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Stereoselective Triplet-Sensitised Radical Reactions of Furanone Derivatives

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Abstract: The stereo- and regioselectivity of triplet-sensitised radical reactions of furanone derivatives have been investigated. Furanones **7a**,**b** were excited to the $^3\pi\pi^*$ state by triplet energy transfer from acetone. Intramolecular hydrogen abstraction then occurred such that hydrogen was transferred from the tetrahydropyran to the β position of the furanone moiety. Radical combination of the tetrahydropyranyl and the oxoallyl radicals led to the final products **8a**,**b**. In the intramolecular reaction, overall, a pyranyl group adds to the α position of the furanone. The effect of conformation was first investigated with compounds **9a**,**b** carrying an additional substituent on the tether between the furanone and pyranyl moiety. Further information on the effect of conformation and the relative configuration at the pyranyl anomeric centre and the furanone moiety was obtained from the transformations of the glucose derivatives **12**, **14**, **17** and **18**. Radical abstraction occurred at the anomeric centre and at the 5′-position of the glucosyl moiety. Computational studies of the hydrogen-abstraction step were carried out with model structures. The activation barriers of this step for different stereoisomers and the abstraction at the anomeric centre and at the 6′-position of the tetrahydropyranyl moiety were calculated. The results of this investigation are in accordance with experimental observations. Furthermore, they reveal that the reactivity and regioselectivity are mainly determined in the hydrogen-abstraction step. Intramolecular hydrogen abstraction (almost simultaneous electron and proton transfer) in $^3\pi\pi^*$ excited furanones only takes place under restricted structural conditions in a limited number of conformations that are defined by the relative configuration of the substrates. It is observed that in the biradical intermediate, back-hydrogen transfer occurs leading to the starting compound. In the case of glucose derivatives, this reaction led to epimerisation at the anomeric centre.

Keywords: density functional calculations · hydrogen transfer · photochemistry · radical reactions · reaction mechanisms

Introduction

Photochemical reaction conditions generally enable transformations that are difficult or impossible under conventional conditions.[1] These phenomena may be fundamentally described by the topology of ground- and excited-state potential energy hypersurfaces.[2] In photochemical reactions at least two of these surfaces are involved. These considerations also raise the question of hydrogen transfer, which is one of the most important transformations in chemistry and biology. Two basic mechanisms[3] exist for this transformation: In the first, an electron is transferred. An acid–base re-

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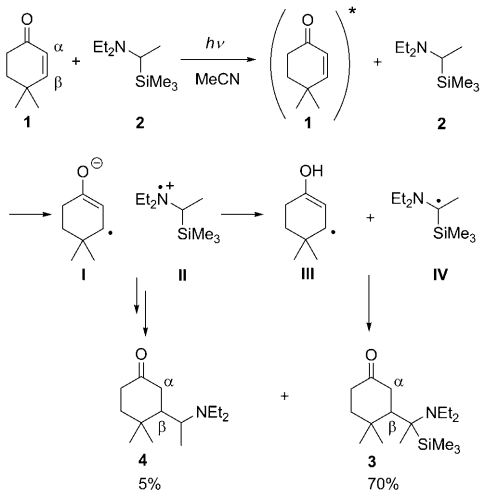
action then follows. The resulting radical cation is deprotonated by the radical anion. In the case of photochemical transformations, the electron transfer between the reaction partners is enabled by the electronic excitation of one of the reaction partners.[4] The thermodynamics of such processes are established by the Rehm–Weller equation,[5,6] whereas the kinetics are determined by Marcus theory.[6,7]

In the second mechanism, the electron and proton are almost simultaneously transferred. This reaction takes place, for example, when electron transfer is unfavourable but the formation of two radical species from a photochemically excited molecule and a hydrogen donor is thermodynamically favourable.

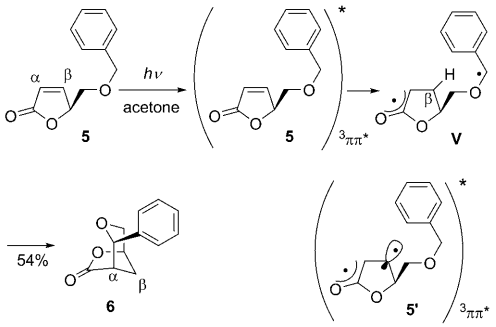
These two processes have also been discussed in the context of proton-coupled electron transfer.[8] The two photochemical reactions may lead to significantly different products, as is illustrated for the photochemical transformations of the α,β-unsaturated carbonyl compounds depicted in Schemes 1 and 2. In the first case (Scheme 1), electron



Scheme 1. Hydrogen transfer takes place in two steps: Photochemical electron transfer followed by proton transfer. The yields are based on consumed enone **1** (60% conversion).

transfer occurs from the tertiary amine **2** to the photochemically excited enone **1** leading to the formation of the radical-ion pair **I** and **II**.[9,10] A proton is then transferred from **II** to the oxygen atom of **I**. At this stage the Brønsted basicity is mainly localised. Combination of the resulting neutral radicals **III** and **IV** leads to the major product **3**. The deprotonation of **II** competes with desilylation, which leads to the minor product **4**. The formation of **4** is favoured when the reaction is carried out in methanol as solvent instead of acetonitrile. Similar intramolecular reactions have also been carried out.[11,12] It is concluded that the two-step hydrogen transfer induces the formation of a C–C bond at the β position of the α,β-unsaturated carbonyl compound. This mechanism is favoured by the increased electron-donating ability of tertiary amines.[10,13] The same kind of products are obtained when α-aminoalkyl radicals are generated by photochemical electron transfer from a tertiary amine to an excited electron-transfer sensitiser.[12,14–21] In this case the α,β-unsaturated carbonyl compound remains in its ground state.

In the second case of hydrogen transfer, the two particles, the electron and the proton, are almost simultaneously transferred. This reaction step is also referred to as hydrogen abstraction. When the furanone derivative **5** is electronically excited, hydrogen is transferred from the benzyl position of the side-chain to the β position of the furanone moiety (Scheme 2).[22] The regioselectivity of this step can



Scheme 2. Hydrogen transfer occurs in one step, by hydrogen abstraction.

be explained by the higher spin density at the β position of the vibrationally relaxed $^3\pi\pi^*$ excited furanone (**5′**).[23,24] As a result of delocalisation, the spin density at the α position is lower. The resulting biradical intermediate **V** undergoes radical combination to give the final product **6**.[25,26] The spin density distribution in the $^3\pi\pi^*$ excited α,β-unsaturated carbonyl compound also induces characteristic regio- and stereoselectivity in other reactions, for example, in photoreduction and [2+2] photocycloaddition reactions with alkenes.[24,27]

As has already been mentioned, in the first case, in addition to α-aminoalkyl radicals, hydroxyalkyl, alkoxyalkyl, acyl, or alkyl radicals can also be added to alkenes using photochemical sensitisation.[15,16,28–31] In these cases, the radicals are generated by hydrogen transfer to the electronically excited sensitiser. They then add to the alkene in its ground state and consequently to the β position. This regiochemistry is mainly a result of the nucleophilic character of the radicals.[32]

We can state here that photochemical transformations induced by electron transfer followed by proton transfer to a $^3\pi\pi^*$ excited α,β-unsaturated carbonyl compound or hydrogen abstraction from the same $^3\pi\pi^*$ state lead to different regioisomers of the final product. In the first case, a C–C bond is generated at the β position (Scheme 1), whereas in the second case the C–C bond is formed at the α position of the α,β-unsaturated carbonyl compound (Scheme 2).

In the context of applications to organic synthesis, we can state that the α,β-unsaturated carbonyl moiety of carboxy compounds in their ground state easily undergoes the addition of nucleophiles (Michael addition)[33,34] or radical species at the β position. Frequently, tandem reactions are used to add substituents first to the β position and then to the α

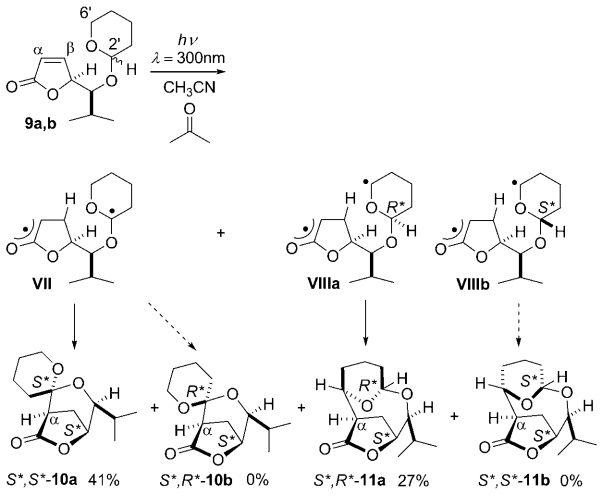
position.[18,19,30,34,35] In general, the simple α functionalisation of such compounds, for example in the case of the Baylis–Hillman[34,36] reaction, is more complex. Recently, a similar Lewis acid catalysed reaction was published.[37] Easy reactions like that described in Scheme 2 are therefore particularly interesting for application in organic synthesis because they enable the selective α functionalisation of α,β-unsaturated carbonyl compounds. Such a transformation has previously been studied in the context of the synthesis of (+)-pleuromutilin.[26]

We thus decided to investigate in more detail the stereoelectronic factors that control the reactivity and stereoselectivity of this type of reaction, that is, successive hydrogen abstraction and cyclisation (Scheme 2). Such studies will be useful for a systematic application of the transformation to organic synthesis later on. Two steps are discussed in particular: 1) the intramolecular hydrogen abstraction in a $^3\pi\pi^*$ excited furanone moiety and 2) the radical combination of the resulting triplet biradical intermediate. To attain the final product, intersystem crossing occurs that is accelerated by increased spin–orbit coupling.[38,39]

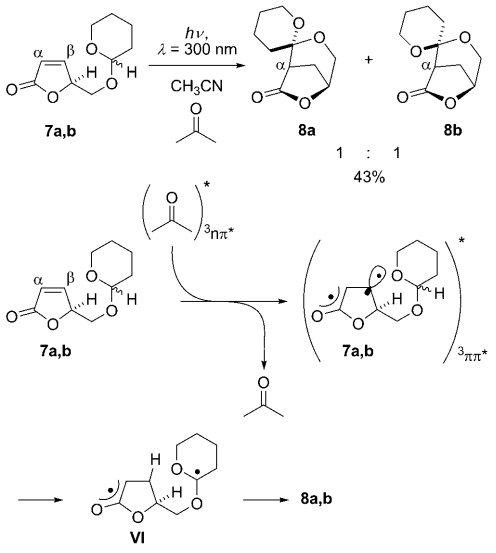
Results and Discussion

We started our investigation by irradiating the racemic furanone derivatives **7a**,**b** in the presence of acetone (Scheme 3). The intramolecular cyclisation products **8a** and **8b** were obtained as a 1:1 diastereomeric mixture in an isolated yield of 43%. Under these reaction conditions, the $^3\pi\pi^*$ excited states of **7a**,**b** are generated by triplet energy transfer from the $^3n\pi^*$ excited acetone. No transformation of **7a**,**b** was observed in the absence of acetone. Thus, the formation of the spirocyclic products can be explained by selective hydrogen abstraction (almost simultaneous transfer of the electron and the proton) at the acetal centre in the $^3\pi\pi^*$ excited state, which gives the biradical **VI**. The radical–radical coupling process leads to the formation of the cyclisation products **8a** and **8b**. This transformation is regioselective but not stereoselective and a C–C bond is established at the α position of the furanone moiety.

To investigate the effect of conformation on the reactivity of the electronically excited state of the furanone, we introduced an isopropyl group at the carbon atom that links the furanone and the tetrahydropyran moieties. The racemic compounds **9a**,**b** were irradiated under similar conditions and two regioisomeric products **10a** and **11a** were isolated (Scheme 4). Once again, C–C bond formation between the



Scheme 4. Photochemical cyclisation of the furanone derivatives **9a**,**b** carrying an additional alkyl substituent in-between the furanone and the tetrahydropyran moiety induced by photochemical hydrogen abstraction.



Scheme 3. Photochemical cyclisation of the furanone derivatives **7a**,**b** induced by photochemical hydrogen abstraction.

furanone and the tetrahydropyran moieties was found to occur only at the α position of the lactone moiety. The formation of the spirocyclic compound **10a** may be explained by hydrogen abstraction at the acetal centre (2′-position) and radical coupling in biradical **VII**. However, only one stereoisomer of this product (*S**,*S**)-**10a** was observed. As in the case of the transformations of **7a**,**b** depicted in Scheme 3, the reactions of **9a**,**b** were also carried out with racemic material. To indicate the relative configurations, the symbols *R** and *S** are used.[40] The second regioisomer **11a** obtained may be formed by hydrogen abstraction at the 6′-position. Because two stereoisomeric substrates **9a**,**b** possessing different relative configurations at the acetal centre (C2′) were transformed, two stereoisomers of the biradical intermediates **VIIIa**,**b** were formed. Only biradical **VIIIa** can generate the final product (*S**,*R**)-**11a**. The corresponding epimer (*S**,*S**)-**11b** would have been formed by cyclisation in the intermediate **VIIIb**. The selective generation of the intermediary biradical **VIIIa** will be discussed later in the section on computational studies. As has already been discussed in detail, the formation of the C–C bond at the α

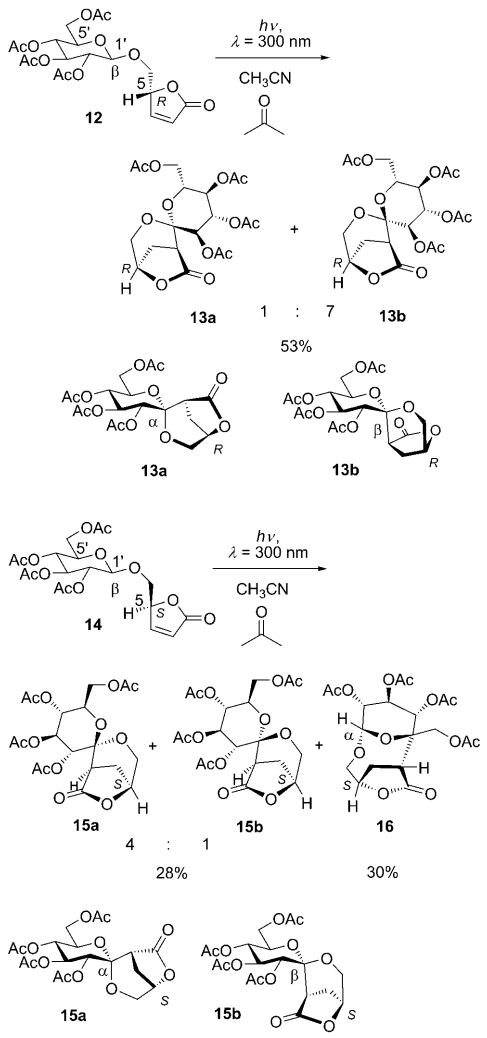
position of the furanone is characteristic of a hydrogen-abstraction mechanism involving an almost simultaneous transfer of the electron and the proton. Note also that in both isomers **10a** and **11a**, the C–O bond of the tetrahydropyranyl ring adjacent to the newly generated C–C bond is orientated more or less *anti* with respect to the lactone group. In contrast to the reaction depicted in Scheme 3, the transformation of compounds **9a**,**b** carrying an isopropyl substituent is stereoselective but not regioselective.

To study stereoelectronic effects such as the anomeric effect, a glucosyl as a substituted pyran moiety was attached to the furanone (Schemes 5 and 6). The transformation of these compounds enables a more precise investigation of the influence of the relative configuration at the acetal centre. We chose glucosides as conformationally rigid tetrahydropyran derivatives. The formation of a C–C bond at the anomeric centre leads to C-glycosides, which have been intensively studied due to their interesting biological activities.[41] The formation of a C–C bond at the anomeric centre of various carbohydrate derivatives was recently established by a Norrish–Yang reaction.[42] The regioselectivity of photochemically induced hydrogen transfer has also been investigated in disaccharide derivatives.[43]

When the β-glucosides **12** and **14** possessing different configurations at the furanone moiety were irradiated, characteristic transformations were observed. Glucoside **12** possesses the β configuration at the acetal centre and an *R* configuration at the 5-position of the furanone moiety (Scheme 5). As in the case of **7a**,**b** depicted in Scheme 3, only spiro compounds **13a**,**b** were obtained. Glucoside **14** also possesses the β configuration at the anomeric centre, but the *S* configuration at the furanone moiety. Once again, we obtained spiro compounds **15a**,**b**. However, the major isomer **15a** possesses the α configuration at the anomeric centre. As in the case of the transformation of compounds **9a**,**b** (Scheme 4), a large part of the hydrogen abstraction occurred at the 5′-position of the glucosyl moiety leading to the regioisomer **16**. This product possesses the α configuration at the anomeric centre.

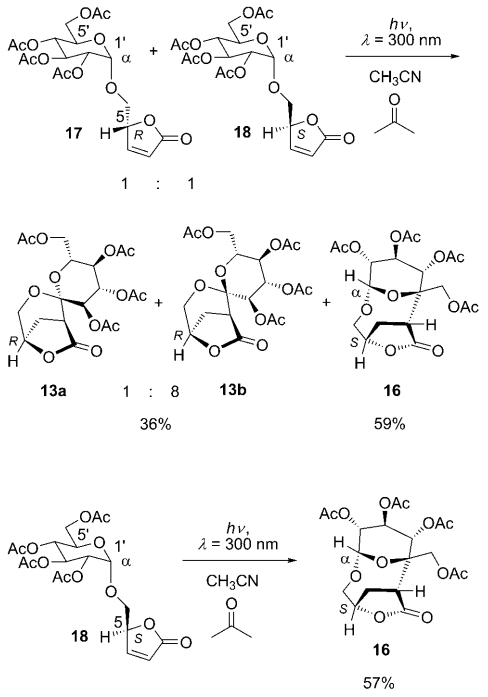
The photochemical reactivity of the α anomers **17** and **18** was also investigated under the same reaction conditions (Scheme 6). These compounds were synthesised as a 1:1 mixture of diastereoisomers[44] and only small amounts of compound **18** could be separated (see the Supporting Information). The 1:1 mixture of **17** and **18** was first irradiated and the spirocyclic compounds **13a**,**b** as well as compound **16** were isolated. The spirocyclic compounds **15a**,**b** were not detected. The structures of the products were identified by comparison with the NMR data of products obtained from the reaction of the β anomers (Scheme 5). A fraction containing the pure 5*S* epimer **18** was irradiated under the same conditions, leading stereo- and regioselectively to compound **16** with almost the same yield as in the preceding transformation.

The formation of compound **16** in the case of the transformation of the β anomer **14** cannot be explained solely by the elementary steps depicted in Schemes 3 and 4. In this



Scheme 5. Photochemical cyclisation of the β-anomeric glucosyl derivatives **12** and **14** induced by photochemical hydrogen abstraction.

case, hydrogen abstraction takes place at the 5′-position (Scheme 5). Radical combination should lead to a highly constrained product with the β configuration at the anomeric centre. However, compound **16** possesses the α configuration at this centre. We wondered whether under the reaction conditions, compounds **12**, **14**, **17** or **18** can epimerise at the anomeric centre. Samples of these compounds were irradiated for only 40 min. In the case of the α anomers, a 1:1 mixture of **17** and **18** was used. In this case no transformation into the corresponding β anomers **12** and **14** was observed. The β anomers **12** and **14**, however, were partially transformed into the epimers **17** and **18**, respectively (Table 1). In the case of **12**, only small amounts of **17** were detected. The major spirocyclic compound **13b** was also detected in the crude material. In the case of the partial transformation of **14**, the corresponding epimer **18** was detected in larger amounts. Once again, the major spirocyclic compound **15a** of this reaction was also detected. Although isolated in high yields after complete conversion (Scheme 5), compound **16** was not detected at this stage. From these ob-



Scheme 6. Photochemical cyclisation of the α-anomeric glucosyl derivatives **17** and **18** induced by photochemical hydrogen abstraction. In the case of the transformation of a 1:1 mixture of the epimers **17** and **18**, the yields of **13a**,**b** and **16** are given with respect to the proportion of the corresponding substrates in the starting product mixture.

Table 1. Partial transformation of the β anomers **12** and **14** after 40 min of irradiation.

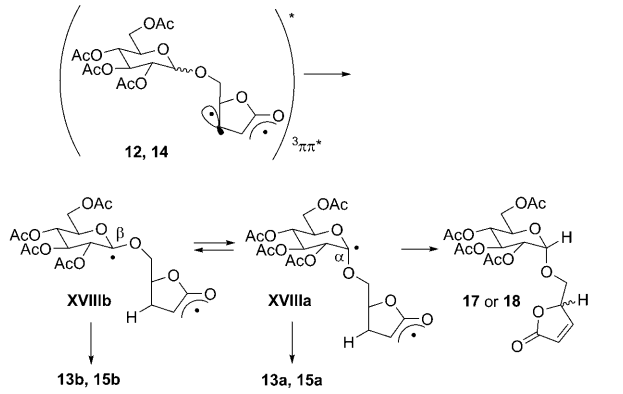
Substrate	Conversion[%]	Product ratio in the reaction mixture [%][a]								
		12	**14**	**17**	**18**	**13a**	**13b**	**15a**	**15b**	**16**
12	30	70	–	7	–	–	23	–	–	–
14	50	–	50	–	33	–	–	17	–	–

[a] Determined after evaporation of the solvent in the crude material.

servations as well as from the results depicted in Schemes 5 and 6, it is concluded that **16** is exclusively formed form the α anomer **18**. Consequently, compounds **13a**,**b** in the transformation of the 1:1 mixture of **17** and **18** (Scheme 6) are only generated from the isomer **17**.

Epimerisation at the β-anomeric centre is efficient in the case of **14** (Table 1) and important mechanistic aspects should be discussed. The epimerisation may occur when after intramolecular hydrogen abstraction in the excited furanones the intermediates **XVIIIa**,**b** are formed (Scheme 7). In the case of the α-anomeric intermediate **XVIIIa**, hydrogen can be transferred back from the furanone moiety (β position) to the glucosyl part leading to the α derivative **17** or **18**.

Under the reaction conditions described, glucosyl radicals may alternatively be generated by intermolecular hydrogen abstraction by the $^3n\pi^*$ excited acetone. In this case, one should observe the intramolecular addition of these radicals to the furanone moiety at the β position.[31] In such a reaction, hydroxyisopropyl radicals are also generated. These



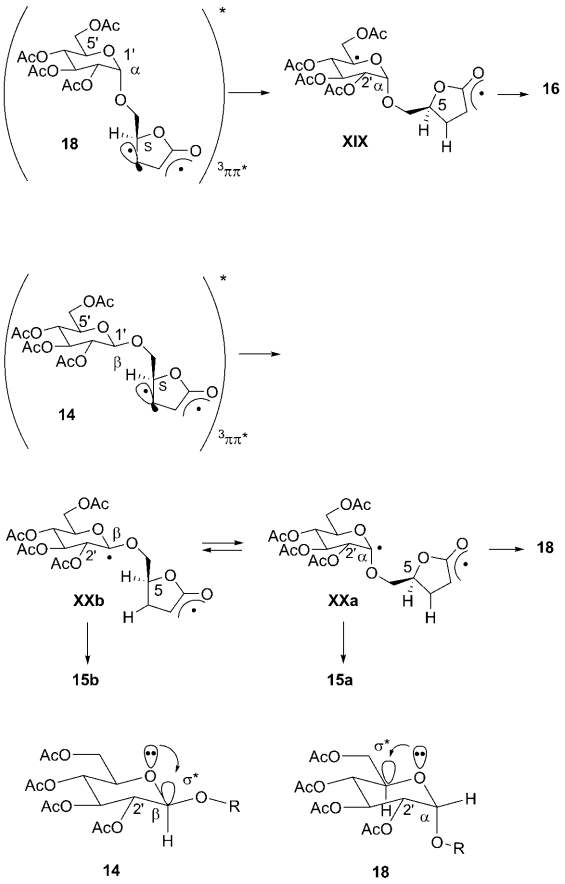
Scheme 7. Transformations of the β anomers **12** and **14**. Formation of diastereoisomeric spirocyclic compounds by combination of biradical intermediates and epimerisation of β isomers **12** and **14** to the corresponding α anomers **17** or **18**, respectively.

radicals are particularly reactive and add very easily to furanones even when they are formed in small amounts (see for example refs.[19,29]). In our transformations, such products were not observed. Clearly, triplet energy transfer is highly competitive with respect to hydrogen abstraction in this step.

The relative configurations of the substrates have a significant influence on the regio- and stereoselectivity of the reaction. The 5*S* configuration in compound **18** enables only hydrogen abstraction at the 5′-position of the glycosyl moiety leading to biradical **XIX** (Scheme 8). In the case of the β anomer **14**, hydrogen abstraction was observed at the anomeric centre (**XXa**,**b**). In both cases, only axial hydrogen abstraction leads to product formation. The kinetic anomeric effect[45,46] of the glucosyl ring oxygen present in the β anomers at the 1′- and 5′-positions contributes to the increased reactivity (Scheme 8). The C–H bonds oriented in the axial position at the anomeric centre are weakened by the interaction of a lone-pair orbital of the ring oxygen with the σ* orbital of this bond.[45,47] Depending on the conformation, the exocyclic anomeric effect[46] based on the OR substituent also contributes to the weakening of this C–H bond at the anomeric centre.[48] In similar systems, hydrogen abstraction, for example, by photochemically excited benzophenone, is about eight times faster at the axial position of a β anomer than at the equatorial position of the corresponding α anomer.[49] A homoanomeric effect results from the presence of the AcO group at the 2′-position.[50,51]

Radical combination in intermediate **XIX** leads to the final product **16** and radical combination in intermediates **XXa**,**b** leads to **15a**,**b**. In the latter case, the α-anomeric product **15a** is preferentially formed.

Compounds **12** and **17** with the 5*R* configuration favour hydrogen abstraction at the anomeric centre and induce a selective transformation to the spirocyclic compounds **13a**,**b** with almost the same stereoselectivity but with a higher yield in the case of the transformation of the β anomer **12** (Schemes 5 and 6). In both cases, the formation of the β-

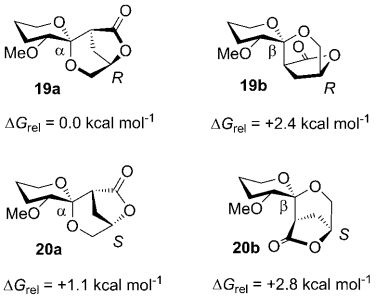


Scheme 8. Reaction of the 5*S* stereoisomers **18** and **14**. Orbital interactions of the kinetic isotope effect leading to regioselective hydrogen abstraction.

anomeric spirocycle **13b** is strongly favoured, which is in contrast to the transformation of the 5*S* compound **14**.

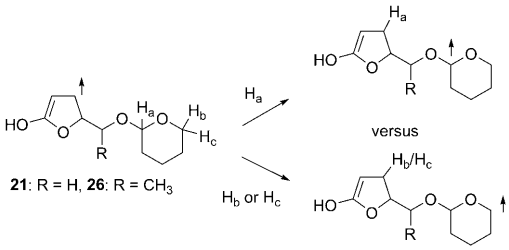
The formation of α- and β-anomeric spirocyclic products depending on the configuration at the furanone moiety indicates that the cyclisation step is kinetically controlled. Neither the relative stability of the anomeric radicals nor the thermodynamic stability of the final products seems to play a decisive role. In general, anomeric radicals with an axial spin orientation (**XVIIIb** in Scheme 7 and **XXb** in Scheme 8) are more stable than their analogues with an equatorial spin orientation.[47,51–53] Calculations on model compounds showed that the α-anomeric products **19a** and **20a** (generated from less stable biradicals with an equatorial spin orientation) are more stable than their β analogues **19b** and **20b**, which are generated from more stable biradicals with an axial spin orientation (Scheme 9).

As mentioned above in the discussion of the experimental results, the mechanism for the formation of the cyclisation products in the photochemical reaction of furanone derivatives is a stepwise process, that is, hydrogen abstraction followed by radical–radical coupling (Schemes 3, 4, 7 and 8). Product selectivity was found to be largely dependent on the alkyl substituent at the tethered carbon atom



Scheme 9. Relative thermodynamic stability of model compounds **19a**,**b** and **20a**,**b**.

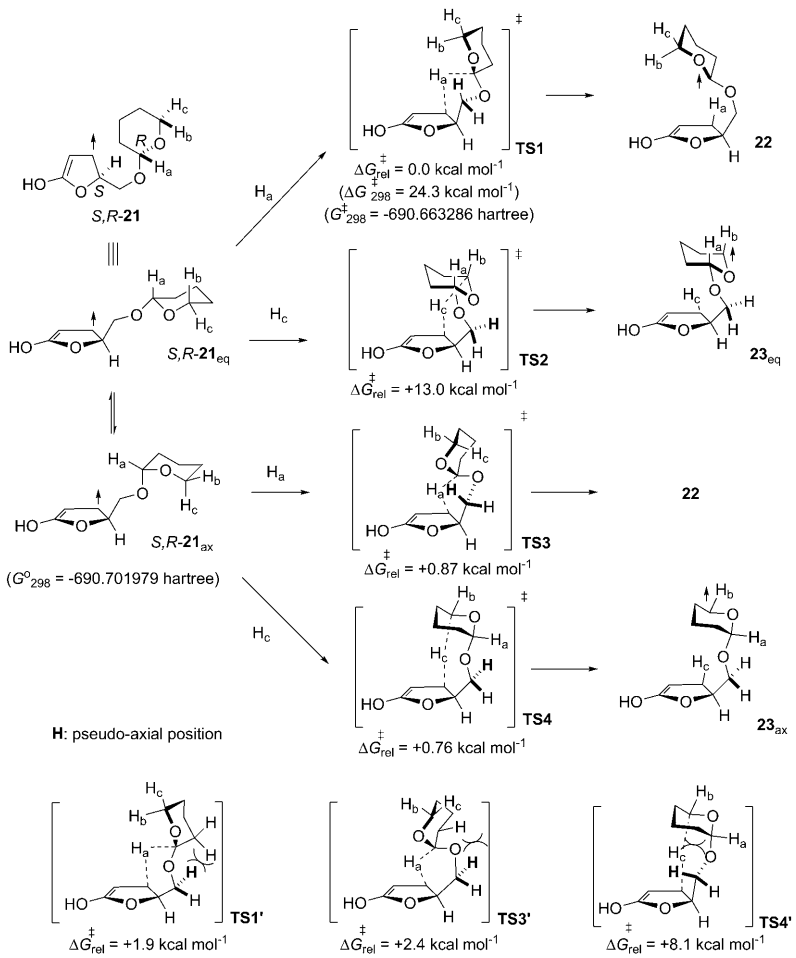
(Schemes 3 and 4) and the stereochemistry of the starting compounds (Schemes 5 and 6). The site selectivity of the first hydrogen-abstraction step, for example, **VII** versus **VIII**, may play an important role in determining the product selectivity, for example, **10** versus **11** (Scheme 4). To obtain information on the site selectivity of the hydrogen-abstraction reaction we decided to calculate the energy barriers of the hydrogen-abstraction steps in the model reactions of radicals **21** and **26** (Scheme 10). Thus, the hydrogen abstrac-



Scheme 10.

tion of H_a is a model reaction for the formation of biradicals, for example, **VI**, **VII** and **XX**, which are the precursors of the spiro compounds **8**, **10**, **13** and **15**. Alternatively, the formation of biradicals **VIII** and **XIX** that are the precursors of the tricyclic compounds **11** and **16** can be investigated by a study of the energy profile of the hydrogen abstraction of H_b/H_c.

First, to obtain information about stereoelectronic effects on the hydrogen-abstraction reaction, the energy barriers for the possible pathways were calculated for the radical (*S*,*R*)-**21**, which is a model for the $^3\pi\pi^*$ excited state of **7**, at the UB3LYP/6-31G(d)[54] level of theory with the Gaussian 03[55] suite of programs (Scheme 11). These computational studies provided important information about the product selectivities observed in our experiments (Schemes 3–6). In principle there are six possible hydrogen-abstraction reactions: 1) H_a abstraction from (*S*,*R*)-$\mathbf{21}_{eq}$, 2) H_b abstraction from (*S*,*R*)-$\mathbf{21}_{eq}$, 3) H_c abstraction from (*S*,*R*)-$\mathbf{21}_{eq}$, 4) H_a abstraction from (*S*,*R*)-$\mathbf{21}_{ax}$, 5) H_b abstraction from (*S*,*R*)-$\mathbf{21}_{ax}$ and 6) H_c abstraction from (*S*,*R*)-$\mathbf{21}_{ax}$. However, as can be easily imagined, the H_b atom abstractions are energetically

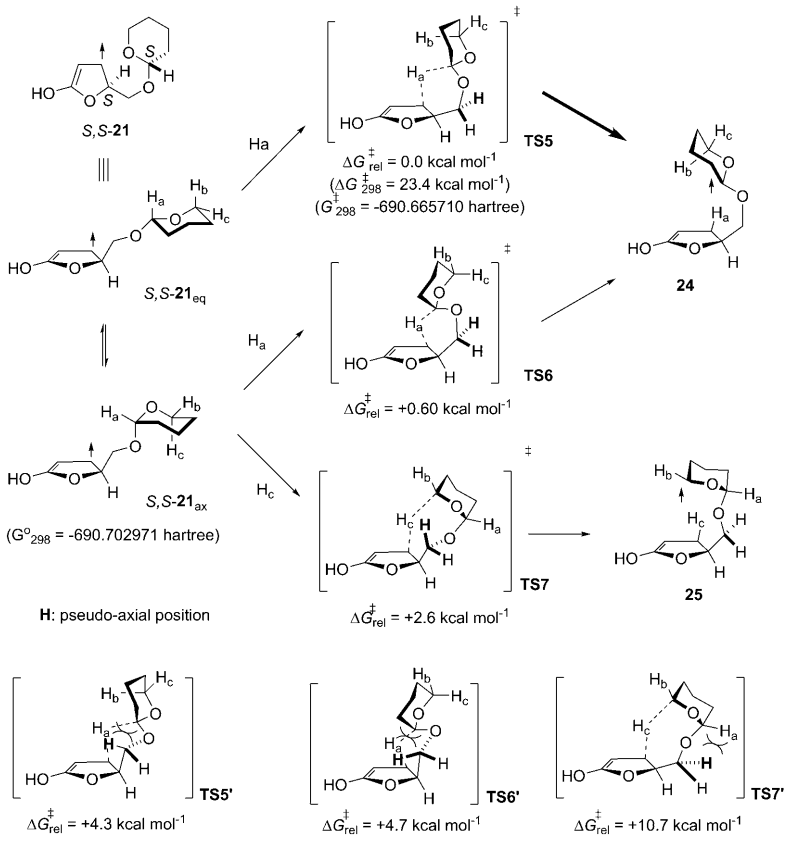


Scheme 11.

unfavourable pathways. Indeed, the activation energies for the hydrogen abstraction of H_b in (*S*,*R*)-**21**$_{eq}$ and (*S*,*R*)-**21**$_{ax}$ conformers were calculated to be 44 and 54 kcal mol^{-1}, respectively. Their transition-state structures are not shown in Scheme 11. In the H_a abstraction reaction in (*S*,*R*)-**21**$_{eq}$, two transition states, that is, **TS1** and **TS1′**, were found to lead to radical **22** (Scheme 11). The hydrogen abstraction via transition state **TS1**, which is located at around 25 kcal mol^{-1} above the starting radical (*S*,*R*)-**21**, was calculated to be the most energetically favoured pathway; the energy of the transition state **TS1′** was found to be energetically less stable than **TS1** by 1.9 kcal mol^{-1}. The sterically repulsive interaction between the pseudo-axial hydrogen (**H**) and the CH_2 group in the pyran ring, which is shown in structure **TS1′**, causes the energetic destabilisation. The stereoelectronic effect can reasonably explain the energetic preference of the axial H_a abstraction process, which has already been highlighted in Scheme 8. The equatorial hydrogen abstraction (H_c) shown in transition state **TS2** was calculated to be the least energetically favoured structure. The energy of transition state **TS3** in the equatorial H_a atom abstraction was found to be 0.87 kcal mol^{-1} higher than the energy of **TS1**. The hydrogen abstraction of H_c via **TS4** was found to have a similar energy to that of transition state **TS3**, and a higher than that of transition state **TS1**. Thus, the site-selective formation of radical **22** is predicted in the hydrogen-abstraction reaction in the model radical (*S*,*R*)-**21**. A similar repulsive interaction to that causing the destabilisation of **TS1′** also exists in the transition-state structures **TS3′** and **TS4′**.

Similarly, H_a abstraction via **TS5** was also calculated to be the energy minimum pathway for the hydrogen abstraction reaction in the model radical (*S*,*S*)-**21** (Scheme 12). The energies of the transition state **TS6** for the equatorial H_a abstraction and the transition state **TS7** for H_c abstraction in the axial conformer (*S*,*S*)-**21**$_{ax}$ were calculated to be higher than the energy of **TS5**. The other transition states **TS5′**–**7′** were also calculated to be much higher in energy than **TS5** and **TS6**, which can reasonably be explained by the energetic destabilising interaction between the pseudo-axial hydrogen (**H**) and the pyran ring. Thus, in the reaction of (*S*,*S*)-**21**, selective hydrogen abstraction is expected to occur at the anomeric centre via **TS5** to give radical **24**. These computational predictions are consistent with the experimental observations in which selective hydrogen-atom abstraction in the excited state of the furanones **7a**,**b** was observed at the acetal carbon atom to give the biradical **VI** (Scheme 3). The energetic preference of the axial hydrogen-atom abstraction is also responsible for the notable substrate effect on the reactivity of the excited state of the furanone derivatives **12**, **14**, **17** and **18** (Schemes 5 and 6).

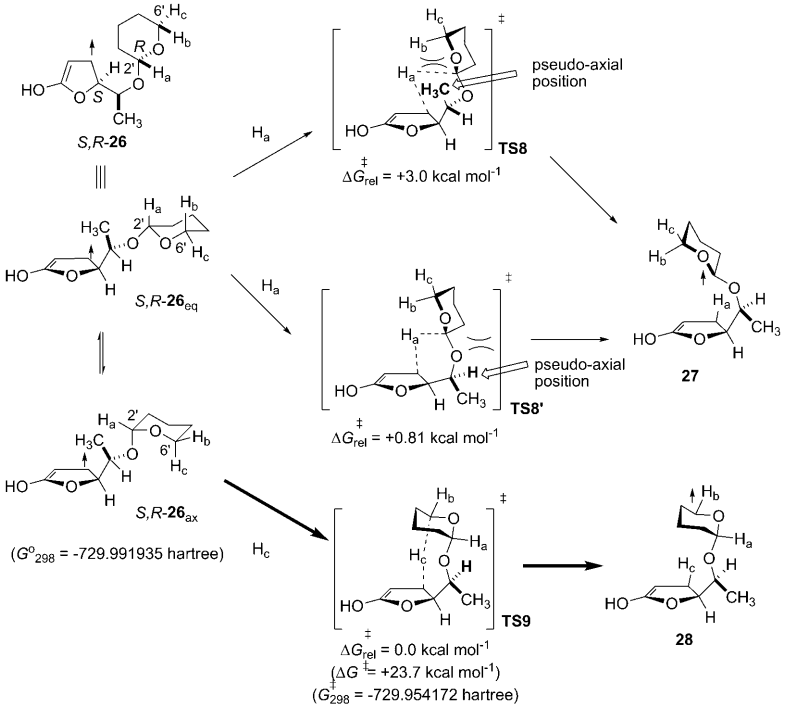
Next, we investigated the energy profile of the hydrogen-abstraction reaction in the radicals (*S*,*R*)- and (*S*,*S*)-**26**, which are model compounds for the $^3\pi\pi^*$ excited state of furanones **9a**,**b**, to obtain information about the effect of the alkyl group of the tethered carbon on the energy profile (Schemes 13 and 14). The computational studies revealed that the methyl substituent significantly affects the energy barriers of the hydrogen-abstraction reactions. Thus, H_c atom abstraction at the 6′-position was calculated to be the energy minimum pathway giving radical **28** via **TS9** (Scheme 13). The formation of the anomeric tetrahydropyranyl radical **27** via **TS8** and **TS8′** was calculated to be energetically unfavourable for the methyl substituted case. The



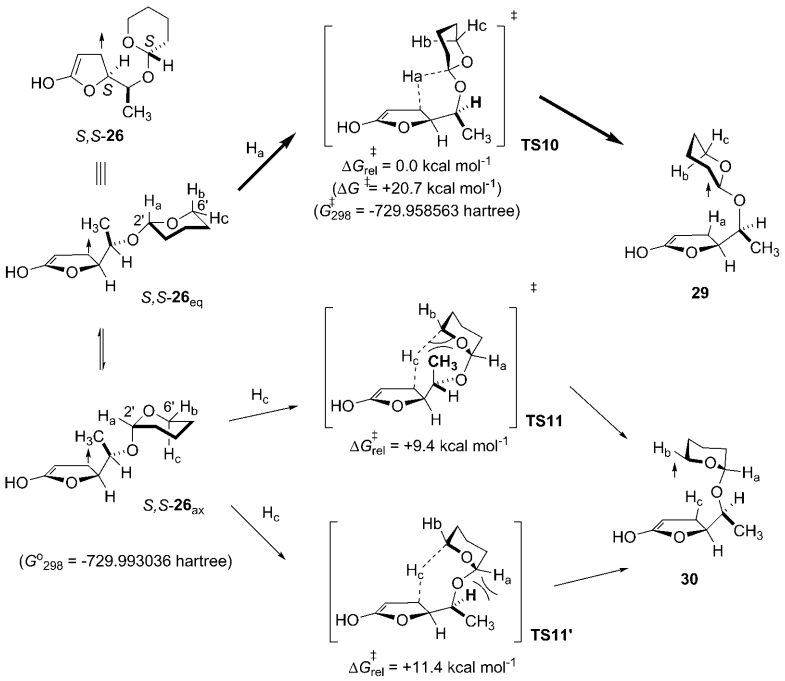
Scheme 12.

significant substituent effect can reasonably be explained by the repulsive non-bonding interactions depicted in structures **TS8** and **TS8′**. In the transition-state structure **TS8**, the methyl group is in the pseudo-axial position and thus a repulsive interaction occurs between the methyl group and the pyran ring. In structure **TS8′**, although the methyl group is in the pseudo-equatorial position, the 1,3-pseudo-diaxial interaction is the reason for the lower stability of structure **TS8′**.

The computational results for the hydrogen-abstraction reactions in (*S*,*S*)-**26** are summarised in Scheme 14. Axial H_a abstraction at the 2′-position was found to be the energy minimum pathway affording the anomeric tetrahydropyranyl radical **29** via **TS10**. H_c abstraction at the 6′-position to give radical **30** via **TS11** and **TS11′** was calculated to be energetically disfavoured by over 9 kcal mol^{-1}. The sterically repulsive-interactions depicted in structures **TS11** and **TS11′** are supposed to be the reason for the energetic destabilisation of these structures. The computational results clearly indicate that the methyl group plays an important role in changing the regioselectivity of the hydrogen-abstraction reaction. Thus, H_a abstraction at the 2′-position is predicted to be the major pathway for the reaction of diastereomer (*S*,*S*)-**26** to give the anomeric radical **29**. With the other diastereomer (*S*,*R*)-**26**, hydrogen abstraction at the 6′-position to give the radical **28** is the energetically favoured process. The computational results provide important information for understanding the experimental observations shown in Scheme 4. Thus, the formation of the spirocyclic compound (*S**,*S**)-**10a** can reasonably be explained by the energetically favoured H_a abstraction at the 2′-position via **TS12**, which is a similar transition state to **TS10** (Scheme 14), and the sub-



Scheme 13.

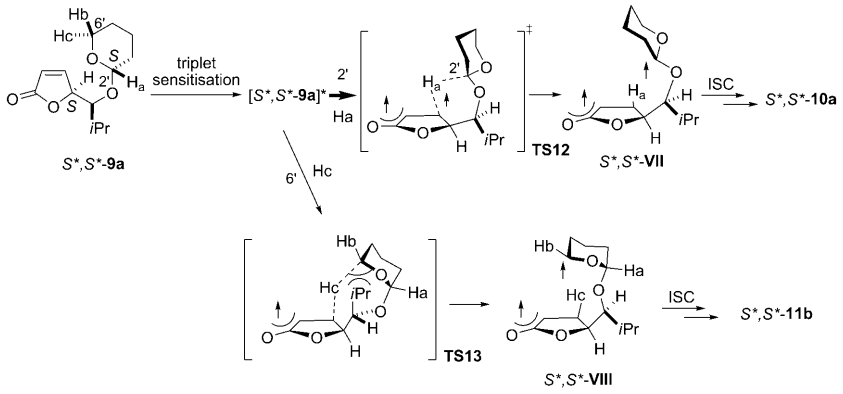


Scheme 14.

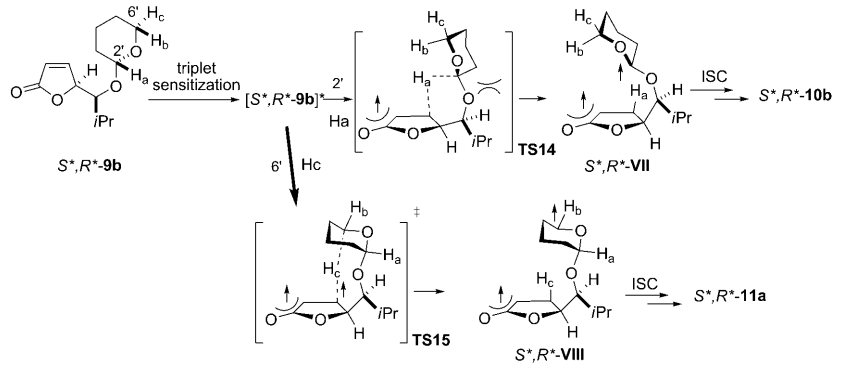
sequent cyclisation reaction via biradical (*S**,*S**)-**VII** after intersystem crossing (ISC; Scheme 15). The generation of biradical (*S**,*S**)-**VIII** via **TS13** (compare with **TS11**), which is derived from hydrogen abstraction at the 6′-position, is expected to be an energetically disfavoured process and thus we did not see any traces of the cyclisation product (*S**,*S**)-**11b**.

From the *S**,*R**-configured furanone derivative **9b**, as found for the model reaction of (*S*,*R*)-**26** (Scheme 13), H_c abstraction from the 6′-position would be the preferred pathway to biradical (*S**,*R**)-**VIII** via **TS15**, which is the precursor of the cyclisation product (*S**,*R**)-**11a** (Scheme 16). The transition state **TS14** for H_a abstraction is the energetically disfavoured one because a sterically repulsive interaction is expected. A similar destabilising steric repulsion was found in transition-state structure **TS8′** in Scheme 13. Although the mass balance of the photoreaction of **9a**,**b** is not so high (Scheme 4), the theoretically predicted regioselectivity of the hydrogen-abstraction reaction is close to the product distribution shown in Scheme 4.

As shown in Schemes 5 and 6, very interestingly, the β-glucosides **12** and **14** and α-glucoside **17** selectively gave the spiro compounds **13** and **15**, whereas the α-glucoside **18** produced selectively the tricyclic compound **16**. The product selectivity is also reasonably explained by the energetic differences in the transition states of the first hydrogen-abstraction steps. Thus, hydrogen abstraction in (*S*,*R*)-**21**$_{eq}$ (Scheme 11) is the model reaction for hydrogen abstraction in the β-glucoside **12**, in which the conformation of the pyran ring is locked by the acetoxy substituents. As shown in **TS1** and **TS2** (Scheme 11), the H_a hydrogen-abstraction pathway is calculated to be much more energetically favoured than



Scheme 15.



Scheme 16.

the H_c hydrogen abstraction. The computational prediction is consistent with the selective formation of the spiro compound **13** from **12**. The energetically favoured H_a hydrogen abstraction in (*S*,*S*)-**21**$_{eq}$ via **TS5** (Scheme 12) reasonably explains the selective formation of the spiro compound **15** from the reaction of **14**. The selective formation of the spiro compound **13** from **17** is also explained by the energetically favoured H_a hydrogen abstraction in (*S*,*S*)-**21**$_{ax}$ via **TS6** (Scheme 12). As shown in Scheme 11, the H_c abstraction in (*S*,*R*)-**21**$_{ax}$ via **TS4**, which is the model of **18**, was calculated to be the energetically favoured pathway compared with the H_a hydrogen abstraction via **TS3**. Indeed, α-glucoside **18** selectively produced the tricyclic compound **16**.

Structure determination of the photochemical products: X-ray structure analysis was performed on compound **8b** (Scheme 3, Figure 1). The structure of **8a** was determined by comparison of the NMR data of compounds **8a**,**b**.

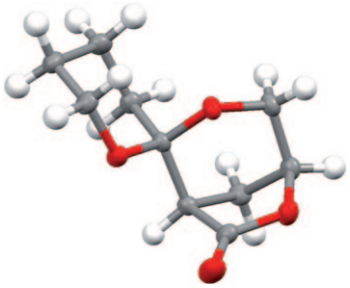


Figure 1. X-ray structure of compound **8b**.

The structure of compound **10a** (Scheme 4, Figure 2) was determined by X-ray structure analysis. NMR NOE measurements were used to determine the structure of compound **11a**.

The relative configurations of the ring systems in compounds **13a**,**b** were determined from their 2D NOESY NMR spectra. For this purpose, molecular models were built using the Macromodel software, the MM2 force field and Monte-Carlo conformational searches. The observed NOESY correlations correspond to short inter-proton distances in the lowest-energy conformers (Scheme 6, Figure 3). The analysis was performed on a mixture of the diastereoisomers because the signals of the major and the minor ones were clearly distinguishable.

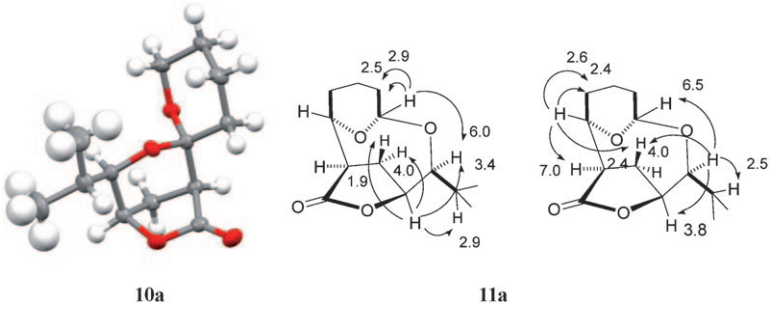


Figure 2. X-ray structure of compound **10a** and NOE enhancements (in %) of compound **11a**.

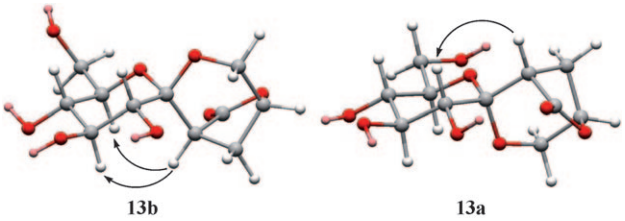


Figure 3. Structure modelling of compounds **13b** (major diastereomer) and **13a** (minor diastereomer) based on NOESY correlations. For simplicity the acetoxy functions have been replaced by hydroxy functions.

The structures of **15a** and **16** were determined by X-ray analysis. The structure of **15b** was determined by comparison of the NMR data of a mixture of compounds **15a**,**b** (Scheme 3, Figure 4).

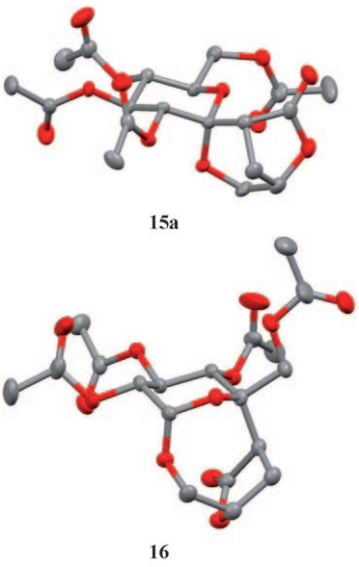


Figure 4. X-ray structures of compounds **15a** and **16**. For reasons of clarity the hydrogen atoms have been omitted.

Conclusion

We have described intramolecular hydrogen abstraction reactions in $^3\pi\pi^*$ excited furanones. Hydrogen is transferred form a tetrahydropyranyl substituent to the β position of the excited furanone. Radical combination of the biradical intermediate leads to the final products. The outcome is significantly dependent on the relative configurations of the

starting molecules. Computational studies indicate that the chemical reactivity and regioselectivity are mainly determined in the hydrogen-abstraction step. The activation barriers are strongly dependent upon the configuration. Hydrogen abstraction in $^3\pi\pi^*$ excited furanones (electron and proton transfer occur at almost the same time) is linked to very defined structural requirements. Hydrogen transfer may also occur by another mechanism. First, an electron is transferred and subsequent proton transfer from the resulting radical cation to the radical anion then leads to neutral radical species. This mechanism does not operate in our reactions. Such a mechanism would be less dependent upon structural requirements. In this case the reactivity is mainly determined by the redox potentials of the reaction partners and the Rehm–Weller or Marcus relationships.

Experimental Section

NMR spectra were recorded with a Bruker AC 250 (250 MHz for ^{1}H and 62 MHz for ^{13}C NMR) or DRX 500 (500 MHz for ^{1}H and 125 MHz for ^{13}C NMR) spectrometer. Chemical shifts are given in ppm relative to TMS using residual solvent signals as secondary references. IR spectra were recorded with a Nicolet AVATAR 320 FT-IR spectrometer. GCMS analyses were performed with Termoquest CE Instruments (Trace GC: 2000 series, Finnigan Trace MS). Optical rotations were recorded with a Perkin–Elmer 341 Polarimeter. UV irradiations were performed with Rayonet reactors (The Southern New England Ultraviolet Company, Branford, Connecticut) at $\lambda = 300$ nm; the reaction mixtures were irradiated in quartz tubes ($\varnothing = 1$ cm). Preparative chromatography was carried out with silica gel 60 from Carlo Erba Reactifs–SDS. Preparative HPLC separations were performed with a HP Series 1100 instrument (UV detection: $\lambda = 230$ nm, column: Macherey–Nagel 100–5 (silica, $\varnothing = 10$ mm, length = 250 mm). TLC was carried out with Kieselgel 60 F254 plates form Merck.

Photochemical transformation of compounds 7a,b: A solution of furanone derivatives **7a**,**b** (2.0 g, 10 mmol) and acetone (53 mL) in acetonitrile (233 mL) was added to quartz tubes, bubbled with argon for 20 min and irradiated for 3 h. After evaporation of the solvent, the residue was subjected to flash chromatography (eluent: ethyl acetate/petroleum ether, 3:7). Yield of compound **8a**: 0.44 g (22 %), m.p. 80–81 °C (R_f = 0.50, eluent: ethyl acetate/petroleum ether, 3:7). Yield of compound **8b**: 0.42 g (21 %), m.p. 110–111 °C (R_f = 0.27, eluent: ethyl acetate/petroleum ether, 3:7). For X-ray structure analysis, compound **8b** was recrystallised from ethyl acetate.

Compound 8a: ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 4.67$ (m, 1H), 3.79–3.84 (m, 2H), 3.70–3.75 (m, 2H), 2.74 (d, $J = 11.5$ Hz, 1H), 2.57 (d, $J = 5.2$ Hz, 1H), 2.21–2.26 (m, 1H), 2.03–2.06 (m, 1H), 1.74–1.83 (m, 1H), 1.54 ppm (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$: $\delta = 175.16$, 94.62, 76.27, 62.77, 62.22, 48.81, 32.87, 30.19, 24.98, 18.02 ppm; IR (KBr): $\tilde{\nu} = 2868$, 1782, 1041 cm^{-1}; HRMS (ESI+H): m/z calcd for $C_{10}H_{15}O_4$: 199.0970; found: 199.0972 $[M+H]^+$; elemental analysis calcd (%) for $C_{10}H_{14}O_4$ (198.22): C 60.59, H 7.12; found: C 60.41, H 7.17.

Compound 8b: ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 4.73$ (m, 1H), 4.01 (d, $J = 12.7$ Hz, 1H), 3.75–3.87 (m, 3H), 2.68 (d, $J = 4.3$ Hz, 1H), 2.35 (m, 1H), 2.22 (d, $J = 11.7$ Hz, 1H), 1.94 (d, $J = 13.2$ Hz, 1H), 1.81 (m, 1H), 1.61–1.67 (m, 2H), 1.45–1.51 ppm (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 175.52$, 96.96, 77.36, 65.11, 62.57, 49.31, 34.42, 29.80, 24.56, 18.82 ppm; IR (KBr): $\tilde{\nu} = 2865$, 1774, 1046 cm^{-1}; HRMS (ESI+H): m/z calcd for $C_{10}H_{15}O_4$: 199.0970; found: 199.0968 $[M+H]^+$; elemental analysis calcd (%) for $C_{10}H_{14}O_4$ (198.22): C 60.59, H 7.12; found: C 60.79, H 7.19.

Photochemical transformation of compounds 9a,b: A solution of furanone derivatives **9a**,**b** (420 mg, 1.75 mmol) and acetone (8 mL) in acetonitrile (52 mL) was added to quartz tubes, bubbled with argon for 20 min and irradiated for 1 h. After evaporation of the solvent, the residue was subjected to flash chromatography (eluent: ethyl acetate/petroleum ether, 1:10 then progressively changed to 1:2). Yield of compound **10a**: 172 mg (41 %), m.p. 93–95 °C. Yield of compound **11a**: 113 mg (27 %).

Compound 10a: ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 4.69$ (d, $J = 5.9$ Hz, 1H), 3.65–3.85 (m, 2H), 3.29 (d, $J = 9.0$ Hz, 1H), 2.68 (d, $J = 11.5$ Hz, 1H), 2.53 (d, $J = 5.2$ Hz, 1H), 2.27 (quint., $J = 5.7$ Hz, 1H), 2.07 (m, 1H), 1.75–1.94 (m, 2H), 1.44–1.68 (m, 4H), 1.01 (d, $J = 6.6$ Hz, 3H), 0.92 ppm (d, $J = 6.8$ Hz, 3H); ^{13}C NMR (62 MHz, $CDCl_3$): $\delta = 175.80$, 94.57, 76.77, 76.68, 62.42, 48.96, 33.30, 31.19, 30.01, 25.58, 19.27, 19.06, 18.59 ppm; IR (KBr): $\tilde{\nu} = 2962$, 2873, 1779, 1008 cm^{-1}; MS (EI): m/z (%): 241 (1) $[M]^+$, 197 (10), 140 (62), 111 (100), 55 (80); elemental analysis calcd (%) for $C_{13}H_{20}O_4$ (240.3): C 64.98, H 8.39; found: C 64.99, H 8.79.

Compound 11a: ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 4.82$ (slightly br s,, 1H), 4.64 (d, $J = 7.8$ Hz, 1H), 4.03 (t, $J = 7.6$ Hz, 1H), 3.13 (d, $J = 8.3$ Hz, 1H), 2.60 (dd, $J = 7.8$, 10.6 Hz, 1H), 2.48 (ddd, $J = 7.9$, 10.6, 13.0 Hz, 1H), 2.37 (d, $J = 12.6$ Hz, 1H), 2.19 (m, 1H), 2.07 (qt, $J = 13.0$, 4.4 Hz, 1H), 1.97 (m, 1H), 1.87 (m, 1H), 1.78 (m, 1H), 1.63 (ddt, $J = 2.7$, 4.7, 13.0 Hz, 1H), 1.55 (m, 1H), 1.38 (m, 1H), 0.95 ppm (d, $J = 6.7$ Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 178.32$, 96.70, 84.69, 76.68, 68.06, 44.43, 31.70, 31.15, 29.00, 24.34, 19.25, 18.67, 12.80 ppm; IR (film): $\tilde{\nu} = 2943$, 2874, 1766, 1161, 1019 cm^{-1}; MS (CI, NH_3): m/z (%): 258 (4) $[M+NH_4]^+$, 241 (1) $[M+H]^+$; elemental analysis calcd (%) for $C_{13}H_{20}O_4$ (240.3): C 64.98, H 8.39; found: C 64.67, H 9.19.

Photochemical transformation of the furanone derivative 12: A solution of the furanone derivative **12** (0.9 g, 2.03 mmol) and acetone (11 mL) in acetonitrile (47 mL) was added to quartz tubes, bubbled with argon for 20 min and irradiated for 3 h. After evaporation of the solvent, the residue was subjected to flash chromatography (eluent: ethyl acetate/petroleum ether: 4:6). Yield of compounds **13a**,**b**: 0.48 g (53 %) isolated as a 1:7 mixture of diastereomers.

Compounds 13a,b: ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 5.45$ (dd, $J = 9.4$/10.2 Hz, 1H-min), 5.28 (dd, $J = 9.2$, 9.4 Hz, 1H-maj), 5.25 (d, $J = 10.0$ Hz, 1H-min), 5.22 (m, 1H-maj), 5.17 (d, $J = 9.1$ Hz, 1H-maj), 5.12 (dd, $J = 9.4$, 10.0 Hz, 1H-min), 4.82 (t, $J = 4.9$ Hz, 1H-maj), 4.71 (dd, $J = 2.5$, 5.2 Hz, 1H-min), 4.30 (m, 1H-maj), 4.28 (m, 1H-maj), 4.26 (m, 1H-min), 4.26 (m, 1H-maj), 4.19 (dd, $J = 2.6$, 12.4 Hz, 1H-min), 4.07 (m, 1H-maj), 4.06 (m, 1H-min), 4.04 (m, 1H-min), 4.04 (m, 1H-maj), 3.83 (d, $J = 11.5$ Hz, 1H-min), 3.32 (d, $J = 4.8$ Hz, 1H-maj), 2.80 (br d, $J = 11.9$ Hz, 1H-min), 2.70 (d, $J = 5.3$ Hz, 1H-min), 2.53 (dt, $J = 5.0$, 11.8 Hz, 1H-maj), 2.39 (ddt, $J = 2.0$, 5.5, 12.0 Hz, 1H-min), 2.27 (d, $J = 11.8$ Hz, 1H-maj), 2.03 (s, 3H-maj), 2.01 (s, 3H-maj), 2.093 (s, 3H-maj), 2.090 ppm (s, 3H-maj); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 174.09$ (maj), 170.90 (maj), 170.29 (maj), 169.55 (maj), 168.81 (maj), 99.85 (min), 98.95 (maj), 76.79 (maj), 75.00 (min), 74.14 (maj), 71.83 (maj), 71.70 (min), 71.08 (maj), 70.87 (min), 69.24 (min), 68.61 (min), 67.67 (maj), 66.67 (maj), 64.15 (min), 62.04 (min), 61.59 (maj), 45.70 (min), 43.91 (maj), 31.29 (min), 30.35 (maj), 20.94 (maj), 20.80 (maj), 20.75 (maj), 20.72 ppm (maj) (maj: major isomer, min: minor isomer); IR (KBr): $\tilde{\nu} = 2960$, 1753, 1372, 1037 cm^{-1}; HRMS (ESI+Na): m/z calcd for $C_{19}H_{24}O_{12}Na$: 467.1165; found: 467.1159 $[M+Na]^+$; elemental analysis calcd (%) for $C_{19}H_{24}O_{12}$ (444.39): C 51.35, H 5.44; found: C 51.03, H 5.69.

Photochemical transformation of the furanone derivative 14: A solution of the furanone derivative **14** (0.69 g, 1.56 mmol) and acetone (8.2 mL) in acetonitrile (36 mL) was added to quartz tubes, bubbled with argon for 20 min and irradiated for 3 h. After evaporation of the solvent, the residue was subjected to flash chromatography (eluent: ethyl acetate/petroleum ether, 4:6). Yield of compounds **15a**,**b**: 0.19 g (28 %) isolated as a 4:1 mixture of diastereomers. For X-ray structure analysis, a pure fraction of the major isomer **15a** was obtained by recrystallisation form diethyl ether (m.p. 136–137 °C);$[\alpha]_D^{20} = +26{,}0$ ($c = 1.1$ in CH_2Cl_2). Yield of compound **16**: 0.21 g (30 %); $[\alpha]_D^{20} = +14.52$ ($c = 0.296$ in CH_2Cl_2). For X-ray structure analysis, a pure fraction of the major isomer **16** was obtained by recrystallisation form methanol (m.p. 254 °C).

Mixture of compounds 15a and 15b: ^{1}H NMR (250 MHz, $CDCl_3$): $\delta =$ 5.40 (m, 1H-maj, 1H-min), 5.17 (m, 1H-min), 5.06 (m, 2H-maj), 5.02 (m, 1H-min), 4.76 (t, $J = 4.6$ Hz, 1H-maj), 4.71 (t, $J = 3.7$ Hz, 1H-min), 4.28 (m, 1H-maj, 1H-min), 3.86–4.13 (m, 4H-maj, 4H-min), 2.93 (m; 1H-maj,

1H-min), 2.65 (d, $J=12.9$ Hz, 1H-min), 2.37 (m, 1H-maj, 1H-min), 2.23 (d, $J=11.5$ Hz, 1H-maj), 2.01 (s, 6H-maj), 1.99 (s, 3H-maj), 1.96 ppm (s, 3H-maj); ^{13}C NMR (62 MHz, $CDCl_3$): $\delta=173.01$ (min), 172.80 (maj), 170.72 (maj), 170.54 (min), 170.15 (maj), 169.91 (min), 169.70 (maj), 169.43 (maj), 168.78 (min), 97.12 (maj), 96.79 (min), 76.32 (maj), 75.44 (min), 74.48 (maj), 73.09 (min), 72.64 (min), 70.89 (min), 70.57 (maj), 69.61 (maj), 68.67 (maj), 68.14 (min), 65.96 (maj), 64.14 (min), 62.54 (min), 61.84 (maj), 45.97 (maj), 43.13 (min), 30.04 (min), 29.06 (maj), 20.86 (min), 20.77 (maj), 20.69 (min), 20.65 (maj), 20.63 (maj), 20.59 ppm (maj) (maj: major isomer, min: minor isomer).

Compound 15a: ^{1}H NMR (250 MHz, $CDCl_3$): $\delta=5.48$ (t, $J=10.0$ Hz, 1H), 5.11 (d, $J=10.0$ Hz, 1H), 5.10 (m, 1H), 4.78 (t, $J=4.8$ Hz, 1H), 4.31 (dd, $J=8.3$, 11.3 Hz, 1H), 3.99–4.15 (m, 4H), 2.97 (d, $J=4.3$ Hz, 1H), 2.28 (m, 1H), 2.25 (d, $J=11.5$ Hz, 1H), 2.092 (s, 3H), 2.088 (s, 3H), 2.02 (s, 3H), 1.99 ppm (s, 3H); ^{13}C NMR (62 MHz, $CDCl_3$): $\delta=172.80$, 170.83, 170.26, 169.76, 169.50, 97.23, 76.35, 74.62, 70.74, 69.78, 68.78, 66.05, 61.94, 46.06, 29.16, 20.86, 20.74, 20.71, 20.68 ppm; IR (KBr): $\tilde{\nu}=2964$, 1812, 1751, 1730, 1371, 1029 cm^{-1}; HRMS (ESI+Na): m/z calcd for $C_{19}H_{24}O_{12}Na$: 467.1165; found: 467.1162 $[M+Na]^+$; elemental analysis calcd (%) for $C_{19}H_{24}O_{12}$ (444.39): C 51.35, H 5.44; found: C 51.22, H 5.32.

Compound 16: ^{1}H NMR (250 MHz, $CDCl_3$): $\delta=5.79$ (t, $J=10.1$ Hz, 1H), 5.51 (d, $J=10.1$ Hz, 1H), 5.13 (d, $J=3.2$ Hz, 1H), 4.84 (dd, $J=3.2$, 10.1 Hz, 1H), 4.61 (dd, $J=3.3$, 7.0 Hz, 1H), 4.23 (dd, $J=3.2$, 12.2 Hz, 1H, H6), 4.06 (d, $J=11.9$ Hz, 1H), 3.80 (d, $J=11.9$ Hz; 1H), 3.53 (d, $J=12.2$ Hz, 1H), 2.67 (d, $J=11.3$ Hz, 1H), 2.55 (m, 1H), 2.35 (d, $J=12.6$ Hz, 1H), 2.14 (s, 3H), 2.12 (s, 3H), 2.06 (s, 3H), 1.99 ppm (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta=173.56$, 170.58, 170.52, 170.24, 169.36, 96.06, 76.54, 74.58, 71.48, 70.93, 69.19, 67.02, 66.94, 42.23, 30.23, 20.95 (2×), 20.88, 20.75 ppm; IR (KBr): $\tilde{\nu}=2967$, 1750, 1371, 1249, 1035 cm^{-1}; HRMS (ESI+Na): m/z calcd for $C_{19}H_{24}O_{12}Na$: 467.1165; found: 467.1172 $[M+Na]^+$; elemental analysis calcd (%) for $C_{19}H_{24}O_{12}$ (444.39): C 51.35, H 5.44; found: C 51.32, H 5.42

Photochemical transformation of the furanone derivatives 17 and 18: A solution of a 1:1 mixture of furanones **17** and **18** (0.44 g, 0.99 mmol) and acetone (5.2 mL) in acetonitrile (23 mL) was added to quartz tubes, bubbled with argon for 20 min and irradiated for 3 h. After evaporation of the solvent, the residue was subjected to flash chromatography (eluent: ethyl acetate/petroleum ether, 4:6). Yield of compounds **13a**,**b** as a 1:8 mixture: 0.08 g (36%). Yield of compound **16**: 0.13 g (59%). Under the same reaction conditions, pure **18** (100 mg, 0.22 mmol) were transformed into compound **16** (yield: 57 mg, 57%).

X-Ray crystal structures of 8b, 10, 15a and 16: Single crystals were obtained by slow evaporation of a solution of diethyl ether/petroleum ether (**8b** and **10a**) or diethyl ether (**15a** and **16**). Data were collected at 173(2) K with a Bruker APEX8 CCD diffractometer equipped with an Oxford Cryosystem liquid N_2 device, using graphite-monochromated $Mo_{K\alpha}$ ($\lambda=0.71073$) radiation. For all structures, diffraction data were corrected for absorption and structural determination was achieved by using the APEX (1.022) software package (APEX 2, version 1.0-22; Bruker AXS Inc., Madison, WI, 2004). The hydrogen atoms were introduced at calculated positions and not refined (riding model).

CCDC-752441 (**8b**), 752442 (**10a**), 752443 (**15a**) and 752444 (**16**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Crystal data for 8b: $C_{10}H_{14}O_4$, $M=198.21$, monoclinic, space group $P2_1/c$, $a=7.6050(2)$, $b=11.9326(3)$, $c=10.1241(3)$ Å, $\beta=92.555(2)°$, $V=917.82(4)$ Å^3, $T=173(2)$ K, $Z=4$, $\rho_{calcd}=1.434$ g cm^{-3}, $\mu=0.111$ mm^{-1}, 14276 collected reflections, 2111 independent ($R_{int}=0.0344$), GooF=1.079, $R_1=0.0420$, $wR_2=0.1018$ for $I>2\sigma(I)$ and $R_1=0.0543$, $wR_2=0.1105$ for all data.

Crystal data for 10a: $C_{13}H_{20}O_4$, $M=240.29$, monoclinic, space group $P2_1/c$, $a=12.8670(6)$, $b=8.2700(4)$, $c=12.0450(9)$ Å, $\beta=95.2740(18)°$, $V=1276.28(13)$ Å^3, $T=173(2)$ K, $Z=4$, $\rho_{calcd}=1.251$ g cm^{-3}, $\mu=0.092$ mm^{-1}, 6283 collected reflections, 3715 independent ($R_{int}=0.0207$), GooF=1.006, $R_1=0.0450$, $wR_2=0.0987$ for $I>2\sigma(I)$ and $R_1=0.0651$, $wR_2=0.1072$ for all data.

Crystal data for 15a: $C_{19}H_{24}O_{12}$, $M=444.38$, orthorhombic, space group $P2_12_12_1$, $a=9.2376(4)$, $b=13.8925(7)$, $c=16.3298(8)$ Å, $V=2095.66(17)$ Å^3, $T=173(2)$ K, $Z=4$, $\rho_{calcd}=1.408$ g cm^{-3}, $\mu=0.119$ mm^{-1}, 19389 collected reflections, 4803 independent ($R_{int}=0.0469$), GooF=1.052, $R_1=0.0428$, $wR_2=0.0864$ for $I>2\sigma(I)$ and $R_1=0.0594$, $wR_2=0.0942$ for all data. The absolute configuration was determined by reference to the configuration of the chiral centre at C7 (configuration *S*), which remains unchanged during the synthetic procedure.

Crystal data for 16: $C_{19}H_{24}O_{12}$, $M=444.38$, orthorhombic, space group $P2_12_12_1$, $a=9.0325(2)$, $b=11.4600(3)$, $c=20.4572(5)$ Å, $V=2117.57(9)$ Å^3, $T=173(2)$ K, $Z=4$, $\rho_{calcd}=1.394$ g cm^{-3}, $\mu=0.118$ mm^{-1}, 22943 collected reflections, 4779 independent ($R_{int}=0.0410$), GooF=1.013, $R_1=0.0533$, $wR_2=0.1106$ for $I>2\sigma(I)$ and $R_1=0.0697$, $wR_2=0.1206$ for all data. The absolute configuration was determined by reference to the configuration of the chiral centre at C7 (configuration *S*), which remains unchanged during the synthetic procedure

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