

A concise synthesis of (–)-centrolobine *via* a diastereoselective ring rearrangement metathesis–isomerisation sequence

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A total synthesis of (–)-centrolobine (**1**) based on a diastereoselective ring rearrangement metathesis–double bond isomerisation sequence and a one-pot cross metathesis–hydrogenation procedure is described.

(–)-Centrolobine **1** is a tetrahydropyranic antibiotic isolated from the heart wood of *Centrolobium robustum* (porcupine tree) and the stem of *Brosimum portabile*.¹ It has shown activity against *Leishmania amazonensis promastigotes*, a major health problem in Brazil.

The asymmetric synthesis of (–)-centrolobine has been reported recently by several groups. The stereoselective construction of the tetrahydropyran core structure has previously been achieved by Prins-cyclisation,^{2,3} reductive etherification⁴ or a one-pot cross metathesis–hydrogenation–lactonisation procedure.⁵ We investigated a new, variable approach towards the core structure of (–)-centrolobine, which should also be of interest in the synthesis of other substituted hetero- and carbocycles.

Among the different types of metathesis known, ring rearrangement metathesis (RRM) has proven to be especially powerful. Stereocenters are easily established in a ring and transferred to the sidechain or *vice versa*. RRM has been applied in the synthesis of fused carbocycles⁶ and polycyclic ethers⁷ as well as piperidines,^{8,9} pyrrolidines⁸ and various natural products.¹⁰ Some years ago, we presented the first case of diastereoselective ring closing metathesis.¹¹ Diastereoselective RCM has been applied in the synthesis of highly functionalised rings,⁴ also those containing quaternary stereocenters¹⁰ as well as natural products, e.g. (–)-limaspermene¹² and the formal synthesis of (–)-eburnamone.¹³ In our laboratories we have now developed a new method of diastereoselective ring rearrangement metathesis (dRRM, Scheme 1).¹⁴ The RRM of prochiral rings with a stereocenter in the sidechain like **A** should lead to carbo- or heterocycles **B** containing a new stereocenter. The challenge for such a process is to shift the reaction to the desired product with a synthetically useful



Scheme 1 Concept (X = O, CHR, NPG, $m = 0, 1; n = 0, 1$).

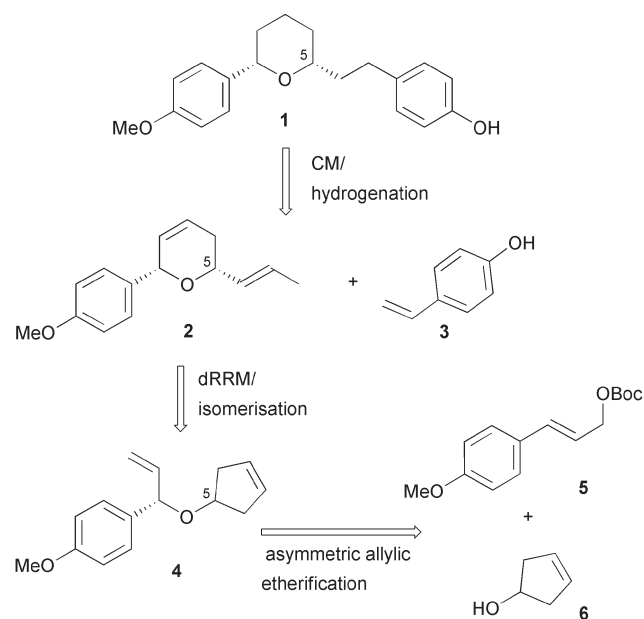
diastereoselectivity, whereby the reaction can be kinetically or thermodynamically controlled.

We report herein the application of this new concept for the stereoselective synthesis of 2,6-substituted dihydropyrans to the total synthesis of (–)-centrolobine.

The retrosynthetic strategy is outlined in Scheme 2. The key features of this approach involve a one-pot cross metathesis (CM)–hydrogenation procedure introducing the *para*-hydroxybenzyl moiety to **2**. The terminal methyl group in **2** should be advantageous in the CM to suppress homodimerisation. We envisaged that the cross partner **2** would be available from **4** *via* ruthenium catalyzed diastereoselective ring rearrangement metathesis (dRRM) followed by double bond isomerisation of the terminal alkene. The stereocenter at C-5 is established in the RRM step diastereoselectively.¹⁴ The enantiopure metathesis precursor **4** was to be obtained by an asymmetric allylic etherification.¹⁵

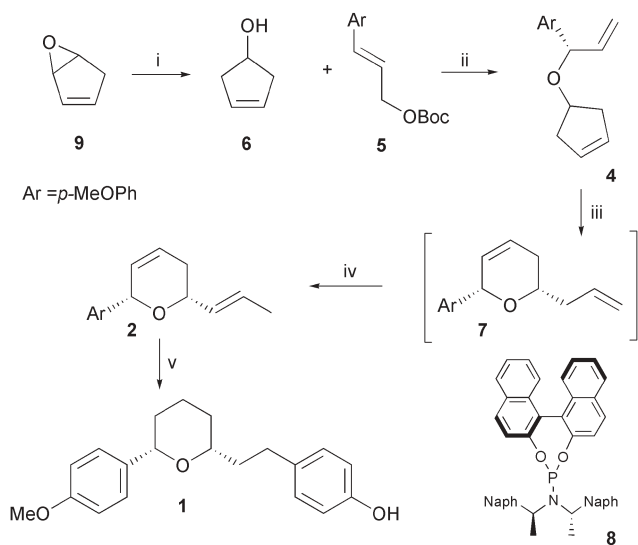
The synthesis of (–)-centrolobine started with a reductive opening of epoxide **9** with LiAlH₄ in quantitative yield to deliver the alcohol **6** as a nucleophile for the ether synthesis (Scheme 3).¹⁶

The next step required an enantioselective allylation of **6**. Transition metal catalyzed asymmetric allylations have been investigated extensively.¹⁷ Palladium catalyzed allylic substitution has been applied widely in synthesis.¹⁸ In the case of non-symmetrical allylic substrates, the bond formation usually takes place at the less substituted position. There are only a few



Scheme 2 Retrosynthetic approach.

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Scheme 3 Reagents and conditions: (i) LiAlH₄, Et₂O, >98%; (ii) BuLi, CuI, then [Ir(COD)Cl]₂, **8**, THF, 0 °C→RT, 87%, >98% ee; (iii) 2 × 5% [Ru(IH₂Mes)PCy₃(=CHPh)Cl]₂, benzene–ethylene, 50 °C, 6 h; (iv) 0.4 equiv. NaBH₄, 55%; (v) 2 equiv. styrene **3**, 10% (IH₂Mes)RuCl₂PCy₃(*o*-iPr)CHPh, toluene, RT then 5% Pd/C (50 wt% water), H₂ (1 atm), 50%. Naph = naphthyl, Boc = *tert*-butylcarbonate.

examples known where the branched products are formed.¹⁹ In our case, we required the branched product of allylic etherification, **4**, in high enantio- and regioselectivity. Recently, iridium catalysts have been described which lead preferentially to the branched products of allylic substitution yielding high regio- and enantioselectivity. Helmchen *et al.* reported asymmetric substitutions with amines and carbon nucleophiles employing iridium complexes with phosphoramidite ligands.²⁰ Reactions with phenoxides and copper alkoxides were published by Hartwig *et al.*^{15,21} Following this procedure, treatment of the copper alkoxide of cyclopentenol **6** with *para*-methoxy cinnamyl carbonate **5** in the presence of [Ir(COD)Cl]₂ and the phosphoramidite ligand **8** gave the cyclopentenyl ether in 87% yield and >98% ee (chiral HPLC).†

Different conditions were tested to investigate the conversion of **4** to **7** via dRRM. In initial studies, different precatalysts were compared. Whereas 5 mol% of the first generation catalysts *Grubbs I* [Ru(PCy₃)₂(=CHPh)Cl]₂²² and *Hoveyda I* [Ru(PCy₃(=CH(*o*-iPr)Ph)Cl)₂]²³ led to poor diastereoselectivities (2 : 1, *cis* : *trans*), the employment of 5 mol% *Grubbs II* [Ru(IH₂Mes)PCy₃(=CHPh)Cl]₂²⁴ gave a significant improvement of the diastereoisomeric ratio, and **7** was obtained in 4 : 1 (*cis* : *trans*) dr. Optimisation of the reaction conditions resulted in lower catalyst loadings. Using 3 mol% of the *Grubbs II* catalyst in DCM, the conversion was complete after 15 h at room temperature. Variation of the reaction temperature did not result in a change of the diastereoisomeric ratio. Performing the reaction under an ethylene atmosphere was advantageous with respect to initiation speed and suppressing dimerisation.

With the rearrangement product **7** in our hands, we now envisaged the isomerisation of the terminal double bond to an internal olefin. Different isomerisation catalysts for double bonds have been described,²⁵ nevertheless an economic *in situ* conversion of the metathesis catalyst into an isomerisation catalyst was desirable. The isomerisation of terminal to internal double bonds

by ruthenium hydride species during the work up is a well known side reaction in olefin metathesis.²⁶ The targeted double bond isomerisation has also been reported by Snapper *et al.* and Schmidt as a one-pot RCM–isomerisation process to synthesize vinylic ethers.²⁷ The challenge in our case was to isomerise the terminal double bond selectively. Because the attack of the ruthenium catalyst at the less substituted, terminal double bond is favoured, we expected that the terminal double bond would isomerise more easily than the ring double bond and therefore hoped to control the selectivity by temperature. Initially, MeOH and base were added to the reaction mixture after dRRM and the vessel was heated to generate the ruthenium hydride catalyst. At 100 °C, reaction took place, but unfortunately the cyclic double bond was also isomerised. The addition of NaBH₄ followed by heating to 100 °C gave the desired product in modest conversion. Changing the solvent to benzene led to a significant improvement. In the optimized procedure, the dRRM reaction was carried out using the *Grubbs II* catalyst in benzene, which had been saturated with ethylene, at 50 °C in a pressure vessel. After complete conversion (dr = 4 : 1, GC-MS), 40 mol% of NaBH₄ was added to convert the metathesis catalyst into an isomerisation catalyst, the vessel was flushed with nitrogen and subsequently heated to 100 °C for 30 h. The desired dihydropyran **2** was obtained in 60% yield (95% purity by ¹H-NMR) with no isomerisation of the endocyclic double bond. The relative stereochemistry was assigned by a positive NOE of the protons in the 2,5-positions of the pyran ring.

With **2** in hand, we had to introduce the phenol group. Cross metathesis has proved to be a useful tool for the introduction of side chains.²⁸ In particular, styrenes react selectively with alkyl substituted double bonds to give the mixed cross product.²⁹ The cross metathesis with *para*-hydroxystyrene **3** was performed at room temperature in toluene with 10 mol% of the *Hoveyda–Grubbs* catalyst.³⁰ After complete conversion, palladium on charcoal (5 wt%, 50% water) was added and a hydrogen atmosphere was introduced. A positive side effect of the use of this carrier is the adsorption of the remaining ruthenium species. (–)-Centrolobine **1** could be isolated in 50% yield and >98% ee. The hydrogenation was also performed by the conversion of the ruthenium catalyst to a hydride species at 70 °C as well as with ethanol as a solvent, but these procedures led to a cleavage of the benzylic ether.⁵

In summary, we have shown that the new concept of diastereoselective ring rearrangement metathesis is a powerful tool in asymmetric synthesis with the example of the natural product (–)-centrolobine. Two effective one-pot reactions have been applied in this short synthesis and (–)-centrolobine **1** was obtained in 5 steps with 22% overall yield and >98% ee.

The application of the method to further natural products is in preparation and will be reported in due course. This work was supported from the DFG (Graduate School 352).

Notes and references

† 1-[1-(Cyclopent-3-enyloxy)-allyl]-4-methoxy benzene (**4**). A solution of *n*BuLi (3.2 mL, 8 mmol, 2.5 M in hexane) was added dropwise to cyclopentenol¹⁶ **6** (0.67 g, 8 mmol) in THF at –78 °C.¹⁵ The mixture was stirred for 10 min and allowed to warm to rt. The solvent was removed *in vacuo* and the residue was dissolved in THF (4 mL). After addition of CuI (1.6 g, 8.4 mmol), the slurry was stirred for 30 min at rt. A solution of [Ir(COD)Cl]₂ (54 mg, 0.08 mmol) and the ligand **8** (102 mg, 0.16 mmol) in THF (8 mL) was added and the mixture was cooled to 0 °C. Carbonate **5**

(1.06 g, 4 mmol) was added and the mixture was stirred at rt for 50 h, poured into water and extracted with Et₂O (3 ×). The organic layers were dried (MgSO₄) and the solvent was distilled at normal pressure. Chromatography (SiO₂, Et₂O : pentane 1 : 20) yielded 800 mg (87%) of **4** as a colourless oil (ee > 98%, HPLC, [α]_D²⁰ = +4° (c = 0.82 CDCl₃)). ¹H-NMR (500 MHz, CDCl₃): δ = 7.28 (d, J = 8.3 Hz, 2H), 6.88 (d, J = 8.3 Hz, 2H), 5.95 (ddd, J = 17.2, 10.2, 6.5 Hz, 1H), 5.66–5.69 (m, 2H), 5.22 (dd, J = 17.2, 1.5 Hz, 1H), 5.14 (dd, J = 10.2, 1.5 Hz, 1H), 4.78 (d, J = 6.5 Hz, 1H), 4.28 (dt, J = 7.2, 3.7 Hz, 1H), 3.80 (s, 3H), 2.35–2.60 (m, 4H). ¹³C-NMR (125.8 MHz): δ = 159.0 (C), 139.6 (CH), 133.6 (C), 128.4 (CH), 128.3 (CH), 128.2 (CH), 128.1 (CH), 115.6 (CH₂), 113.8 (CH), 80.5 (CH), 76.5 (CH), 55.3 (CH₃), 39.5 (CH₂), 39.3 (CH₂), 27.8 (CH). IR (ATR): 3062 (m), 2930 (m), 2835 (m), 1161 (m), 1511 (vs), 1247 (vs), 1036 (m), 925 (m), 827 (m). EI-MS: 230 (12, [M]⁺), 163 (30, [M – C₂H₅]⁺), 147 (100, [M – C₅H₇O]⁺). HR-MS calc.: [M]⁺: 230.1308, found: 230.1307. EA calc.: C 78.23%, H 7.88%, found: C 77.80%, H 7.91%.

6-(4-Methoxy-phenyl)-2-propenyl-3,6-dihydro-2H-pyran (2): 230 mg (1 mmol) of **4** were dissolved in benzene (c = 0.02 M), which had been saturated with ethylene in a pressure vessel (0.33 L). 85 mg (0.1 mmol) Grubbs II catalyst was added in two portions and the reaction mixture was heated to 50 °C for 6 h. The conversion was monitored via GC-MS. Subsequently, 15 mg (0.4 mmol) of NaBH₄ were added. The vessel was flushed with nitrogen and heated for 30 h to 100 °C. The solvent was distilled over a Vigreux-column and the residue was purified by flash chromatography (SiO₂, Et₂O : pentane 1 : 100) to yield 130 mg (60%) of the product contaminated with 5% impurity (trans-isomer of the non-isomerised RRM product). ¹H-NMR (500 MHz, CDCl₃, 25 °C): δ = 7.29 (d, J = 8.3 Hz, 2H), 6.87 (d, J = 8.3 Hz, 2H), 5.89–5.94 (m, 1H), 5.69–5.74 (m, 2H), 5.59 (ddq, J = 15.5, 6.6, 1.5 Hz, 1H), 5.17 (bs, 1H), 4.21 (ddd, J = 7.0, 6.5, 3.0 Hz, 1H), 3.79 (s, 3H), 2.20–2.30 (m, 1H), 2.01–2.08 (m, 1H), 1.69 (dd, J = 6.6, 1.5 Hz, 3H). NOE (5.17 → 4.21: 1.9%). ¹³C-NMR (125.8 MHz): δ = 160.7 (C), 133.7 (C), 131.9 (CH), 130.2 (CH), 128.7 (CH), 112.8 (CH), 124.5 (CH), 113.8 (CH), 77.3 (CH), 75.0 (CH), 55.3 (CH₃), 31.0 (CH₂), 17.8 (CH₃). IR (ATR): 3435 (m), 3035 (vw), 2926 (w), 2854 (w), 1703 (vw), 1598 (w), 1325 (m), 1158 (vs), 1095 (m), 815 (m). EI-MS: 230 (20, [M]⁺), 187 (30, [M – C₃H₇]⁺), 135 (100), 108 (15, [C₇H₈O]⁺). HR-MS calc.: [M]⁺: 230.1307, found: 230.1306.

(–)-Centrolobine (1): To 22 mg (0.1 mmol) **2** and 24 mg (0.2 mmol) **3**³¹ in 0.2 mL toluene, 6.2 mg (0.01 mmol) Hoveyda–Blechert catalyst were added and the mixture was stirred at rt overnight. Subsequently, 6 mg Pd/C (5%, 50 wt% H₂O) were added and an H₂ atmosphere was introduced. The mixture was stirred for 4 d at rt and filtered over a pad of cotton wool. The solvent was evaporated and the product was purified by flash chromatography (SiO₂, EtOAc : hexane 1 : 15–1 : 10). 14 mg (50%) of **1** were obtained. The spectroscopic data were consistent with the literature.³ ¹H-NMR (500 MHz, CDCl₃): δ = 7.31 (d, J = 8.5 Hz, 2H), 7.05 (d, J = 8.8 Hz, 2H), 6.87 (d, J = 8.5 Hz, 2H), 6.74 (d, J = 8.8 Hz, 2H), 4.59 (bs, 1H), 4.29 (dd, J = 11.1, 2.0 Hz, 1H), 3.80 (s, 3H), 3.44 (dddd, J = 12.6, 6.4, 4.7, 1.8 Hz, 1H), 2.78–2.60 (m, 2H), 1.96–1.82 (m, 4H), 1.79–1.70 (m, 1H), 1.69–1.50 (m, 2H), 1.41–1.27 (m, 1H). [α]_D²⁰ = 60.0 (c = 0.25, CH₂Cl₂).

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