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Quinoid BINOL-type compounds as a novel class of chiral ligands☆

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Dedicated to Professor José Barluenga on the occasion of his 65th birthday

Abstract—A short and efficient synthesis of a novel family of quinone-substituted BINOL-type ligands exploiting the chromium-templated [3+2+1]benzannulation reaction as the key step is reported.

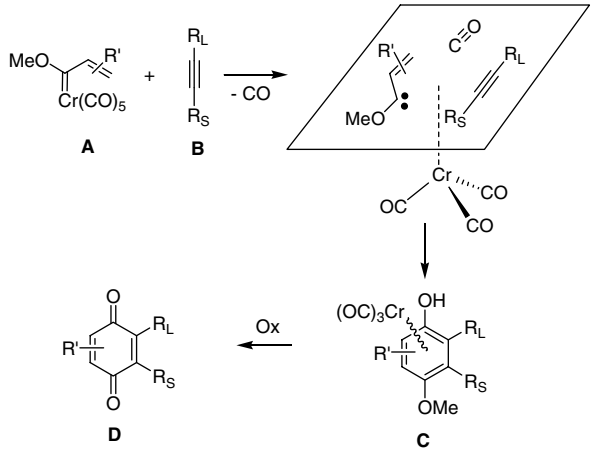
1. Introduction

Enantiopure BINOL is one of the most prominent C_2-symmetric, axial-chiral ligands for both stoichiometric and catalytic asymmetric reactions.[1] Nevertheless, the modification of the chiral backbone in a symmetrical or non-symmetrical fashion is of great interest as substitution of BINOL may affect not only the steric environment around the coordinated metal centre but also the electronic properties of the oxygen atoms, which are common constituents in many Lewis acidic metal complexes.[2,3] The most frequently modified positions at the binaphthol core are those at the aromatic carbon atoms 3 and 6. To the best of our knowledge, no quinoid moieties have ever been attached to BINOL. Herein, we report a novel class of modified BINOL ligands, which bear redox-active quinoid functionalities either attached to the binaphthol core in positions 3 and 6 through a C–C-single bond or directly annulated. We envisaged to synthesise this new BINOL-type ligand family using the chromium-templated [3+2+1]benzannulation reaction as the key step in the synthetic approach. Until now, we are only aware of a single example of this synthetic strategy applied to the synthesis of the vaulted 2,2′-binaphthol- and 3,3′-biphenanthrol ligands VANOL and VAPOL by Wulff et al.[4]

2. Results and discussion

The chromium-templated [3+2+1]benzannulation reaction between a pentacarbonylchromium(0)-carbene complex **A** and an alkyne **B** provides one of the most powerful tools for generating densely substituted benzenoid compounds (Scheme 1).[5]

This unique type of metal carbene reaction proceeds via a formal [3+2+1] cycloaddition, which involves an α,β-unsaturated carbene ligand, an alkyne and a carbonyl ligand and takes place within the coordination sphere of the chromium(0) metal centre, which acts as a



Scheme 1. Atom connectivity in the regioselective [3+2+1]benzannulation reaction (R_L = large substituent; R_S = small substituent).

☆ Reactions of Complex Ligands Part 107. For Part 106 see Bennewitz, J.; Nieger, M.; Lewall, B.; Dötz, K. H. *J. Organometal. Chem.*, in press.

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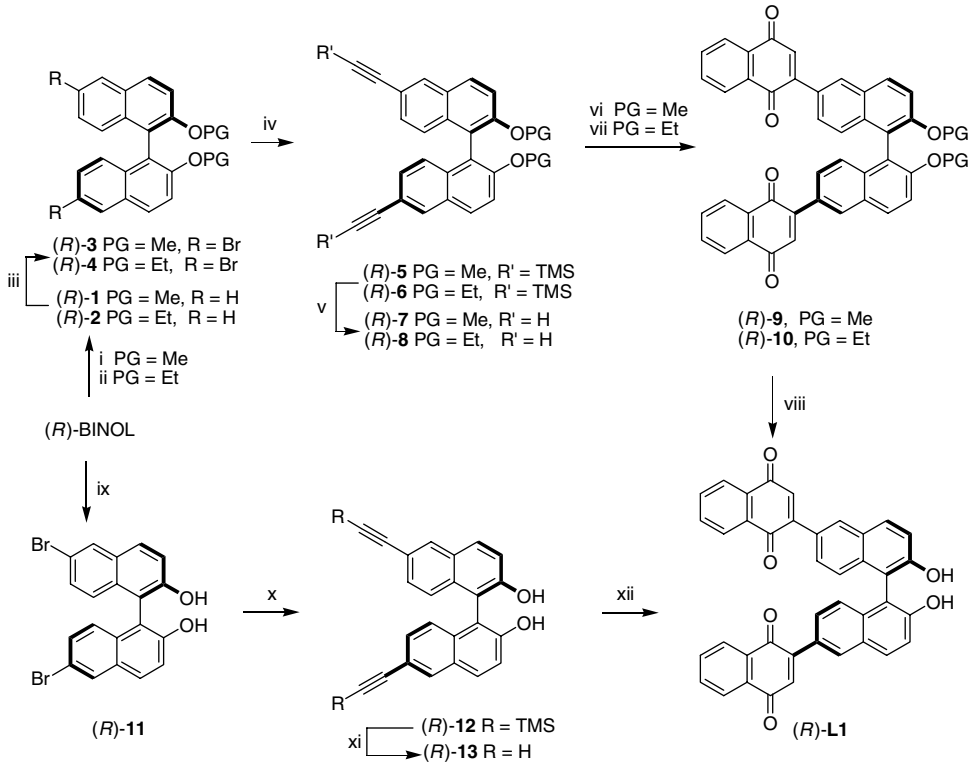
template. The initially formed $Cr(CO)_3$-coordinated 4-methoxyphenol or 4-methoxy-1-naphthol skeleton **C** can subsequently be cleaved from the chromium template and readily oxidised to the corresponding quinone **D** with CAN in a one-pot procedure.[6] This highly valuable transformation was used to synthesise (*R*)-BINOL-derived ligands with either quinoid functionalities attached to the binaphthol core through a C–C-single bond or directly annulated quinone moities starting from commercially available, enantiomerically pure (*R*)-BINOL. The two different structural patterns could be generated depending on the functionalisation of the binaphthol compound.

The synthetic approach to chiral ligand (*R*)-**L1** is outlined in Scheme 2, and two different strategies concerning the protecting groups are presented. The protection of the free hydroxy groups as methoxy or ethoxy ethers was the first step following the strategy of maximum protection. Compound (*R*)-**1** was synthesised according to the procedure of Cram et al. in 95% yield.[7] The use of Cs_2CO_3 instead of K_2CO_3 allowed for the synthesis of the ethoxy-protected compound (*R*)-**2** under milder conditions [shorter reaction time (3 vs 36 h) and lower reaction temperature (25 vs 56 °C)] compared to the literature procedure.[8] Compound (*R*)-**2** revealed two major advantages compared to its methyl analogue (*R*)-**1**: the use of a less toxic alkylation reagent in their syntheses (EtBr vs MeI) and its easy purification by recrystallisation. The bromination of (*R*)-**2** in positions 6,6′ with bromine in CH_2Cl_2 was achieved in 86%.[8] Application of this procedure in the synthesis of compound (*R*)-**3** resulted in an easier protocol compared to the literature synthesis yielding compound (*R*)-**3** in 95%.[9] The brominated derivatives (*R*)-**3** and (*R*)-**4** reacted with trimethylsilyl acetylene in a Sonogashira-coupling at 80 °C according to the known literature procedure, to give (*R*)-**5** and (*R*)-**6** in 99% and 79% yields, respectively.[10] Cleavage of the remaining TMS-group under basic conditions led to the free alkynes (*R*)-**7** (87%) and (*R*)-**8** (85%), respectively,[10a] which were subsequently subjected to a double chromium-templated [3+2+1]benzannulation reaction. Each alkyne functionality was reacted with 2.2 equiv of pentacarbonyl-[methoxy(phenyl)carbene]chromium(0) under optimised reaction conditions to afford the red 6,6′-bis(naphthoquinone)-substituted binaphthyl compounds (*R*)-**9** and (*R*)-**10** after in situ oxidation of the initially formed $Cr(CO)_3$-(η^6-hydronaphthoquinone) complexes. The double benzannulation reaction with (*R*)-**7** was performed in CH_2Cl_2 at 55 °C to give 73% yield of (*R*)-**9** after oxidation with CAN at room temperature for 12 h. A significant increase of the chemical yield up to 87% was achieved for the benzannulation product (*R*)-**10**, as the benzannulation reaction was performed in TBME and the final oxidation was carried out at 0 °C

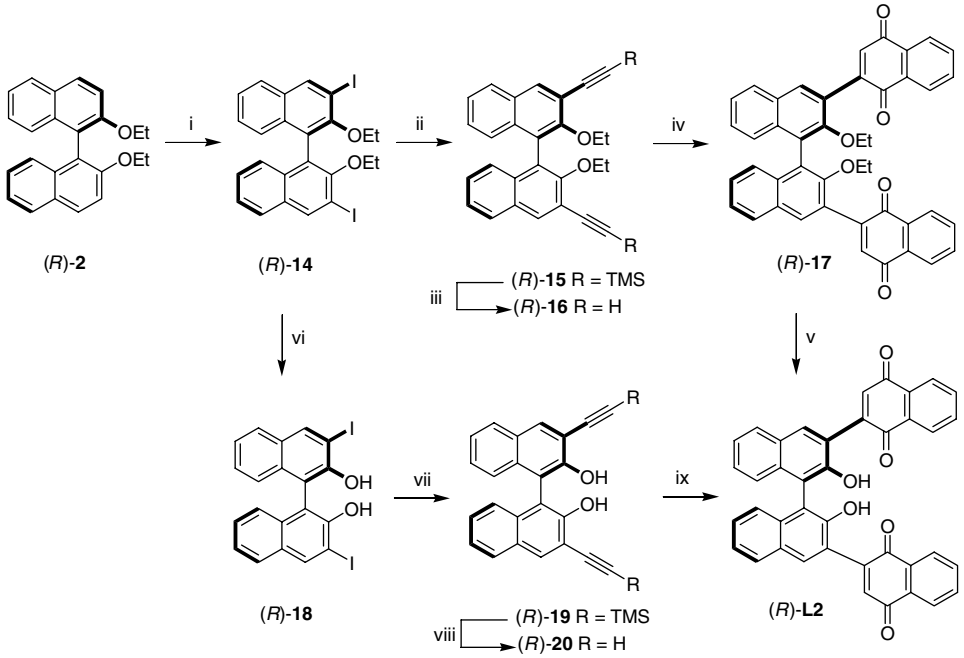


Scheme 2. Reagents and conditions: (i) K_2CO_3, MeI, acetone, 36 h, reflux, 95%; (ii) Cs_2CO_3, EtBr, acetone, 3 h, rt, 99%; (iii) Br_2, CH_2Cl_2, 0 °C to rt, 95% (PG = Me), 86% (PG = Et); (iv) TMSC≡CH, $Pd(PPh_3)_2Cl_2$, CuI, NEt_3, 12 h, 80 °C, 99% (PG = Me), 79% (PG = Et); (v) KOH, MeOH/THF, 3 h, rt, 87% (PG = Me), 85% (PG = Et); (vi) $(CO)_5Cr{=}C(OMe)Ph$, CH_2Cl_2, 3 h, 55 °C, CAN, H_2O, 12 h, 73%; (vii) $(CO)_5Cr{=}C(OMe)Ph$, TBME, 12 h, 60 °C, CAN, H_2O, 1 h, 0 °C, 87%; (viii) BBr_3, CH_2Cl_2, 1 h, −78 °C, 2 h, rt, 84% (PG = Et); (ix) Br_2, CH_2Cl_2, −75 °C to rt, 3 h, 99%; (x) TMSC≡CH, $Pd(PPh_3)_2Cl_2$, CuI, NEt_3, 12 h, 80 °C, 89%; (xi) KOH, MeOH/THF, 3 h, rt, 97%; (xii) $(CO)_5Cr{=}C(OMe)Ph$, TBME, 12 h, 60 °C, CAN, H_2O, 1 h, 0 °C, 25%.

for 1 h. This excellent chemical yield was obtained even at high scale up to 10 mmol. Compound (*R*)-**10** afforded the enantiopure 6,6′-bis(naphthoquinone)-BINOL-type ligand (*R*)-**L1** in 84% yield after cleavage of the ethoxy groups within 3 h with BBr_3 in CH_2Cl_2 at −78 °C to room temperature. These time- and temperature-controlled conditions were necessary as cleavage of the ethoxy groups with BBr_3 under standard conditions resulted only in decomposition. In conclusion, ligand (*R*)-**L1** was synthesised in six steps with an overall yield of 46% following the 'maximised' protecting group strategy (PG = Et).

We were also interested in whether BINOL-bisquinone (*R*)-**L1** could be obtained without the introduction of any protecting groups. The bisalkyne-substituted binaphthyl compound (*R*)-**13** was synthesised according to the literature procedures involving the bromination of (*R*)-BINOL (99%),[9] the Sonogashira-coupling with trimethylsilyl acetylene (89%)[11] and the cleavage of the TMS-groups under basic conditions (97%).[11] Bisalkyne (*R*)-**13** was reacted in a double benzannulation reaction with 4.5 equiv of pentacarbonyl[methoxy(phenyl)carbene]chromium(0) to give bisquinone (*R*)-**L1** in 25% yield. This demonstrates that the benzannulation reaction is compatible with the presence of the free hydroxy groups, although this results in a decrease in chemical yield. Thus, the syntheis of (*R*)-**L1** could be shortened to four steps providing an overall yield of 21% in the absence of any protecting groups.

The synthetic route to the regioisomeric chiral ligand (*R*)-**L2** is outlined in Scheme 3; again two complementary strategies concerning the protecting groups are presented. As observed for the synthesis of (*R*)-**L1**, the ethoxy-protected derivatives generally showed higher solubility than their methoxy analogues and could be easily purified by recrystallisation. This prompted us to synthesise ligand (*R*)-**L2** starting from ethoxy-protected BINOL-(*R*)-**2**, as a successful directed *ortho*-lithiation demands complete solubility in limited amounts of solvent. Elementary iodine proved to be the electrophile of choice to react with the in situ *ortho*-lithiated species as the use of Br_2 or $(BrCl_2C)_2$ afforded only mixtures of bis- and monobrominated species. Bisiodide (*R*)-**14** was synthesised in 88% yield by lithiation of (*R*)-**2** with *n*-BuLi in the presence of TMEDA in Et_2O at room temperature and subsequent reaction with I_2. Subsequent Sonogashira-coupling in positions 3,3′ with trimethylsilyl acetylene at 40 °C in NEt_3 as solvent gave compound (*R*)-**15** in 78% yield. The cleavage of the TMS-groups to afford the terminal alkyne (*R*)-**16** was effected under basic conditions with 90% yield. The double benzannulation reaction of 3,3′-bisalkyne (*R*)-**16** and an excess of pentacarbonyl[methoxy(phenyl)carbene]-chromium was performed under different reaction conditions. The best result was obtained in CH_2Cl_2 at 55 °C with an in situ oxidation with CAN at room temperature for 12 h, affording an orange 3,3′-bis(naphthoquinone)-substituted binaphthyl compound (*R*)-**17** in 24% yield even at a 10 mmol scale. Several deprotecting reagents were tested for the cleavage of the ethoxy groups in (*R*)-**17**. The use of the common Lewis-acids BB_3 and BI_3[12] did not meet with success, and TMSI seemed to be an inappropriate choice as previous experiments have indicated a preference for furanohelicene cyclisation under these conditions.[13] Quantitative reaction was observed with $AlCl_3$,[14] although only analytical



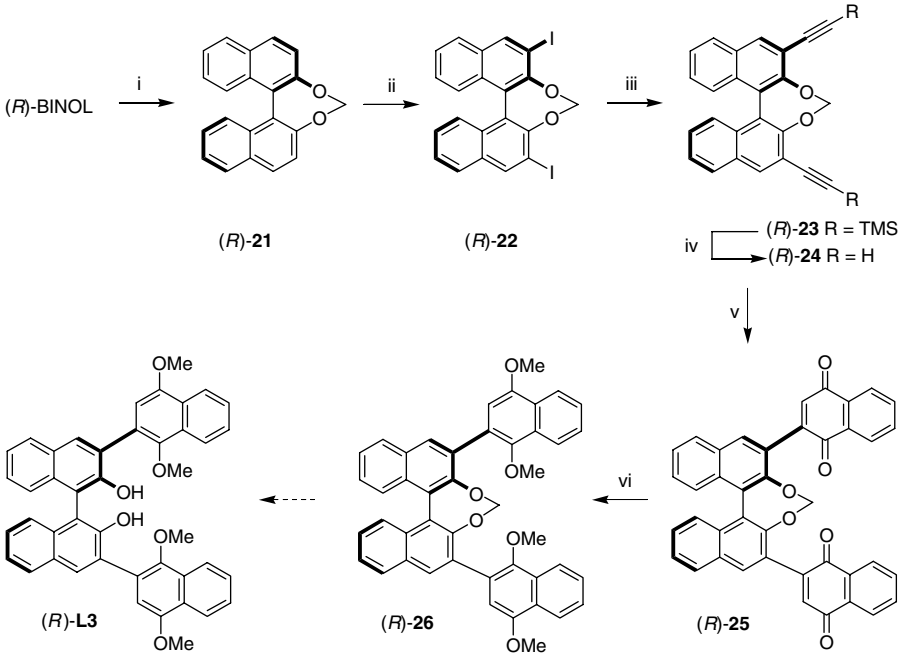
Scheme 3. Reagents and conditions: (i) *n*-BuLi, TMEDA, Et_2O, 6 h, rt, I_2, −78 °C to rt, 88%; (ii) TMSC≡CH, $Pd(PPh_3)_2Cl_2$, CuI, NEt_3, 20 h, 40 °C, 78%; (iii) KOH, MeOH/THF, 3 h, rt, 90%; (iv) $(CO)_5Cr{=}C(OMe)Ph$, CH_2Cl_2, 5 h, 55 °C, CAN, H_2O, 12 h, rt, 24%; (v) $AlCl_3$, CH_2Cl_2, 12 h, rt; (vi) BBr_3, CH_2Cl_2, 12 h, −40 °C to rt, 99%; (vii) TMSC≡CH, $Pd(PPh_3)_2Cl_2$, CuI, NEt_3, 20 h, 40 °C, 99%; (viii) KOH, MeOH/THF, 3 h, rt, 99%; (ix) $(CO)_5Cr{=}C(OMe)Ph$, CH_2Cl_2, 12 h, 55 °C, CAN, H_2O, 1 h, 0 °C, 0%.

amounts of the enantiopure 3,3′-bis(naphthoquinone)-BINOL-type ligand (*R*)-**L2** could be isolated after column chromatography. Again, the possibility of applying a 'minimised' protecting group strategy was studied — 'minimised' as the absence of any protecting group is incompatible with the *ortho*-lithiation step. The ethoxy-groups were removed after the iodination in positions 3,3′ with BBr_3 in CH_2Cl_2 to yield compound (*R*)-**18**[15] quantitatively. Sonogashira-coupling with trimethylsilyl acetylene and subsequent cleavage of the TMS-groups under basic conditions gave bisalkynes (*R*)-**19**[16] and (*R*)-**20**[17] in quantitative yields, respectively. Although quantitative consumption of the alkyne was observed, unfortunately, no product arising from the double benzannulation of (*R*)-**20** and pentacarbonyl[methoxy(phenyl)carbene]chromium could be isolated after in situ oxidation with CAN. As already observed for (*R*)-**L1**, the benzannulation reaction proceeded with significantly lower yield in the presence of free hydroxy groups compared to the hydroxy protection situation (87% vs 25%). Unfortunately, this trend was confirmed for the benzannulation approach to (*R*)-**L2**, and reduced the 24% yield obtained for the protected BINOL derivative (*R*)-**16** to virtually 0% for its unprotected analogue (*R*)-**20**.

BINOL-derived ligands bearing an alkyl-protected benzohydroquinoid moiety in positions 3,3′ have proven to be highly effective in asymmetric catalysis.[18] These functional groups are introduced via a Suzuki-coupling between the halogenated binaphthol and the corresponding arylboronic acids. As an alternative synthetic approach to those types of ligands, we envisaged to attach a naphthohydroquinone to the binaphthol core by following our [3+2+1]benzannulation protocol. In view of the last step — the deprotection of the hydroxy groups — an orthogonal protecting group strategy was necessary in order to cleave the hydroxy protecting group in the presence of the methoxy-groups of the hydro(naphthoquinone)-functionalities (Scheme 4).

Following this approach, (*R*)-BINOL was cycloprotected with diiodomethane in DMF and K_2CO_3 as base to give acetal (*R*)-**21** in 87% yield.[19] Iodination of (*R*)-**21** in positions 3,3′ was achieved in 65% yield following the experimental protocol established for compound (*R*)-**14**. A subsequent Sonogashira-coupling with trimethylsilyl acetylene under standard conditions gave compound (*R*)-**23** in 84% yield; deprotection of the TMS-groups under basic conditions yielded (*R*)-**24** nearly quantitatively. Bisalkyne (*R*)-**24** was reacted with pentacarbonyl[methoxy(phenyl)carbene]chromium in a double [3+2+1]benzannulation reaction in TBME at 60 °C; after in situ oxidation with CAN at 0 °C for 1 h the 3,3′-bis(naphthoquinone)-substituted binaphthyl, compound (*R*)-**25**, was isolated in 22% yield. The reductive methylation of the naphthoquinone moieties proceeded nicely under phase transfer catalytic conditions.[20] The bis(naphthoquinone) (*R*)-**25** was reduced in the first step with $Na_2S_2O_4$ to the bis(naphthohydroquinone), which was subsequently deprotonated with KOH and methylated with Me_2SO_4 to give a 76% yield of the methyl-protected 3,3′-bis(naphthohydroquinone)-substituted binaphthyl compound (*R*)-**26**, which represents a direct precursor of bis(naphthohydroquinoid) derivative (*R*)-**L3**.[21]

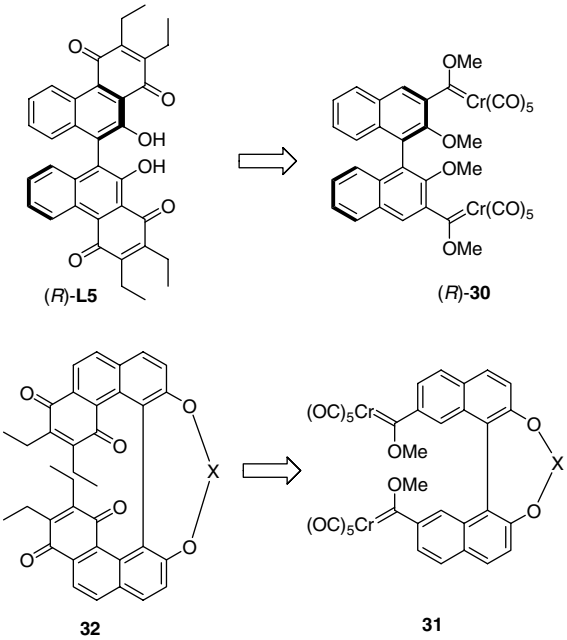
The NMR-data of ligands (*R*)-**L1**, (*R*)-**L2** and compound (*R*)-**26** revealed that these structures suffer from a strong distortion of the naphthoquinone and the



Scheme 4. Reagents and conditions: (i) I_2CH_2, K_2CO_3, DMF, 16 h, 80 °C, 87%; (ii) *n*-BuLi, TMEDA, Et_2O, 6 h, rt, I_2, −78 °C to rt, 65%; (iii) TMSC≡CH, $Pd(PPh_3)_2Cl_2$, CuI, NEt_3, 20 h, 40 °C, 84%; (iv) KOH, MeOH/THF, 3 h, rt, 98%; (v) $(CO)_5Cr{=}C(OMe)Ph$, TBME, 12 h, 60 °C, CAN, H_2O, 1 h, 0 °C, 22%; (vi) $Na_2S_2O_4$, THF/H_2O, *n*-Bu_4NBr, KOH, Me_2SO_4, 76%.

naphthohydroquinone moieties with respect to the BINOL naphthol unit as the remaining H-atom in the *ortho*-position to the quinone or the methoxy group, respectively, indicating an enhanced upfield shift compared to the aromatic H-atoms [(*R*)-**L1**: 6.93 vs 7.2–8.2 ppm; (*R*)-**L2**: 7.20 vs 7.2–8.1 ppm; and (*R*)-**26**: 6.7 vs 7.3–8.2 ppm]. This finding suggests that the H-atom points onto the aromatic system resulting in shielding due to the ring current effect. MM3-minimised molecular models of compounds (*R*)-**L1** and (*R*)-**L2**, which are in agreement with this argument, are shown in Figure 1.

Finally, the synthesis of the C_2-symmetric bis(phenanthrenequinone) ligand (*R*)-**L4** was envisaged following a different synthetic strategy as the alkyne component for the [3+2+1]benzannulation reaction is no longer attached to the binaphthol core. Instead, the chromium carbene functionality is incorporated into the binaphthol moiety and properly placed to allow for an angular benzannulation regiochemistry (Scheme 5). There have been two preliminary reports on the synthesis of structurally related compounds, for example, chiral ligand (*R*)-**L5**, which has been synthesised starting from biscarbene complex (*R*)-**30** and racemic compound **32** generated from the racemic biscarbene complex precursor **31** (Scheme 6).[13,22] BINOL bisbromide (*R*)-**3** was applied to the classical Fischer-Route; lithiation with *t*-BuLi in THF for 30 min at −78 °C, treatment with $Cr(CO)_6$ at −20 °C to give the non-stable bis(acylmetalate), and in situ methylation with Me_3OBF_4 in water afforded the bis(carbene) complex (*R*)-**27** in 80% yield.



Scheme 6. Retrosynthetic approach to bisquinones (*R*)-**L5** and **32**.

The use of water in the methylating step is crucial for a high yield; the syntheses of the related biscarbene complexes (*R*)-**30** and **31**, in which the alkylation was performed in dichloromethane, resulted in yields of only 56% and 48%, respectively. Double [3+2+1]benzannulation of bis(carbene) complex (*R*)-**27** with 3-hexyne in

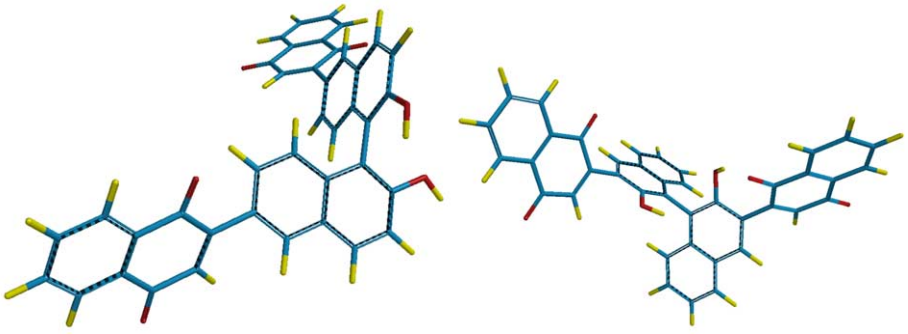
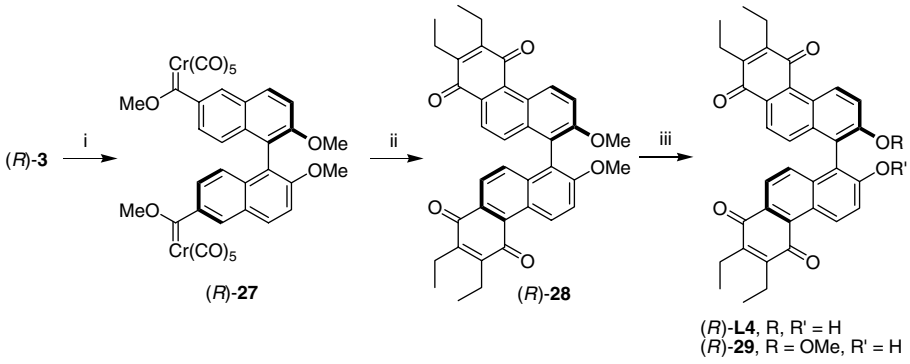


Figure 1. MM3-minimised 3D representation of (*R*)-**L1** and (*R*)-**L2**.



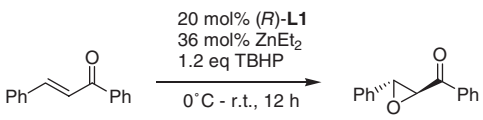
Scheme 5. Reagents and conditions: (i) *t*-BuLi, THF, 30 min, −78 °C, $Cr(CO)_6$, 40 min, −20 °C to rt, Me_3OBF_4, H_2O, 30 min, rt, 80%; (ii) 3-hexyne, CH_2Cl_2, 12 h, 55 °C, CAN, H_2O, 1 h, 0 °C, 40%; (iii) BBr_3, CH_2Cl_2, −12 h, 10 °C to rt, 70% [(*R*)-**L4**], 30% [(*R*)-**29**].

CH_2Cl_2 at 55 °C afforded — after in situ oxidation with CAN at 0 °C — the bis(phenanthrenquinone) (*R*)-**28** in 40% yield. As expected, the exclusive formation of the bis-angular benzannulation product was observed.[23]

The C_2-symmetric free ligand (*R*)-**L4** was isolated in 70% yield after cleavage of the methoxy groups with BBr_3 in CH_2Cl_2; in addition, the non-symmetrical monodentate ligand (*R*)-**29** was isolated in 30% yield. The synthesis of (*R*)-**L4** was accomplished in five steps with 18% overall yield providing the missing complementary structure to the already existing compounds (*R*)-**L5** and **32**.

In order to test the potential of the chiral ligands (*R*)-**L1** and (*R*)-**L2** in an enantioselective catalysis, two model reactions were chosen. The catalytic activity of ligand (*R*)-**L1** was probed in the zinc-mediated asymmetric epoxidation of chalcone (Scheme 7).[24,25] The reaction was performed in different solvents by the sequential treatment of chiral ligand (*R*)-**L1** with $ZnEt_2$, chalcone and *tert*-butyl hydroperoxide (TBHP) as the terminal oxidant. The epoxidation proceeded in all cases with perfect diastereoselectivity; only the *trans*-epoxide was formed (Table 1). The solvent has a significant effect on both the yield and the enantioselectivity. An exceptionally high reactivity was observed when the reaction was conducted in Et_2O, and the epoxide was isolated in 99% yield and 32% enantiomeric excess (Table 1, entry 3). A slight enantiomeric excess was observed for CH_2Cl_2 (40% ee), although the yield dropped dramatically to 45% (Table 1, entry 1). Toluene gave only a modest yield (27%), while the asymmetric induction remained nearly unchanged (38% ee) (Table 1, entry 2). No epoxidation was observed when the reaction was performed in THF (Table 1, entry 4).

The chiral ligand (*R*)-**L2** has been used in the zinc-mediated Hetero-Diels–Alder reaction (Scheme 8).[27,28] The



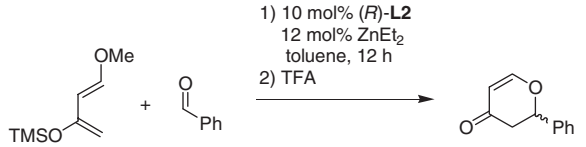
Scheme 7. Zinc-mediated enantioselective epoxidation of chalcone.

Table 1. Enantioselective epoxidation of chalcone catalysed by a chiral Zn-(*R*)-**L1** complex

Entry	Solvent	Yield (%)[a]	de (%)[b]	ee (%)[c,d]
1	CH_2Cl_2	45	>99	40
2	Toluene	27	>99	38
3	Et_2O	99	>99	32
4	THF	—	—	—

[a] Yield of isolated epoxide.
[b] Only the *trans*-isomer was formed as determined from the ^1H NMR coupling constant of the vicinal protons on the oxirane ring.
[c] Determined by HPLC analysis on a chiral stationary phase.
[d] Absolute configuration of the major enantiomer was determined to be (2*S*,3*R*) by comparison of the specific rotation and HPLC retention times with those reported in the literature.[26]

chiral catalyst was generated in situ by adding $ZnEt_2$ to the (*R*)-**L2**. The results of the Hetero-Diels–Alder reaction between Danishefsky's diene and benzaldehyde are shown in Table 2.



Scheme 8. Zinc-mediated enantioselective hetero-Diels–Alder reaction.

Table 2. Enantioselective hetero-Diels–Alder reaction catalysed by a chiral Zn-(*R*)-**L2** complex

Entry	*T* (°C)	Yield (%)[a]	ee (%)[b]
1	25	99	20
2	0	99	10

[a] Yield of isolated product.
[b] Determined by HPLC analysis on a chiral stationary phase.

The 2-phenyl-substituted 2,3-dihydro-4*H*-pyran-4-one was isolated in quantitative yield and low ee when conducting the reaction either at room temperature or at 0 °C (Table 2, entries 1 and 2). Remarkably, the ee was further decreased when the reaction temperature was lowered from 25 to 0 °C.

3. Conclusion

In summary, the (*R*)-BINOL-derived quinoid ligands (*R*)-**L1**, (*R*)-**L2**, (*R*)-**L4** and ligand precursor (*R*)-**26** were synthesised in a straightforward manner employing the [3+2+1]benzannulation reaction as the key step. Depending on the functionalisation of the binaphthol compound, two different structural patterns could be generated. The alkyne-functionalised binaphthol compounds generated quinone-funtionalities, which were attached to the binaphthol core through a C–C-single bond [(*R*)-**L1**, (*R*)-**L2**], while a chromium carbene-functionalised binaphthol was reacted to give directly annulated quinone moieties [(*R*)-**L4**]. Preliminary results have shown moderate activity of these ligands in enantioselective epoxidation and Hetero-Diels–Alder catalysis. Further studies aimed at the elucidation of the scope of these ligands in other metal-catalysed enantioselective reactions are currently in progress.

4. Experimental

4.1. General procedures

Reactions involving moisture- or/and air-sensitive intermediates were performed under argon atmosphere. Dichloromethane was distilled from CaH_2 under argon. Diethyl ether and tetrahydrofuran were freshly distilled from benzophenone ketyl radical under argon prior to use. Column chromatography was performed with silica

gel 60 (0.063–0.2 mm). All yields given refer to as isolated yields. Optical rotation data [$c = g/100$ ml] were measured on a Perkin–Elmer 431 polarimeter. NMR spectra were recorded on a 300 MHz spectrometer. The chemical shifts reported are in parts per million relative to TMS. IR spectra [cm^{-1}] were recorded on a Nicolet Magna 550 FT-IR spectrometer. MS (EI) [m/z (%)] and HRMS measurements were performed on a Kratos MS 50. MS (FAB) [m/z (%)] was performed on a Kratos Concept 1H-spectrometer.

The following compounds were prepared according to the literature procedures: (*R*)-2,2′-dimethoxy-1,1′-binaphthyl,[7] (*R*)-6,6′-dibrom-2,2′-diethoxy-1,1′-binaphthyl,[8] (*R*)-6,6′-di[(trimethylsilyl)ethynyl]-2,2′-diethoxy-1,1′-binaphthyl,[10] (*R*)-6,6′-di[(trimethylsilyl)ethynyl]-2,2′-dimethoxy-1,1′-binaphthyl,[10] (*R*)-6,6′-diethynyl-2,2′-diethoxy-1,1′-binaphthyl,[10a] (*R*)-6,6′-diethynyl-2,2′-dimethoxy-1,1′-binaphthyl,[10a] (*R*)-6,6′-dibrom-2,2′-dihydroxy-1,1′-binaphthyl,[9] (*R*)-6,6′-di[(trimethylsilyl)ethynyl]-2,2′-dihydroxy-1,1′-binaphthyl,[11] (*R*)-6,6′-diethynyl-2,2′-dihydroxy-1,1′-binaphthyl,[11] pentacarbonyl[methoxy(phenyl)-carbene]chromium,[29] borontriodide,[12] (*R*)-2,2′-methylenedioxy-1,1′-binaphthyl.[19]

4.2. (*R*)-2,2′-Diethoxy-1,1′-binaphthyl, 2

Ethylbromide (24 ml, 315 mmol) was added to a solution of (*R*)-BINOL (6.0 g, 21 mmol) and Cs_2CO_3 (27.4 g, 84 mmol) in acetone (250 ml). After stirring the solution at room temperature for 3 h, the reaction mixture was poured into H_2O (300 ml) and extracted with CH_2Cl_2 (3×100 ml). The combined organic layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The product was purified by recrystallisation from PE to give compound **2** (7.1 g, 99%) as colourless crystals; the spectroscopic and chiroptical data were in agreement with those reported in the literature.[8]

4.3. (*R*)-6,6′-Dibromo-2,2′-dimethoxy-1,1′-binaphthyl, 3

(*R*)-2,2′-Dimethoxy-1,1′-binaphthyl **1** (4.7 g, 15 mmol) was dissolved in CH_2Cl_2 (250 ml) and stirred at 0 °C. Bromine (1.68 ml, 33 mmol) was added in one portion with stirring and a stream of argon was bubbled through the solution to remove the evolving HBr. The reaction mixture was stirred for 5 h while the flask was allowed to warm to room temperature. During this procedure, the product precipitated as a white solid and was filtered off and dried in vacuo to give compound **3** (4.9 g, 95%) as a white powder; the spectroscopic and chiroptical data were in agreement with those reported in the literature.[9]

4.4. (*R*)-6,6′-Di(naphthalene-1,4-dione-2-yl)-2,2′-dimethoxy-1,1′-binaphthyl, 9

A solution of compound **7** (0.38 g, 1 mmol) and $(CO)_5Cr{=}C(OMe)(Ph)$ (1.41 g, 4.5 mmol) in CH_2Cl_2 (20 ml) was degassed by three freeze–pump–thaw cycles and warmed to 55 °C for 3 h under an inert atmosphere. The benzannulation reaction mixture was cooled to 0 °C and a 0.25 M solution of $(NH_4)_2Ce(NO_3)_6$ in H_2O (40 ml) slowly added. The mixture was stirred for 12 h and extracted with Et_2O (50 ml). The organic layer was washed with $NaHCO_3$ and NaCl, and finally dried over $MgSO_4$. After removing the solvents under reduced pressure, the residue was purified by column chromatography (CH_2Cl_2; $R_f = 0.5$) to afford the title compound **9** (0.48 g, 73%) as a red solid; $[\alpha]_D^{23} = -286$ (*c* 0.048, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 3.81 (s, 6H, OCH_3), 7.15 (s, 2H), 7.19 (d, 2H, $J = 9$ Hz), 7.41 (dd, 2H, $J = 9$, 2 Hz), 7.51 (d, 2H $J = 9$ Hz), 7.75 (m, 4H), 8.08 (d, 2H, $J = 9$ Hz), 8.10–8.22 (m, 4H), 8.23 (d, 2H, $J = 2$ Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 185.72 (C=O), 185.43 (C=O), 156.99 (C2), 148.56 (C2″), 135.36, 135.29, 134.42, 133.32, 132.85, 131.49, 131.08, 129.32, 129.06, 127.71, 127.39, 126.58, 126.12, 119.63, 115.13, 57.34 (OCH_3); MS (EI): m/z 626 (199), 580 (10); HRMS (EI) calcd for $C_{42}H_{26}O_6$ 626.1729, found 626.1706; IR (KBr) ν 3066, 2935, 2836, 1730, 1654, 1618, 1592, 1573, 1477, 1332, 1303, 1249, 1099, 1064, 1022, 889, 804, 779, 719.

4.5. (*R*)-6,6′-Di(naphthalene-1,4-dione-2-yl)-2,2′-diethoxy-1,1′-binaphthyl, 10

A solution of compound **8** (3.9 g, 10 mmol) and $(CO)_5Cr{=}C(OMe)(Ph)$ (14.1 g, 45 mmol) in *t*-BuOMe (50 ml) was degassed by three freeze–pump–thaw cycles and warmed to 60 °C for 12 h under an inert atmosphere. The benzannulation reaction mixture was cooled to 0 °C, and a 0.25 M solution of $(NH_4)_2Ce(NO_3)_6$ in H_2O (400 ml) was slowly added. The mixture was stirred for 1 h at 0 °C and extracted with Et_2O (500 ml). The organic layer was washed with $NaHCO_3$ and NaCl and finally dried over $MgSO_4$. After removing the solvents under a reduced pressure, the residue was purified by column chromatography (CH_2Cl_2; $R_f = 0.5$) to afford the title compound **10** (5.72 g, 87%) as a red solid; $[\alpha]_D^{23} = -265$ (*c* 0.022, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 1.01 (t, 6H, $J = 7$ Hz, CH3), 4.00 (m, 4H, OCH_2), 7.05 (s, 2H,), 7.10 (d, 2H, $J = 9$ Hz), 7.29 (dd, 2H, $J = 9$, 2 Hz), 7.37 (d, 2H, $J = 9$ Hz), 7.64 (m, 4H), 7.93 (d, 2H, $J = 9$ Hz), 8.00–8.10 (m, 4H), 8.11 (d, 2H, $J = 2$ Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 185.13 (C=O), 184.84 (C=O), 155.75 (C2), 147.97 (C2″), 137.82, 134.67, 133.79, 132.71, 132.22, 130.60, 130.40, 128.68, 128.35, 128.29, 127.08, 126.51, 125.95, 125.71, 119.86, 115.91, 65.00 (OCH_2), 14.98 (CH_3); MS (EI): m/z 654 (100); HRMS (EI) calcd for $C_{44}H_{30}O_6$ 654.2042, found 654.2042; IR (KBr) ν 2975, 2919, 1730, 1664, 1654, 1616, 1590, 1572, 1466, 1342, 1302, 1247, 1113, 888, 779, 717.

4.6. (*R*)-6,6′-Di(naphthalene-1,4-dione-2-yl)-2,2′-dihydroxy-1,1′-binaphthyl, (*R*)-L1

A stirred solution of compound **10** (0.65 g, 1 mmol) in CH_2Cl_2 (40 ml) was cooled to −78 °C and BBr_3 (0.52 ml, 5.5 mmol) was added dropwise under an inert atmosphere. After the reaction mixture was stirred for 1 h at −78 °C, it was warmed to room temperature and stirred for a further 2.5 h. H_2O (20 ml) was then added, and the reaction mixture was vigorously stirred

for 30 min and extracted with CH_2Cl_2 (100 ml). The organic phase was washed with H_2O and dried over $MgSO_4$. After removing the solvents under reduced pressure, the residue was purified by column chromatography [PE/AcOEt, 3/1 (v/v); $R_f = 0.8$] to afford the title compound (*R*)-**L1** (0.5 g, 84%) as a red solid; $[\alpha]_D^{23} = -310$ (*c* 0.06, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 5.8 (br s, 2H, OH), 6.93 (s, 2H), 7.17 (d, 2H, $J = 9$ Hz), 7.37 (m, 4H), 7.74 (m, 4H), 7.92 (d, 2H, $J = 9$ Hz), 8.04 (m, 2H), 8.11 (m, 2H), 8.15 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 185.57 (C=O), 185.25 (C=O), 155.10 (C2), 148.02 (C2″), 135.24, 134.96, 134.56, 134.51, 133.18, 133.09, 132.67, 131.37, 129.56, 129.36, 128.36, 127.75, 126.69, 125.23, 119.55, 111.72; MS (EI): *m*/*z* 598 (100); HRMS (EI) calcd for $C_{40}H_{22}O_6$ 598.1416, found 598.1408; IR (KBr) *v* 3416, 3066, 1664, 1618, 1591, 1571, 1473, 1276, 1250, 1214, 1154, 887, 815, 779, 717.

4.7. (*R*)-3,3′-Diodo-2,2′-diethoxy-1,1′-binaphthyl, 14

TMEDA (0.55 ml, 3.7 mmol) and a 1.6 M solution of *n*-BuLi in *n*-hexane (2.3 ml, 3.7 mmol) were subsequently added at room temperature to a solution of compound **2** (0.34 g, 1 mmol) in Et_2O (15 ml) under an inert atmosphere. After stirring the solution for 6 h at room temperature, the reaction mixture was cooled to −78 °C, and a solution of iodine (1 g, 4 mmol) in Et_2O (8 ml) was added. The reaction mixture was warmed to room temperature and stirred for an additional 10 h. The excess iodine was reduced with 1 M NaS_2O_5 (5 ml). The organic layer was separated, washed with NaCl and dried over $MgSO_4$. The solvent was removed under reduced pressure. Purification by column chromatography [PE/CH_2Cl_2, 2/1 (v/v); $R_f = 0.4$] afforded compound **14** (0.52 g, 88%) as a white solid; $[\alpha]_D^{23} = -78$ (*c* 0.35, $CHCl_3$), ^1H NMR (300 MHz, $CDCl_3$) δ 0.84 (t, 6H, $J = 7$ Hz, CH_3), 3.33 (m, 2H, OCH_AH_B), 3.73 (m, 2H, OCH_AH_B), 7.00 (d, 2H, $J = 8$ Hz), 7.18 (m, 2H), 7.32 (m, 2H), 7.70 (d, 2H, $J = 8$ Hz), 8.44 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.28 (C2), 139.67, 133.96, 132.01, 126.98, 126.93, 125.88, 125.55, 125.48, 93.07 (C3), 69.74 (OCH_2), 15.43 (CH_3); MS (EI): *m*/*z* 594 (100), 566 (10), 538 (35), 468 (30); HRMS (EI) calcd for $C_{24}H_{20}I_2O_2$ 593.9552, found 593.9551; IR (KBr) *v* 3052, 2975, 2933, 2885, 1560, 1490, 1413, 1382, 1344, 1226, 1149, 1041, 1022, 885, 748.

4.8. (*R*)-3,3′-Di[(trimethylsilyl)ethynyl]-2,2′-diethoxy-1,1′-binaphthyl, 15

To a stirred solution of compound **14** (1.6 g, 2.7 mmol), $PdCl_2(PPh_3)_2$ (0.11 g, 6 mol %), CuI (0.05 g, 6 mol %) in NEt_3 (18 ml) and under an inert atmosphere, freshly distilled trimethylsilyl acetylene (2.16 ml, 16.2 mmol) was added in one portion. After heating the reaction mixture to 40 °C for 20 h, it was cooled to room temperature and filtered through a pad of Celite. Additionally, the residue was washed with Et_2O (50 ml). The organic layers were combined and the solvents removed under reduced pressure. The remaining solid was purified by column chromatography [PE/CH_2Cl_2, 2/1 (v/v); $R_f = 0.6$] to yield the title compound **15** (1.1 g, 78%) as a white solid; $[\alpha]_D^{23} = -50$ (*c* 0.36, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 0.28 (s, 18H, $Si(CH_3)_3$), 0.92 (t, 6H, $J = 7$ Hz, CH_3), 3.71 (m, 2H, OCH_AH_B), 4.03 (m, 2H, OCH_AH_B), 7.06 (d, 2H, $J = 8$ Hz), 7.22 (m, 2H), 7.36 (m, 2H), 7.80 (d, 2H, $J = 8$ Hz), 8.14 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.24 (C2), 135.23, 134.73, 130.59, 128.41, 127.78, 126.50, 125.87, 125.73, 118.26, 102.92 (C≡C), 99.23 (C≡C), 70.13 (OCH_2), 16.29 (CH_3), 0.63 ($Si(CH_3)_3$); MS (EI): *m*/*z* 534 (100), 461 (5); HRMS (EI) calcd for $C_{34}H_{38}O_2Si_2$ 534.2410, found 534.2405; IR (KBr) *v* 3061, 2955, 2929, 2163, 1621, 1591, 1492, 1434, 1382, 1254, 1170, 1111, 840, 760.

4.9. (*R*)-3,3′-Diethynyl-2,2′-diethoxy-1,1′-binaphthyl, 16

A 1 M solution of KOH (81 ml) was added dropwise to a solution of compound **15** (14.4 g, 27 mmol) in MeOH/THF [540 ml, 1/1 (v/v)]. After stirring the reaction mixture for 3 h at room temperature, the solvents were removed under reduced pressure, and the residue was dissolved in AcOEt (30 ml). The organic phase was washed with H_2O and dried over $MgSO_4$. The solvent was removed under reduced pressure. Purification by column chromatography [PE/CH_2Cl_2, 2/1 (v/v); $R_f = 0.3$] afforded compound **16** (9.5 g, 90%) as a yellow solid; $[\alpha]_D^{23} = -7.5$ (*c* 0.39, $CHCl_3$); $[\alpha]_{436}^{23} = -25$ (*c* 0.39, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 0.75 (t, 6H, $J = 7$ Hz, CH_3), 3.17 (s, 2H, C≡H), 3.61 (m, 2H, OCH_AH_B), 3.87 (m, 2H, OCH_AH_B), 6.92 (d, 2H, $J = 8$ Hz), 7.08 (m, 2H), 7.22 (m, 2H), 7.66 (d, 2H, $J = 8$ Hz), 8.02 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.63 (C2), 135.01, 134.15, 129.90, 127.77, 127.35, 125.82, 125.24, 125.22, 116.60, 81.17 (C≡H), 80.90 (C≡C), 69.71 (OCH_2), 15.55 (CH_3); MS (EI): *m*/*z* 390 (100); HRMS (EI) calcd for $C_{28}H_{22}O_2$ 390.1619, found 390.1618; IR (KBr) *v* 3286, 3056, 2975, 2928, 2102, 1733, 1618, 1587, 1490, 1427, 1384, 1349, 1235, 1097, 1022, 890, 752, 617 cm^{-1}.

4.10. (*R*)-3,3′-Di(naphthalene-1,4-dione-2-yl)-2,2′-diethoxy-1,1′-binaphthyl, 17

A solution of compound **16** (0.5 g, 1.3 mmol) and $(CO)_5Cr{=}C(OMe)(Ph)$ (1.83 g, 5.85 mmol) in CH_2Cl_2 (25 ml) was degassed by three freeze–pump–thaw cycles and warmed to 55 °C for 5 h under inert atmosphere. The benzannulation reaction mixture was cooled to 0 °C and a 0.25 M solution of $(NH_4)_2Ce(NO_3)_6$ in H_2O (52 ml) was slowly added. The mixture was stirred for 12 h and extracted with Et_2O (50 ml). The organic layer was washed with $NaHCO_3$ and NaCl and finally dried over $MgSO_4$. After removing the solvents under reduced pressure, the residue was purified by column chromatography (CH_2Cl_2; $R_f = 0.4$) to afford the title compound **17** (0.2 g, 24%) as an orange solid; $[\alpha]_D^{23} = -110$ (*c* 0.05, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 0.70 (t, 6H, $J = 7$ Hz, CH_3), 3.40 (m, 2H, OCH_AH_B), 3.54 (m, 2H, OCH_AH_B), 7.14 (s, 2H), 7.24 (d, 2H, $J = 8$ Hz), 7.28 (m, 2H), 7.37 (m, 2H), 7.70 (m, 4H), 7.84 (d, 2H, $J = 8$ Hz), 7.87 (s, 2H), 8.10 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 185.77 (C=O), 184.81 (C=O), 154.46 (C2), 149.49 (C2″), 137.24, 135.72, 134.56, 134.42, 133.22, 132.94, 131.53, 130.57,

129.44, 129.10, 128.22, 127.65, 126.85, 126.59, 125.92, 124.88, 70.15 (OCH_2), 16.18 (CH_3); MS (EI): *m*/*z* 654 (100), 580 (50); HRMS (EI) calcd for $C_{44}H_{30}O_6$ 654.2042, found 654.2038; IR (KBr) *v* 3062, 2974, 2925, 2906, 1664, 1619, 1597, 1426, 1390, 1350, 1302, 1251, 1107, 1045, 1024, 892, 790.

4.11. (*R*)-3,3′-Di(naphthalene-1,4-dione-2-yl)-2,2′-diol-1,1′-binaphthyl, (*R*)-L2

A solution of compound **17** (0.08 g, 0.12 mmol) and $AlCl_3$ (0.16 g, 1.2 mmol) in CH_2Cl_2 (5 ml) was stirred for 12 h at room temperature under an inert atmosphere. After adding a 1 M solution of HCl (20 ml), the reaction mixture was vigorously stirred for another 12 h. The reaction mixture was extracted with CH_2Cl_2 (50 ml) and the organic layer subsequently washed with $NaHCO_3$ and NaCl. The organic phase was dried over $MgSO_4$ and the solvents were removed under reduced pressure. The remaining residue was purified by column chromatography with silica gel 60 (0.015–0.25 mm), [CH_2Cl_2/MeOH, 15/0.1 (v/v); $R_f = 0.64$] to afford the title compound (*R*)-**L2** as an orange solid; $[\alpha]_D^{26} = +63$ (*c* 0.15, THF); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.92 (s, 2H, OH), 7.17 (d, 2H, $J = 8$ Hz), 7.20 (s, 2H), 7.28–7.37 (m, 4H), 7.73 (d, 2H, $J = 6$ Hz), 7.74 (d, 2H, $J = 6$ Hz), 7.87 (d, 2H, $J = 8$ Hz), 7.96 (s, 2H), 8.03 (dd, 2H, $J = 6$, 3 Hz), 8.08 (dd, 2H, $J = 6$, 3 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 185.04 (C=O), 183.94 (C=O), 150.52 (C2), 147.50 (C2″), 137.06, 134.13, 133.90, 133.78, 132.37, 132.29, 132.13, 128.85, 128.73, 128.39, 127.11, 126.13, 124.69, 124.39, 124.21, 112.13; MS (EI): *m*/*z* 598 (33), 597 (38), 596 (91), 580 (100); IR (KBr) *v* 3428, 3062, 2962, 2926, 2854, 1662, 1621, 1593, 1446, 1301, 1252, 1128, 893, 785, 737.

4.12. (*R*)-3,3′-Diiodo-2,2-dihydroxy-1,1′-binaphthyl, 18

A solution of compound **14** (0.42 g, 0.7 mmol) in CH_2Cl_2 (10 ml) was cooled to −40 °C and a 1 M solution of BBr_3 in CH_2Cl_2 (7 ml) was added dropwise under an inert atmosphere. The solution was warmed to room temperature and stirred for 12 h. H_2O (30 ml) was added and the reaction mixture vigorously stirred for 30 min. The solution was extracted with CH_2Cl_2 (50 ml) and the organic layer dried over $MgSO_4$. After removing the solvent under reduced pressure, the remaining residue was purified by column chromatography [PE/AcOEt, 5/1 (v/v); $R_f = 0.5$] to afford the title compound **18** (0.38 g, 99%) as a pale yellow solid; the spectroscopic and chiroptical data were in agreement with those reported in the literature.[15]

4.13. (*R*)-3,3′-Di[(trimethylsilyl)ethynyl]-2,2′-dihydroxy-1,1′-binaphthyl, 19

To a stirred solution of compound **18** (0.38 g, 0.7 mmol), $PdCl_2(PPh_3)_2$ (0.03 g, 6 mol %), CuI (8 mg, 6 mol %) in NEt_3 (20 ml) and under an inert atmosphere, freshly distilled trimethylsilyl acetylene (0.6 ml, 4.2 mmol) was added in one portion. After heating the reaction mixture to 40 °C for 20 h, it was cooled to room temperature, and the solvent removed under reduced pressure. The remaining residue was dissolved in AcOEt and filtered through a pad of Celite. The filtrate was washed with a 1 M solution of HCl and dried over $MgSO_4$. After removing the solvent under reduced pressure, the remaining residue was dried in vacuo to give compound **19** (0.34 g, 99%) as a white solid; the spectroscopic and chiroptical data were in agreement with those reported in the literature.[16]

4.14. (*R*)-3,3′-Diethynyl-2,2′-dihydroxy-1,1′-binaphthyl, 20

A 1 M solution of KOH (3 ml) was added dropwise to a solution of compound **19** (0.34 g, 0.7 mmol) in MeOH/THF [20 ml, 1/1 (v/v)]. After stirring the reaction mixture for 3 h at room temperature, the solvents were removed under reduced pressure. The residue was dissolved in AcOEt (30 ml) and washed with a 1 M solution of HCl and H_2O. The organic layer was dried over $MgSO_4$ and the solvent removed under reduced pressure. Purification by column chromatography (CH_2Cl_2; $R_f = 0.3$) afforded compound **20** (0.23 g, 99%) as a yellow solid; the spectroscopic and chiroptical data were in agreement with those reported in the literature.[17]

4.15. (*R*)-3,3′-Diiodo-2,2′-methylenedioxy-1,1′-binaphthyl, 22

TMEDA (3.5 ml, 23.5 mmol) and a 1.6 M solution of *n*-BuLi in *n*-hexane (14.6 ml, 23.5 mmol) were subsequently added at room temperature to a solution of compound **21** (1.89 g, 6.34 mmol) in Et_2O (95 ml) under an inert atmosphere. After stirring the solution for 6 h at room temperature, the reaction mixture was cooled to −78 °C and a solution of iodine (6.34 g, 25.4 mmol) in Et_2O (50 ml) added. The reaction mixture was warmed to room temperature and stirred for an additional 10 h. The excess iodine was reduced with 1 M NaS_2O_5 (20 ml). The organic layer was separated, washed with NaCl and dried over $MgSO_4$. The solvent was removed under reduced pressure. Purification by column chromatography [PE/CH_2Cl_2, 3/1 (v/v); $R_f = 0.5$] afforded compound **22** (2.26 g, 65%) as a white solid; $[\alpha]_D^{23} = -542$ (*c* 0.35, $CHCl_3$); ^{1}H NMR (300 MHz, C_6D_6) δ 5.51 (s, 2H, CH_2), 6.91 (m, 2H), 7.08 (m, 2H), 7.35 (m, 4H), 8.23 (s, 2H); ^{13}C NMR (75 MHz, C_6D_6) δ 150.26 (C2), 140.02, 133.37, 132.21, 127.62, 127.08, 126.95, 126.79, 125.86, 102.20 (OCH_2O), 90.46 (C3); MS (EI): *m*/*z* 550 (40), 424 (70), 298 (100); HRMS (EI) calcd for $C_{21}H_{12}I_2O_2$ 549.8927, found 549.8928; IR (KBr) *v* 3056, 2966, 2906, 1571, 1496, 1384, 1344, 1236, 1201, 1153, 1152, 1041, 997, 888, 749.

4.16. (*R*)-3,3′-Di[(trimethylsilyl)ethynyl]-2,2′-methylenedioxy-1,1′-binaphthyl, 23

To a stirred solution of compound **22** (5.6 g, 10.2 mmol), $PdCl_2(PPh_3)_2$ (0.44 g, 6 mol %), CuI (0.12 g, 6 mol %) in NEt_3 (65 ml) and under an inert atmosphere, freshly distilled trimethylsilyl acetylene (8.7 ml, 61.2 mmol) was added in one portion. After heating the reaction mixture to 40 °C for 20 h, it was cooled to room temperature and filtered through a pad

of Celite. Additionally, the residue was washed with Et_2O (250 ml). The organic fractions were combined and the solvents were removed under reduced pressure. The remaining solid was purified by column chromatography [PE/CH_2Cl_2, 2/1 (v/v); $R_f = 0.7$] to yield the title compound **23** (4.2 g, 78%) as a light yellow solid; $[\alpha]_D^{23} = -729$ (*c* 0.28, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 0.12 (s, 18H, $Si(CH_3)_3$), 5.60 (s, 2H, CH_2), 7.03–7.25 (m, 6H), 7.65 (d, 2H, $J = 8$ Hz), 7.97 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 150.74 (C2), 134.39, 131.86, 131.04, 128.23, 126.86, 126.71, 126.40, 125.61, 116.44, 102.62 (OCH_2O), 100.44 (C≡C), 99.10 (C≡C), 0.00 ($Si(CH_3)_3$); MS (EI): *m*/*z* 490 (100), 462 (20); HRMS (EI) calcd for $C_{31}H_{30}O_2Si_2$ 490.1784, found 490.1787; IR (KBr) *v* 3054, 2958, 2898, 2156, 1592, 1498, 1411, 1330, 1249, 1151, 1091, 1020, 997, 842, 750.

4.17. (*R*)-3,3′-Diethynyl-2,2′-methylenedioxy-1,1′-binaphthyl, 24

A 1 M solution of KOH (26 ml) was added dropwise to a solution of compound **23** (4.2 g, 8.6 mmol) in MeOH/THF [170 ml, 1/1 (v/v)]. After stirring the reaction mixture for 3 h at room temperature, the solvents were removed under reduced pressure and the residue was dissolved in AcOEt (45 ml). The organic phase was washed with H_2O and dried over $MgSO_4$. The solvent was removed under reduced pressure. Purification by column chromatography [PE/CH_2Cl_2, 1/1 (v/v); $R_f = 0.6$] afforded compound **24** (2.9 g, 98%) as a yellow solid; $[\alpha]_D^{23} = -769$ (*c* 0.4, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 3.33 (s, 2H, C≡H), 5.80 (s, 2H, CH_2), 7.26–7.47 (m, 6H), 7.86 (d, 2H, $J = 8$ Hz), 8.20 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 150.85 (C2), 135.01, 132.03, 131.05, 128.30, 127.14, 126.77, 126.40, 125.80, 115.42, 103.01 (OCH_2O), 81.44 (C≡H), 79.28 (C≡C); MS (EI): *m*/*z* 346 (100), 318 (36); HRMS (EI) calcd for $C_{25}H_{14}O_2$ 346.0994, found 346.0995; IR (KBr) *v* 3289, 3052, 2967, 2910, 2100, 1619, 1592, 1498, 1413, 1357, 1328, 1265, 1243, 989, 891, 750, 684, 619.

4.18. (*R*)-3,3′-Di(naphthalene-1,4-dione-2-yl)-2,2′-methylenedioxy-1,1′-binaphthyl, 25

A solution of compound **24** (1.38 g, 4 mmol) and $(CO)_5Cr{=}C(OMe)(Ph)$ (5.64 g, 18 mmol) in *t*-BuOMe (20 ml) was degassed by three freeze–pump–thaw cycles and warmed to 60 °C for 12 h under an inert atmosphere. The benzannulation reaction mixture was cooled to 0 °C and a 0.25 M solution of $(NO_3)_6Ce(NH_4)_2$ (160 ml) was slowly added. The mixture was stirred for 1 h at 0 °C and extracted with Et_2O (200 ml). The organic layer was washed with $NaHCO_3$ and NaCl and finally dried over $MgSO_4$. After removing the solvents under reduced pressure, the residue was purified by column chromatography (CH_2Cl_2; $R_f = 0.4$) to afford the title compound **25** (0.53 g, 22%) as an orange solid; $[\alpha]_D^{23} = -158$ (*c* 0.36, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 5.50 (s, 2H, CH_2), 7.18 (s, 2H), 7.35–7.55 (m, 6H), 7.78 (m, 4H), 7.97 (d, 2H, $J = 8$ Hz), 7.99 (s, 2H), 8.16 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 184.84 (C=O), 184.03 (C=O), 148.69 (C2), 147.84 (C2″), 137.24, 133.95, 133.87, 132.92, 132.36, 132.19, 131.10, 130.90, 128.69, 127.31, 127.04, 127.01, 126.98, 126.21, 126.02, 125.73, 103.42 (OCH_2O); MS (EI): *m*/*z* 610 (100), 582 (23); HRMS (EI) calcd for $C_{41}H_{22}O_6$ 610.1416, found 610.1418; IR (KBr) *v* 3057, 2915, 1718, 1672, 1596, 1299, 1251, 993, 725.

4.19. (*R*)-3,3′-Di(2-naphthalene-1,4-dimethoxy)-2,2′-methylenedioxy-1,1′-binaphthyl, 26

NaS_2O_4 (1.8 g, 10.4 mmol) was added to a solution of compound **25** (0.53 g, 0.87 mmol) and $(n\text{-Bu})_4NBr$ (66 mg, 2 mmol) in THF (5 ml) and H_2O (2 ml) at room temperature. After 15 min, KOH (2.25 g, 40 mmol) was added and after 5 min Me_2SO_4 (3.48 ml, 36.6 mmol). The reaction mixture was stirred for 12 h at room temperature and extracted with CH_2Cl_2 (10 ml). The organic layer was dried over $MgSO_4$ and the solvent removed under reduced pressure. Purification by column chromatography [PE/CH_2Cl_2, 3/1 (v/v); $R_f = 0.7$] afforded compound **26** (0.44 g, 76%) as a yellow solid; $[\alpha]_D^{23} = -184$ (*c* 0.2, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 3.51 (s, 6H, CH_3), 3.85 (s, 6H, CH_3), 5.35 (s, 2H, CH_2), 6.72 (s, 2H), 7.28 (m, 2H), 7.42 (m, 6H), 7.55 (d, 2H, $J = 8$ Hz), 7.89 (d, 2H, $J = 8$ Hz), 8.03 (s, 2H), 8.04 (m, 2H), 8.18 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.32 (C2), 149.37(C1″), 147.60 (C4″), 132.10, 131.92, 131.45, 131.20, 128.79, 128.50, 127.06, 127.02, 126.74, 126.37, 126.08, 126.02, 125.72, 125.32, 122.32, 106.97, 102.82 (OCH_2O), 61.84 (OCH_3), 55.81 (OCH_3); MS (EI): *m*/*z* 670 (50), 639 (8), 608 (10); HRMS (EI) calcd for $C_{45}H_{34}O_6$ 670.2355, found 670.2351; IR (KBr) *v* 3068, 2931, 2836, 1625, 1591, 1506, 1456, 1413, 1364, 1228, 1095, 997, 769, 750.

4.20. (*R*)-6,6′-(2,2′-Dimethoxy-1,1′-binaphthyl)-bis-[pentacarbonyl(methoxy)carbene-chromium], 27

A solution of compound **3** (0.94 g, 2 mmol) in THF (50 ml) was cooled to −78 °C, and 3.5 ml (5.1 mmol) of a 1.48 M solution of *t*-BuLi in *n*-pentane added dropwise to the solution under an inert atmosphere. The resulting yellow solution was stirred for 30 min at −78 °C and then warmed to −20 °C. After adding $Cr(CO)_6$ (1.11 g, 5.1 mmol) in one portion at this temperature, the reaction mixture was warmed to room temperature. The solvent was evaporated under reduced pressure and the remaining residue dissolved in H_2O (40 ml). Me_3OBF_4 (0.77 g, 5.1 mmol) was added in one portion and the resulting red solution was stirred for 30 min. The organic layer was extracted with CH_2Cl_2 (3×30 ml) under an inert atmosphere and the combined organic layers were filtered through a pad of $MgSO_4$. The solvent was evaporated under reduced pressure and the remaining residue was purified by column chromatography [Et_2O/PE, 3/1 (v/v); $R_f = 0.6$] to afford the title compound **27** (1.25 g, 80%) as a red solid; ^1H NMR (300 MHz, $CDCl_3$) δ 3.82 (s, 6H, OCH_3), 4.85 (s, 6H, $OCH_{3Carbene}$), 7.11 (d, 2H, $J = 9$ Hz), 7.43 (dd, 2H, $J = 9$, 1.7 Hz), 7.53 (d, 2H, $J = 9$ Hz), 8.15 (d, 2H, $J = 9$ Hz), 8.22 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 345.74 (C=Cr), 224.68 (CO_{trans}), 217.31 (CO_{cis}), 157.78

(C2), 148.95 (C6), 135.93, 132.88, 128.94, 128.30, 125.46, 123.32, 119.19, 115.24, 67.97 ($OCH_{3Carbene}$), 57.17 (OCH_3); MS (FAB): *m/z* 782 (10), 698 (5), 642 (100), 613 (42), 586 (8), 558 (10), 502 (20); IR (CH_2Cl_2) *v* 2060, 1983, 1944.

4.21. (−)-2,2′,3,3′-Tetraethyl-8,8′-dimethoxy-7,7′-bis(phenanthrene-1,4-dione), 28

A solution of freshly distilled 3-hexyne (0.26 ml, 2.28 mmol) and biscarbene complex **27** (0.3 g, 0.38 mmol) in CH_2Cl_2 (5 ml) was degassed by three freeze–pump–thaw cycles and warmed to 55 °C for 12 h under an inert atmosphere. The benzannulation reaction mixture was cooled to 0 °C and a 0.25 M solution of $(NH_4)_2Ca(NO_3)_6$ (15 ml) was slowly added. The mixture was stirred for 1 h at 0 °C and extracted with Et_2O (20 ml). The organic layer was washed with $NaHCO_3$ and NaCl and finally dried over $MgSO_4$. After removing the solvents under reduced pressure, the residue was purified by column chromatography (CH_2Cl_2; $R_f = 0.67$) to afford the title compound **28** (90 mg, 40%) as an orange solid; $[\alpha]_D^{23} = -10$ (*c* 0.14, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.14 (t, 6H, $J = 7$ Hz, CH_3), 1.21 (t, 6H, $J = 7$ Hz, CH_3), 2.61 (q, 4H, $J = 7$ Hz, CH_2), 2.70 (q, 4H, $J = 7$ Hz, CH_2), 3.78 (s, 3H, OCH_3), 7.32 (d, 2H, $J = 9$ Hz), 7.61 (d, 2H, $J = 9$ Hz), 7.87 (d, 2H, $J = 9$ Hz), 9.70 (d, 2H, $J = 9$ Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 188.8 (C=O), 185.8 (C=O), 156.7 (C8), 149.2, 145.3, 137.2, 130.8, 130.6, 128.4, 125.1, 122.7, 118.9, 116.6, 56.4 (OCH_3), 20.5 (CH_2), 19.8 (CH_2), 14.2 (CH_3), 14.0 (CH_3); MS (EI): *m/z* 586 (100), 543 (7); HRMS (EI) calcd for $C_{38}H_{34}O_6$ 586.2355, found 586.2355; IR (KBr) *v* 2968, 2935, 2873, 2843, 1651, 1605, 1468, 1309, 1267, 1250, 1095, 1088, 1065, 808.

4.22. (−)-2,2′,3,3′-Tetraethyl-8,8′-dihydroxy-7,7′-bis(phenanthrene-1,4-dione), (*R*)-L4

A solution of compound **28** (65 mg, 0.11 mmol) in CH_2Cl_2 (1 ml) was cooled to −10 °C and BBr_3 (0.8 ml) was added dropwise under an inert atmosphere. The solution was warmed to room temperature and stirred for 12 h. H_2O (2 ml) was added and the reaction mixture vigorously stirred for 30 min. The solution was extracted with CH_2Cl_2 (10 ml) and the organic layer dried over $MgSO_4$. After removing the solvent under reduced pressure, the remaining residue was purified by column chromatography (Et_2O) to afford the title compound (*R*)-**L4** (43 mg, 70%) as an orange solid; $[\alpha]_D^{23} = -160$ (*c* 0.11, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.02 (t, 6H, $J = 7$ Hz, CH_3), 1.22 (t, 6H, $J = 7$ Hz, CH_3), 2.44 (m, 4H, CH_2), 2.64 (m, 4H, CH_2), 6.97 (d, 2H, $J = 9$ Hz), 7.02 (s, 2H, OH), 7.39 (d, 2H, $J = 9$ Hz), 7.44 (d, 2H, $J = 9$ Hz), 9.44 (d, 2H, $J = 9$ Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 188.0, 185.6, 155.6, 149.8, 145.19, 137.3, 131.6, 129.8, 129.7, 127.9, 125.3, 123.6, 121.9, 111.4, 20.6, 19.7, 14.1, 13.8; MS (EI): *m/z* 558 (100), 515 (10); HRMS (EI) calcd for $C_{36}H_{30}O_6$ 558.2042, found 558.2044; IR (KBr) *v* 3434, 2976, 2935, 2875, 1653, 1603, 1468, 1308, 1281, 1248, 818.

4.23. (−)-2,2′,3,3′-Tetraethyl-(8-hydroxy,8′-methoxy)-7,7′-bis(phenanthrene-1,4-dione), 29

Purification by column chromatography (CH_2Cl_2; $R_f = 0.5$) afforded the title compound **29** (19 mg, 30%) as an orange solid; $[\alpha]_D^{23} = -30$ (*c* 0.136, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.11 (m, 6H, CH_3), 1.21 (m, 6H, CH_3), 2.59 (m, 4H, CH_2), 2.69 (m, 4H, CH_2), 3.84 (s, 3H, OCH_3), 5.57 (s, 1H, OH), 7.17 (d, 1H, $J = 9$ Hz), 7.32 (d, 1H, $J = 9$ Hz), 7.52 (d, 1H, $J = 9$ Hz), 7.61 (d, 1H, $J = 9$ Hz), 7.80 (d, 1H, $J = 9$ Hz), 7.85 (d, 1H, $J = 9$ Hz), 9.60 (d, 1H, $J = 9$ Hz), 9.72 (d, 1H, $J = 9$ Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 188.7 (C=O), 188.4 (C=O), 185.8 (C=O), 185.5 (C=O), 157.7 (C), 153.6 (C), 149.4, 145.4, 145.3, 137.3, 137.2, 132.1, 130.5, 130.4, 130.2, 128.5, 128.2, 125.4, 125.3, 123.7, 122.9, 121.3, 116.3, 115.1, 114.9, 56.4 (OCH_3), 20.5 (CH_2), 20.5 (CH_2), 19.8 (CH_2), 14.2 (CH_3), 14.0 (CH_3), 13.9 (CH_3); MS (EI): *m/z* 572 (100), 529 (9); HRMS (EI) calcd for $C_{37}H_{32}O_6$ 572.2199, found 572.2203; IR (KBr) *v* 3421, 2970, 2935, 2875, 2843, 1650, 1603, 1468, 1308, 1269, 1250, 1093, 812.

4.24. General procedure for the enantioselective epoxidation

(*R*)-**L1** (0.12 g, 0.2 mmol) was dissolved in Et_2O (20 ml) in a Schlenk flask equipped with a magnetic stirring bar under an inert atmosphere. After cooling to 0 °C with an ice-bath, $ZnEt_2$ (0.33 ml, 0.36 mmol, 1.1 M solution in toluene) was added under stirring. After 15 min, chalcone (1 mmol) and TBHP (0.24 ml, 1.2 mmol, 5–6 M in decane) were added, and the resulting mixture allowed to warm to room temperature overnight. The reaction was quenched with aq satd $NaHSO_3$ and extracted with EtOAc. The organic layer was washed with aq Na_2CO_3 and brine. The combined organic layers were dried over $MgSO_4$ and the solvent evaporated in vacuo. The residue was purified by column chromatography (CH_2Cl_2). In all cases, (*R*)-**L1** was recovered almost quantitatively. The enantiomeric excesses of the epoxide were determined by HPLC analysis on a stationary phase: Chiralcel OD column with *n*-hexane/2-propanol as eluent (95:5, 0.7 ml/min) and 254 nm UV detector. The absolute configuration of the product has been assigned by comparison of specific rotation with literature values and the elution order of the two enantiomers on the HPLC column.

4.25. General procedure for the enantioselective Hetero-Diels–Alder reaction

A solution of (*R*)-**L2** (0.06 g, 0.1 mmol) and $ZnEt_2$ (0.11 ml, 0.12 mmol, 1.1 M solution in toluene) in toluene (4 ml) was stirred in a Schlenk flask equipped with a magnetic stirring bar under an inert atmosphere for 30 min. Freshly distilled benzaldehyde (0.1 ml, 1 mmol) was added and after the reaction mixture was kept for 30 min at 0 °C, Danishefsky's diene (0.2 ml, 1 mmol) was charged. The reaction was quenched after 12 h by introducing TFA (2 ml). The reaction mixture was extracted with Et_2O and the organic layer was washed

with aq satd $NaHCO_3$. The organic layer was dried over $MgSO_4$ and the solvent was evaporated in vacuo. The residue was purified by column chromatography [PE/EE, 4/1 (v/v)]. The enantiomeric excess of the product was determined by HPLC analysis on a stationary phase: Chiralcel OD column with *n*-hexane/2-propanol as eluent (90:10, 1.0 ml/min) and 254 nm UV detector.

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