Tandem RCM–Claisen Rearrangement–[2+2] Cycloaddition of $O,O'$-(But-2-en-1,4-diyl)-bridged Binaphthols

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Received: 30 October 2012; in revised form: 29 November 2012 / Accepted: 3 December 2012 / Published: 7 December 2012

Abstract: Attempted RCM of 2,2'-bis(allyloxy)-1,1'-binaphthyl resulted in a Claisen-type rearrangement of a postulated labile dioxacyclodecine proceeding at room temperature and followed by [2+2] cycloaddition. Structures of products were confirmed by X-ray crystallography. A mechanistic rationalisation based on relative stabilities of proposed intermediates and transition states is provided.

Keywords: DFT calculations; Grubbs II catalyst; cage compounds; spiro-compounds; chiral macrocycle

1. Introduction

A sequence of reactions is designated as a tandem process if the reacting functional group(s) of each step are formed or activated only in the preceding one and with no need of adding reagents for
individual steps. A further requirement is that all reactions proceed under the same conditions with no mutual interference of by-products. Since advantages over conventional multistep synthesis by avoiding work-up and purification of intermediates are obvious, such processes have found widespread application [1–11]. With increasing complexity of target structures functional group tolerance and stereoselectivity of transformations become crucial and are particularly challenging in the synthesis of natural products and biologically active compounds. Consequently, the usefulness of tandem reactions will also rely on a sufficient high degree of stereocontrol in each step. This requirement is often fulfilled with rearrangements proceeding via cyclic transition states and with sigmatropic rearrangements which represent stereospecific transformations. Typical examples are Cope and Claisen rearrangements and variations like Claisen-Ireland, Claisen-Johnsen, Meerwein-Eschenmoser-Claisen, thio- and aza-Claisen, and Carrol rearrangement [12–21]. A special situation arises when atropisomeric biaryls are involved translating axial-chirality of the substrates into centro-chirality of the products provided the reaction proceeds at a temperature where no racemisation of the biaryl takes place. Particularly O,O'-disubstituted binaphthol derivatives have shown various rearrangements and cyclisations ending up with configurationally stable polycyclic structures formed on cost of the aromaticity of one of the benzene rings [22,23]. While most of published procedures require elevated temperature to proceed, the present process takes place below 60 °C and affords a single rearranged product in excellent yield. Such transformations offer a unique access to otherwise difficult to synthesize centrochiral compounds, eventually useful as chiral building blocks [24]. The present paper reports on a tandem sequence where up to three intramolecular transformations are involved producing stereoselectively spiro- and finally chiral cage-compounds from simple binaphthyl precursors.

2. Results and Discussion

2.1. Synthesis and Rearrangements

In course of our attempts to synthesize macrocyclic chiral (di)olefins with incorporation of biaryl units, eventually useful as chiral ligand in asymmetric catalysis, we investigated the RCM of 2,2'-bis(allyloxy)-1,1'-binaphthyl \( (2a) \), a versatile precursor previously applied in the synthesis of ring systems [25–27]. While RCM of a homologue of \( 2a \) (4-butenyloxy instead allyloxy in positions 2 and 2') proceeded as expected, bridging positions 2 and 2' of the binaphthol and yielding the dioxacyclododecine product as a cis/trans mixture [28], compound \( 2a \) behaved completely different (Scheme 1). Treatment with Grubbs II catalyst (DCM, reflux) resulted in the formation of a \( C_1 \) symmetrical species (35%) and a product with higher symmetry (59%). While in the latter case ESI-MS gave a molecular peak of \( m/z \) 699.3 and correct HRMS for a dimeric structure \( 3a \) with \( D_2 \) symmetry, the former one gave the correct mass of \( m/z \) 338.2 for the desired product, but disagreeing NMR spectra for structure \( 4a \), with the spectroscopic data pointing rather to a rearranged product \( 5a \) [29,30]. In order to increase the yield of the macrocycle we repeated the cyclisation at r.t. with enantiopure precursor \((R)-2a\). Under these conditions 15% of starting material was recovered after 10 h and only small amounts (4%) of \( 5a \) were formed. As the main product 70% of dimer \( 3a \) ([\( \alpha \]D]_{20} +110) was isolated (82% rel. to recovered starting material) thus confirming the relative biaryl configurations in the racemic product to be \((R)_{ax}(R)_{ax}(S)_{ax}(S)_{ax}\) and absence of “meso-\(3a\)” with \((R)_{ax}(S)_{ax}\) configuration. The trans-geometry of double bonds was confirmed by macrocyclisation of
dibromide \((R)-10\) with \((R)-1a\) yielding the same product obtained by RCM (Scheme 2). A crystal structure of \(3a\) was published \[24\].

**Scheme 1.** Rearrangement of 1,1'-binaphthyl derivatives with 2,2'-O-allyl fragments.

\[
\begin{align*}
R = & H & 1a \\
& Br & 1c \\
& Ph & 1d \\
\end{align*}
\]

- **Reagents and Conditions:**
  a. reference \[26\] (2a); allylbromide, K₂CO₃, acetone, reflux, 24 h (2b–d); b. Grubbs II (10%), DCM, r.t., 6–8 h; c. hv, toluene (see text); d. \(E\)-1,4-dibromobut-2-ene, Cs₂CO₃, acetone, reflux, 24 h.

* See text.  § From 1a. Reagents and Conditions: a. reference [26] (2a); allylbromide, K₂CO₃, acetone, reflux, 24 h (2b–d); b. Grubbs II (10%), DCM, r.t., 6–8 h; c. hv, toluene (see text); d. \(E\)-1,4-dibromobut-2-ene, Cs₂CO₃, acetone, reflux, 24 h.
Scheme 2. Synthesis of (R,R)-3a through macrocyclisation.

Reagents and Conditions: a. Methyl 4-bromocrotonate, K₂CO₃, 24 h, r.t.; b. DIBAL, DCM, –78 °C → –20 °C, 12 h; c. PBr₃, THF, –40 °C → r.t. overnight; d. (R)-1a, KOH, THF, 3 days, reflux.

It is interesting to note that the temperature plays a decisive role in the outcome of this reaction. According to Piedra et al. the formation of dimers can be suppressed at elevated temperature (3 h, 120 °C, MW) and at higher dilution, while variation of the catalyst showed little influence. This behaviour seems nearly unaffected from substituents in positions 6 or 7 of the naphthalene rings [24]. In contrast, when using substrates 2b–d with substituents in position 3 no dimeric species could be detected (see below).

The rearrangement of an aryl-allylether undergoing a Claisen-type rearrangement is usually formulated via a concerted or radical mechanism generating an arylxy- and allyl radical in the latter case (photo-Claisen rearrangement) [31]. As the most likely precursor for 5a we postulated labile (E)-dioxacyclodecine 4a, which might smoothly traverse a chair-like transition state TS I to give spiro compound 5a. The involvement of (labile) 4a with an E-double bond was supported since 5a was obtained as the exclusive product when reacting 1a with E-1,4-dibromobut-2-ene (Cs₂CO₃, acetone, 20 h reflux, 94%) [32]. Mechanistic implications will be discussed below.

If 5a was irradiated with long wave-length UV light (>300 nm) in toluene for 3 h at ambient temperature, a mixture of two rearranged products 6a (67%) and 7a (10%) was formed through intramolecular [2+2] cycloaddition (6% of starting material was recovered). Inspection of a wire model revealed that particularly for the formation of the predominating isomer 6a the required conformation for a transition state like TS IIA can be easily adopted. While intramolecular [2+2] cycloadditions of enones with olefins have been frequently observed [33,34], an analogous cyclisation of 1-allyl-naphthalen-2(1H)-one was only reported in 1980 [35,36].

Similar treatment of 3,3′-diiodo substituted substrate 2b showed similar conversions and corresponding products obtained, but displaying significantly different stability/reactivity. Thus, RCM of 2b at r.t. in the dark yielded exclusively 5b (95%) without detectable amounts of dimerisation product. If light was not rigorously excluded some rearranged product 6b (10%) was also detected. Its structure was confirmed by crystal structure analysis (Figure 1). When a solution of 5b in toluene was irradiated with visible light (60 W light bulb) for several hours, complete photoaddition took place yielding a mixture of 6b and 7b (approx. 9:1). The isomers were separable by chromatography and fully characterized by NMR and MS. The ease of accessing cyclobutanes 6b and 7b prompted us to perform the sequence 2b → 4b → 5b → 6b/7b in one pot. Conducting the RCM in toluene under irradiation with visible light resulted in exclusive formation of 6b/7b (85:15, 89% total yield). For comparative studies also bromo- as well as phenyl-substituted O-allyl precursors 2c and 2d, respectively were investigated. Their behavior on treatment with Grubbs II catalyst was virtually the
same, yielding 5c and 5d in excellent yield (91% and 98%, respectively) and subsequent photoisomerisation under UV irradiation gave 6c/7c (64%/10%) and 6d/7d (7%/39%), respectively.

**Figure 1.** Crystal structures of 5b (left), 6a (middle) and 6b (right). H-atoms and solvent molecules omitted for clarity.

In view of intended use in asymmetric catalysis macrocyclic diolefin 3a was treated with [RhCl(C₂H₄)₂], [C₃H₅PdCl]₂, and Pd₂(dbata)₃ precursors which did not result in the formation of complexes, instead Pd(PPh₃)₄ caused complete cleavage yielding a mixture of 5a (56%) and epi-5a (20%). (Scheme 3) A tentative mechanistic interpretation is discussed in the Supporting Information.

**Scheme 3.** Pd(0) mediated cleavage of 3a and subsequent photoisomerisation of epi-5a.

Subsequent irradiation of epi-5a for 0.5 h afforded two products. The main product was expectedly the corresponding epimer of 6a, epi-6a (36%) while no epi-7a could be detected. Instead cyclobutanone 11 (25%) was formed. Both structures were confirmed by X-ray analysis (Figure 2).

**Figure 2.** Crystal structures of epi-5a (left), epi-6a (middle), and 11 (right). H-atoms and solvent molecules omitted for clarity.
2.2. Calculations, Evidence for Existence of 4a, Its Geometry and Rearrangement to 5a

Geometries and energies of ground state structures as well as transition states were obtained using program packages SPARTAN (B3LYP, MO6 and MP2) and GAUSSIAN09 (B3LYP) [37,38]. For comparability reasons B3LYP data as determined in the absence of solvent and, where appropriate, also in DCM (values in parenthesis) are collected in Table 1 and are discussed below.

Table 1. B3LYP (Ru: sdd, all other atoms: 6-31G**), MO6, and MP2 calculated free energies of activation based on ground state and transition state energies for conversion of 2a-pro-cis- and 2a-pro-trans-Ru, cis- and trans-Ru-Cycl, E- and Z-4a, and E-12. Asterisks (*) denote results obtained with the corresponding biphenyl system.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>ΔG‡ b</th>
</tr>
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<tbody>
<tr>
<td>B3LYP</td>
<td>MO6</td>
</tr>
<tr>
<td>2a-pro-trans-Ru* → trans-Ru-Cycl*</td>
<td>1.0 (1.8)</td>
</tr>
<tr>
<td>2a-pro-cis-Ru* → cis-Ru-Cycl*</td>
<td>2.2 (3.2)</td>
</tr>
<tr>
<td>trans-Ru-Cycl* → E-4a-Ru*</td>
<td>17.2 (19.4)</td>
</tr>
<tr>
<td>cis-Ru-Cycl* → Z-4a-Ru*</td>
<td>7.7 (9.4)</td>
</tr>
<tr>
<td>E-4a → 5a</td>
<td>26.4 (26.2)</td>
</tr>
<tr>
<td>Z-4a → 5a</td>
<td>32.3 (33.0)</td>
</tr>
<tr>
<td>E-12 → E-4a</td>
<td>3.9 (6.2)</td>
</tr>
<tr>
<td>E-12 → 5a</td>
<td>8.3 (9.7)</td>
</tr>
<tr>
<td>E-12 → epi-5a</td>
<td>8.6 (9.8)</td>
</tr>
<tr>
<td>E-12 → E-13</td>
<td>39.1</td>
</tr>
<tr>
<td>E-12 → 14</td>
<td>7.3</td>
</tr>
<tr>
<td>E-12 → epi-14</td>
<td>7.1</td>
</tr>
<tr>
<td>E-4a → epi-5a</td>
<td>39.1</td>
</tr>
</tbody>
</table>

a For details see Supporting Information; b kcal/mol in vacuo and DCM (in parentheses).

To trace the transformation from 2a into 5a under metathesis conditions several possibilities had to be taken into account as outlined in Scheme 4 and energy profiles of alternative reaction paths were determined. Our calculations are based on the established mechanism of the olefin metathesis cyclisation with Grubbs II catalyst [39–41] and are carried out on a corresponding biphenyl skeleton which is expected to be a realistic model for the transformation 2a → 4a. Calculations on olefin metathesis reaction with ethylene and Grubbs II catalyst supported a dissociative path with trans-coordination of the olefin as a barrierless step [42]. Applied to our system an olefin-Ru-carbene, 2a-Ru, is postulated which coordinates the pending olefin with either re- or si-side to form (transient) intermediates in the configuration determining step from which 2,3-cis- or 2,3-trans-substituted metalla-cyclobutanes are obtained. Cycloreversion leads to Ru-olefin complexes of 4a and after dissociation Z- and E-4a could undergo Claisen rearrangement to 5a. A direct transformation of a Ru-cycle into 5a without traversing 4a would proceed via an anti-aromatic transition state (8π electrons) and seems highly unfavourable.

It was found that the metallacycle with trans geometry is more stable (∆G0 = 3.3 kcal/mol), but less reactive [ΔG‡ = 17.2 kcal/mol versus 7.7 kcal/mol, (19.4 kcal/mol versus 9.4 kcal/mol)] yielding E-4a-Ru in a slightly more endergonic reaction (Figure 3, top and middle).
Scheme 4. Formation of 5a from 2a and postulated intermediates of RCM.

Figure 3. Energy profile (B3LYP, single point energies in DCM in parenthesis) for the formation of E and Z-olefin-carben-Ru complexes formed in course of a RCM with Grubbs II catalyst. Calculations were performed on a simplified system using the corresponding biphenyl species.
The subsequent (presumably) barrierless dissociation delivers $E$- and $Z$-olefins. Although ground state energies of $E$- and $Z$-4a are very similar ($\Delta G^0 < 0.2$ kcal/mol), the barriers for the Claisen rearrangement (Figure 3, bottom) differ significantly from each other with 26.2 kcal/mol (from $E$-4a) and 33.0 kcal/mol (from $Z$-4a) and moreover, both are markedly higher than all barriers between intermediates of the preceding RCM. Accordingly, these intermediates are in equilibrium and the Claisen rearrangement is rate determining proceeding exclusively via $E$-4a with the equilibrium on the product side ($\Delta G^0 = 1.2$ kcal/mol, 0.8 kcal/mol in DCM). It should be pointed out that the overall reaction proceeds under Curtin–Hammett conditions and as a consequence the formation of 5a via $E$-4a and Z-4a depends only on energy differences of corresponding transition states $\Delta \Delta G^\ddagger = 5.7$ kcal/mol (5.6 kcal).
This is also in agreement with the course of the base catalyzed reaction of 1a with E-1,4-dibromo-but-2-ene at elevated temperature. The first step obviously forms the (mono)anion E-12 through O-allylation of 1a (Scheme 5). Formally this intermediate can undergo four intramolecular nucleophilic substitutions (i)–(iv) with attack of either phenolate or carbanion at either C1 or C3 of the allyl moiety (SN or SN’ reaction).

Scheme 5. Hypothetic reaction paths (i)–(iv) of anion E-12.

Since all steps yielding neutral intermediates/products from a charged species E-12 concomitant with precipitation of KBr, these will proceed under kinetic control and are virtually irreversible. Under the applied conditions E/Z isomerisation of 12 can be ruled out, but the flexibility of the key intermediate E-12 resulted in a Boltzmann distribution of conformations with several local minima [43]. The lowest transition state with 3.9 kcal/mol (6.2 kcal/mol) was found for path (i) yielding E-4a. For all other processes significantly higher barriers were obtained with 7.3 kcal/mol and 7.1 kcal/mol for (ii), 8.3 kcal/mol (9.7 kcal/mol) and 8.6 kcal/mol (9.8 kcal/mol) for (iv), and even more pronounced for (iii) with 39.1 kcal/mol. This clearly points to a two-step process with E-4a as an intermediate as depicted in Figure 4 [44]. Energies obtained with MP2 and MO6 show similar trends.

Transformations of 5a–d into 6a–d and 7a–d, as well as the formation of 11 from epi-5a, are triggered by light and exited states are obviously involved. Due to their sufficient energy content various diradical structures may be readily derived therefrom and have to be considered as feasible intermediates [45–47]. A detailed investigation for better understanding of these processes is presently under way and will be published in near future.
**Figure 4.** Energy profile (B3LYP) for the formation of 5a from E-12 under vacuum and in DCM (values in parenthesis).

3. Experimental

3.1. General

Melting points: Kofler melting point apparatus, uncorrected. NMR: recorded at 400.27 MHz ($^1$H) and 100.66 MHz ($^{13}$C), respectively on a Bruker AVIII400 spectrometer. Chemical shifts $\delta$ are reported in ppm; for $^1$H rel. to (residuals non-deuterated) solvent signals (chloroform-$d$: 7.24, toluene-$d_8$: 2.08 ppm), for $^{13}$C to CDCl$_3$ at 77.00 ppm, or CD$_2$C$_6$D$_5$ at 21.40 ppm, respectively. Coupling patterns are designated as s(inglet), d(oublet), t(riplet), q(uartet), m(ultiplet), p(seudo), and br(oad).
$^{13}$C\({}^1{\text{H}}\)-NMR spectra are recorded in a $J$-modulated mode; signals are assigned as C, CH$_2$, and CH$_3$; undesignated signals refer to CH-resonances. MS: ESI or El (ESI-Qq ao TOF mass spectrometer, Bruker, 70 eV).

For photo rearrangements a mercury medium pressure lamp doped with FeI$_2$ (Heraeus TQ718-Z4, 700 W) was used operating at >300 nm in ice cooled Pyrex glass vessels.

Hexane fraction (PE), dichloromethane (DCM), and ethyl acetate (EtOAc) were distilled, absolute THF from sodium benzophenone ketyl, toluene from LiAlH$_4$, DCM and acetonitrile from CaH$_2$; DIBAL was used as a 1.0 molar solution in toluene. All the other chemicals were analytical grade and used without further purification. Column chromatography was performed on SiO$_2$, 40-63 µm. Reported procedures have been followed to obtain 3,3’-disubstituted 2,2’-dihydroxy-1,1’-binaphthyl precursors 1b–d [48–52] and diallyloxy compound 2a [26].

3.2. Syntheses and Rearrangements

3.2.1. Typical Procedure: 2,2’-Bis(allyloxy)-3,3’-diiodo-1,1’-binaphthyl (2b)

To a degassed solution of 2,2’-dihydroxy-3,3’-diiodo-1,1’-binaphthyl (1b, 269 mg, 0.5 mM) in acetone (50 mL) was added allylbromide (242 mg, 2.0 mM, 173 µL), pulverised K$_2$CO$_3$ (208 mg, 1.5 mM) and the mixture was refluxed for 24 h. The solids were filtered off and washed with DCM. After removal of solvents the product was purified by chromatography (DCM/PE, 25:75) to give 273 mg (91%) of 2b; mp: 143–146 °C (DCM/PE). $^1$H-NMR (CDCl$_3$) $\delta$: 8.50 (s, 2H), 7.77 (dm, $J = 8.3$ Hz, 2H), 7.25 (dd, $J = 8.3$, 6.7, 1.3 Hz, 2H), 7.08 (dm, $J = 8.6$ Hz, 2H), 5.52 (ddpt, $J = 17.1$, 10.5, 5.6 Hz, 2H), 4.81 (m, 4H), 4.29 (ddpt, $J = 11.9$, 5.7, 1.4 Hz, 2H), 3.93 ppm. 13C-NMR (CDCl$_3$) $\delta$: 153.90 (C), 139.74, 133.84 (C), 133.08, 132.15 (C), 127.03, 126.94, 125.88, 125.64 (C), 125.62, 117.28 (CH$_2$), 92.70 (C), 74.42 (CH$_2$) ppm. HRMS (ESI): calcd for C$_{26}$H$_{20}$I$_2$O$_2$ NH$_4$: 635.9896, found: 635.9901.

2,2’-Bis(allyloxy)-3,3’-dibromo-1,1’-binaphthyl (2c). Yield: 89%; mp: 98–101 °C (DCM/PE). $^1$H-NMR (CDCl$_3$) $\delta$: 8.23 (s, 2H), 7.80 (dm, $J = 8.5$ Hz, 2H), 7.40 (dd, $J = 8.1$, 6.6, 1.1 Hz, 2H), 7.25 (dd, $J = 8.4$, 6.9, 1.3 Hz, 2H), 7.08 (dm, $J = 8.6$ Hz, 2H), 5.52 (ddpt, $J = 17.0$, 10.6, 5.6 Hz, 2H), 4.82 (m, 4H), 4.36 (ddpt, $J = 11.9$, 5.6, 1.4 Hz, 2H), 4.05 ppm. $^{13}$C-NMR (CDCl$_3$) $\delta$: 151.95 (C), 133.16, 133.10 (C), 132.81, 131.42 (C), 127.11, 126.89 (C), 126.81, 125.92, 125.83, 117.76 (C), 117.17 (CH$_2$), 74.46 ppm. HRMS (ESI): calcd for C$_{26}$H$_{20}$Br$_2$O$_2$Na: 544.9728, found: 544.9732.

2,2’-Bis(allyloxy)-3,3’-diphenyl-1,1’-binaphthyl (2d). Yield: 90%; foam. $^1$H-NMR (CDCl$_3$) $\delta$: 7.94 (s, 2H), 7.89 (br d, $J = 8.2$ Hz, 2H), 7.73 (m, 4H), 7.33–7.46 (m, 8H), 7.24 (m, 4H), 5.27 (ddpt, $J = 17.2$, 10.4, 5.5 Hz, 2H), 4.64 (dm, $J = 10.3$ Hz, 2H), 4.54 (dpq, $J = 17.1$, 1.8 Hz, 2H), 3.94 (ddpt, $J = 12.1$, 5.4, 1.4 Hz, 2H), 3.70 ppm. $^{13}$C-NMR (CDCl$_3$) (One CH signal not detected) $\delta$: 153.30 (C), 139.03 (C), 135.42 (C), 133.81, 133.67 (C), 130.77 (C), 130.25, 129.48, 128.23, 127.99, 127.25, 126.28 (C), 126.17, 125.98, 124.92, 116.17 (CH$_2$), 73.73 ppm. HRMS (ESI): calcd for C$_{38}$H$_{30}$O$_2$Na: 544.9728, found: 544.9732.
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3.2.2. (15E,33E)-14,17,32,35-Tetrahydrotetranaphtho[2,1-b:1',2'-d:2'',1''-l:1''',2'''-n][1,6,11,16]tetraoxacycloicosine (3a) and 2-Vinyl-2,3-dihydro-2'H-spiro[benzo[f]chromene-1,1'-naphthalen]-2'-one (5a)

Diallylether 2a (37 mg, 0.1 mM) was dissolved in DCM (7 mL) and Grubbs II catalyst (8.5 mg, 10 mol%) in DCM (3 mL) was added under Ar at 40 °C during 6 h using a syringe pump. After removal of solvent the products were separated by chromatography (EtOAc/PE, 10:90 → 30:70) to give 12 mg (35%) of 5a followed by 20 mg (59%) of 3a (If the reaction was performed at r.t (10 h) 3a and 5a were isolated in 70% and 4%, respectively). Spectroscopic date are in agreement with reference [24].

(15E,33E)-14,17,32,35-Tetrahydrotetranaphtho[2,1-b:1',2'-d:2'',1''-l:1''',2'''-n][1,6,11,16]tetraoxacycloicosine (3a). White solid; 1H-NMR (CDCl3) δ: 7.92 (d, J = 8.2 Hz, 4H), 7.80 (d, J = 9.0 Hz, 4H), 7.36 (ddd, J = 7.8, 6.9, 0.8 Hz, 4H), 7.22 (ddd, J = 8.0, 6.7, 1.2 Hz, 4H), 7.12 (d, J = 8.8 Hz, 4H), 7.09 (d, J = 8.2 Hz, 4H), 5.54 (m, 4H), 4.39 (m, 8H) ppm. 13C-NMR (CDCl3) δ: 153.72 (C), 134.07 (C), 129.05, 129.02 (C), 127.87, 127.84, 126.15, 125.37, 123.37, 119.76 (C), 114.81, 68.42 (CH2) ppm. HRMS (ESI): calcd for C48H36O4Na: 699.2511, found: 699.2508.

2-Vinyl-2,3-dihydro-2'H-spiro[benzo[f]chromene-1,1'-naphthalen]-2'-one (5a). White solid; mp: 213–216 °C (EtOAc/PE). 1H-NMR (CDCl3) δ: 7.71 (d, J = 8.9 Hz, 1H), 7.66 (d, J = 8.1 Hz, 1H), 7.63 (d, J = 9.8 Hz, 1H), 7.41 (dd, J = 7.7, 1.2 Hz, 1H), 7.24 (ptd, J = 7.5, 1.2 Hz, 1H), 7.20 (d, J = 8.9 Hz, 1H), 7.13 (m, 2H), 7.01 (ddd, J = 8.5, 7.5, 1.4 Hz, 1H), 6.80 (d, J = 7.9 Hz, 1H), 6.65 (d, J = 8.4 Hz, 1H), 6.37 (d, J = 9.7 Hz, 1H), 5.52 (ddd, J = 17.0, 10.3, 8.8 Hz, 1H), 4.94 (dd, J = 10.3, 1.1 Hz, 1H), 4.66 (dpt, J = 17.0, 1.1 Hz, 1H), 4.56 (pt, J = 6.5, 1.1 Hz, 1H), 4.12 (dd, J = 10.9, 3.4 Hz, 1H), 2.99 (m, 1H) ppm. 13C-NMR (CDCl3) δ: 201.46 (C), 154.99 (C), 147.66 (C), 145.38, 131.71 (C), 131.20 (br), 130.66, 130.41 (C), 130.24 (C), 129.89, 129.06, 128.57, 127.61, 126.95, 126.40, 126.31, 123.84, 123.00, 119.06, 118.49 (C), 115.79 (C), 63.05 (CH2), 56.96 (C), 54.44 ppm. HRMS (ESI): calcd for C24H19O2: 339.1385, found: 339.1381. (R,R)-5a was obtained similarly from (R)-2a; mp: 140–143 °C (DCM/PE), [α]D20 +457 (c 1.51, toluene).

3.2.3. One Step Preparation of 5a from 1a

A degassed mixture of binaphthol 1a (286 mg, 1 mmol) and Cs2CO3 (977 mg, 3 mmol) in dry acetone (20 mL) was heated to reflux and 1,4-dibromo-2-butene (214 mg, 1 mmol) in acetone (50 mL) was added over 30 min. After reflux overnight the solids were separated, washed with DCM and the filtrate evaporated. The residue was dissolved in DCM/water (30 mL/30 mL) and the aqueous phase was separated and extracted with DCM (10 mL). The organic phases were dried and the residue subjected to chromatography (EtOAc/PE 10:90) to give 318 mg (94%) of 5a.

3.2.4. Photoisomerisation of 5a

A solution of 5a (252 mg, 0.746 mM) in toluene (10 mL) was irradiated (>300 nm) at 15–20 °C for 3 h. After removal of the solvent the mixture was subjected to chromatography (EtOAc/PE, 15:85) to yield 26 mg (10%) of 7a and 168 mg (67%) of 6a; 16 mg (6%) of starting material were recovered.
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(1R,10cR)-1,2,2a,2b,3,14b-Hexahydro-1,10c-methanobenzo[f]cyclobuta[3,4]naphtho[2,1-c]chromen-15-one (6a). Mp: 164–165 °C (EtOAc/PE). 1H-NMR (CDCl3) δ: 7.79 (dm, J = 8.3 Hz, 1H), 7.78 (d, J = 8.9 Hz, 1H), 7.30 (m, 2H), 7.16-7.24 (m, 3H), 7.18 (d, J = 8.9 Hz, 1H), 6.97 (m, 1H), 6.51 (br d, J = 7.9 Hz, 1H), 4.41 (dd, J = 10.8, 3.5 Hz, 1H), 4.09 (br m, 1H), 4.08 (dd, J = 11.8, 11.1 Hz, 1H), 3.09 (dpt, J = 7.2, 5.0 Hz, 1H), 2.95 (dpt, J = 10.9, 5.7 Hz, 1H), 2.71 (m, 1H), 2.31 (m, 1H), 1.97 (d, J = 10.5 Hz, 1H) ppm. 13C-NMR (CDCl3) (one C(quart.) not detected) δ: 208.92 (C), 155.10 (C), 141.74 (C), 136.64 (C), 133.58 (C), 130.21, 129.96 (C), 128.83, 128.38, 126.76, 126.69, 125.81, 125.34, 124.55, 123.22, 119.41, 112.10 (C), 66.49 (CH2), 48.19, 45.77, 44.73, 37.44, 32.46 (CH2) ppm. HRMS (EI, 40 °C): calcd for C24H18O2: 338.1307, found: 338.1299.

(6R,11bR)-4a,5,6,7-Tetrahydro-4H-5,7:6,11b-dimethanobenzo[3,4]cyclohepta[1,2-c]benzo[f]chromen-16-one (7a). Mp: 248–249 °C (EtOAc/PE). 1H-NMR (CDCl3) δ: 7.75 (2 × d, J ~ 8 Hz, 2H), 7.24 (m, 1H), 7.17 (d, J = 8.8 Hz, 1H), 7.11–7.17 (m, 2H), 7.04–7.17 (m, 2H), 6.85 (ddd, J = 8.8, 6.7, 2.0 Hz, 1H), 4.23 (dd, J = 10.8, 4.8 Hz, 1H), 3.99 (m, 1H), 3.37 (dd, J = 13.0, 11.0 Hz, 1H), 3.28 (ddd, J = 7.4, 5.8, 0.8 Hz, 1H), 3.11 (ddd, J = 11.0, 8.4, 7.8 Hz, 1H), 2.92 (ddd, J = 12.9, 4.8, 0.7 Hz, 1H), 2.49 (m, 1H), 1.78 (dm, J = 11.0 Hz, 1H) ppm. 13C-NMR (CDCl3) δ: 213.22 (C), 155.45 (C), 142.28 (C), 139.87 (C), 133.18 (C), 130.34 (C), 129.94, 128.85, 128.26, 127.69, 127.01, 126.77, 126.52, 124.21, 118.89, 111.77 (C), 66.87 (CH2), 57.11 (C), 50.55, 44.53, 42.09, 37.17 (CH2), 32.37 ppm. HRMS (ESI): calcd for C24H18O2: 338.1307, found: 338.1301.

3.2.5. Photoisomerisation of ep-i-5a

A solution of ep-i-5a (18 mg in toluene-d8, 0.7 mL) was irradiated in a NMR tube for 0.5 h (300 nm). 1H-NMR showed complete conversion and the mixture was separated by chromatography (EtOAc/PE, 15:85) to give 11 (4 mg) and ep-i-6a (6 mg).

(2aR,2bS)-1,2,2a,2b,3,14b-Hexahydro-1,10c-methanobenzo[f]cyclobuta[3,4]naphtho[2,1-c]chromen-15-one (ep-i-6a). Yield: 36%, mp: 230–234 °C (EtOAc/PE). 1H-NMR (CDCl3) δ: 7.78 (dd, J = 8.0, 1.3 Hz, 1H), 7.77 (d, J = 8.9 Hz, 1H), 7.36 (dm, J = 8.5 Hz, 1H), 7.31 (m, 1H), 7.28 (m, 1H), 7.25 (m, 1H), 7.23 (m, 1H), 7.10 (d, J = 8.8 Hz, 1H), 7.06 (ptd, J = 7.7, 1.6 Hz, 1H), 6.69 (dm, J = 7.8 Hz, 1H), 3.96 (dd, J = 10.4, 3.2 Hz, 1H), 3.94 (dd, J = 5.3, 5.0 Hz, 1H), 3.39 (dd, J = 12.0, 10.1 Hz, 1H), 2.99 (ddd, J = 7.0, 5.4, 4.7 Hz, 1H), 2.82 (ddd, J = 9.4, 6.9, 5.4 Hz, 1H), 2.77 (dd, J = 11.9, 3.0 Hz, 1H), 2.60 (pq, J = 5.3 Hz, 1H), 1.78 (d, J = 9.4 Hz, 1H) ppm. 13C-NMR (CDCl3) δ: 207.74 (C), 153.44 (C), 138.63 (C), 136.10 (C), 132.73 (C), 130.30, 129.40, 129.37 (C), 128.08, 127.90, 127.38, 127.35, 124.64, 124.56, 123.13, 119.07, 112.49 (C), 64.92 (CH2), 59.02 (C), 48.40, 46.01, 43.75, 40.49 (CH2), 38.48 ppm. HRMS (ESI): calcd for C24H18O2K: 377.0933, found: 377.0948.

(8aS)-8a,9,13b,14-Tetrahydro-9,14-methanobenzo[f]cyclobuta[3,4]naphtho[2,1-c]chromen-15(8H)-one (11). Yield: 25%, mp: 245–248 °C, (EtOAc/PE). 1H-NMR (CDCl3) δ: 7.78 (br d, J = 8.0 Hz, 1H), 7.63 (br d, J = 8.5 Hz, 1H), 7.62 (br d, J = 8.8 Hz, 1H), 7.52 (ddd, J = 8.5, 6.9, 1.5 Hz, 1H), 7.37 (ddd, J = 8.0, 6.9, 1.1 Hz, 1H), 7.28 (m, 1H), 7.17–7.25 (m, 3H), 6.92 (d, J = 8.8 Hz, 1H), 4.69 (d, J = 5.7 Hz, 1H), 4.00 (dd, J = 10.9, 4.2 Hz, 1H), 3.40 (br dd, J = 8.2, 5.7 Hz, 1H), 3.31 (ptd, J = 4.0, 1.0 Hz, 1H), 2.91 (br dpt, J = 12.0, 4.0 Hz, 1H), 2.71 (dd, J = 12.9, 4.2 Hz, 1H), 2.59 (dd, J = 11.9, 10.9 Hz, 1H),
1.88 (ddd, J = 12.9, 8.2, 1.1 Hz, 1H) ppm. $^{13}$C-NMR (CDCl$_3$) δ: 211.87 (C), 154.15 (C), 139.89 (C), 132.38 (C), 132.25 (C), 130.30, 130.21 (C), 129.50, 127.81, 127.37, 127.35, 126.32, 124.50, 124.11, 123.37, 119.09, 110.41 (C), 66.06 (CH$_2$), 64.40 (C), 54.20, 45.26, 37.60, 36.62 (CH$_2$), 35.65 ppm. HRMS (ESI): calcd for C$_{24}$H$_{18}$O$_2$Na: 361.1204, found: 361.1194.

3.2.6. 3',5-Diiodo-2-vinyl-2,3-dihydro-2'H-spiro[benzo[f]chromene-1,1'-naphthalen]-2'-one (5b)

To a degassed solution of 2b (189 mg, 0.3 mM) in DCM (18 mL) was added Grubbs II catalyst (15 mg, 5 mol%) dissolved in DCM (2 mL) over 10 h at r.t. in the dark using a syringe pump. Removal of the solvent was followed by column chromatography (EtOAc/PE, 10:90; the column was wrapped with aluminium foil) to give 172 mg (95%) of 5b.

3',5-Diiodo-2-vinyl-2,3-dihydro-2'H-spiro[benzo[f]chromene-1,1'-naphthalen]-2'-one (5b). Mp: 254–259 °C (EtOAc/PE). $^1$H-NMR (CDCl$_3$) δ: 8.37 (s, 1H), 8.31 (s, 1H), 7.56 (dm, J = 8.1 Hz, 1H), 7.34 (dd, J = 7.7, 1.5 Hz, 1H), 7.24 (ptd, J = 7.5, 1.3 Hz, 1H), 7.15 (m, 1H), 7.13 (m, 1H), 7.02 (ddd, J = 8.5, 10.3, 8.8 Hz, 1H), 5.01 (ddd, J = 10.3, 1.3, 0.5 Hz, 1H), 4.68 (dpt, J = 17.0, 1.1 Hz, 1H), 4.53 (dd, J = 10.8, 1H), 4.20 (dd, J = 11.0, 3.4 Hz, 1H), 2.91 (m, 1H) ppm. $^{13}$C-NMR (CDCl$_3$) δ: 54.43, 57.89 (C), 63.78 (CH$_2$), 88.06 (C), 102.32 (C), 116.60 (C), 119.36 (CH$_2$), 123.55, 123.82, 127.12, 127.40, 127.59, 127.68, 128.62, 130.23, 131.28, 131.36 (C), 131.42 (C), 131.54 (C), 140.10, 147.29 (C), 152.24 (C), 154.40, 194.70 (C) ppm. HRMS (EI, 30 °C): calcd for C$_{24}$H$_{16}$I$_2$O$_2$: 589.9240, found: 589.9230.

3',5-Dibromo-2-vinyl-2,3-dihydro-2'H-spiro[benzo[f]chromene-1,1'-naphthalen]-2'-one (5c). Yield: 91%; pale yellow foam. $^1$H-NMR (CDCl$_3$) δ: 8.08 (s, 1H), 8.05 (s, 1H), 7.59 (dm, J = 8.1 Hz, 1H), 7.37 (dd, J = 7.6, 1.4 Hz, 1H), 7.25 (ptd, J = 7.5, 1.3 Hz, 1H), 7.15 (m, 2H), 7.03 (ddd, J = 8.5, 6.9, 1.4 Hz, 1H), 6.72 (dm, J = 7.8 Hz, 1H), 6.54 (dm, J = 8.6 Hz, 1H), 5.42 (ddd, J = 17.0, 10.5, 8.9 Hz, 1H), 5.01 (dd, J = 10.4, 1.2 Hz, 1H), 4.69 (dpt, J = 17.0, 1.1 Hz, 1H), 4.56 (pt, J = 11.1 Hz, 1H), 4.23 (dd, J = 11.1, 3.4 Hz, 1H), 2.99 (ddd, J = 11.7, 8.9, 3.5 Hz, 1H) ppm. $^{13}$C-NMR (CDCl$_3$) δ: 193.67 (C), 151.05 (C), 146.93, 146.67 (C), 133.15, 131.13, 130.62 (C), 130.47 (C), 130.29 (C), 129.89, 128.84, 127.85, 127.56 (2× CH), 126.97, 124.04, 123.53, 122.70 (C), 119.60 (CH$_2$), 117.37 (C), 113.25 (C), 63.57 (CH$_2$), 58.72 (C), 54.34 ppm. HRMS (ESI): calcd for C$_{24}$H$_{16}$Br$_2$O$_2$Na: 516.9415, found: 516.9415.

3',5-Diphenyl-2-vinyl-2,3-dihydro-2'H-spiro[benzo[f]chromene-1,1'-naphthalen]-2'-one (5d). Yield: 98%; pale yellow solid. $^1$H-NMR (CDCl$_3$) δ: 7.73 (2 × s, 2H), 7.69 (m, 1H), 7.68 (m, 2H), 7.54 (m, 2H), 7.44–7.50 (m, 3H), 7.31-7.41 (m, 4H), 7.27 (ptd, J = 7.5, 1.3 Hz, 1H), 7.15 (m, 2H), 7.02 (ddd, J = 8.5, 6.9, 1.5 Hz, 1H), 6.88 (dm, J = 7.7 Hz, 1H), 6.78 (dm, J = 8.6 Hz, 1H), 5.60 (ddd, J = 17.1, 10.4, 8.8 Hz, 1H), 4.96 (ddd, J = 10.3, 1.4, 0.5 Hz, 1H), 4.71 (dm, J = 17.1 Hz, 1H), 4.54 (dd, J = 10.2, 10.0 Hz, 1H), 4.13 (dd, J = 10.8, 3.3 Hz, 1H), 3.05 (ddd, J = 9.9, 8.9, 3.3 Hz, 1H) ppm. $^{13}$C-NMR (CDCl$_3$) δ: 199.83 (C), 152.82 (C), 147.56 (C), 142.90, 138.45 (C), 136.47 (C), 135.51 (C), 131.92 (C), 131.56, 131.36 (C), 130.71 (C), 130.59, 130.33, 129.94, 129.88 (C), 129.35, 128.90, 128.73,
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128.20, 128.14, 128.01, 127.51, 127.12, 126.30, 123.82, 123.39, 118.32 (C), 116.69 (C), 63.16 (CH₂), 57.79 (C), 54.13 ppm. HRMS (ESI): calcd for C₃₆H₂₆O₂Na: 513.1830, found: 513.1847.

3.2.7. Photoisomerisation of 5b (Typical Procedure)

A sample containing ca.15 mg of 5b in toluene-d₈ in a NMR tube was irradiated for a total of 10 h (60 W, light bulb) after which ¹H-NMR indicated absence of 5b and formation of 6b and 7b (ca. 9:1), separable by chromatography (EtOAc/PE, 10:90).

(1R,10cR)-1,5-Diiodo-1,2,2a,2b,3,14b-hexahydro-1,10c-methanobenzo[f]cyclobuta[3,4]naphtho[2,1-c]chromen-15-one (6b). Yield: 75%; mp: 248–249 °C (EtOAc/PE). ¹H-NMR (CDCl₃) δ: 8.35 (s, 1H), 7.64 (dm, J = 8.0 Hz, 1H), 7.32 (dd, J = 7.4, 1.4 Hz, 1H), 7.26 (ddd, J = 8.0, 6.8, 1.2 Hz, 1H), 7.21 (ptd, J = 7.4, 1.2 Hz, 1H), 7.17 (ddd, J = 8.3, 6.8, 1.5 Hz, 1H), 6.98 (m, 2H), 6.38 (br d, J = 7.9 Hz, 1H), 4.46 (br d, J = 6.8 Hz, 1H), 4.45 (ddd, J = 11.0, 3.5 Hz, 1H), 3.97 (dd, J = 11.8, 11.1 Hz, 1H), 3.11 (m, 1H), 2.95 (ddd, J = 10.8, 7.1, 1.4 Hz, 1H), 2.46 (d, J = 10.7 Hz, 1H), 2.26 (m, 1H) ppm. ¹³C-NMR (CDCl₃) δ: 201.23 (C), 152.37 (C), 140.48, 139.98 (C), 133.56 (C), 133.10 (C), 131.23 (C), 128.58, 127.79, 127.57, 127.40, 126.48, 125.88, 125.46, 124.14, 112.46 (C), 87.90 (C), 65.72 (CH₂), 58.16 (C), 56.58, 44.10, 43.33 (CH₂), 39.88, 35.86 (C) ppm. HRMS (EI, 30 °C): calcd for C₂₄H₁₆I₂O₂: 589.9240, found: 589.9231.

(6R,11bR)-2,6-Diiodo-4a,5,6,7-tetrahydro-4H-5,7:6,11b-dimethanobenzo[3,4]cyclohepta[1,2-c]benzo[f]chromen-16-one (7b). Yield: 12%, mp: 151–152 °C (EtOAc/PE). ¹H-NMR (CDCl₃) δ: 8.37 (s, 1H), 7.65 (dm, J = 8.1 Hz, 1H), 7.26 (ddd, J = 8.0, 6.8, 1.1 Hz, 1H), 7.17 (ptd, J = 7.5, 1.2 Hz, 1H), 7.08 (m, 1H), 7.07 (m, 1H), 6.96 (dm, J = 8.8 Hz, 1H), 6.87 (m, 1H), 6.29 (dd, J = 8.0, 1.2 Hz, 1H), 4.36 (dd, J = 11.2, 4.9 Hz, 1H), 4.16 (ddd, J = 8.5, 4.9, 0.9 Hz, 1H), 3.17 (dpt, J = 11.1, 8.1 Hz, 1H), 3.45 (dd, J = 13.0, 11.1 Hz, 1H), 3.06 (ddd, J = 13.0, 4.8, 0.6 Hz, 1H), 2.57 (ddm, J = 7.8, 4.8 Hz, 1H), 1.73 (dm, J = 11.1 Hz, 1H) ppm. ¹³C-NMR (CDCl₃) δ: 205.34 (C), 152.37 (C), 140.48, 139.98 (C), 133.56 (C), 133.10 (C), 131.23 (C), 128.58, 127.79, 127.57, 127.40, 126.48, 125.88, 125.46, 124.14, 112.46 (C), 87.90 (C), 65.72 (CH₂), 58.16 (C), 56.58, 44.10, 43.33 (CH₂), 39.88, 35.86 (C) ppm. HRMS (ESI): calcd for C₂₄H₁₆I₂O₂: 589.9240, found: 589.9231.

(1R,10cR)-1,5-Dibromo-1,2,2a,2b,3,14b-hexahydro-1,10c-methanobenzo[f]cyclobuta[3,4]naphtho[2,1-c]chromen-15-one (6c). Yield: 64%, crystalline precipitate, mp: 324–328 °C (EtOAc/PE, dec.). ¹H-NMR (CDCl₃) δ: 8.14 (s, 1H), 7.72 (dm, J = 8.2 Hz, 1H), 7.39 (dd, J = 7.4, 1.3 Hz, 1H), 7.33 (ddd, J = 8.0, 6.8, 1.0 Hz, 1H), 7.27 (ptd, J = 7.6, 1.3 Hz, 1H), 7.22 (ddd, J = 8.3, 6.8, 1.4 Hz, 1H), 7.07 (dm, J = 8.8 Hz, 1H), 7.03 (ptd, J = 7.5, 1.4 Hz, 1H), 6.44 (br d, J = 7.8 Hz, 1H), 4.55 (dd, J = 11.0, 3.4 Hz, 1H), 4.40 (d, J = 6.9 Hz, 1H), 4.03 (dd, J = 11.9, 11.1 Hz, 1H), 3.20 (m, 1H), 2.97 (ddd, J = 10.8, 7.2, 1.5 Hz, 1H), 2.49 (d, J = 10.8 Hz, 1H), 2.31 (dm, J = 12.1 Hz, 1H) ppm. ¹³C-NMR (CDCl₃) δ: 200.42 (C), 150.97 (C), 139.77 (C), 133.58, 133.40 (C), 132.42 (C), 130.15 (C), 128.67, 127.84, 127.64, 127.54, 126.55, 125.91, 125.26, 124.39, 113.28 (C), 113.22 (C), 65.71 (CH₂), 58.80 (C), 57.38 (C), 54.93, 44.27, 41.55 (CH₂), 35.85 ppm. HRMS (ESI): calcd for C₂₄H₁₆Br₂NaO₂: 516.9415, found: 516.9425.
(6R,11bR)-2,6-dibromo-4a,5,6,7-tetrahydro-4H-5,7:6,11b-dimethanobenzo[3,4]cyclohepta[1,2-c]benzo[ff]chromen-16-one (7c). Yield: 10%, mp: 240–246 °C (EtOAc/PE), colorless prisms. 1H-NMR (CDCl3) δ: 8.11 (s, 1H), 7.68 (br d, J = 8.3 Hz, 1H), 7.28 (m, 1H), 7.18 (ptd, J = 7.5, 1.5 Hz, 1H), 7.10 (br d, J = 7.4 Hz, 1H), 7.09 (m, 1H), 6.96 (d, J = 8.6 Hz, 1H), 6.88 (ptd, J = 7.6, 1.4 Hz, 1H), 6.27 (br d, J = 8.0 Hz, 1H), 4.39 (dd, J = 11.1, 4.8 Hz, 1H), 4.16 (dd, J = 8.1, 5.1 Hz, 1H), 3.57 (dpt, J = 11.2, 8.2 Hz, 1H), 3.47 (dd, J = 11.1, 11.1 Hz, 1H), 3.01 (dd, J = 13.0, 4.9 Hz, 1H), 2.58 (dd, J = 7.8, 5.1 Hz, 1H), 1.81 (d, J = 11.2 Hz, 1H) ppm. 13C-NMR (CDCl3) δ: 203.99 (C), 151.50 (C), 140.24 (C), 138.69 (C), 133.27, 132.10 (C), 130.53 (C), 128.74, 128.38, 127.42, 127.09, 127.06, 126.49, 125.04, 124.37, 113.24 (C), 112.80 (C), 67.17 (CH2), 58.83 (C), 56.07, 55.87 (C), 50.01, 42.10, 35.68 (CH2) ppm. HRMS (ESI): calcd for C24H16Br2NaO2: 518.9394, found: 518.9372.

(1R,10cR)-1,5-Diphenyl-1,2,2a,2b,3,14b-hexahydro-1,10c-methanobenzo[f]cyclobuta[3,4]naphtho[2,1-c]chromen-15-one (6d). Yield: 7%, mp: 322–327 °C (EtOAc/PE), colorless prisms. 1H-NMR (CDCl3) δ: 7.79 (s, 1H), 7.78 (d, J = 8.4 Hz, 1H), 7.61 (m, 2H), 7.48 (dd, J = 7.5, 1.2 Hz, 1H), 7.44 (m, 2H), 7.36 (m, 1H), 7.21–7.33 (m, 5H), 7.11 (m, 2H), 7.07 (ptd, J = 7.7, 1.4 Hz, 1H), 7.00 (d, J = 8.6 Hz, 1H), 6.61 (d, J = 7.8 Hz, 1H), 4.46 (dd, J = 11.1, 3.6 Hz, 1H), 4.24 (d, J = 6.2 Hz, 1H), 4.14 (dd, J = 11.6, 11.0 Hz, 1H), 3.00 (pq, J = 6.0 Hz, 1H), 2.81 (ddd, J = 10.3, 6.4, 1.7 Hz, 1H), 2.41 (m, 1H), 2.40 (d, J = 10.3 Hz, 1H) ppm. 13C-NMR (CDCl3) δ: 207.29 (C), 152.92 (C), 141.15 (C), 140.09 (C), 138.65 (C), 136.65 (C), 132.97 (C), 132.35 (C), 131.00, 129.86, 129.52 (C), 128.47, 128.40, 128.30, 127.96, 127.17, 127.14, 127.05, 127.02, 126.35, 126.07, 125.68, 124.69, 123.43, 112.72 (C), 65.44 (CH2), 58.76 (C), 57.88 (C), 49.80, 46.07, 36.89 (CH2), 34.08 ppm. HRMS (ESI): calcd for C36H26NaO2: 513.1825, found: 513.1824.

(6R,11bR)-2,6-Diphenyl-4a,5,6,7-tetrahydro-4H-5,7:6,11b-dimethanobenzo[3,4]cyclohepta[1,2-c]benzo[ff]chromen-16-one (7d). Yield: 39%, oil. 1H-NMR (CDCl3) δ: 7.82 (s, 1H), 7.80 (br d, J = 8.3 Hz, 1H), 7.65 (m, 2H), 7.41–7.52 (m, 7H), 7.38 (m, 1H), 7.29 (m, 1H), 7.26 (m, 2H), 7.11 (m, 2H), 6.98 (m, 1H), 6.51 (d, J = 7.8 Hz, 1H), 4.39 (dd, J = 10.9, 4.9 Hz, 1H), 4.26 (dd, J = 8.4, 4.7 Hz, 1H), 3.54 (dd, J = 13.1, 10.9 Hz, 1H), 3.22 (dpt, J = 10.9, 8.3 Hz, 1H), 3.08 (dd, J = 12.9, 4.9 Hz, 1H), 2.82 (dd, J = 7.9, 4.7 Hz, 1H), 1.90 (d, J = 10.9 Hz, 1H) ppm. 13C-NMR (CDCl3) δ: 211.38 (C), 153.10 (C), 142.06 (C), 139.75 (C), 138.48 (C), 136.54 (C), 132.67 (C), 132.35 (C), 131.00, 129.86, 129.52 (C), 128.47, 128.40, 128.30, 127.96, 127.17, 127.14, 127.05, 127.02, 126.35, 126.07, 125.68, 124.69, 123.43, 112.72 (C), 65.44 (CH2), 58.76 (C), 57.88 (C), 49.80, 46.07, 36.89 (CH2), 34.08 ppm. HRMS (ESI): calcd for C36H26NaO2: 513.1825, found: 513.1824.

3.2.8. Synthesis of 6b/7b from 2b (One Pot Procedure)

Grubbs II catalyst (12.6 mg, 0.015 mM) dissolved in toluene (1.5 mL) was slowly added during 6 h to a stirred solution of 2b (145 mg, 0.235 mM) in toluene (14 mL) at r.t. During this time the reaction mixture was irradiated using a desk lamp. Extractive work-up and chromatographic purification afforded 103 mg (76%) of 6b and 17 mg (13%) of 7b.

(2E,2'E)-Dimethyl 4,4'-(R)-1,1'-binaphthyl-2,2'-diylbis(oxy)dibut-2-enoate [(R)-8]. (R)-2,2'-Dihydroxy-1,1'-binaphthyl 1a (859 mg, 3 mM) was dissolved in acetonitrile (25 mL). After addition of methyl
4-bromocrotonate (1.61 g, 9 mM) and K₂CO₃ (1.26 g, 9 mM) the mixture was stirred at r.t. under Ar for 24 h. Standard work-up with water/DCM and drying (MgSO₄) was followed by column chromatography (EtOAc/PE, 30:70) to yield 1.07 g (74%) of \((R)\)-8; oil; \([\alpha]_D^{20} +30.6 \text{ (c 1.00, CHCl₃)}\).

\(^1\text{H-NMR (CDC}_{13}\text{)} \delta: 7.94 \text{ (d, } J = 9.0 \text{ Hz, 2H)}, 7.86 \text{ (br d, } J = 8.2 \text{ Hz, 2H)}, 7.33 \text{ (ddd, } J = 8.0, 6.5, 1.4 \text{ Hz, 2H}), 7.32 \text{ (d, } J = 9.0 \text{ Hz, 2H)}, 7.22 \text{ (ddd, } J = 8.2, 6.7, 1.4 \text{ Hz, 2H)}, 7.14 \text{ (dm, } J = 8.6 \text{ Hz, 2H)}, 6.81 \text{ (dpt, } J = 15.7, 3.9 \text{ Hz, 2H}), 5.63 \text{ (dpt, } J = 15.8, 2.2 \text{ Hz, 2H}), 4.66 \text{ (m, 4H)}, 3.63 \text{ (s, 6H)} \text{ ppm.}

\(^13\text{C-NMR (CDC}_{13}\text{)} \delta: 166.44 \text{ (C)}, 153.33 \text{ (C)}, 143.07, 134.02 \text{ (C)}, 129.62, 129.53 \text{ (C)}, 127.99, 126.56, 125.32, 123.94, 123.94, 120.17 \text{ (C)}, 115.01, 67.79 \text{ (CH} \text{₂)}, 51.45 \text{ (CH} \text{₃)} \text{ ppm. HRMS (ESI): calcd for C}_{30}\text{H}_{26}\text{O}_{6}\text{Na: 505.1627, found: 505.1616.}

(2E,2'E)-4,4'-(R)-1,1'-Binaphthyl-2,2'-diylbis(oxy)dibut-2-en-1-ol \([{(R)}-9]\). To a degassed solution of \((R)\)-8 (1.07 g, 2.22 mM) in abs. DCM (30 mL) was added at −78 °C DIBAL (1 mol solution in toluene, 8.9 mL, 8.9 mM) and the reaction was kept at −20 °C for 12 h after which time TLC (EtOAc, 100%) indicated complete conversion. A saturated solution of potassium sodium tartrate (30 mL) and glycol (0.5 mL) was added and the mixture was stirred at r.t. for 3 h. The organic phase was separated and the aqueous phase was extracted with DCM (10 mL). The combined organic extracts were washed with brine and dried (Na₂SO₄). After evaporation the crude product was purified by chromatography (EtOAc / PE 50:50 → 100:0) to give 672 mg (71%) of \((R)\)-9; white solid; mp: 38–40 °C; \([\alpha]_D^{20} +65.2 \text{ (c 1.00, CHCl₃)}\). \(^1\text{H-NMR (CDCl₃)} \delta: 7.91 \text{ (d, } J = 9.1 \text{ Hz, 2H)}, 7.84 \text{ (d, } J = 8.1 \text{ Hz, 2H)}, 7.19 \text{ (dd, } J = 8.4, 6.7, 1.3 \text{ Hz, 2H}), 7.11 \text{ (br d, } J = 8.4 \text{ Hz, 2H)}, 5.55 \text{ (m, 4H)}, 4.50 \text{ (m, 4H)}, 3.90 \text{ (m, 4H)}, 1.73 \text{ (br s, 2H)} \text{ ppm.}

\(^13\text{C-NMR (CDCl₃)} \delta: 153.93 \text{ (C)}, 134.13 \text{ (C)}, 131.61, 129.39 \text{ (C)}, 129.20, 127.86, 126.72, 126.23, 125.48, 123.68, 120.66 \text{ (C)}, 115.99, 69.25 \text{ (CH₂)}, 62.71 \text{ (CH₂)} \text{ ppm. HRMS (ESI) calcd for C}_{28}\text{H}_{26}\text{O}_{4}\text{Na: 449.1729, found: 449.1727.}

(2E,2'E)-4,4'-(R)-1,1'-Binaphthyl-2,2'-diylbis(oxy)dibut-2-en-1-ylbromide \([{(R)}-10]\). To a solution of \((R)\)-9 (580 mg, 1.36 mM) in dry THF (15 mL) was dropwise added at −40 °C PBr₃ (810 mg, 3.06 mM, 2.2 equiv, 284 µL) in THF (1 mL) and the mixture was slowly warmed up overnight. Sat. sodium bicarbonate solution (5 mL) was added, followed by water (10 mL) and DCM (20 mL). The aqueous layer was extracted with DCM (2 × 15 mL) and the combined extracts were washed with brine and dried (MgSO₄). After evaporation the crude bromide was purified by chromatography (DCM/PE, 30:70) to give 544 mg (72%) of \((R)\)-10 as a colorless oil; \([\alpha]_D^{20} +13.7 \text{ (c 1.00, THF)}\). \(^1\text{H-NMR (CDCl₃)} \delta: 7.94 \text{ (d, } J = 9.0 \text{ Hz, 2H)}, 7.86 \text{ (d, } J = 8.2 \text{ Hz, 2H)}, 7.37 \text{ (d, } J = 9.1 \text{ Hz, 2H)}, 7.30 \text{ (dd, } J = 8.0, 6.7, 1.2 \text{ Hz, 2H}), 7.19 \text{ (dd, } J = 8.4, 6.7, 1.3 \text{ Hz, 2H}), 7.11 \text{ (br d, } J = 8.4 \text{ Hz, 2H}), 5.55 \text{ (m, 4H)}, 4.50 \text{ (m, 4H)}, 3.90 \text{ (m, 4H)}, 1.73 \text{ (br s, 2H)} \text{ ppm.}

\(^13\text{C-NMR (CDCl₃)} \delta: 153.93 \text{ (C)}, 134.13 \text{ (C)}, 131.61, 129.39 \text{ (C)}, 129.20, 127.86, 126.72, 126.23, 125.48, 123.68, 120.66 \text{ (C)}, 115.99, 69.25 \text{ (CH₂)}, 62.71 \text{ (CH₂)} \text{ ppm. HRMS (ESI) calcd for C}_{28}\text{H}_{24}\text{Br}_{81}\text{BrO}_{2}\text{Na: 575.0023, found: 575.0045.}

Macrocyclisation of \((R)\)-10 with \((R)\)-1. To a degassed solution of \((R)\)-binaphthol 1 (57 mg, 0.2 mM) in THF (7 mL) was added KOH (22 mg, 0.4 mM, 0.4 mL of a 1 N aqueous solution) and the mixture was refluxed for 30 min. Dibromide \((R)\)-10 (110 mg, 0.2 mM) dissolved in THF (3 mL) was added and the reaction was refluxed for 3 d. Extractive work-up with DCM/water and chromatographic purification
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(EtOAc / PE, 20:80) yielded 95 mg (70%) of (R,R)-3a; mp: 159–160 °C (EtOAc/PE); $[\alpha]_D^{20} +110$ (c 0.42, CHCl3). Spectroscopic data fully agreed with the racemic compound.

**Palladium mediated cleavage of (R,R)-3a.** Macrocycle (R,R)-3a (80 mg, 0.12 mmol) and Pd(PPh3)4 (14 mg, 0.012 mmol) were heated in toluene (60 °C) for 48 h. The crude mixture was separated by column chromatography (EtOAc/PE, 10:90→20:80) to give a 44 mg fraction consisting of (R,R)-5a (36 mg, 45%) and 6a (8 mg, 10%) followed by 19 mg (24%) of (R,S)-epi-5a; mp: 153–155 °C (EtOAc/PE). $^1$H-NMR (CDCl3) δ: 7.70 (d, $J = 9.3$ Hz, 1H), 7.68 (d, $J = 8.0$ Hz, 1H), 7.61 (d, $J = 9.9$ Hz, 1H), 7.44 (dd, $J = 7.5, 1.4$ Hz, 1H), 7.29 (ptd, $J = 7.3, 1.2$ Hz, 1H), 7.18 (ptd, $J = 7.7, 1.4$ Hz, 1H), 7.17 (d, $J = 9.1$ Hz, 1H), 7.15 (ddd, $J = 8.1, 6.9, 1.2$ Hz, 1H), 7.07 (br d, $J = 7.6$ Hz, 1H), 7.07 (ddd, $J = 8.4, 6.9, 1.4$ Hz, 1H), 6.62 (dm, $J = 8.5$ Hz, 1H), 6.41 (d, $J = 10.0$ Hz, 1H), 5.00 (m, 2H), 4.94 (m, 1H), 4.24 (pt, $J = 11.3$ Hz, 1H), 4.07 (dd, $J = 11.3, 4.0$ Hz, 1H), 3.11 (m, 1H) ppm. $^{13}$C-NMR (CDCl3) δ: 203.10 (C), 154.17 (C), 145.01, 143.65 (C), 131.54 (C), 131.00, 130.70 (C), 130.25 (C), 129.60, 129.44 (2 × CH), 128.74, 127.48, 126.51, 126.46, 123.86, 123.11, 119.75 (CH2), 118.86, 115.35 (C), 64.09 (CH2), 57.18 (C), 51.34 ppm. HRMS (ESI): calcd for C24H18O2Na: 361.1207, found: 361.1204.

### 3.3. Crystallographic Structure Determination

X-ray diffraction measurements were performed on an X8 APEX II CCD diffractometer at 100 or 150 K. Single crystals were positioned at 50, 35, 35, 45 and 35 mm from the detector and 1270, 1831, 2488, 1406, 1467 and 1278 frames were measured, each for 60, 10, 30, 5, 10 and 10 s over 1° scan width for epi-5a, 6b, 6a, epi-6a, 6b and 11, respectively. The data were processed using SAINT software [53]. Crystal data, data collection parameters, and structure refinement details are given in Table 2. The structures were solved by direct methods and refined by full-matrix least-squares techniques. Non-hydrogen atoms were refined with anisotropic displacement parameters. H atoms were placed at calculated positions and refined as riding atoms in the subsequent least squares model refinements. The isotropic thermal parameters were estimated to be 1.2 times the values of the equivalent isotropic thermal parameters of the non-hydrogen atoms to which hydrogen atoms are bonded. The following computer programs were used: structure solution, SHELXS-97 refinement, SHELXL-97 [54] molecular diagrams, ORTEP [55] computer: Pentium IV. CCDC 907285–907290 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.
Table 2. Crystal data and details of data collection for epi-5a, 5b, 6a, epi-6a, 6b and 11.

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<th>6a</th>
<th>epi-6a</th>
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^a R_1 = \Sigma||F_o||-|F_c||\Sigma|F_o|.
^b wR_2 = (\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2)^{1/2}.
^c GOF = (\Sigma w(F_o^2-F_c^2)^2/(n-p))^{1/2}, where n is the number of reflections and p is the total number of parameters refined.
3.4. Calculations

All calculations were performed using software packages SPARTAN (B3LYP, MO6 and MP2) and the Gaussian09 on the Phoenix Linux Cluster of the Vienna University of Technology [38]. The geometry and energy of the ruthenium model compounds and the transition states were optimized at the B3LYP level [56–58] with the Stuttgart/Dresden ECP (SDD) basis set to describe the electrons of the ruthenium atom [59–61], and a standard 6-31g** basis set was employed for all other atoms [62–68]. All geometries were optimized without symmetry constraints. Frequency calculations were performed to confirm the nature of the stationary points, yielding one imaginary frequency for the transition states and none for the minima. Each transition state was further confirmed by following its vibrational mode downhill on both sides and obtaining the minima presented on the energy profiles. All energies reported are Gibbs free energies and thus contain zero-point, thermal, and entropy effects at 298 K and 1 atm pressure. The solvation energies were calculated on the geometries from B3LYP gas phase optimizations via the polarizable continuum model (PCM) [69,70] with the radii and nonelectrostatic terms based on Truhlar and co-workers’ solute electron density (SMD) solvation model [71] with solvation parameters corresponding to CH₂Cl₂.

4. Conclusions

Summarising, we have developed an operationally simple one-pot procedure for transforming O,O'-diallyl substituted axial chiral binaphthols into centro-chiral species through a RCM followed by a Claisen-type rearrangement of reactive (E)-dioxacyclodecine intermediates 4a–d. This mechanistic assumption was supported and rationalized by DFT calculations performed on E-4a, corresponding precursors and hypothetical intermediates. Under irradiation further rearrangement took place yielding strained cage compounds 6a–d and 7a–d through a formal [2+2] cycloaddition.

References and Notes


43. Since more than 85% of conformers were found within a narrow energy range of ~1 kcal the *Curtin-Hammet Principle for Competing Reactions* can be applied.

44. Moreover, calculations showed very similar activation energies for direct transformations $E_{-12} \rightarrow 5a$ and $E_{-12} \rightarrow epi-5a$. If such reaction path would be operative similar amounts of products $5a$ and $epi-5a$ should be isolated which disagrees with experimental results.


53. SAINT-Plus (version 7.06a) and APEX2. Bruker-Nonius AXS Inc.: Madison, WI, USA, 2004.


Sample Availability: Samples of the compounds 3a and 5a are available from the authors.

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