc. for $C_{24}H_{22}O_8N_2Cr$ (MW 518.44): C, 55.60; H, 4.28; N, 5.40%.

4.6.3. {1′-Phenyl-3′-acetoxy-4′-[η⁶-5-(N,N-dimethylamino)-1,3-benzodioxole]-azetidin-2′-one}tricarbonylchromium (**6c**)

Imine **5c** (0.17 g, 0.43 mmol), Et_3N (0.36 ml, 2.56 mmol) and acetoxyacetyl chloride (0.15 ml, 1.41 mmol) after 20 h of reaction at r.t. afforded **6c**. Recrystallisation yielded yellow crystals (0.092 g, 43%), m.p. (dec.) 142–144°C. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 2.06 (s, 3H, CH_3COO), 2.71 [s, 6H, $(NCH_3)_2$], 4.40 (s, 1H, ArH), 5.09 (s, 1H, ArH), 5.47 (s, 1H, CH_2), 5.69 (d, 1H, J = 5.7 Hz, CH), 5.87 (s, 1H, CH_2), 6.45 (d, 1H, J = 5.7 Hz, CH), 7.19–7.72 (m, 5H, Ar′H). EIMS; m/z (%): 504 ([M^+], 6), 420 (13), 368 (41), 268 (100). IR (KBr, cm^{-1}): ν_{max} 1935, 1850 (C≡O), 1775, 1755 (C=O). Anal. Found: C, 55.06; H, 3.99; N, 5.44. Calc. for $C_{23}H_{20}O_8N_2Cr$ (MW 504.42): C, 54.77; H, 4.00; N, 5.55%.

4.6.4. {η⁶-5-(N,N-Dimethylamino)-7-[N′-(N″-phenyl-acetoxyacetyl)imino]-1,3-benzodioxole}-tricarbonylchromium (**7**)

Imine **5d** (0.10 g, 0.24 mmol), Et_3N (0.20 ml, 1.43 mmol) and acetoxyacetyl chloride (0.15 ml, 1.43 mmol) after 20 h of reaction at r.t. afforded **7**. Recrystallisation yielded orange powder (0.060 g, 48%), m.p. (dec.) 135–138°C. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 2.21 (s, 3H, CH_3COO), 2.91 [s, 6H, $(NCH_3)_2$], 4.66 (s, 1H, ArH), 5.14 (s, 1H, ArH), 5.33 (dd, 2H, J = 18.3 and 49.7 Hz, OCH_2), 5.66 (s, 1H, CH_2), 5.93 (s, 1H, CH_2), 7.23–7.59 (m, 5H, Ar′H). ^{13}C-NMR ($CDCl_3$, 100 MHz): δ = 20.75 (CH_3), 40.46 [$N(CH_3)_2$], 60.90 (Ar), 61.46 (Ar), 62.34 (OCH_2), 87.18 (C_{quat}), 100.25 (CH_2), 119.60 (C_{quat}), 128.80 (Ar′), 130.05 (Ar′), 130.51 (Ar′), 132.74 (C_{quat}), 133.77 (C_{quat}), 135.82 (CHN), 167.96 (C=O), 170.98 (C=O), 234.57 (C≡O). EIMS; m/z (%): 520 ([MH^+], 7), 519 ([M^+], 8), 463 (9), 435 (64), 383 (83), 327 (100). IR (KBr, cm^{-1}): ν_{max} 1946, 1857 (C≡O), 1751, 1708 (C=O), 1578 (C=N).

4.7. General procedure for the decomplexation of β-lactams **6a**–**6d** and complex **7**

A solution of complexes **6** and **7** in ether was exposed to air and sunlight at r.t. until TLC indicated that the reaction had gone to completion. Filtration through silica or celite and removal of the solvent gave decomplexed products which, when necessary, were further

purified by preparative layer chromatography (*n*-hexane–Et_2O, 70:30) to afford products **8** and **9**.

*4.7.1. 1′-(4″-Fluorophenyl)-3′-acetoxy-4′-[5-(N,N-dimethylamino)-1,3-benzodioxole]azetidin-2′-one (**8a**)*

Complex **6a** (0.016 g, 0.043 mmol) afforded β-lactam **8a** as a colourless oil (0.010 g, 60%). ^{1}H-NMR ($CDCl_3$, 300 MHz): $\delta = 1.86$ (s, 3H, CH_3COO), 2.82 [s, 6H, $(NCH_3)_2$], 5.38 (d, 1H, $J = 4.8$ Hz, CH), 5.80 (s, 1H, CH_2), 5.90 (s, 1H, CH_2), 5.98 (d, 1H, $J = 4.8$ Hz, CH), 6.01 (d, 1H, $J = 2.4$ Hz, ArH), 6.37 (d, 1H, $J = 2.4$ Hz, ArH), 6.98 (t, 2H, $J = 8.4$ Hz, Ar′H), 7.34 (m, 2H, Ar′H). ^{13}C-NMR ($CDCl_3$, 75 MHz): $\delta = 20.12$ (CH_3), 41.56 [$N(CH_3)_2$], 57.48 (CH), 76.09 (CH), 96.51 (Ar), 101.21 (CH_2), 104.05 (Ar), 113.23 (Ar, C_{quat}), 115.97 (d, 2Ar′, $J = 22.6$ Hz), 118.80 (d, 2Ar′, $J = 8.2$ Hz), 133.25 (Ar′, C_{quat}), 138.13 (Ar, C_{quat}), 146.94 (Ar, C_{quat}), 148.56 (Ar, C_{quat}), 159.46 (d, Ar′, $J = 242.9$ Hz, C_{quat}), 161.65 (C=O), 169.07 (OCO). EIMS; *m*/*z* (%): 386 ([M^+], 52), 286 (88), 43 (100). IR (film, cm^{-1}): ν_{max} 1762, 1637 (C=O). EIHRMS Found: 386.12724. Calc. for $C_{20}H_{19}O_5N_2F$: 386.12725.

*4.7.2. 1′-Benzyl-3′-acetoxy-4′-[5-(N,N-dimethylamino)-1,3-benzodioxole]azetidin-2′-one (**8b**)*

Complex **6b** (0.010 g, 0.019 mmol) afforded β-lactam **8b** as a colourless oil (0.006 g, 80%). ^{1}H-NMR ($CDCl_3$, 300 MHz): $\delta = 1.81$ (s, 3H, CH_3COO), 2.83 [s, 6H, $(NCH_3)_2$], 3.98 (d, 1H, $J = 15.0$ Hz, NCH_2), 4.79 (d, 1H, $J = 15.0$ Hz, NCH_2), 4.83 (d, 1H, $J = 4.5$ Hz, CH), 5.80 (d, 1H, $J = 4.5$ Hz, CH), 5.84 (s, 2H, CH_2), 5.92 (d, 1H, $J = 2.4$ Hz, ArH), 6.37 (d, 1H, $J = 2.4$ Hz, ArH), 7.25 (m, 5H, Ar′H). ^{13}C-NMR ($CDCl_3$, 100 MHz): $\delta = 20.16$ (CH_3), 41.66 [$N(CH_3)_2$], 44.73 (CH_2), 56.81 (CH), 76.89 (CH), 96.39 (Ar), 101.02 (CH_2), 104.48 (Ar), 113.51 (Ar, C_{quat}), 127.88 (Ar′), 128.45 (Ar′), 128.74 (Ar′), 134.47 (Ar, C_{quat}), 138.24 (Ar, C_{quat}), 146.62 (Ar, C_{quat}), 148.28 (Ar′, C_{quat}), 164.64 (C=O), 169.16 (OCO). EIMS; *m*/*z* (%): 382 ([M^+], 11), 282 (6), 207 (7), 162 (18), 120 (67), 91 (98), 43 (100). IR (film, cm^{-1}): ν_{max} 1752, 1677 (C=O). EIHRMS Found: 382.15212. Calc. for $C_{21}H_{22}O_5N_2$: 382.15232.

*4.7.3. 1′-Phenyl-3′-acetoxy-4′-[5-(N,N-dimethylamino)-1,3-benzodioxole]azetidin-2′-one (**8c**)*

Complex **6c** (0.022 g, 0.043 mmol) afforded β-lactam **8c** as a colourless oil (0.016 g, 74%). ^{1}H-NMR ($CDCl_3$, 300 MHz): $\delta = 1.86$ (s, 3H, CH_3COO), 2.81 [s, 6H, $(NCH_3)_2$], 5.41 (d, 1H, $J = 4.8$ Hz, CH), 5.81 (s, 1H, CH_2), 5.90 (s, 1H, CH_2), 5.98 (d, 1H, $J = 4.8$ Hz, CH), 6.04 (d, 1H, $J = 2.1$ Hz, ArH), 6.37 (d, 1H, $J = 2.1$ Hz, ArH), 7.07–7.38 (m, 5H, Ar′H). ^{13}C-NMR ($CDCl_3$, 75 MHz): $\delta = 19.77$ (CH_3), 41.33 [$N(CH_3)_2$], 57.22 (CH), 75.98 (CH), 96.44 (Ar), 101.01 (CH_2), 104.44 (Ar), 113.85 (Ar, C_{quat}), 117.66 (2Ar′), 124.44 (Ar′), 128.89 (2Ar′), 137.20 (Ar, C_{quat}), 138.24 (Ar, C_{quat}), 147.10 (Ar, C_{quat}), 148.57 (Ar′, C_{quat}), 161.80 (C=O), 168.69 (OCO). EIMS; *m*/*z* (%): 368 ([M^+], 82), 268 (100), 249 (19), 207 (37). IR (film, cm^{-1}): ν_{max} 1770, 1751 (C=O). EIHRMS Found: 368.13667. Calc. for $C_{20}H_{20}O_5N_2$: 368.13669.

*4.7.4. 5-(N,N-Dimethylamino)-7-[N′-(N″-phenyl-acetoxyacetyl)imino]-1,3-benzodioxole (**9**)*

Complex **7** (0.010 g, 0.019 mmol) afforded product **9** as a yellow powder (0.0064 g, 86%), m.p. (dec.) 160–163°C. ^{1}H-NMR ($CDCl_3$, 300 MHz): $\delta = 2.21$ (s, 3H, CH_3COO), 2.88 [s, 6H, $(NCH_3)_2$], 5.40 (s, 2H, CH_2), 5.88 (s, 2H, CH_2), 6.40 (d, 1H, $J = 2.4$ Hz, ArH), 6.43 (d, 1H, $J = 2.4$ Hz, ArH), 7.22 (m, 2H, Ar′H), 7.39 (s, 1H, CHN), 7.52 (m, 3H, Ar′H). ^{13}C-NMR ($CDCl_3$, 100 MHz): $\delta = 20.87$ (CH_3), 41.71 [$N(CH_3)_2$], 62.74 (OCH_2), 98.03 (Ar), 101.12 (CH_2), 101.34 (Ar), 115.38 (Ar, C_{quat}), 129.11 (Ar′), 129.79 (Ar′), 130.35 (Ar′), 134.23 (C_{quat}), 137.93 (CHN), 146.90 (C_{quat}), 148.98 (C_{quat}), 168.34 (C=O), 171.16 (OCO). EIMS; *m*/*z* (%): 383 ([M^+], 81), 283 (17), 190 (48), 164 (72), 43 (100). IR (KBr, cm^{-1}): ν_{max} 1742, 1698 (C=O), 1638 (C=N). EIHRMS Found: 383.14879. Calc. for $C_{20}H_{21}O_5N_3$: 383.14757.

*4.8. (7R,1′S)-[η^6-5-(N,N-Dimethylamino)-7-(N′-methylbenzylimino)-1,3-benzodixole]tricarbonylchromium (**10I**) and (7S,1S′)-[η^6-5-(N,N-dimethylamino)-7-(N′-methylbenzylimino)-1,3-benzodioxole]tricarbonylchromium (**10II**)*

(*S*)-(−)-(α)-Methylbenzylamine (0.40 ml, 2.89 mmol) was added to an Et_2O (50 ml) solution of complex **4** (0.95 g, 2.89 mmol) containing 4 Å molecular sieves. The mixture was stirred for 4 h at r.t. and filtered through celite. TLC (Et_2O–*n*-hexane–Et_3N, 80:15:5 and Et_2O–*n*-hexane, 75:25) and ^{1}H-NMR spectrum showed a mixture of two compounds in a 1:1 ratio. Separation of the two complexes was only possible by recrystallisation from CH_2Cl_2–Et_2O–*n*-hexane and afforded complexes **10I** and **10II**. First, the complex **10I** was afforded (0.35 g, 30%) as red crystals. With no more complex **10I** in solution the complex **10II** recrystallised as an orange powder (0.15 g, 12%). Following the order of recrystallisation — complex **10I**: m.p. (dec.) 138–140°C. ^{1}H-NMR ($CDCl_3$, 300 MHz): $\delta = 1.61$ (d, 3H, $J = 6.6$ Hz, CH_3), 2.89 [s, 6H, $N(CH_3)_2$], 4.67 (q, 1H, $J = 6.6$ and 13.4 Hz, CH), 4.89 (d, 1H, $J = 2.1$ Hz, ArH), 5.20 (d, 1H, $J = 2.1$ Hz, ArH), 5.77 (s, 1H, CH_2), 6.01 (s, 1H, CH_2), 7.38–7.40 (m, 5H, Ar′H), 8.35 (s, 1H, CHN). ^{13}C-NMR ($CDCl_3$, 75 MHz): $\delta = 23.72$ (CH_3), 40.55 [$(NCH_3)_2$], 62.38 (2Ar), 68.79 (CHAr′), 88.31 (Ar, C_{quat}), 100.44 (CH_2), 121.22 (Ar, C_{quat}), 126.89 (Ar′), 127.09 (Ar′), 128.44

(Ar′), 129.64 (Ar, C_{quat}), 132.41 (Ar, C_{quat}), 143.40 (Ar′, C_{quat}), 152.83 (CHN), 234.44 (C≡O). EIMS; m/z (%): 376 ([$M^+ - 2CO$], 1), 348 (4), 296 (100). IR (KBr, cm^{-1}): ν_{max} 1939, 1880, 1848 (C≡O), 1641 (C=N). Anal. Found: C, 58.39; H, 4.67; N, 6.34. Calc. for $C_{12}H_{20}O_5N_2Cr$ (MW 432.40): C, 58.33; H, 4.66; N, 6.48%. Complex **10II**: m.p. (dec.) 122–125°C. ^{1}H-NMR ($CDCl_3$, 300 MHz): $\delta = 1.61$ (d, 3H, $J = 6.6$ Hz, CH_3), 2.90 [s, 6H, $N(CH_3)_2$], 4.59 (q, 1H, $J = 6.6$ and 13.1 Hz, CH), 4.98 (d, 1H, $J = 1.8$ Hz, ArH), 5.20 (d, 1H, $J = 1.8$ Hz, ArH), 5.77 (s, 1H, CH_2), 5.98 (s, 1H, CH_2), 7.23–7.43 (m, 5H, Ar′H), 8.40 (s, 1H, CHN). ^{13}C-NMR ($CDCl_3$, 75 MHz): $\delta = 24.96$ (CH_3), 40.48 [$(NCH_3)_2$], 62.14 (Ar), 62.44 (Ar), 69.97 (CHAr′), 87.90 (Ar, C_{quat}), 100.54 (CH_2), 121.51 (Ar, C_{quat}), 126.65 (Ar′), 127.06 (Ar′), 128.47 (Ar′), 129.66 (Ar, C_{quat}), 132.53 (Ar, C_{quat}), 144.24 (Ar′, C_{quat}), 152.20 (CHN), 234.61 (C≡O). EIMS; m/z (%): 376 ([$M^+ - 2CO$], 1), 348 (4), 296 (100). IR (KBr, cm^{-1}): ν_{max} 1937, 1883, 1852 (C=O), 1646 (C=N). Anal. Found: C, 58.22; H, 4.59; N, 6.42. Calc. for $C_{12}H_{20}O_5N_2Cr$ (MW 432.40): C, 58.33; H, 4.66; N, 6.48%.

*4.9. (7R)-[η^6-5-(N,N-Dimethylamino)-7-formyl-1,3-benzodioxole]tricarbonylchromium **(4I)***

Complex **10I** (0.42 g, 0.97 mmol) was dissolved in THF (15 ml) and a solution of concentrated HCl (six drops) in H_2O (2 ml) was added. After stirring for 30 min, a saturated solution of NH_4Cl (20 ml) and Et_2O (20 ml) was added. The organic phase was dried, concentrated and purified by column chromatography (n-hexane–Et_2O, 50:50) to yield complex **4I**. Recrystallisation from CH_2Cl_2–n-hexane gave a red powder (0.23g, 72%), m.p. (dec.) 119–121°C. $[\alpha]_D^{25} = -364$ ($c = 0.23$, $CHCl_3$). ^{1}H-NMR ($CDCl_3$, 300 MHz): $\delta =$ 2.88 [s, 6H, $N(CH_3)_2$], 4.64 (d, 1H, $J = 2.4$ Hz, ArH), 5.47 (d, 1H, $J = 2.4$ Hz, ArH), 5.85 (s, 1H, CH_2), 6.11 (s, 1H, CH_2), 10.01 (s, 1H, CHO). ^{13}C-NMR ($CDCl_3$, 75 MHz): $\delta = 40.56$ [$(NCH_3)_2$], 61.46 (Ar), 64.40 (Ar), 82.99 (Ar, C_{quat}), 101.50 (CH_2), 124.83 (Ar, C_{quat}), 128.14 (Ar, C_{quat}), 131.08 (Ar, C_{quat}), 185.96 (C=O), 233.37 (C≡O). EIMS; m/z (%): 329 ([M^+], 9), 273 (7), 245 (18), 193 (100). IR (KBr, cm^{-1}): ν_{max} 1946, 1891, 1847 (C≡O), 1688 (C=O). Anal. Found: C, 47.29; H, 39; N, 4.06. Calc. for $C_{13}H_{11}O_6NCr$ (MW 329.23): C, 47.43; H, 3.37; N, 4.25%.

*4.10. Synthesis of enantiomerically pure imine complexes **11***

*4.10.1. (7R)-[η^6-5-(N,N-Dimethylamino)-7-(N′-4′-fluoro-phenylimino)-1,3-benzodioxole]-tricarbonylchromium **(11a)***

4-Fluoroaniline (0.33 ml, 3.50 mmol) in THF (20 ml) and complex **4I** (0.23 g, 0.70 mmol) afforded **11a**, according to the general procedure for the preparation of imine complexes. Recrystallisation from CH_2Cl_2–n-hexane afforded **11a** as a red powder (0.21 g, 70%), m.p. (dec.) 145–147°C. $[\alpha]_D^{25} = -490$ ($c = 0.10$, $CHCl_3$). ^{1}H-NMR ($CDCl_3$, 300 MHz): $\delta = 2.94$ [s, 6H, $N(CH_3)_2$], 5.04 (d, 1H, $J = 1.2$ Hz, ArH), 5.29 (d, 1H, $J = 1.2$ Hz, ArH), 5.82 (s, 1H, CH_2), 6.06 (s, 1H, CH_2), 7.05–7.24 (m, 4H, Ar′H), 8.47 (s, 1H, CHN). ^{13}C-NMR ($CDCl_3$, 75 MHz): $\delta = 40.57$ [$N(CH_3)_2$], 61.81 (Ar), 62.56 (Ar), 87.08 (Ar, C_{quat}), 100.72 (CH_2), 115.99 (d, 2Ar′, $J = 23.3$ Hz), 122.02 (Ar, C_{quat}), 122.53 (d, 2Ar′, $J = 8.3$ Hz), 129.76 (Ar, C_{quat}), 132.42 (Ar, C_{quat}), 147.12 (Ar′, C_{quat}), 153.52 (CHN), 161.61 (d, Ar′, $J =$ 243.6 Hz, C_{quat}), 234.51 (C≡O). EIMS; m/z (%): 422 ([M^+], 1), 366 (2), 338 (6), 286 (100). IR (KBr, cm^{-1}): ν_{max} 1938, 1873, 1848 (C≡O), 1629 (C=N). EIHRMS Found: 422.03631. Calc. for $C_{19}H_{15}O_5N_2CrF$: 422.03646.

*4.10.2. (7R)-[η^6-5-(N,N-Dimethylamino)-7-(N′-benzylimino)-1,3-benzodioxole]tricarbonylchromium **(11b)***

Benzylamine (five equivalents, 0.18 ml, 1.66 mmol) in CH_2Cl_2 (20 ml) and complex **4I** (0.11 g, 0.33 mmol) afforded **11b**, according to the general procedure for the preparation of racemic imine complexes. Recrystallisation from CH_2Cl_2–n-hexane afforded **11b** as an orange powder (0.12 g, 86%), m.p. (dec.) 128–130°C. $[\alpha]_D^{25} = -835$ ($c = 0.15$, $CHCl_3$). ^{1}H-NMR ($CDCl_3$, 300 MHz): $\delta = 2.89$ [s, 6H, $N(CH_3)_2$], 4.70–4.92 (m, 3H, CH_2 and ArH), 5.22 (d, 1H, $J = 2.1$ Hz, ArH), 5.78 (s, 1H, CH_2), 6.02 (s, 1H, CH_2), 7.26–7.40 (m, 5H, Ar′H), 8.40 (s, 1H, CHN). ^{13}C-NMR ($CDCl_3$, 100 MHz): $\delta = 40.52$ [$N(CH_3)_2$], 61.92 (Ar), 62.23 (Ar), 64.99 (CH_2), 87.99 (Ar, C_{quat}), 100.47 (CH_2), 121.04 (Ar, C_{quat}), 127.39 (Ar′), 128.41 (Ar′), 128.66 (Ar′), 129.89 (Ar, C_{quat}), 132.60 (Ar, C_{quat}), 138.04 (Ar′, C_{quat}), 155.29 (CHN), 234.82 (C≡O). EIMS; m/z (%): 418 ([M^+], 1), 362 (9), 334 (34), 282 (87), 179 (41), 91 (99), 52 (100). IR (KBr, cm^{-1}): ν_{max} 1938, 1870, 1844 (C≡O), 1646 (C = N). Anal. Found: C, 57.19; H, 4.28; N, 6.52. Calc. for $C_{20}H_{18}O_5N_2Cr$ (MW 418.37): C, 57.42; H, 4.34; N, 6.70%.

*4.11. Synthesis of enantiomerically pure β-lactams **12** and **13***

*4.11.1. (7R,3′R,4′S)-{1′-(4″-Fluorophenyl)-3′-acetoxy-4′-[η^6-5-(N,N-dimethylamino)-1,3-benzodioxole]-azetidin-2′-one}tricarbonylchromium **(12a)** and the corresponding decomplexed product (3′R,4′S)-{1′-(4″-fluorophenyl)-3′-acetoxy-4′-[5-(N,N-dimethyl-amino)-1,3-benzodioxole]azetidin-2′-one} **(13a)***

These complexes were prepared from imine **11a** (0.15 g, 0.36 mmol), Et_3N (0.30 ml, 2.13 mmol) and acetoxy-

acetyl chloride (0.24 ml, 2.14 mmol) after 3 days at r.t., according to the general method for preparation of β-lactam complexes. The crude product was obtained as an orange oil, which corresponded to a mixture of β-lactam complex **12a** and its decomplexed form **13a**. Column chromatography (*n*-hexane–Et_2O, 25:75) of this mixture yielded product **13a** as a colourless oil (0.066 g, 48%) and complex **12a**, which recrystallised from Et_2O–*n*-hexane as yellow crystals (0.060 g, 32%). Following the order of elution — β-lactam **13a**: $[\alpha]_D^{25} = -17$ ($c = 0.14$, $CHCl_3$). ^{1}H-NMR ($CDCl_3$, 300 MHz): $\delta = 1.86$ (s, 3H, CH_3COO), 2.82 [s, 6H, $(NCH_3)_2$], 5.38 (d, 1H, $J = 4.8$ Hz, CH), 5.80 (s, 1H, CH_2), 5.90 (s, 1H, CH_2), 5.98 (d, 1H, $J = 4.8$ Hz, CH), 6.01 (d, 1H, $J = 2.4$ Hz, ArH), 6.37 (d, 1H, $J = 2.4$ Hz, ArH), 6.98 (t, 2H, $J = 8.4$ Hz, Ar′H), 7.34 (m, 2H, Ar′H). ^{13}C-NMR ($CDCl_3$, 75 MHz): $\delta = 20.12$ (CH_3), 41.56 [$N(CH_3)_2$], 57.48 (CH), 76.09 (CH), 96.51 (Ar), 101.21 (CH_2), 104.05 (Ar), 113.23 (Ar, C_{quat}), 115.97 (d, 2Ar′, $J = 22.6$ Hz), 118.80 (d, 2Ar′, $J = 8.2$ Hz), 133.25 (Ar′, C_{quat}), 138.13 (Ar, C_{quat}), 146.94 (Ar, C_{quat}), 148.56 (Ar, C_{quat}), 159.46 (d, Ar′, $J = 242.9$, C_{quat}), 161.65 (C=O), 169.07 (OCO). EIMS; *m*/*z* (%): 386 ([M^+], 18), 286 (100). IR (film, cm^{-1}): ν_{max} 1762, 1637 (C=O). EIHRMS Found: 386.12727. Calc. for $C_{20}H_{19}O_5N_2F$: 386.12725. β-lactam complex **12a**: m.p. (dec.) 143–145°C. $[\alpha]_D^{25} = +10$ ($c = 0.10$, $CHCl_3$). ^{1}H-NMR ($CDCl_3$, 300 MHz): $\delta = 2.05$ (s, 3H, CH_3COO), 2.72 [s, 6H, $(NCH_3)_2$], 4.37 (d, 1H, $J = 1.8$ Hz, ArH), 5.11 (d, 1H, $J = 1.8$ Hz, ArH), 5.46 (s, 1H, CH_2), 5.67 (d, 1H, $J = 5.4$ Hz, CH), 5.88 (s, 1H, CH_2), 6.43 (d, 1H, $J = 5.4$ Hz, CH), 7.13 (t, 2H, $J = 9.0$ Hz, Ar′H), 7.70 (m, 2H, Ar′H). EIMS; *m*/*z* (%): 438 ([$M^+ - 3CO$], 1), 386 (66), 286 (100). IR (KBr, cm^{-1}): ν_{max} 1947, 1880, 1862 (C≡O), 1773, 1753 (C=O). Found: 522.05253. Calc. for $C_{23}H_{19}O_8N_2CrF$: 522.05251.

*4.11.2. (7R,3′R,4′S)-{1′-Benzyl-3′-acetoxy-4′-[η^6-5-(N,N-dimethylamino)-1,3-benzodioxole]-azetidin-2′-one}tricarbonylchromium (**12b**)*

Imine **11b** (0.10 g, 0.20 mmol), Et_3N (0.24 ml, 1.44 mmol) and acetoxyacetyl chloride (0.08 ml, 0.72 mmol) after 4 h of reaction at r.t. afforded **12b**. Recrystallisation from Et_2O–*n*-hexane yielded a yellow powder (0.050g, 40%), m.p. (dec.) 112–114°C. $[\alpha]_D^{25} = +6$ ($c = 0.10$, Et_2O). ^{1}H-NMR ($CDCl_3$, 300 MHz): $\delta = 1.94$ (s, 3H, CH_3COO), 2.50 [s, 6H, $(NCH_3)_2$], 3.88 (d, 1H, $J = 2.1$ Hz, ArH), 4.44 (d, 1H, $J = 15.0$ Hz, NCH_2), 4.86 (d, 1H, $J = 15.0$ Hz, NCH_2), 4.94 (d, 1H, $J = 2.1$ Hz, ArH), 5.26 (d, 1H, $J = 5.1$ Hz, CH), 5.44 (s, 1H, CH_2), 5.87 (s, 1H, CH_2), 6.15 (d, 1H, $J = 5.1$ Hz, CH), 7.28–7.57 (m, 5H, Ar′H). EIMS; *m*/*z* (%): 434 ([$M^+ - 3CO$]), 2), 382 (100), 282 (52), 91 (85), 43 (61). IR (KBr, cm^{-1}): ν_{max} 1937, 1871, 1851 (C≡O), 1782, 1762 (C=O). Found: 518.07770. Calc. for $C_{24}H_{22}O_8N_2Cr$: 518.07758.

*4.11.3. (3′R,4′S)-{1′-Benzyl-3′-acetoxy-4′-[5-(N,N-dimethylamino)-1,3-benzodioxole]azetidin-2′-one} (**13b**)*

Complex **12b** (0.050 g, 0.096 mmol) afforded after decomplexation procedure β-lactam **12b** as a colourless oil (0.025 g, 70%). $[\alpha]_D^{25} = +18$ ($c = 0.30$, $CHCl_3$). ^{1}H-NMR ($CDCl_3$, 300 MHz): $\delta = 1.81$ (s, 3H, CH_3COO), 2.83 [s, 6H, $(NCH_3)_2$], 3.98 (d, 1H, $J = 15.0$ Hz, NCH_2), 4.79 (d, 1H, $J = 15.0$ Hz, NCH_2), 4.83 (d, 1H, $J = 4.5$ Hz, CH), 5.80 (d, 1H, $J = 4.5$ Hz, CH), 5.84 (s, 2H, CH_2), 5.92 (d, 1H, $J = 2.4$ Hz, ArH), 6.37 (d, 1H, $J = 2.4$ Hz, ArH), 7.25 (m, 5H, Ar′H). ^{13}C-NMR ($CDCl_3$, 100 MHz): $\delta = 20.16$ (CH_3), 41.66 [$N(CH_3)_2$], 44.73 (CH_2), 56.81 (CH), 76.89 (CH), 96.39 (Ar), 101.02 (CH_2), 104.48 (Ar), 113.51 (Ar, C_{quat}), 127.88 (Ar′), 128.45 (Ar′), 128.74 (Ar′) 134.47 (Ar, C_{quat}), 138.24 (Ar, C_{quat}), 146.62 (Ar, C_{quat}), 148.28 (Ar′, C_{quat}), 164.64 (C=O), 169.16 (OCO). EIMS; *m*/*z* (%): 382 ([M^+], 100), 282 (52), 91 (98), 43 (84). IR (film, cm^{-1}): ν_{max} 1752, 1677 (C=O). EIHRMS Found: 382.15358. Calc. for $C_{21}H_{22}O_5N_2$: 382.15232.

*4.12. Crystal structure determination of complex **4l***

4.12.1. Crystal data

$C_{13}H_{11}CrNO_6$, $M_r = 329.23$. The crystals are monoclinic and belong to the space group $P2_1$, with cell dimensions $a = 7.688(3)$ Å, $b = 13.245(4)$ Å, $c = 13.463(5)$ Å, $\beta = 97.16(4)°$, $V = 1360.2(8)$ Å^3, $Z = 2$ (with two molecules in the asymmetric unit with the same configuration), $D_{calc} = 1.61$ g cm^{-3}, $\mu = 0.868$ mm^{-1}, $F(000) = 672$. Of the 8654 reflections measured, 4227 were independent ($R_{int} = 0.0415$) and 3896 were observed [$I > 2\sigma(I)$]. Full anisotropic refinement for all non-hydrogen atoms yielded the final *R*-values: R_1 [$I > 2\sigma(I)$] = 4.30%, wR_2 [$I > 2\sigma(I)$] = 11.00%, R_1 (all data) = 4.95% and wR_2 (all data) = 12.65%.

*4.13. Crystal structure determination of complex **12a***

4.13.1. Crystal data

$C_{23}H_{19}CrN_2O_8F$, $M_r = 522.40$. The crystals are monoclinic and belong to the space group $P2_1$, with cell dimensions $a = 18.122(10)$ Å, $b = 7.277(2)$ Å, $c = 19.173(11)$ Å, $\beta = 108.36(6)°$, $V = 2400(2)$ Å^3, $Z = 2$ (with two molecules in the asymmetric unit with the same configuration), $D_{calc} = 1.45$ g cm^{-3}, $\mu = 0.535$ mm^{-1}, $F(000) = 1072$. Of the 15 669 reflections measured, 7196 were independent ($R_{int} = 0.0581$) and 5713 were observed [$I > 2\sigma(I)$]. Full anisotropic refinement for all non-hydrogen atoms yielded the final *R*-values: R_1 [$I > 2\sigma(I)$] = 4.44%, wR_2 [$I > 2\sigma(I)$] = 11.25%, R_1 (all data) = 5.57% and wR_2 (all data) = 13.14%.

5. Supplementary material

Full details of data collection and refinement, tables of final atomic coordinates, anisotropic thermal parameters for all non-hydrogen atoms, hydrogen atomic coordinates, complete tables for bond lengths and angles as well as torsion angles have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 157891 for complex **4l** and no. 157871 for complex **12a**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: 44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

The authors gratefully acknowledge Catarina J. Alves for some preliminary experiments.

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