# Novel [6]- and [7]Helicene-Like Quinones via Mono- and Bidirectional Chromium-Templated Benzannulation of Bridged Binaphthyl Carbene Complexes[‡]

**Jochen F. Schneider,[a] Martin Nieger,[b] Kalle Nättinen,[c] Burhanshah Lewall,[b] Edgar Niecke,[b] and Karl Heinz Dötz*[a]**

*Dedicated to Professor Helmut G. Alt on the occasion of his 60th birthday*

**Keywords:** Benzannulation / Carbene complexes / Chromium / Circular Dichroism / Cyclic voltammetry / Quinones

A new organometallic approach to novel, functionalised, helicene-like quinones and bisquinones has been developed based on the chromium-templated [3+2+1] benzannulation reaction. The [5]helicene-analogous monocarbene chromium complexes **4**, **5**, **17** and **19**, derived from dibromo-substituted methylene- or silylene-tethered binaphthols **2** and **3**, react with various alkynes to give [6]helicene-like quinones **6**–**13** and **20**–**29** after oxidative work-up. A rare competition of angular vs. linear annulation is observed for the incorporation of phenylacetylene that affords quinones **21/22** and **28/29**. Protection of the phenolic benzannulation product with camphanic acid chloride **14**, followed by chromatographic separation, provides access to enantiopure [6]helicene-like derivatives. Bidirectional benzannulation of helical biscarbene complexes **16** and **18** results in bisangular and angular-linear bisquinones **30**–**36** after oxidative work-up. X-ray crystal structures of the heterocyclic [5]-, [6]- and [7]helicene-derivatives and the angular-linear annulation products indicate an increasing distortion of the helical framework with progressive annulation. The CD spectra of the methylene-tethered biaryls (**3**, **9**, **14**, **36**) reflect the different interactions between the aryl chromophores; cyclovoltammetric studies of bisangular bisquinones **30** and **33** reveal three reversible, one-electron reduction steps.


## Introduction

Helicenes are screw-shaped benzologues of phenanthrene consisting of *ortho*-fused aromatic rings,[2] of which hexahelicene was the first example to be synthesised and optically resolved by Newman and Lednicer in 1955.[3] Replacement of a benzene ring by a heteroarene leads to heterohelicenes[4] with different bond angles at the specific positions affecting the whole helical framework. An even greater influence arises from the incorporation of larger rings, for example seven-membered heterocycles,[5] which reduce the helicene's rigidity but restrict the conformational flexibility of the parent axial-chiral biaryls.[6] Most representatives of this class of compounds are metal-tethered or differently bridged binaphthyls, which have a wealth of applications in asymmetric catalysis.[7] Beyond that only a few higher homologues are hitherto known.[8] Recently, helicenes have also encouraged intense studies on the use as chiral ligands[9] for molecular recognition, asymmetric induction, kinetic resolution or enantioselective catalysis, or for inducing unusual chiroptical or electronic properties[10] in materials science.[11]

The classical synthesis of helicenes provides only scarce amounts of product because the key reaction step − the oxidative photocyclisation of stilbene-type precursors[12] − is restricted to very dilute solutions. Several new, non-photochemical routes have now emerged[13] that rely, for example, on the cross-coupling of condensed (hetero)aromatic units followed by ring closure, or on the Diels–Alder cycloaddition of *p*-benzoquinone to divinyl arenes, as elaborated by Katz and co-workers.[14] An enantioselective modification has been developed by Carreño et al.,[15] who use ($S_S$)-2-(*p*-tolylsulfinyl)-1,4-benzoquinone and vinyl dihydrophenanthrenes to obtain enantio-enriched dihydro[5]helicene quinones or bisquinones. Moreover, various synthetic methodologies involving transition metals have been reported,[16] in particular double or triple $Co^I$-catalysed

[‡] Reactions of Complex Ligands, 101. Part 100: Ref.[1]

[a] Kekulé-Institut für Organische Chemie und Biochemie der Rheinischen Friedrich-Wilhelms-Universität,
Gerhard-Domagk-Straße 1, 53121 Bonn, Germany
Fax: +49-228-735813
E-mail: doetz@uni-bonn.de
[b] Institut für Anorganische Chemie der Rheinischen Friedrich-Wilhelms-Universität,
Gerhard-Domagk-Straße 1, 53121 Bonn, Germany
[c] Department of Chemistry, University of Jyväskylä,
P. O. Box 35, 40014 Jyväskylä, Finland

 **DOI: 10.1002/ejoc.200400800**  

[2+2+2] cycloisomerisation reactions of aromatic hexa- or nonaynes to heliphenes, $Pd^0$-catalysed [2+2+2] cyclotrimerisation of arynes to double helicenes or $Co^0/Ni^0$-catalysed [2+2+2] cycloisomerisation of aromatic triynes to tetrahydrohelicenes.

Here we report a novel organometallic approach based on the chromium-templated [3+2+1] benzannulation reaction[17] of Fischer-type carbene complexes.[18] So far, this strategy has been restricted to small helicene derivatives like allocolchicin[19] or TBDMS-protected hydroquinoid tri- or tetracyclic (hetero)arenes.[20] We now present the formation of extended heterocyclic helicene-like quinones derived from the benzannulation of bridged binaphthyl carbene complexes with different alkynes, followed by oxidative work-up.

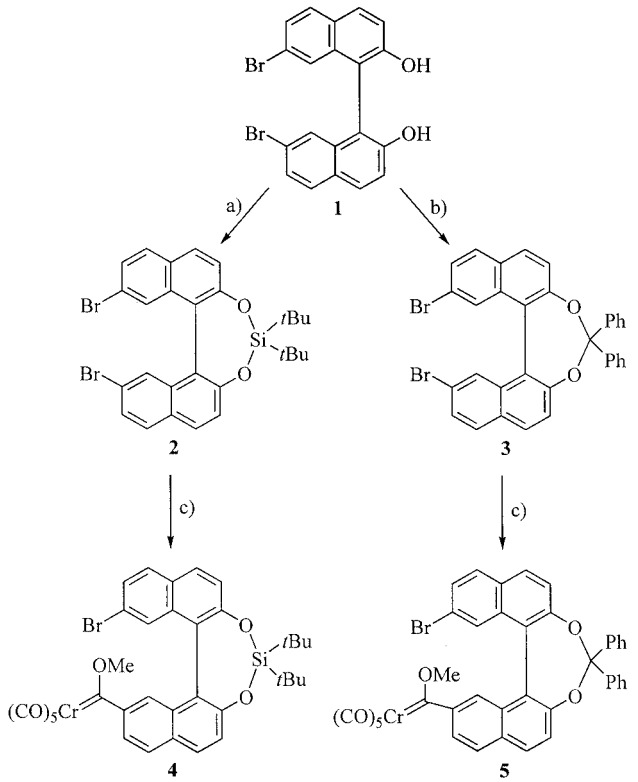
## Results and Discussion

### Bromo-Substituted [6]Helicene-Like Quinones

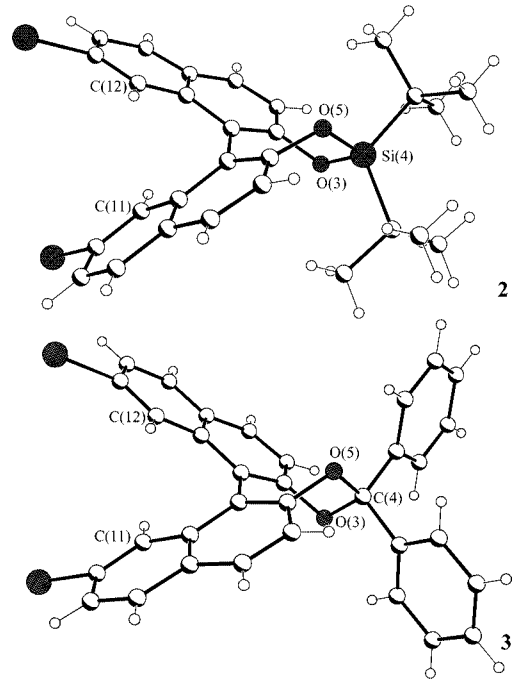
7,7′-Dibromo-2,2′-dihydroxy-1,1′-binaphthyl (**1**) was prepared according to a literature procedure[21] starting from 2,7-dihydroxynaphthalene, which was transformed into 7-bromo-2-hydroxynaphthalene and oxidatively coupled with $CuCl_2$/*tert*-butylamine. Optical resolution of this compound has been reported by chromatographic separation of the diastereomeric camphor sulfonates or the menthyl chloroformates. For the present work, binaphthyl **1** emerged as a suitable precursor for the construction of helical shapes as the 2,2′-position allows a facile bridging or cyclisation to pentahelicene-like structures suited for adjustable conformation. Moreover, the bromo substituents allow for a straightforward conversion into mono- or biscarbene complexes, which in turn serve as starting materials for homologisation of the parent helicenoids by benzannulation.

Di-*tert*-butyldichlorosilane and dichlorodiphenylmethane turned out to form appropriate linkers, as already described for other systems.[22] Advantageously, they withstand chromatographic conditions, subsequent lithiation or oxidative work-up, and the bulky *tert*-butyl or phenyl groups effectively shield the 3,3′-position and prevent undesired lithiation, as reported for the preparation of 3,3′-biscarbene functionalised 2,2′-dimethoxy-1,1′-binaphthyl.[23]

At first we focused on the incorporation of one metal carbene moiety to study the feasibility of a monobenzannulation and leave a bromo substituent for further modifications.[14c] A single metal–halogen exchange in racemic **2** or **3** with 1.1 equivalents of *n*-butyllithium was carried out at –88 °C (to prevent Wurtz-like reactions), followed by ad-




Scheme 1. Synthesis of monocarbene complexes **4** and **5**; reagents and conditions: a) $tBu_2SiCl_2$, $NEt_3$, DMF, room temp., 12 h, 77%; b) $Ph_2CCl_2$, 145 °C, 30 min, 68%; c) *n*BuLi, $Cr(CO)_6$, $Me_3OBF_4$, 71% for **4**, 75% for **5**.




| | 2 | 3 |
|---|---|---|
| C(11)···C(12) | 3.05 | 3.09 |
| X – O(3/5) | 1.66 | 1.43 |
| O(3)···O(5) | 2.66 | 2.35 |
| O(3) – X – O(5) | 106.6 | 110.1 |
| C(2a/5a) – O(3/5) – X | 121.1 | 115.0 |

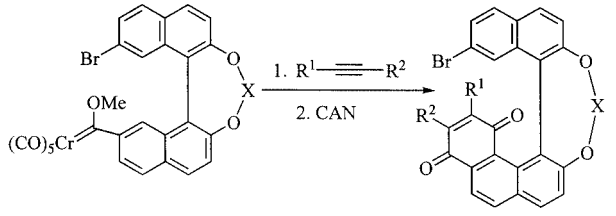
Figure 1. Molecular structures of silylene- and methylene-tethered binaphthols **2** and **3** with selected bond distances [Å] and angles [°] (average values for various independent molecules and the corresponding parts in each molecule).

dition of hexacarbonyl chromium to afford the pentacarbonyl acyl chromate, which underwent *O*-alkylation with trimethyloxonium tetrafluoroborate to give helical (methoxy)carbene complexes **4** and **5**, respectively (Scheme 1).

X-ray studies of **2** and **3** (Figure 1) revealed a similar dihedral angle along the biaryl axis (ca. 53.5°), compared to 60° reported for other binaphthyl derivatives bearing the same tethers,[24] which suggests conformational flexibility. The dihedral angle is twice as large as for substituted [5]helicenes and derivatives doubly functionalised with bulky diphenylphosphanyl groups at complementary positions C(10) and C(13) (25.5–31.4°).[25]

A typical angular [3+2+1] benzannulation of the two racemic monocarbene complexes with various alkynes in dichloromethane at 55 °C led, after oxidative work-up with ceric ammonium nitrate (CAN), to the substituted [6]helicene-like quinones **6**–**13** in moderate yields (Scheme 2). Oxidative demetallation was applied to avoid a tedious chromatographic purification of the air-sensitive mixture of metal-coordinated and uncomplexed hydroquinones which resist *O*-protection with *tert*-butyldimethylsilyl chloride.



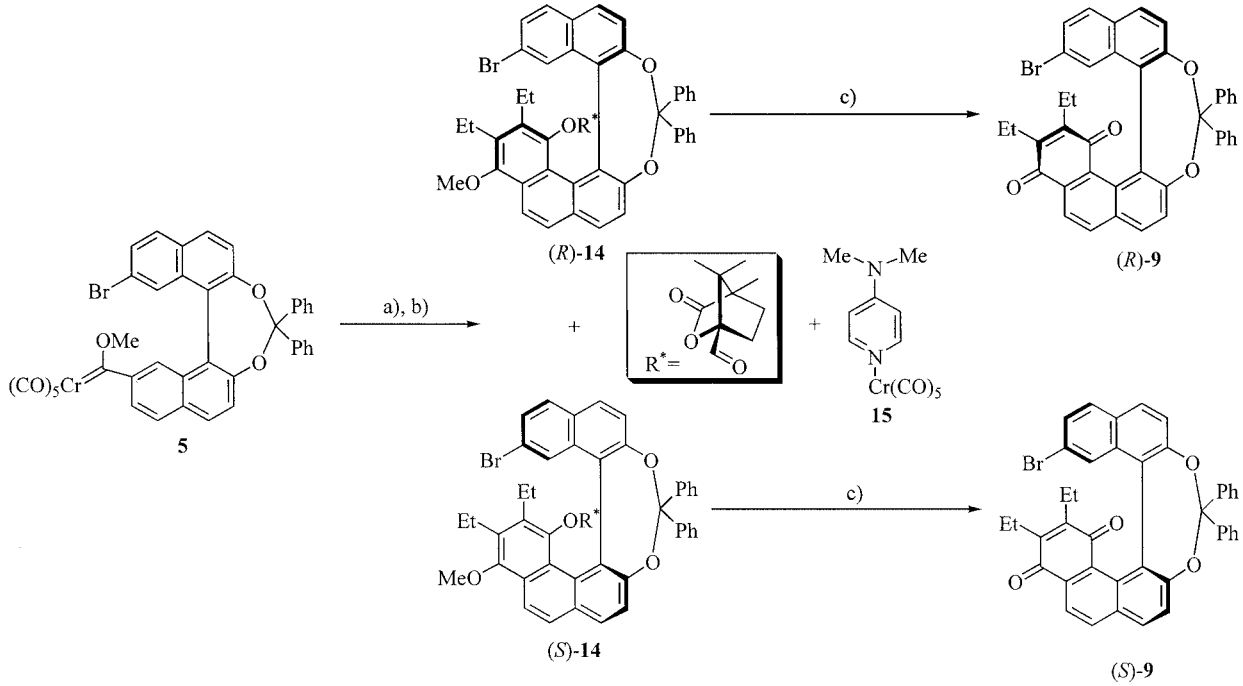

| | | $R^1$ | $R^2$ | |
|---|---|---|---|---|
| **4** | X = Si-*t*Bu$_2$ | | | |
| **6** | | Et | Et | 52 % |
| **7** | | *t*Bu | H | 49 % |
| **8** | | Ph | H | 36 % |
| **5** | X = C-Ph$_2$ | | | |
| **9** | | Et | Et | 46 % |
| **10** | | *t*Bu | H | 44 % |
| **11** | | *n*Pr | H | 40 % |
| **12** | | Oct | H | 33 % |
| **13** | | Ph | H | 18 % |

Scheme 2. Monodirectional benzannulation to [6]helicene-like quinones **6**–**13**.

## Optical Resolution of Heterocyclic Helicene Quinones by Protection as the Camphanate Ester

Whilst searching for a chiral protective group we turned our attention to camphanate ester, which has previously been applied to the protection of naphthohydroquinone.[26] For the present work it is an eminently practical, one-pot reaction to get the non-racemic annulation product after chromatographic separation (Scheme 3), in comparison with Katz's access to analogous mono- or dicamphanates.[27]

Since our preliminary studies showed good results for the benzannulation of **5** with 3-hexyne, we extended this reaction to obtain pure enantiomers of [6]helicene derivatives. The phenolic group on the outer periphery is already methylated, leaving the more important one for optical resolution on the inside of the ring system for subsequent acylation with (1*S*)-(–)-camphanoyl chloride in the presence of triethylamine and DMAP. The latter is known to assist acylation of sterically hindered phenols.[28] Moreover, it nips off the shielding $Cr(CO)_3$ moiety to form the isolated by-product DMAP·$Cr(CO)_5$, presumably with participation




Scheme 3. Angular benzannulation and preparation of non-racemic monoquinone **9**; reagents and conditions: a) 3-hexyne, THF, 55 °C, 3 h; b) (1*S*)-(–)-camphanoyl chloride, DMAP, $NEt_3$, room temp., 12 h, 19% yield of each diastereomer; c) KOH powder, then CAN, 82%.

of solvated carbon monoxide. A similar abstraction has been previously observed for $Cr(CO)_5$ carbene complexes.[29]

The resulting diastereomers were separated by column chromatography, with the (*R*)- or (*M*)-helicene derivative, whose absolute configuration was determined by X-ray crystallography, eluting first, followed by the (*S*)- or (*P*)-counterpart. In helicen-1-ol (1*S*)-camphanates, these differences of $R_f$ are due to the variable O=CCO conformation, which is antiperiplanar in (*M*)-helicene frameworks (Figure 2) and synperiplanar in the others.[30] In the former the lactone carbonyl points towards the helix, whereas it points away in the latter.

Treatment with KOH powder and oxidation with CAN converted the diastereomers of **14** into the enantiomerically pure samples of heterocyclic [6]helicene-like quinone **9**.

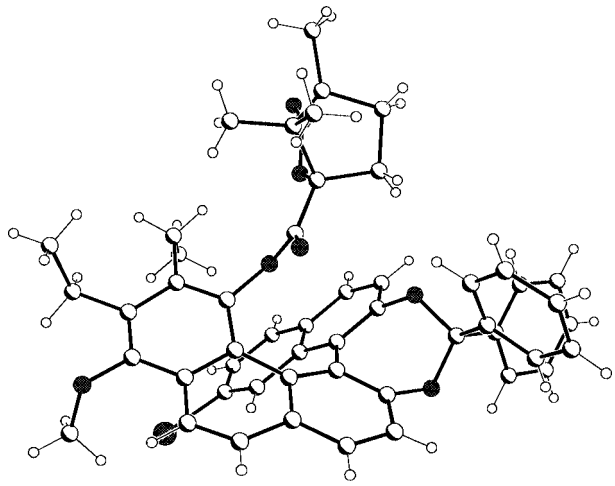
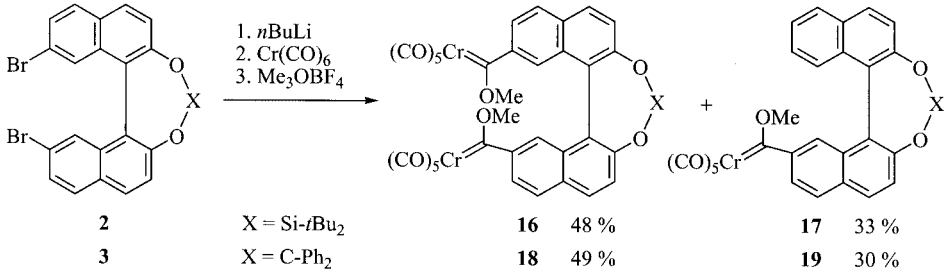


Figure 2. Molecular structure of camphanate (*R*)-**14** (see Figure 3 for selected bond lengths and angles).

## Synthesis of Helical Biscarbene Complexes

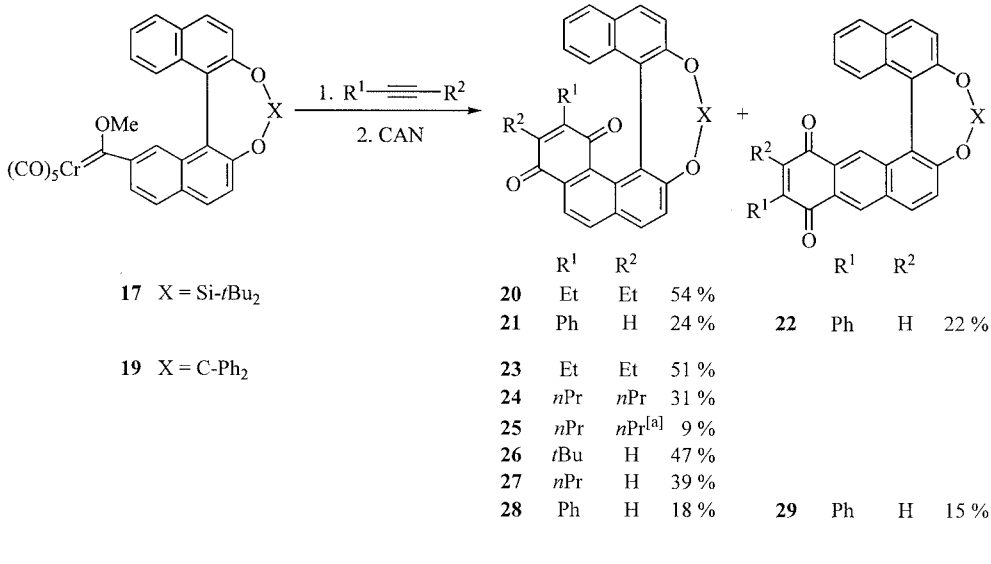
The synthesis of the racemic biscarbene complexes **16** and **18** followed the previously described Fischer route using two equivalents of the respective reagents to afford the bimetallated helicene derivatives along with monometallated by-product **17** or **19**, respectively (Scheme 4). The problem of incomplete biscarbene functionalisation has been previously reported for other (hetero)arenes.[31] A feasible route to metal monocarbenes is a dilithiation with subsequent addition of only one equivalent of hexacarbonyl chromium. The acyl chromate intermediate formed hampers the second addition of $Cr(CO)_6$, resulting in final hydrolysis during purification on silica gel.[32]




**2** X = Si-*t*Bu$_2$
**3** X = C-Ph$_2$

**16** 48 %
**18** 49 %
**17** 33 %
**19** 30 %

Scheme 4. Synthesis of helical mono- and biscarbene complexes **16**–**19**.

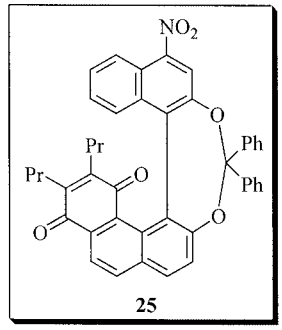



**17** X = Si-*t*Bu$_2$

**19** X = C-Ph$_2$

| | $R^1$ | $R^2$ | |
|---|---|---|---|
| **20** | Et | Et | 54 % |
| **21** | Ph | H | 24 % |
| **23** | Et | Et | 51 % |
| **24** | *n*Pr | *n*Pr | 31 % |
| **25** | *n*Pr | *n*Pr[a] | 9 % |
| **26** | *t*Bu | H | 47 % |
| **27** | *n*Pr | H | 39 % |
| **28** | Ph | H | 18 % |

| | $R^1$ | $R^2$ | |
|---|---|---|---|
| **22** | Ph | H | 22 % |
| **29** | Ph | H | 15 % |




**25**

Scheme 5. Angular vs. linear monobenzannulation of unsubstituted carbene complexes **17** and **19**. [a] 1-$NO_2$-substituted by-product.

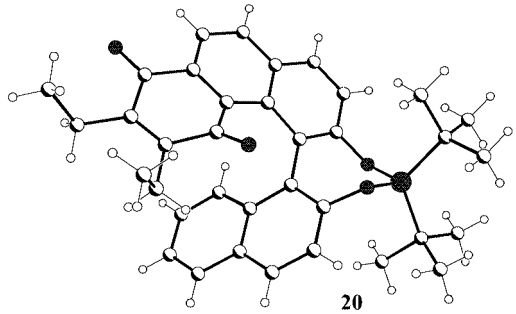
  

### Angular vs. Linear Benzannulation of Helical Monocarbene Complexes

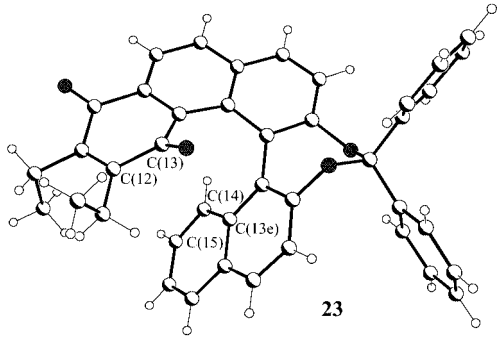
A series of additional monobenzannulation reactions was performed under the same conditions (Scheme 5) to study the cycloaddition without the steric influence of the halide. Apart from generally slightly better yields, the reaction with phenylacetylene surprisingly afforded a unique example of competing regioselectivity of benzannulation. This rare observation[33] is unprecedented for the half counterpart,[34] chromium 2-naphthylcarbene, which in principle also offers two regiochemical alternatives but undergoes only angular benzannulation. The angular regiopreference may be rationalised in terms of the higher electron density at C(1) of the naphthalene skeleton compared with C(3), which controls the electrophilic ring closure of the $\eta^4$-vinyl ketene intermediate.[17a] Obviously, the regiodiversity reflects the energy difference between the two modes of electrocyclisation (angular vs. linear), which is smaller for the vinyl carbene moiety arising from insertion of phenylacetylene than from the insertion of aliphatic alkynes. A possible reason is the enhanced reactivity of the vinyl ketene for electrocyclic ring-closure due to the larger electron withdrawal by the phenyl ring compared with an alkyl chain, which reduces the regioselectivity. However, bromo substitution of the naphthyl unit seems to hamper the free rotation of the metallated vinyl ketene unit, which significantly enlarges the regioselectivity towards angular electrocyclisation and results in suppression of the linear benzannulation product.

A similar competition of regiochemistry has been observed for single photocyclisations of stilbene derivatives, which depend on steric repulsions or electronic effects of adjacent aromatic or heteroaromatic rings,[35] as well as for the thermolysis of a naphthyl-2-cyclobutenone derivative.[36]

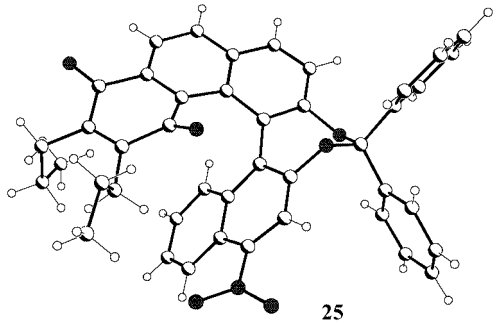
Oxidative work-up with CAN implies additional nitration,[37] as exemplified for the incorporation of 4-octyne: the resulting quinone shows a 1-$NO_2$-substitution, as established by X-ray analysis (Figure 3). Oxidation at 0 °C for less than 2 h suppressed the aromatic nitration in the other cases. Contrary to an earlier reported nitration of 1,1′-binaphthyl 2,2′-ethers with nitric acid in glacial acetic acid[38] where the positions 6,6′ or 3 are substituted, this substitution occurs *meta* to the (sila)ketal moiety, thus suggesting a completely different mechanism.



**20**




**23**



**25**

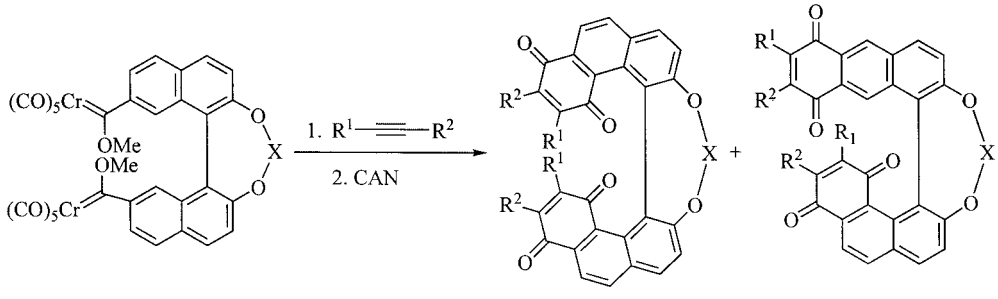
| | (*R*)-**14** | **20** | **23** | **25** |
|---|---|---|---|---|
| C(12)···C(15) | 4.12 | 4.21 | 3.87 | 4.04 |
| C(13)···C(14) | 3.18 | 3.37 | 3.16 | 3.11 |
| O(13)···C(13e) | 3.03 | 3.18 | 3.21 | 3.31 |
| $\varphi_1$ | 25.8 | 24.8 | 24.2 | 22.6 |
| $\varphi_2$ | 4.4 | 4.2 | 4.2 | 6.0 |
| $\varphi_3$ | 12.8 | 26.9 | 29.6 | 29.6 |

Figure 3. Molecular structures of [6]helicene-like quinones **20**, **23** and **25**. Selected transannular distances [Å] and torsional angles $\varphi$ [°] are also given (average values for various independent molecules; see Figure 4 for atom numbering.) $\varphi_1$ = C(13), C(13a), C(13b), C(13c); $\varphi_2$ = O(10), C(10), C(9a), C(9); $\varphi_3$ = O(13), C(13), C(13a), C(13b).

### Bidirectional Benzannulation of Helical Biscarbene Complexes

Finally, we applied the benzannulation to a bidirectional route to more extended helical bisquinones. So far, only rare examples of double and quadruple benzannulations[39] have been reported in general. We used similar reaction conditions as for the monodirectional version but with double the amount of alkyne and oxidizing agent. As expected, the helical biscarbene complexes reveal an even more delicate regiochemistry. In addition to the electronic or steric properties of the alkynes, the different biaryl bridges reflect another potential parameter of influence: whereas bisannulation with 3-hexyne or 3,3-dimethyl-1-butyne yield the bisangular or the angular-linear products independently of the tether, 1-pentyne yields different regioisomers that depend on the nature of the tether (Scheme 6). We speculate that first one naphthyl undergoes angular annulation and that steric effects are responsible for the regiopreference of the second annulation, which affords the benzo[*n*]hexahelicene[40] derivatives **31**, **32**, **34** and the bisangular annulation products **30**, **33**, **35** and **36**. Sim-




| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | $R^1$ | $R^2$ | | | $R^1$ | $R^2$ | |
| **16** | X = Si-*t*Bu$_2$ | **30** | Et | Et | 39 % | **31** | *t*Bu | H | 31 % |
| | | | | | | **32** | *n*Pr | H | 26 % |
| **18** | X = C-Ph$_2$ | **33** | Et | Et | 35 % | **34** | *t*Bu | H | 26 % |
| | | **35** | *n*Pr | H | 20 % | | | | |
| | | **36** | Oct | H | 13 % | | | | |

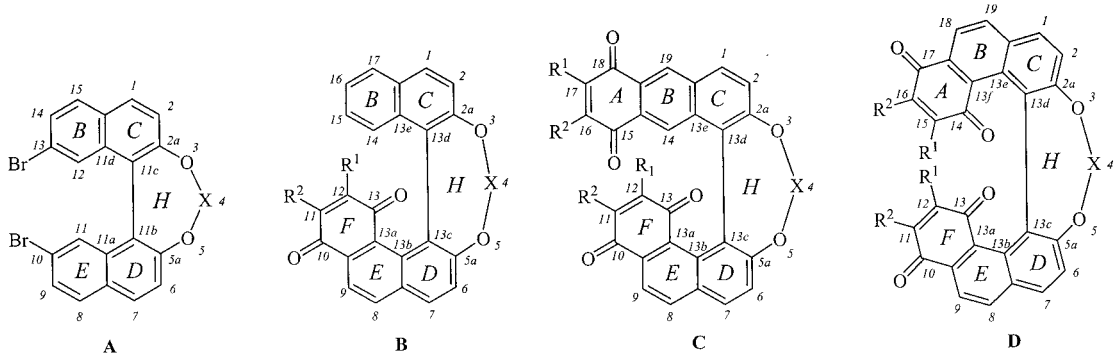
Scheme 6. Bidirectional benzannulation of helical biscarbene complexes **16** and **18**.

ilar unsymmetrical cyclisation products have been encountered in other helicene syntheses by photochemical, radical or Diels–Alder processes.[41]

### Comparative X-ray Structural Studies

A comparison between the X-ray structures of this series of biaryl-substituted seven-membered heterocycles bearing central, conformationally flexible 1,3-dioxepin and 1,3,2-dioxasilepin rings highlights the effect of increasing distortion of the molecules with progressive annulation and also reflects the differences with the fully aromatic carbohelicenes, where the torsion over the inner helical rim and the inner pitch elevations quantify the molecules' helicity. Carbohelicenes form a regular cylindrical helix, often with slightly different torsions of the opposite sides resulting in a lack of $C_2$-symmetry. These torsional angles are even more conspicuous for the heterocyclic helicene-like quinones (Figure 4). The wide diaryl dihedral angle $\varphi$(CHD) (40.6–53.7°) contrasts the small angles in the direct neighbourhood [$\varphi$(BCH) and $\varphi$(HDE) = 1.2–19.7°], which also partly differ among each other, forming an irregular overall screw.

The comparison reveals an inversely proportional relation between the number of fused rings and the resulting dihedral angle about the chirality axis (53.2–44.8° for silaketals and 53.7–40.6° for ketals). This is in agreement with




| | A | | B | | | | C | | | D | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | **2**[a] | **3** | (*R*)-**14** | **20**[a] | **23** | **25** | **31** | **32**[a] | **34**[a] | **30**[a] | **33** | **35** | **36**[a] |
| φ(*CHD*) | **53.2** | 53.7 | 48.5 | **52.1** | 47.0 | 48.8 | **47.8** | **47.2** | 47.7 | **44.8** | 42.7 | 40.6 | 43.1 |
| φ(*BCH*) | **10.0** | 5.8 | 2.2 | **7.4** | 5.5 | 11.6 | **2.4** | **11.5** | 1.2 | **14.4** | 9.5 | 19.7 | 15.0 |
| φ(*HDE*) | **7.8** | 3.3 | 9.5 | **9.5** | 10.8 | 10.4 | **19.6** | **13.2** | 15.3 | **14.4** | 9.3 | 16.9 | 15.1 |
| φ(*BHE*) | **57.4** | 56.1 | 41.2 | **52.2** | 46.8 | 51.2 | **47.4** | **48.8** | 46.3 | **42.7** | 38.2 | 42.0 | 43.7 |
| φ(*CHD*)* | **55.3** | 47.5 | 48.1 | **57.0** | 49.1 | 50.6 | **54.7** | **56.5** | 48.9 | **61.0** | 50.3 | 53.2 | 53.0 |
| Θ(*CH*) | **120.0** | 123.5 | 124.1 | **121.5** | 123.2 | 123.8 | **118.9** | **120.3** | 123.0 | **120.8** | 124.6 | 122.2 | 124.7 |
| Θ(*HD*) | **119.9** | 123.3 | 126.3 | **122.4** | 124.3 | 123.4 | **122.2** | **121.3** | 124.5 | **120.8** | 125.5 | 122.0 | 124.5 |

Figure 4. Numbering scheme of the homologous helicene derivatives **A**–**D** along with torsional angles $\varphi$ [°] and angles $\Theta$ [°] (bold printed values symbolize the silaketals). $\Theta$(XX), $\varphi$(XXX): angle and torsional angle of the inner helix bonds of the respective rings A–F and H; $\varphi$(CHD)*: torsional angle between the four aromatic carbons of the seven-membered ring. [a] Average values for various independent molecules

the torsion values $\varphi$(BHE) between C(10) and C(13) of rings B and E (for system **A** and the same positions for compounds **B**–**D**) and the biaryl bond (57.4–42.7° and 56.1–38.2°), which describe the out-of-plane bending of the two respective aryl units more completely. This snap shut motion towards higher homologues should be transmitted over the axis to the biarylic minor groove. Instead, the $\varphi$(CHD)* angles increase (55.3–61.0° and 47.5–53.2°) except for compounds **C**, thereby reflecting the puckering of the flexible heterocyclic ring.

A comparison of silaketal **2** with its carbo analogue **3** indicates an increase of the C–O–X angle (121.1° vs. 115.0°) and a decrease of the O–X–O angle (106.6° vs. 110.1°) for the sila compounds, thus reflecting the longer Si–O bond (1.66 vs. 1.43 Å for the ketal) and the non-bonding O(3)···O(5) distance (2.66 vs. 2.35 Å).

As a result of the steric strain imposed by the different seven-membered rings, angles $\Theta$(CH) and $\Theta$(HD) between the biaryl bond and the adjacent carbon atoms [C(11a), C(11d) for **A** or C(13b), C(13e) for **B**–**D**, Figure 4 and Figure 5] are slightly larger than 120°. This is independent of the degree of annulation and leads to a larger outward bending of the methylene tether.

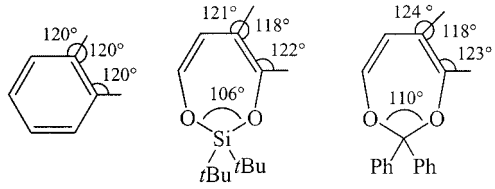



Figure 5. Comparison of differing average angles.

The main structural features of the heterocyclic [6]helicene quinones **B** (Figure 3) are the overlapping terminal edges with a shortest C(13)···C(14) distance of 3.11–3.37 Å, which is in the range of the all-benzene analogues (2.94–3.22 Å).[42] The O(13)···C(13e) gap is even shorter (3.03–3.31 Å) and leads to a distortion of the quinone ring into a boat shape. Thus, the inner carbonyl group is strikingly twisted out of plane ($\varphi_3$: 26.9–29.6°); in contrast, the distortion involving the inner alkoxy oxygen atom in camphanate **14** is far less pronounced (12.8°). The distortion of the outer carbonyl groups is only marginal ($\varphi_2$: 4.2–6.0°). Additionally, the dihedral angles characterising the phenanthryl ring (22.6–25.8°) or the biaryl axis (47.0–52.1°) are distinctly larger than those reported for carbo[6]helicenes (11.7–18.8° or 22.9–27.8°).[42]

The overlapping terminal rings in the bridged biphenanthryl derivatives **D** (Figure 6) are separated by distances that exceed the sum of the respective van der Waals radii (4.01–5.25 Å at the periphery of helix), although they come into very close contact on the interior rim (3.16–3.56 Å), as observed for carbo[7]helicene bisquinone.[27b] Figure 6 shows the greatest through-space interaction of the *pseudoortho* arranged quinone units for the tetraethyl-substituted ketal **33** (3.16–3.18 Å), which is similar to the all-benzene analogue (3.11–3.13 Å). The disubstituted bisquinones **35** and **36**, as well as the silylene-tethered derivative **30**, have larger distances. The dihedral angles of the phenanthryl rings (24.6–28.2°) or the biaryl axis (40.6–44.8°) are also larger than the analogous dihedral angles of the [7]helicene bisquinone (21.3°/23.2° or 23.8°). As already observed for the monoquinone system **B**, the quinone rings reveal a strong out-of-plane bending which can also be quantified by the large torsional angle at the inwards pointing carbonyl groups (21.2–25.7°) with respect to the less-pronounced distortion of the outer counterparts (1.8–6.2°). These characteristics resemble the structural details observed for carbo[7]helicene (average of 1.9° and 19.1°).[27b]

The angular-linear benzannulation products **C** show a similar close contact of the terminal edges [C(13)···C(14): 3.12–3.49 Å]. The anthryl quinones are less distorted (0.3–5.6°) than their phenanthryl quinone counterparts (4.0–5.8° and 19.9–23.3°). The dihedral angles of the biaryl axis (47.2–47.8°) lie between those of compounds **B** and **D**; the phenanthryl unit shows the highest distortion of the studied examples (26.5–29.9°) due to the embedded bulky *tert*-butyl group (Figure 7).

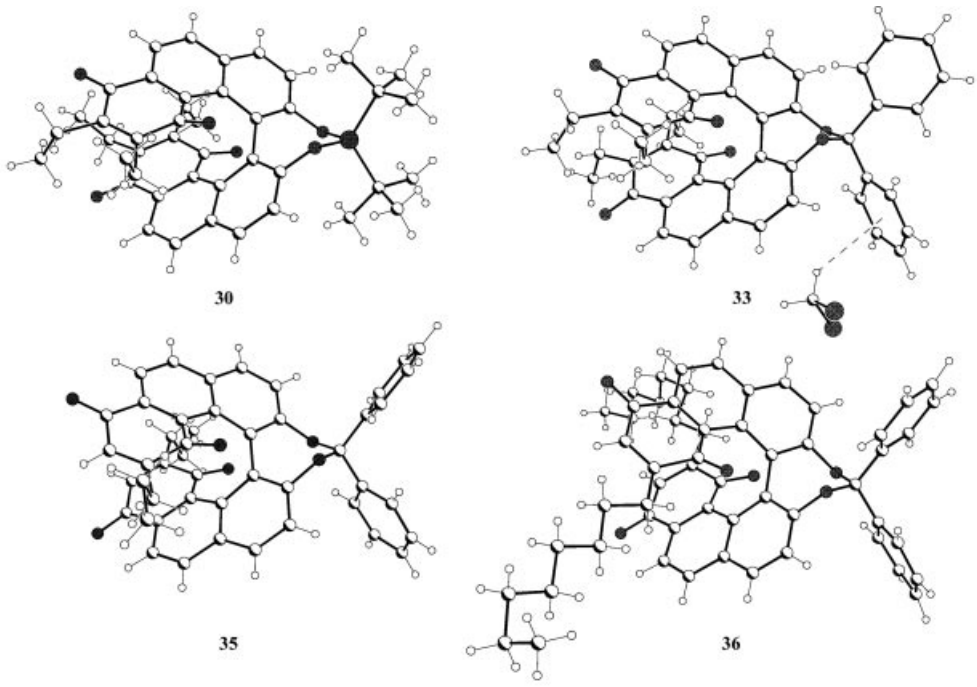
In conclusion, the X-ray data demonstrate that the molecular structures of the heterocyclic helicenes are determined by the nature and the conformational flexibility of the central heterocyclic ring and by the degree of annulation. These elements mainly determine the structural parameters, such as the spreading of the biaryl dihedral and bond angles, the twist of the terminal quinoid rings and the out-of-plane bending of the biaryl halves. Some parameters do not necessarily vary linearly with the number of fused rings or the ketalic centre. They are also partly influenced by the packing arrangement. The various weak intermolecular C–H···O interactions play the most important role for the crystal packing of compounds **B**–**D**. π-π Interactions, which are common for (hetero)helicenes, are not observed; instead, compound **33** shows an interesting C–H···π interaction[43] (2.95 Å) between a clathrated dichloromethane and a phenyl group. The packing situation is different for the dihalogenated compounds **2** and **3** due to dominating C–H···Br interactions (3.04–3.12 Å for **2** vs. 2.95–2.97 Å for **3**) or Br···Br interactions (3.51–3.87 Å, with 3.72 Å for the sum of the van der Waals radii)[44] forming a planar $Br_4$ square cluster.

## Optical Resolution and Chiroptical Properties

In order to explore some chiroptical properties of the heterocyclic helicenes we aimed at an enantioresolution of the racemic mixtures by HPLC on a chiralcel OD column, as has previously been reported for the separation of various helical compounds.[45] The recommended eluent (*n*-hexane/2-propanol) turned out to be unsuitable for the dissolution and for optical base-line separations of our heterocyclic helicene derivatives. However, the incorporation of two long alkyl chains in bisquinone **36** increased the solubility sufficiently and thus allowed an antipode separation.

Besides the diastereomeric camphanate pair **14** and the enantiopure monoquinone **9** derived therefrom, non-race-




| | 30 | 33 | 35 | 36 |
|---|---|---|---|---|
| C(17)···C(11) | 4.53 | 4.16 | 4.60 | 5.25 |
| C(16)···C(10) | 4.53 | 4.01 | 4.69 | 5.24 |
| C(13f)···C(13) | 3.48 | 3.18 | 3.44 | 3.56 |
| C(14)···C(13a) | 3.48 | 3.16 | 3.50 | 3.55 |
| C(13e)···O(13) | 3.28 | 3.03 | 3.19 | 3.14 |
| O(14)···C(13c) | 3.28 | 3.03 | 3.22 | 3.12 |
| $\varphi_1$ | 28.2 | 27.1 | 26.5 | 26.0 |
| $\varphi_{1a}$ | 28.2 | 25.2 | 26.1 | 24.6 |
| $\varphi_2$ | 5.8 | 6.2 | 2.2 | 3.1 |
| $\varphi_{2a}$ | 5.8 | 1.9 | 2.9 | 1.8 |
| $\varphi_3$ | 25.7 | 23.1 | 21.4 | 21.7 |
| $\varphi_{3a}$ | 25.7 | 24.7 | 25.4 | 21.2 |

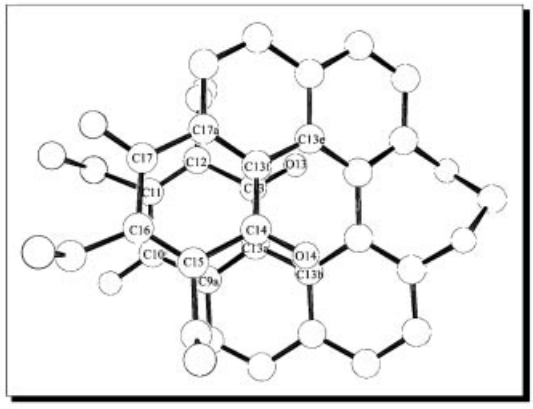


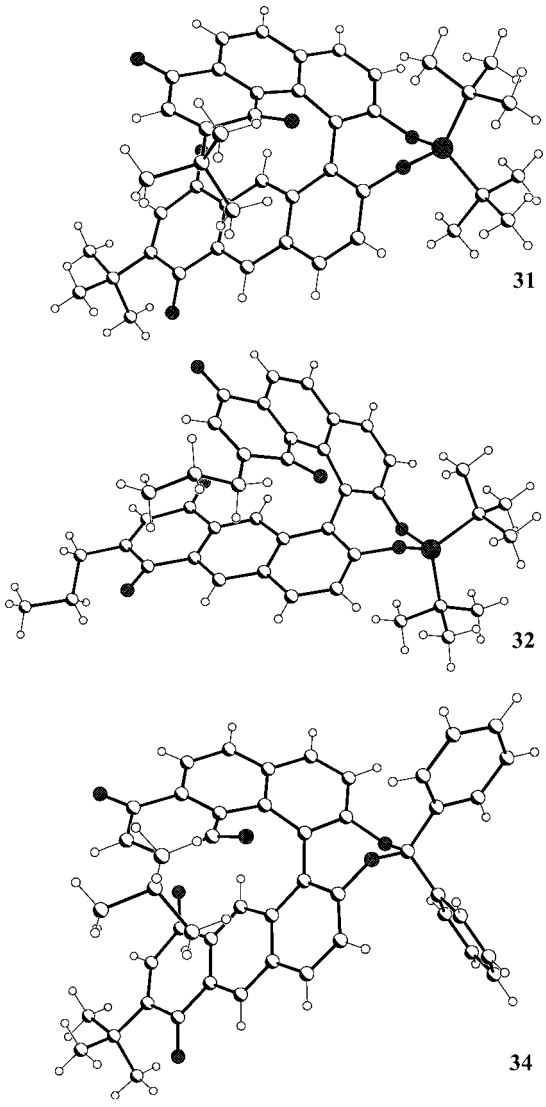

Figure 6. Molecular structures of [7]helicene-like bisquinones **30**, **33**, **35** and **36**, and selected transannular distances [Å] and torsional angles $\varphi$ [°] (average values for various independent molecules; see Figure 4 for atom numbering). $\varphi_1$ = C(13), C(13a), C(13b), C(13c); $\varphi_{1a}$ = C(13d), C(13e), C(13f), C(14); $\varphi_2$ = O(10), C(10), C(9a), C(9); $\varphi_{2a}$ = O(17), C(17), C(17°), C(18); $\varphi_3$ = O(13), C(13), C(13°), C(13b); $\varphi_{3a}$ = O(14), C(14), C(13f), C(13e).

mic **3** could be obtained from the brominated (*R*)- or (*S*)-BINOL **1**, which was resolved according to the method published by Diederich.[21a]

The CD spectra obtained for each pair of isomers of **3**, **14**, **9** and **36** (Figure 8) are mirror images over the entire spectra in all cases, thereby indicating that complete optical resolution had occurred. The bridged binaphthyl (*R*)-**3** shows an intense negative couplet centred at 231 nm, which corresponds to the allowed, long-axis-polarized $^1$B transition of the 2-naphthol chromophore. Following the analysis of other methylene-tethered binaphthols,[46] this spectral feature is indicative of a dihedral angle, $\theta$, between the naphthyl moieties of less than 110° for the (*R*)-configuration. This absolute configuration is corroborated by a dihedral angle of 54° determined by X-ray analysis. Two additional CD signals of opposite signs at 333 and 268 nm are in the $^1L_b$ and $^1L_a$ spectral range; two other distinct extrema found at 251 and 202 nm are of uncertain origin, although they might be connected with a complex interaction of the $^1$B naphthyl transition with the adjacent phenyl groups. This situation hampers a proper estimation of the dihedral angle from the $\Delta\varepsilon_{max}$ value of the low-energy component at 230 nm.[47]

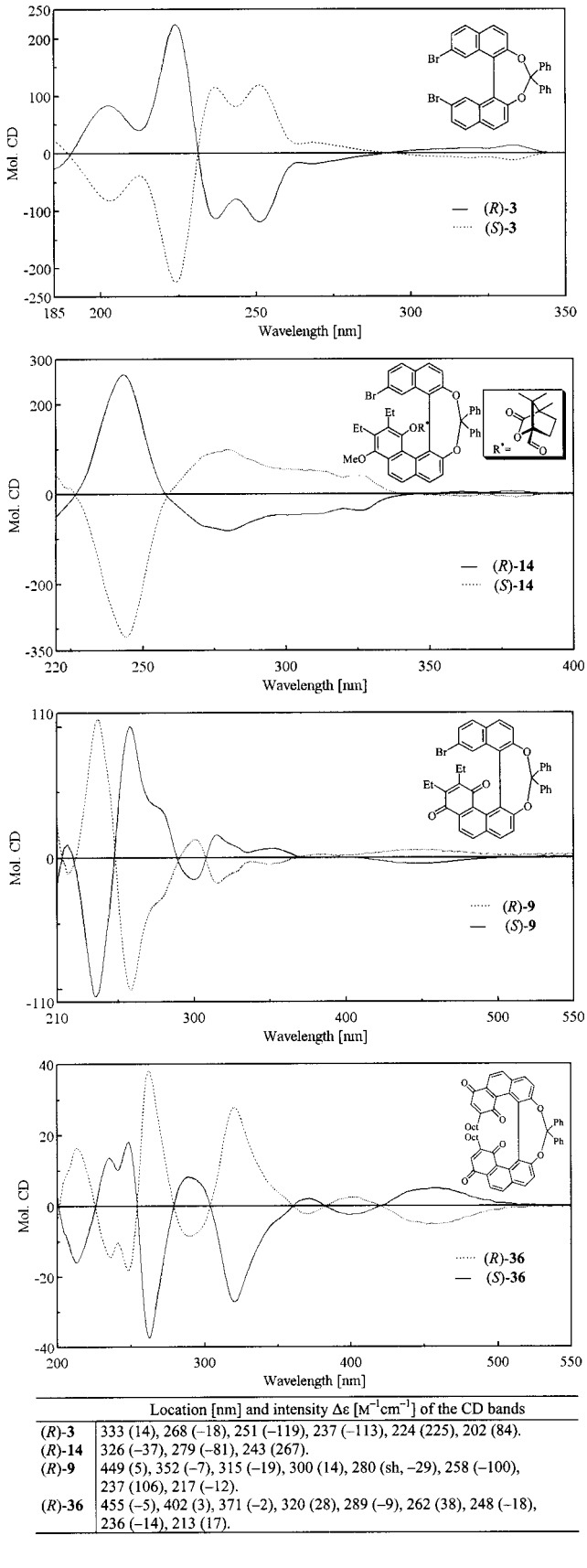
The CD spectra of diastereomer (*R*)-**14** and enantiomer (*R*)-**9**, whose absolute configurations were established unambiguously by X-ray diffraction, are dominated by a nega-




| | 31 | 32 | 34 |
|---|---|---|---|
| C(12)···C(14a) | 4.50 | 4.11 | 4.41 |
| C(13)···C(14) | 3.49 | 3.12 | 3.42 |
| O(13)···C(13c) | 3.38 | 3.33 | 3.35 |
| $\varphi_1$ | 27.7 | 26.5 | 29.9 |
| $\varphi_2$ | 5.8 | 4.1 | 4.0 |
| $\varphi_3$ | 19.9 | 23.3 | 20.8 |
| $\varphi_4$ | 0.3 | 4.8 | 5.6 |
| $\varphi_5$ | 2.0 | 2.4 | 3.1 |

Figure 7. Molecular structures of bisquinoid angular-linear benzannulation products **31**, **32** and **34**, and selected transannular distances [Å] and torsional angles $\varphi$ [°] (average values for various independent molecules; see Figure 4 for atom numbering). $\varphi_1$ = C(13), C(13a), C(13b), C(13c); $\varphi_2$ = O(10), C(10), C(9a), C(9); $\varphi_3$ = O(13), C(13), C(13a), C(13b); $\varphi_4$ = O(18), C(18), C(18a), C(19); $\varphi_5$ = O(15), C(15), C(14a), C(14).




| | Location [nm] and intensity $\Delta\varepsilon$ [$M^{-1}cm^{-1}$] of the CD bands |
|---|---|
| (*R*)-**3** | 333 (14), 268 (–18), 251 (–119), 237 (–113), 224 (225), 202 (84). |
| (*R*)-**14** | 326 (–37), 279 (–81), 243 (267). |
| (*R*)-**9** | 449 (5), 352 (–7), 315 (–19), 300 (14), 280 (sh, –29), 258 (–100), 237 (106), 217 (–12). |
| (*R*)-**36** | 455 (–5), 402 (3), 371 (–2), 320 (28), 289 (–9), 262 (38), 248 (–18), 236 (–14), 213 (17). |

Figure 8. CD spectra of heterocyclic helicene derivatives **3**, **14**, **9** and **36** in *n*-hexane.

tive couplet at 258 and 248 nm. The latter shows a simple split-type Cotton effect with a shoulder at 280 nm and some distinct CD signals in the long-wave range, whereas the former shows a stronger positive CD band which is broadened and a smaller negative dichroic signal which merges into a region of overlapping further signals of $^1L_b$ and $^1L_a$ transitions. Both observations suggest that the two exitons in the different biaryl moiety cannot be treated as being independent because of strong but diverse interactions between these two aryl units and an additional disturbance by the diphenyl or camphanate group. Finally, these spectral features are quite similar to those reported for the purely methylene-bridged (*R*)-biaryl analogue.[48]

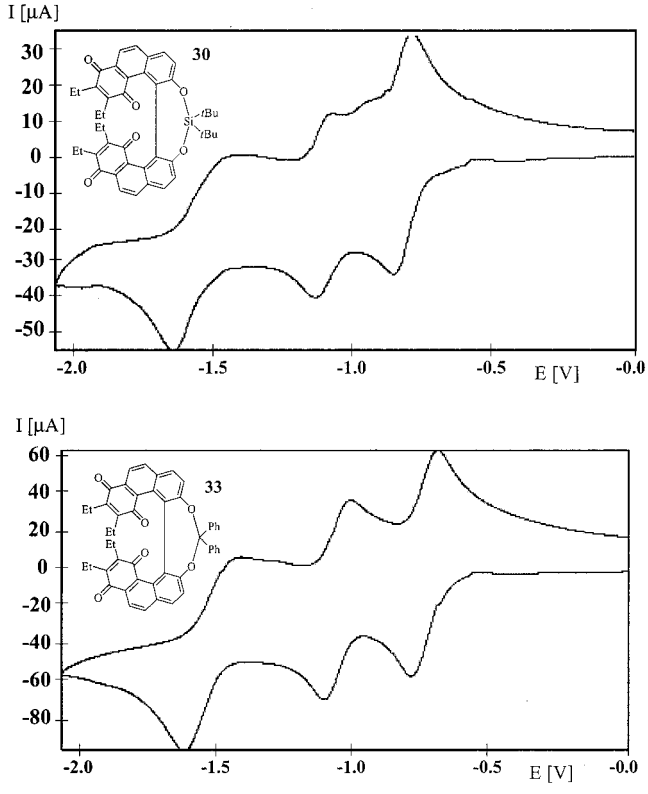
The spectrum of the bridged (*R*)-4,4′-biphenanthrene-3,3′-diol **36** exhibits a positive, single-signed band with a maximum at 262 nm instead of a clear couplet, as reported for some analogous compounds with an (*R*)-configuration.[49] Apart from this pattern, which also indicates strong interaction of the two chromophoric units due to the small dihedral angle (ca. 43° from X-ray diffraction), a second unusually intense positive CD signal is found in the region of $L_b$ transitions at 320 nm.

### Redox Properties of Bisquinones 30 and 33

The electrochemical properties of the two [7]helicene-like bisquinones **30** and **33** were investigated by cyclic voltammetry to provide further information on the intramolecular interaction. Both show the same electrochemical behaviour with very similar voltammograms: three, distinctly separate and reversible one-electron reduction steps, a pattern also found for a bisquinoid [2.2](1,4)naphthalenophane.[50] The first two peaks correspond to the consecutive one-electron reduction of each quinone moiety, which leads to the semiquinone species; the last broader peak corresponds to a third one-electron reduction, which represents the formation of a radical trianion. Bisquinone **30** shows a further small anodic wave around the first redox couple indicative of slow decomposition of a reduced intermediate species.

Reduction potentials can sometimes be used to distinguish localised and delocalised electronic structures. If an added electron occupies an orbital extending over both quinones, more-positive first reduction potentials $E_1$ are observed. A comparison of some related $E_1$ values shows first reduction potentials of about –1.1 V for a bianthrylic or biphenanthrylic bisquinone anion radical[51] having a localised odd electron, and a potential of –0.56 V for the undoubtedly delocalised electron of the [7]helicene bisquinone.[52] This suggests that structures **30** and **33** (Figure 9), characterised by $E_1$ values between –0.87 V and –0.79 V, exhibit intermediate behaviour.

A better estimation of the intramolecular interaction between both electrophores comes from a comparison of the separation between the first two reduction potentials. The large potential differences $\Delta E^0$ of **30** (290 mV) and **33** (310 mV) suggest that the odd electron of the corresponding radical anions should be delocalised over the whole




| | $-E_1^0$ [V] | $-E_2^0$ [V] | $\Delta E^0$ [V] | $-E_3^0$ [V] |
|---|---|---|---|---|
| **30** | 0.84 | 1.13 | 0.29 | 1.58 |
| **33** | 0.79 | 1.10 | 0.31 | 1.65 |

Figure 9. Cyclic voltammograms of **30** and **33** in $CH_3CN/(Bu_4)NBF_4$ at 200 mV s$^{-1}$ with potentials $E^0$ and potential differences $\Delta E^0 = |E_2^0 - E_1^0|$ ($E^0$ is the average of the anodic and cathodic peak potentials vs. SCE).

molecule, most probably even in a transannular manner across the helical array's extremities, which could be proved for [7]helicene bisquinone (310 mV) and ruled out for the linear 1,4,8,11-pentacenetetrone (160 mV).[53] The small differences of the $E_1$ and $\Delta E^0$ values of **30** and **33** indicate a slightly better delocalisation for the ketal-tethered binaphthyl **33**. This view is supported by their crystal structures, which show a better overlap for the *pseudoortho* orientation of the latter quinone units (Figure 6) and a slightly smaller dihedral angle for the biphenanthryl system (45° vs. 43°).

## Conclusions

In summary, we present a novel synthetic non-photochemical access to a broad series of helical scaffolds bearing five, six and seven *ortho*-fused carbo- or heterocycles. The syntheses are based on a progressive mono- and bidirectional chromium-templated [3+2+1] benzannulation of racemic (sila)ketal-tethered binaphthyl carbene complexes with various alkynes showing an unprecedented competition between bisangular and angular-linear bisannulation. A practical enantiomeric resolution of a monobenzannul-

ation product has been carried out by subsequent protection with camphanate.

The X-ray crystal structures indicate an increasing helical distortion as a result of progressive annulation. The CD spectra of ketal-tethered biaryls reflect various interactions between the aryl chromophores, and CV studies of bisangular bisquinones reveal three one-electron reduction steps.

## Experimental Section

**General Remarks:** All reactions were carried out under argon atmosphere using standard Schlenk techniques. Solvents used for reactions, crystallisations and chromatography were dried by distillation from calcium hydride (petroleum ether, *t*BuOMe, $CH_2Cl_2$, DMF) or sodium ($NEt_3$) and saturated with argon. THF was freshly distilled from potassium. All alkynes were degassed under vacuum and saturated with argon prior to use. 7,7′-Dibromo-2,2′-dihydroxy-1,1′-binaphthyl (**1**) was prepared according to a literature procedure.[21] Column chromatography was performed with degassed silica gel (Macherey–Nagel, type 60, 0.015–0.025 mm).

FT-IR spectra: Nicolet Magna 550. NMR spectra: Bruker DPX 300, AM 400 and DRX 500. MS and HR-MS: Kratos MS-50 and Thermoquest MAT 95 XL. FAB-MS: Concept 1H (matrix: *m*-nitrobenzyl alcohol). CD spectrometer: Jasco J-720 and J-810. CV: EG & G Princeton Applied Research potentiostat Model 173 attached to an EG & G electrochemical microcell with a glassy carbon working electrode ($3.55 \times 10^{-6}$ m$^2$), SCE as reference electrode, and a platinum wire counter electrode. The measurements were carried out on degassed anhydrous acetonitrile solution containing the sample (2.2–2.9 mM) and $(Bu)_4NBF_4$ (0.1 M) as supporting electrolyte at 296 K with a sweep rate of 200 mV s$^{-1}$. Enantiomeric separation by HPLC: Knauer Wellchrom, column: Chiralcel OD, 10 × 250 mm (DAICEL).

**(*R*,*S*)-10,13-Dibromo-4,4-di-*tert*-butyldinaphtho[2,1-*d*:1′,2′-*f*][1,3,2]-dioxasilepin (2):** Triethylamine (3.3 mL, 23.4 mmol) and di-*tert*-butyldichlorosilane (1.3 mL, 6.0 mmol) were added sequentially to a solution of (*R*,*S*)-**1** in DMF at room temperature. After 10 min a yellow precipitate had formed and the reaction was completed overnight. After addition of $CH_2Cl_2$ and water (20 mL), the organic phase was washed with a saturated aqueous solution of $NaHCO_3$ (3 × 10 mL). The product was extracted with $CH_2Cl_2$, dried with $MgSO_4$ and concentrated in vacuo. The residue was purified by chromatography on silica gel ($CH_2Cl_2$/PE, 2:1, $R_f$ = 0.72) to give **2** as a colourless solid. Yield: 2.43 g (4.2 mmol, 77%). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 0.96 [s, 18 H, C(C$H_3$)$_3$], 7.12 (d, $^4J_{H,H}$ = 1.9 Hz, 2 H, 11/12-H), 7.40 (d, $^3J_{H,H}$ = 8.7 Hz, 2 H, 8/15-H), 7.41 (dd, $^3J_{H,H}$ = 8.7, $^4J_{H,H}$ = 1.9 Hz, 2 H, 9/14-H), 7.70 (d, $^3J_{H,H}$ = 8.3 Hz, 2 H), 7.83 (d, $^3J_{H,H}$ = 8.3 Hz, 2 H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 21.3 [Si*C*(CH$_3$)], 27.6 [SiC(*C*H$_3$)], 118.8, 120.8, 122.8 (ArCH), 127.5 (ArCH), 128.5, 128.7 (ArCH), 129.8 (ArCH), 129.9 (ArCH), 134.9, 153.0 (2a/5a-C) ppm. MS (70 eV, EI): *m*/*z* (%) = 584 (100) [M$^+$], 528 (32) [M$^+$ – $C_4H_8$], 485 (96) [M$^+$ – $C_4H_8$ – $C_3H_7$], 403 [M$^+$ – $C_{10}H_{17}OSi$], 361 (53) [M$^+$ – $C_{10}H_{17}OSi$ – $C_2H_2O$], 281 (75) [M$^+$ – $C_{10}H_{17}OSi$ – $C_2H_2O$ – Br], 202 (60) [M$^+$ – $C_{10}H_{17}OSi$ – $C_2H_2O$ – 2Br]. HR-MS ($C_{28}H_{28}{}^{79}Br_2O_2Si$): calcd. 582.0225; found 582.0224.

**(*R*,*S*)-10,13-Dibromo-4,4-diphenyldinaphtho[2,1-*d*:1′,2′-*f*][1,3]dioxepin (3):** Dichlorodiphenylmethane (0.89 mL, 4.63 mmol) and (*R*,*S*)-**1** (1.87 g, 4.21 mmol) were stirred in $CH_2Cl_2$ for a short time for homogenisation. After removal of the solvent, the mixture was heated in an oil bath at 145 °C for 30 min to generate HCl at about 120 °C. The crude product was chromatographed on silica gel ($CH_2Cl_2$/PE, 1:1, $R_f$ = 0.88) to yield **3** as a colourless solid. Yield: 1.75 g (2.88 mmol, 68%). $^1$H NMR (500 MHz, $CD_2Cl_2$): $\delta$ = 6.96 (d, $^3J_{H,H}$ = 8.7 Hz, 2 H), 7.32–7.30 (m, 6 H), 7.56–7.53 (m, 6 H), 7.67 (d, $^4J_{H,H}$ = 1.8 Hz, 2 H, 11/12-H), 7.70 (d, $^3J_{H,H}$ = 8.7 Hz, 2 H), 7.77 (d, $^3J_{H,H}$ = 8.7 Hz, 2 H) ppm. $^{13}$C NMR(125 MHz, $CD_2Cl_2$): $\delta$ = 120.6, 123.6, 125.2, 127.1, 127.9, 128.5 (×2), 129.4, 130.2, 130.3, 133.0, 140.8, 151.2 (2a/5a-C) ppm. MS (70 eV, EI): *m*/*z* (%) = 608 (3) [M$^+$], 426 (4) [M$^+$ – OC($C_6H_5$)$_2$], 57 (100). HR-MS ($C_{33}H_{20}{}^{79}Br_2O_2$): calcd. 605.9830; found 605.9814.

**General Procedure A. Synthesis of Monocarbene Complexes 4 and 5:** *n*BuLi (1.6 M in hexane, 1.2 mL, 1.88 mmol) was slowly syringed into a solution of 2,2′-bridged dibromo-1,1′-binaphthyl **2** (1.00 g, 1.71 mmol) or **3** (1.04 g, 1.71 mmol) in THF (30 mL) at –88 °C. The mixture was stirred at –88 to –78 °C for 90 min, and hexacarbonyl chromium (0.56 g, 2.57 mmol) was then added. After stirring for 30 min at this temperature and an additional 2 h while warming to room temp., the solvent was removed in vacuo. The resulting residue was dissolved in $CH_2Cl_2$, combined with trimethyloxonium tetrafluoroborate (Meerwein's reagent, 0.28 g, 1.88 mmol), and the suspension was stirred for 90 min at room temperature. The solvent was evaporated in vacuo and the crude product was purified by column chromatography on silica gel to afford the monocarbene complex **4** or **5** as a red solid.

**(*R*,*S*)-10-[13-Bromo-4,4-di-*tert*-butyldinaphtho[2,1-*d*:1′,2′-*f*][1,3,2]-dioxasilepinyl](methoxycarbene)(pentacarbonyl)chromium (4):** $R_f$ = 0.54 ($CH_2Cl_2$/PE, 1:4). Yield: 0.89 g (1.21 mmol, 71%). IR (petroleum ether): ν(CO) = 2063 (m), 1988 (w), 1956 (vs), 1938 (sh) cm$^{-1}$. $^1$H NMR (300 MHz, $CD_2Cl_2$): $\delta$ = 0.99 [s, 9 H, C(C$H_3$)$_3$], 1.00 [s, 9 H, C(C$H_3$)$_3$], 4.40 (s, 3 H, OC$H_3$), 6.77 (s, 1 H), 7.14 (s, 1 H), 7.28 (dd, $^3J_{H,H}$ = 8.4, $^4J_{H,H}$ = 0.8 Hz, 1 H), 7.41 (dd, $^3J_{H,H}$ = 8.p, $^4J_{H,H}$ = 1.8 Hz, 1 H), 7.47 (d, $^3J_{H,H}$ = 8.9 Hz, 1 H), 7.52 (d, $^3J_{H,H}$ = 8.9 Hz, 1 H), 7.73 (d, $^3J_{H,H}$ = 8.4 Hz, 1 H), 7.88 (d, $^3J_{H,H}$ = 8.9 Hz, 1 H), 7.94 (2d, $^3J_{H,H}$ = 8.5 Hz, 2 H) ppm. $^{13}$C NMR (75 MHz, $CD_2Cl_2$): $\delta$ = 21.3 [Si*C*(CH$_3$)], 27.4 [SiC(*C*H$_3$)], 27.5 [SiC(*C*H$_3$)], 67.2 (O*C*H$_3$), 119.0, 120.1, 121.0, 121.0, 122.3, 122.9, 124.2, 126.5, 127.5, 128.3, 128.5, 128.6, 128.9, 130.0, 130.1, 130.2, 130.5, 132.9, 135.2, 151.3, 153.3, 153.4, 216.0 (*cis*-CO), 224.8 (*trans*-CO), 351.0 (C=Cr) ppm. MS (FAB): *m*/*z* (%) = 740 (1) [M$^+$], 600 (100) [M$^+$ – 5CO], 520 (100) [M$^+$ – 5CO – Br], 505 (20) [M$^+$ – 5CO].

**(*R*,*S*)-10-[13-Bromo-4,4-diphenyldinaphtho[2,1-*d*:1′,2′-*f*][1,3]-dioxepinyl](methoxycarbene)(pentacarbonyl)chromium (5):** $R_f$ = 0.32 (*t*BuOMe/PE, 1:3). Yield: 0.98 g (1.28 mmol, 75%). IR (petroleum ether): ν(CO) = 2063 (m), 1990 (w), 1956 (vs), 1940 (sh) cm$^{-1}$. $^1$H NMR (300 MHz, $CD_2Cl_2$): $\delta$ = 4.52 (s, 3 H, OC$H_3$), 6.96 (d, $^3J_{H,H}$ = 8.7 Hz, 1 H), 7.02 (d, $^3J_{H,H}$ = 8.7 Hz, 1 H), 7.19 (s, 1 H), 7.35–7.28 (m, 6 H), 7.47 (dd, $^3J_{H,H}$ = 8.6, $^4J_{H,H}$ = 1.6 Hz, 1 H), 7.52 (dd, $^3J_{H,H}$ = 8.9, $^4J_{H,H}$ = 2.1 Hz, 1 H), 7.61–7.54 (m, 4 H), 7.69 (d, $^3J_{H,H}$ = 8.9 Hz, 2 H), 7.74 (d, $^3J_{H,H}$ = 8.7 Hz, 2 H), 7.95 (d, $^3J_{H,H}$ = 8.5 Hz, 1 H) ppm. $^{13}$C NMR (75 MHz, $CD_2Cl_2$): $\delta$ = 67.5 (O*C*H$_3$), 117.8, 118.8, 121.0, 123.0, 123.6 (Ar*C*H), 124.8 (Ar*C*H), 125.3, 126.6, 127.2 (Ph*C*H), 127.5, 128.0 (2 × Ph*C*H), 128.5 (Ar*C*H), 128.6 (2 × Ar*C*H), 128.7 (Ar*C*H), 129.5 (Ar*C*H), 128.9, 129.4 (Ar*C*H), 129.5 (Ar*C*H), 130.3 (Ar*C*H), 131.0, 131.9, 132.3, 141.0 (×2), 150.3, 151.5, 216.1 (*cis*-CO), 224.7 (*trans*-CO), 350.6 (C=Cr) ppm. MS (FAB): *m*/*z* (%) = 764 (6) [M$^+$], 708 (5) [M$^+$ – 2CO], 652 (18) [M$^+$ – 4CO], 624 (100) [M$^+$ – 5CO], 544 (28) [M$^+$ – 5CO – Br], 442 (25) [M$^+$ – 5CO – OC($C_6H_5$)$_2$].

**General Procedure B. Benzannulation of Monocarbene Complexes 4 and 5 (and 17 and 19) with Oxidative Work-Up to Give Helical Monoquinones 6–13 (and 20–29):** A Schlenk tube fitted with a con-

denser jacket and containing a solution of 1 mmol of carbene complex and 4 mmol of alkyne in $CH_2Cl_2$ (10 mL) was warmed in an oil bath at 55 °C for 4 h. The reaction mixture was cooled in an ice bath and a solution of ceric ammonium nitrate (3.84 g, 7 mmol) in water (20 mL) was added. After stirring for 2 h at 0 °C, the organic layer was separated, and the aqueous layer was extracted with $CH_2Cl_2$ (3 × 10 mL). The combined organic layers were subsequently washed with brine (3 × 25 mL) and dried with $MgSO_4$. Filtration, evaporation of the solvent and column chromatography afforded the respective helical monoquinone as an orange solid.

**(*R*,*S*)-15-Bromo-4,4-di-*tert*-butyl-11,12-diethylnaphtho[1,2-*f*]phenanthro[2,1-*d*][1,3,2]-dioxasilepin-10,13-dione (6):** Benzannulation of carbene complex **4** (0.74 g) with 3-hexyne (0.45 mL). $R_f$ = 0.63 ($CH_2Cl_2$/PE, 1:1). Yield: 0.33 g (0.52 mmol, 52%). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 0.60 (t, $^3J_{H,H}$ = 7.5 Hz, 3 H, $CH_3$), 0.94 (t, $^3J_{H,H}$ = 7.5 Hz, 3 H, $CH_3$), 1.05 [s, 9 H, $C(CH_3)_3$], 1.10 [s, 9 H, $C(CH_3)_3$], 1.30 (dq, $^2J_{H,H}$ = 12.9, $^3J_{H,H}$ = 7.5 Hz, 2 H, $CH_2$), 1.72 (dq, $^2J_{H,H}$ = 12.9, $^3J_{H,H}$ = 7.5 Hz, 1 H, $CH_2$), 2.11 (dq, $^2J_{H,H}$ = 12.9, $^3J_{H,H}$ = 7.5 Hz, 1 H, $CH_2$), 2.53 (dq, $^2J_{H,H}$ = 12.9, $^3J_{H,H}$ = 7.5 Hz, 1 H, $CH_2$), 6.43 (d, $^4J_{H,H}$ = 1.9 Hz, 1 H, 14-H), 7.21 (dd, $^3J_{H,H}$ = 8.6, $^4J_{H,H}$ = 1.9 Hz, 1 H, 16-H), 7.49 (d, $^3J_{H,H}$ = 8.7 Hz, 1 H), 7.51 (d, $^3J_{H,H}$ = 8.7 Hz,, 1 H), 7.53 (d, $^3J_{H,H}$ = 8.6 Hz, 1 H), 7.71 (d, $^3J_{H,H}$ = 8.7 Hz, 1 H), 7.92 (d, $^3J_{H,H}$ = 8.7 Hz, 1 H), 8.03 (d, $^3J_{H,H}$ = 8.6 Hz, 1 H), 8.05 (d, $^3J_{H,H}$ = 8.6 Hz, 1 H) ppm. $^1$H NMR (400 MHz, [D$_6$]acetone): $\delta$ = 0.64 (t, $^3J_{H,H}$ = 7.5 Hz, 3 H, $CH_3$), 0.93 (t, $^3J_{H,H}$ = 7.5 Hz, 3 H, $CH_3$), 1.08 [s, 9 H, $C(CH_3)_3$], 1.13 [s, 9 H, $C(CH_3)_3$], 1.30 (dq, $^2J_{H,H}$ = 12.7, $^3J_{H,H}$ = 7.5 Hz, 2 H, $CH_2$), 1.30 (dq, $^2J_{H,H}$ = 12.7, $^3J_{H,H}$ = 7.5 Hz, 2 H, $CH_2$), 1.76 (dq, $^2J_{H,H}$ = 12.7, $^3J_{H,H}$ = 7.5 Hz, 1 H, $CH_2$), 2.14 (dq, $^2J_{H,H}$ = 12.8, $^3J_{H,H}$ = 7.5 Hz, 1 H, $CH_2$), 2.53 (dq, $^2J_{H,H}$ = 12.8, $^3J_{H,H}$ = 7.5 Hz, 1 H, $CH_2$), 6.40 (d, $^4J_{H,H}$ = 1.9 Hz, 1 H, H14), 7.31 (dd, $^3J_{H,H}$ = 8.7, $^4J_{H,H}$ = 1.9 Hz, 1 H, H16), 7.56 (d, $^3J_{H,H}$ = 8.8 Hz, 1 H), 7.69 (d, $^3J_{H,H}$ = 8.7 Hz,, 1 H), 7.77 (d, $^3J_{H,H}$ = 8.7 Hz, 1 H), 7.92 (d, $^3J_{H,H}$ = 8.7 Hz, 1 H), 8.03 (d, $^3J_{H,H}$ = 8.3 Hz, 1 H), 8.18 (d, $^3J_{H,H}$ = 8.8 Hz, 1 H), 8.28 (d, $^3J_{H,H}$ = 8.3 Hz, 1 H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 13.8 (2 × *C*H$_2$CH$_3$), 19.1 (CH$_2$*C*H$_3$), 19.9 (CH$_2$*C*H$_3$), 21.4 [Si*C*(CH$_3$)], 21.6 [Si*C*(CH$_3$)], 27.6 [SiC(*C*H$_3$)], 27.8 [SiC(*C*H$_3$)], 120.1, 120.2 (ArCH), 121.2, 123.1, 123.4 (ArCH), 124.8 (ArCH), 126.7 (ArCH), 129.2, 129.2 (ArCH), 129.3 (ArCH), 129.6 (ArCH), 130.4 (ArCH), 130.8, 132.0, 132.2, 132.7 (ArCH), 135.5 (×2), 144.5, 147.9, 152.7, 155.2, 184.7 (C=O), 185.9 (C=O) ppm. MS (70 eV, EI): *m*/*z* (%) = 642 (100) [M$^+$], 586 (23) [M$^+$ – C$_4$H$_8$], 562 (33) [M$^+$ – Br]. HR-MS (C$_{36}$H$_{37}$$^{79}$BrO$_4$Si): calcd. 640.1644; found 640.1644.

**(*R*,*S*)-15-Bromo-4,4,12-tri-*tert*-butylnaphtho[1,2-*f*]phenanthro[2,1-*d*]-[1,3,2]dioxasilepin-10,13-dione (7):** Benzannulation of carbene complex **4** (0.74 g) with 3,3-dimethyl-1-butyne (0.47 mL). $R_f$ = 0.63 (*t*BuOMe/PE, 1:3). Yield: 0.31 g (0.49 mmol, 49%). $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 0.69 [s, 9 H, $C(CH_3)_3$], 1.05 [s, 9 H, $C(CH_3)_3$], 1.09 [s, 9 H, $C(CH_3)_3$], 6.35 (d, $^4J_{H,H}$ = 1.9 Hz, 1 H, 14-H), 6.40 (s, 1 H, 11-H), 7.20 (d, $^3J_{H,H}$ = 8.7, $^4J_{H,H}$ = 1.9 Hz, 1 H, 16-H), 7.43 (d, $^3J_{H,H}$ = 8.9 Hz, 1 H), 7.49 (d, $^3J_{H,H}$ = 8.7 Hz, 2 H), 7.63 (d, $^3J_{H,H}$ = 8.7 Hz, 1 H), 7.91 (d, $^3J_{H,H}$ = 8.9 Hz, 1 H), 8.02 (d, $^3J_{H,H}$ = 8.4 Hz, 1 H), 8.08 (d, $^3J_{H,H}$ = 8.4 Hz, 1 H) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 21.4 [Si*C*(CH$_3$)], 21.7 [Si*C*(CH$_3$)], 27.6 [C(*C*H$_3$)], 27.9 [C(*C*H$_3$)], 29.2 [C(*C*H$_3$)], 35.2 [*C*(CH$_3$)], 119.9 (ArCH), 120.1, 121.8, 123.3 (ArCH), 125.0 (ArCH), 126.7 (ArCH), 128.7 (ArCH), 129.6, 129.6 (ArCH), 129.7 (ArCH), 130.1, 130.3 (ArCH), 130.6 (ArCH), 130.6 (ArCH), 131.7, 132.0, 132.2, 133.2, 133.3 (ArCH), 133.3 (ArCH), 135.4, 152.4 (2a/5a-C), 155.5 (2a/5a-C), 159.5 (C-*t*Bu), 184.2 (C=O), 186.0 (C=O) ppm. MS (70 eV, EI): *m*/*z* (%) = 642 (100) [M$^+$], 586 (13) [M$^+$ – C$_4$H$_8$], 562 (32) [M$^+$ – Br]. HR-MS (C$_{36}$H$_{37}$$^{79}$BrO$_4$Si): calcd. 640.1644; found 640.1641.

**(*R*,*S*)-15-Bromo-4,4-di-*tert*-butyl-12-phenylnaphtho[1,2-*f*]phenanthro[2,1-*d*][1,3,2]-dioxasilepin-10,13-dione (8):** Benzannulation of carbene complex **4** (0.74 g) with phenylacetylene (0.44 mL). $R_f$ = 0.24 ($CH_2Cl_2$). Yield: 0.24 g (0.36 mmol, 36%). $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 1.03 [s, 9 H, $C(CH_3)_3$], 1.07 [s, 9 H, $C(CH_3)_3$], 6.49 (d, $^4J_{H,H}$ = 1.9 Hz, 1 H, 14-H), 6.60 (s, 1 H, 11-H), 7.11 (dd, $^3J_{H,H}$ = 8.7, $^4J_{H,H}$ = 1.9 Hz, 1 H, 16-H), 7.32 (d, $^3J_{H,H}$ = 8.7 Hz, 1 H), 7.32 (d, $^3J_{H,H}$ = 8.7 Hz, 1 H), 7.42 (d, $^3J_{H,H}$ = 8.9 Hz, 1 H), 7.50 (d, $^3J_{H,H}$ = 8.7 Hz, 1 H), 7.55 (d, $^3J_{H,H}$ = 8.7 Hz, 1 H), 7.96 (d, $^3J_{H,H}$ = 8.9 Hz, 1 H), 8.08 (d, $^3J_{H,H}$ = 8.5 Hz, 1 H), 8.13 (d, $^3J_{H,H}$ = 8.5 Hz, 1 H) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 21.4 [Si*C*(CH$_3$)], 21.7 [Si*C*(CH$_3$)], 27.6 [C(*C*H$_3$)], 27.8 [C(*C*H$_3$)], 120.0 (ArCH), 120.3, 123.3 (ArCH), 125.2 (ArCH), 126.9 (ArCH), 127.6, 127.8 (2 × Ph*C*H), 128.7 (2 × Ph*C*H), 128.8 (ArCH), 129.3, 129.5 (ArCH), 129.8 (ArCH), 129.9 (ArCH), 130.0 (ArCH), 130.6 (ArCH), 131.3, 132.0, 132.1, 132.6, 133.1, 133.4 (ArCH), 135.7, 149.2, 152.7, 155.6, 162.3, 184.9 (C=O), 185.2 (C=O) ppm. MS (70 eV, EI): *m*/*z* (%) = 662 (100) [M$^+$], 606 (181) [M$^+$ – C$_4$H$_8$], 563 (16) [M$^+$ – C$_4$H$_8$ – C$_3$H$_7$], 582 (8) [M$^+$ – Br]. HR-MS (C$_{38}$H$_{33}$$^{79}$BrO$_4$Si): calcd. 660.1331; found 660.1334.

**(*R*,*S*)-15-Bromo-11,12-diethyl-4,4-diphenylnaphtho[1,2-*f*]phenanthro[2,1-*d*][1,3]-dioxepin-10,13-dione (9):** Benzannulation of carbene complex **5** (0.76 g) with 3-hexyne (0.45 mL). $R_f$ = 0.52 ($CH_2Cl_2$/PE, 1:1). Yield: 0.30 g (0.46 mmol, 46%). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 0.41 (t, $^3J_{H,H}$ = 7.5 Hz, 3 H, CH$_2$C*H*$_3$), 1.06 (t, $^3J_{H,H}$ = 7.5 Hz, 3 H, CH$_2$C*H*$_3$), 1.22 (dq, $^2J_{H,H}$ = 12.8, $^3J_{H,H}$ = 7.5 Hz, 1 H, C*H*$_2$CH$_3$), 1.78 (dq, $^2J_{H,H}$ = 12.8, $^3J_{H,H}$ = 7.5 Hz, 1 H, C*H*$_2$CH$_3$), 2.23 (dq, $^2J_{H,H}$ = 12.8, $^3J_{H,H}$ = 7.5 Hz, 1 H, C*H*$_2$CH$_3$), 2.60 (dq, $^2J_{H,H}$ = 12.8, $^3J_{H,H}$ = 7.5 Hz, 1 H, C*H*$_2$CH$_3$), 6.97 (d, $^3J_{H,H}$ = 8.7 Hz, 1 H), 7.03 (d, $^3J_{H,H}$ = 8.7 Hz, 1 H), 7.09 (d, $^4J_{H,H}$ = 1.5 Hz, 1 H, 14-H), 7.35–7.25 (m, 7 H), 7.63–7.52 (m, 4 H), 7.71–7.66 (m, 2 H), 7.73 (d, $^3J_{H,H}$ = 8.7 Hz, 1 H), 8.04 (d, $^3J_{H,H}$ = 8.5 Hz, 1 H), 8.14 (d, $^3J_{H,H}$ = 8.5 Hz, 1 H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 13.3 (*C*H$_2$CH$_3$), 14.1 (*C*H$_2$CH$_3$), 19.4 (CH$_2$*C*H$_3$), 19.8 (CH$_2$*C*H$_3$), 116.6 (C4), 120.6, 121.2 (ArCH), 124.0 (ArCH), 125.9 (ArCH), 127.3, 127.3 (2 × Ph*C*H), 127.5 (2 × Ph*C*H), 127.6 (ArCH), 127.7 (ArCH), 127.8 (2 × Ph*C*H), 127.9 (2 × Ph*C*H), 128.3 (ArCH), 128.4 (ArCH), 128.5 (ArCH), 130.0 (ArCH), 130.1, 130.4 (ArCH), 131.5, 131.9, 133.4 (ArCH), 134.3, 134.9, 140.6, 141.0, 148.7, 149.8, 184.9 (C=O), 186.0 (C=O) ppm. MS (70 eV, EI): *m*/*z* (%) = 666 (83) [M$^+$], 588 (92) [M$^+$ – C$_6$H$_6$], 484 (48) [M$^+$ – OC(C$_6$H$_5$)$_2$], 404 (100) [M$^+$ – OC(C$_6$H$_5$)$_2$ – Br]. HR-MS (C$_{41}$H$_{29}$$^{79}$BrO$_4$): calcd. 664.1249; found 664.1225.

**(*R*,*S*)-15-Bromo-12-*tert*-butyl-4,4-diphenylnaphtho[1,2-*f*]phenanthro[2,1-*d*][1,3]dioxepin-10,13-dione (10):** Benzannulation of carbene complex **5** (0.76 g) with 3,3-dimethyl-1-butyne (0.47 mL). $R_f$ = 0.62 ($CH_2Cl_2$/PE, 1:1). Yield: 0.29 g (0.44 mmol, 44%). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 0.58 [s, 9 H, $C(CH_3)_3$], 6.55 (s, 1 H, 11-H), 6.90 (d, $^3J_{H,H}$ = 8.7 Hz, 1 H), 7.00 (d, $^3J_{H,H}$ = 8.6 Hz, 1 H), 7.04 (d, $^4J_{H,H}$ = 1.9 Hz, 1 H, 14-H), 7.34–7.25 (m, 7 H), 7.47 (d, $^3J_{H,H}$ = 8.7 Hz, 1 H), 7.54 (d, $^3J_{H,H}$ = 8.7 Hz, 1 H), 7.60–7.56 (m, 2 H), 7.70–7.64 (m, 2 H), 7.72 (d, $^3J_{H,H}$ = 8.7 Hz, 1 H), 8.05 (d, $^3J_{H,H}$ = 8.6 Hz, 1 H), 8.11 (d, $^3J_{H,H}$ = 8.3 Hz, 1 H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 28.9 [C(*C*H$_3$)$_3$], 35.2 [*C*(CH$_3$)$_3$], 116.5 (C4), 120.5, 120.7 (ArCH), 123.7 (ArCH), 126.0 (ArCH), 127.3 (×2), 127.3 (2 × Ph*C*H), 127.5 (ArCH), 127.5 (2 × Ph*C*H), 127.7 (ArCH), 127.8 (4 × Ph*C*H), 128.3 (ArCH), 128.3 (ArCH), 128.5 (2 × ArCH), 129.1, 130.1 (ArCH), 130.5 (ArCH), 130.6 (ArCH), 133.7 (ArCH), 134.7, 135.6, 140.5, 140.9, 149.8, 152.6, 159.9, 184.6 (C=O), 185.8 (C=O) ppm. MS (70 eV, EI): *m*/*z* (%) = 666 (72) [M$^+$], 586 (10) [M$^+$ – C$_6$H$_6$], 484 (57) [M$^+$ – OC(C$_6$H$_5$)$_2$], 404 (25) [M$^+$ – OC(C$_6$H$_5$)$_2$ – Br], 57 (100) [C$_4$H$_9$$^+$]. HR-MS (C$_{41}$H$_{29}$$^{79}$BrO$_4$): calcd. 664.1249; found 664.1247.

**(*R*,*S*)-15-Bromo-4,4-diphenyl-12-propylnaphtho[1,2-*f*]phenanthro-[2,1-*d*][1,3]dioxepin-10,13-dione (11):** Benzannulation of carbene complex **5** (0.76 g) with 1-pentyne (0.39 mL). $R_f$ = 0.48 ($CH_2Cl_2$/PE, 1:1). Yield: 0.26 g (0.40 mmol, 40%). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 0.67 (t, $^3J_{H,H}$ = 7.3 Hz, 3 H, $CH_2CH_2CH_3$), 0.67 (t, $^3J_{H,H}$ = 7.3 Hz, 3 H, $CH_2CH_2CH_3$), 0.86–0.68 (m, 2 H, $CH_2CH_2CH_3$), 1.09 (dddd, $^2J_{H,H}$ = 16.5, $^3J_{H,H}$ = 8.4, $^3J_{H,H}$ = 6.6, $^4J_{H,H}$ = 1.7 Hz, 1 H, $CH_2CH_2CH_3$), 1.63 (dddd, $^2J_{H,H}$ = 16.5, $^3J_{H,H}$ = 8.7, $^3J_{H,H}$ = 6.5, $^4J_{H,H}$ = 1.6 Hz, 1 H, $CH_2CH_2CH_3$), 6.39 (t, $^4J_{H,H}$ = 1.6 Hz, 1 H, 11-H), 6.98 (d, $^3J_{H,H}$ = 8.7 Hz, 1 H), 7.06 (d, $^3J_{H,H}$ = 8.6 Hz, 1 H), 7.13 (d, $^4J_{H,H}$ = 1.9 Hz, 1 H, 14-H), 7.33–7.27 (m, 6 H), 7.35 (dd, $^3J_{H,H}$ = 8.7, $^4J_{H,H}$ = 1.9 Hz, 1 H, 16-H), 7.56 (d, $^3J_{H,H}$ = 8.3 Hz, 1 H), 7.60–7.57 (m, 2 H), 7.61 (d, $^3J_{H,H}$ = 8.7 Hz, 1 H), 7.70–7.67 (m, 2 H), 7.73 (d, $^3J_{H,H}$ = 8.7 Hz, 1 H), 8.06 (d, $^3J_{H,H}$ = 8.6 Hz, 1 H), 8.11 (d, $^3J_{H,H}$ = 8.3 Hz, 1 H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 13.4 ($CH_2CH_2CH_3$), 19.5 ($CH_2CH_2CH_3$), 30.0 ($CH_2CH_2CH_3$), 116.6 (C4), 120.9, 120.9 (ArCH), 124.0 (ArCH), 126.1 (ArCH), 127.2 (2×PhCH), 127.4 (2×PhCH), 127.5 (ArCH), 127.8 (2×PhCH), 127.9 (ArCH), 127.9 (2×PhCH), 128.2, 128.4 (2×ArCH), 128.5 (ArCH), 128.9, 130.0 (×2), 130.0 (ArCH), 130.0 (ArCH), 130.1 (ArCH), 130.3 (ArCH), 131.5, 131.8, 132.4, 133.8 (ArCH), 134.4, 135.1, 140.5, 140.9, 149.9, 152.8, 153.9, 184.9 (C=O), 186.1 (C=O) ppm. MS (70 eV, EI): *m*/*z* (%) = 652 (100) [M$^+$], 572 (19) [M$^+$ – Br], 470 (90) [M$^+$ – OC($C_6H_5$)$_2$], 390 (30) [M$^+$ – OC($C_6H_5$)$_2$ – Br]. HR-MS ($C_{40}H_{27}{}^{79}BrO_4$): calcd. 650.1093; found 650.1094.

**(*R*,*S*)-15-Bromo-12-octyl-4,4-diphenylnaphtho[1,2-*f*]phenanthro-[2,1-*d*][1,3]dioxepin-10,13-dione (12):** Benzannulation of carbene complex **5** (0.76 g) with 1-decyne (0.72 mL). $R_f$ = 0.46 ($CH_2Cl_2$/PE, 1:1). Yield: 0.13 g (0.18 mmol, 18%). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 0.86–0.78 (m, 1 H, $CH_2$), 0.89 (t, $^3J_{H,H}$ = 7.1 Hz, 3 H, $CH_2CH_2CH_3$), 1.08–0.98 (m, 2 H, $CH_2$), 1.17–1.11 (m, 2 H, $CH_2$), 1.35–1.19 (m, 8 H, $CH_2$), 1.63 (dddd, $^2J_{H,H}$ = 16.4, $^3J_{H,H}$ = 9.9, $^3J_{H,H}$ = 5.2, $^4J_{H,H}$ = 1.5 Hz, 1 H, $CH_2$), 6.38 (t, $^4J_{H,H}$ = 1.5 Hz, 1 H, 11-H), 6.97 (d, $^3J_{H,H}$ = 8.7 Hz, 1 H), 6.97 (d, $^3J_{H,H}$ = 8.7 Hz, 1 H), 7.05 (d, $^3J_{H,H}$ = 8.6 Hz, 1 H), 7.11 (d, $^4J_{H,H}$ = 1.9 Hz, 1 H, 14-H), 7.32–7.26 (m, 6 H), 7.34 (dd, $^3J_{H,H}$ = 8.7, $^4J_{H,H}$ = 1.9 Hz, 1 H, 16-H), 7.55 (d, $^3J_{H,H}$ = 8.7 Hz, 1 H), 7.60 (d, $^3J_{H,H}$ = 8.7 Hz, 1 H), 7.60–7.55 (m, 2 H), 7.69–7.65 (m, 2 H), 7.74 (d, $^3J_{H,H}$ = 8.5 Hz, 1 H), 8.07 (d, $^3J_{H,H}$ = 8.6 Hz, 1 H), 8.11 (d, $^3J_{H,H}$ = 8.5 Hz, 1 H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 14.1 ($CH_3$), 22.6 (7$CH_2$), 26.2, 28.2, 29.1, 29.2 (×2), 31.8, 114.0, 116.6, 120.8, 120.9 (ArCH), 124.0 (ArCH), 126.1 (ArCH), 127.2, 127.2 (2×PhCH), 127.4 (2×PhCH), 127.4 (2×PhCH), 127.5 (ArCH), 127.8 (2×PhCH), 127.9 (2×PhCH), 128.4 (2×ArCH), 128.5 (ArCH), 128.9, 129.9 (ArCH), 130.0, 130.1 (ArCH), 130.4 (ArCH), 131.5, 131.8, 133.7 (ArCH), 134.4, 135.1, 140.5, 140.9, 143.9, 149.9, 152.8, 154.3, 184.9 (C=O), 186.1 (C=O) ppm. MS (70 eV, EI): *m*/*z* (%) = 722 (100) [M$^+$], 642 (9) [M$^+$ – Br], 540 (19) [M$^+$ – OC($C_6H_5$)$_2$]. HR-MS ($C_{45}H_{37}{}^{79}BrO_4$): calcd. 720.1875; found 720.1806.

**(*R*,*S*)-15-Bromo-4,4,12-triphenylnaphtho[1,2-*f*]phenanthro-[2,1-*d*][1,3]dioxepin-10,13-dione (13):** Benzannulation of carbene complex **5** (0.76 g) with phenylacetylene (0.44 mL). $R_f$ = 0.61 ($CH_2Cl_2$). Yield: 0.23 g (0.33 mmol, 33%). $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 6.64 (dd, $^3J_{H,H}$ = 8.6, $^4J_{H,H}$ = 1.2 Hz, 1 H), 6.95 (d, $^3J_{H,H}$ = 8.7 Hz, 1 H), 6.78 (s, 1 H, 11-H), 7.07 (d, $^3J_{H,H}$ = 8.7 Hz, 1 H), 7.13 (d, $^3J_{H,H}$ = 8.3 Hz, 1 H), 7.18 (d, $^4J_{H,H}$ = 1.9 Hz, 1 H, 14-H), 7.25 (d, $^3J_{H,H}$ = 8.3 Hz, 1 H), 7.30 (d, $^3J_{H,H}$ = 8.9 Hz, 1 H), 7.77 (d, $^3J_{H,H}$ = 8.7 Hz, 1 H), 8.11 (d, $^3J_{H,H}$ = 8.5 Hz, 1 H), 8.17 (d, $^3J_{H,H}$ = 8.3 Hz, 1 H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 116.7 (C4), 120.8, 120.8 (ArCH), 124.1 (ArCH), 126.2 (ArCH), 127.3 (2×PhCH), 127.4 (2×PhCH), 127.7 (2×PhCH), 127.8 (2×PhCH), 127.9 (2×PhCH), 128.1 (ArCH), 128.3, 128.3 (ArCH), 128.4 (2×PhCH), 128.5 (2×ArCH), 128.7, 129.7 (ArCH), 129.9 (ArCH), 130.0 (ArCH), 130.1 (ArCH), 130.2 (ArCH), 130.3, 131.1, 131.7, 132.2, 132.4, 133.9 (ArCH), 134.6, 135.8, 140.5, 149.5, 150.0, 152.9, 184.9 (C=O), 185.8 (C=O) ppm. MS (70 eV, EI): *m*/*z* (%) = 686 (100) [M$^+$], 504 (31) [M$^+$ – OC($C_6H_5$)$_2$], 423 (26) [M$^+$ – OC($C_6H_5$)$_2$ – HBr]. HR-MS ($C_{43}H_{25}{}^{79}BrO_4$): calcd. 684.0936; found 684.0933.

**Resolution of Helical Monohydroquinone 9:** A solution of racemic carbene complex **5** (1.15 g, 1.5 mmol) and 3-hexyne (0.68 mL, 6 mmol) in THF (10 mL) was warmed to 55 °C for 3 h. The mixture was cooled to –10 °C and combined with triethylamine (0.31 mL, 2.25 mmol), (1*S*)-(–)-camphanoyl chloride and 4-(dimethylamino)pyridine (DMAP, 92 mg, 0.75 mmol). Stirring was continued overnight whilst allowing the Schlenk tube to reach room temperature. The solvent was removed, and the residue was purified by column chromatography on silica gel ($CH_2Cl_2$/PE, 1:1) to yield the yellow monocamphanate esters (*M*)-**14** and (*P*)-**14** along with DMAP·$Cr(CO)_5$ **15** ($R_f$ = 0.35) as by-product.

**Monocamphanate (*M*)-14:** $R_f$ = 0.27 ($CH_2Cl_2$/PE, 1:1). Yield: 0.25 g (0.29 mmol, 38% based on one diastereomer). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 0.23 (t, $^3J_{H,H}$ = 7.5 Hz, 3 H, $CH_2CH_3$), 0.74 (s, 3 H, $CH_3$), 0.84 (s, 3 H, $CH_3$), 1.04 (s, 3 H, $CH_3$), 1.09 (t, $^3J_{H,H}$ = 7.5 Hz, 3 H, $CH_2CH_3$), 1.77 (ddd, $^2J_{H,H}$ = 13.1, $^3J_{H,H}$ = 8.9, $^3J_{H,H}$ = 4.7 Hz, 1 H, $CH_2$), 1.80 (dq, $^2J_{H,H}$ = 14.2, $^3J_{H,H}$ = 7.5 Hz, 1 H, $CH_2CH_3$), 1.83 (ddd, $^2J_{H,H}$ = 13.1, $^3J_{H,H}$ = 10.1, $^3J_{H,H}$ = 4.9 Hz, 1 H, $CH_2$), 2.05 (ddd, $^2J_{H,H}$ = 13.4, $^3J_{H,H}$ = 10.1, $^3J_{H,H}$ = 4.9 Hz, 1 H, $CH_2$), 2.17 (dq, $^2J_{H,H}$ = 14.2, $^3J_{H,H}$ = 7.5 Hz, 1 H, $CH_2CH_3$), 2.56 (dq, $^2J_{H,H}$ = 13.7, $^3J_{H,H}$ = 7.5 Hz, 1 H, $CH_2CH_3$), 2.60 (ddd, $^2J_{H,H}$ = 13.4, $^3J_{H,H}$ = 8.9, $^3J_{H,H}$ = 4.7 Hz, 1 H, $CH_2$), 2.85 (dq, $^2J_{H,H}$ = 13.7, $^3J_{H,H}$ = 7.5 Hz, 1 H, $CH_2CH_3$), 4.01 (s, 3 H, $OCH_3$), 6.41 (d, $^4J_{H,H}$ = 2.0 Hz, 1 H, 14-H), 7.06 (d, $^3J_{H,H}$ = 8.7 Hz, 1 H), 7.07 (dd, $^3J_{H,H}$ = 8.7, $^4J_{H,H}$ = 2.0 Hz, 1 H, 16-H), 7.10 (d, $^3J_{H,H}$ = 8.5 Hz, 1 H), 7.20–7.16 (m, 3 H), 7.34–7.26 (m, 2 H), 7.48–7.42 (m, 3 H), 7.52 (d, $^3J_{H,H}$ = 8.5 Hz, 1 H), 7.60 (d, $^3J_{H,H}$ = 8.7 Hz, 1 H), 7.69–7.66 (m, 2 H), 7.70 (d, $^3J_{H,H}$ = 8.5 Hz, 1 H), 7.89 (d, $^3J_{H,H}$ = 8.7 Hz, 1 H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 9.6 [C($CH_3$)], 13.7 ($CH_2CH_3$), 15.3 ($CH_2CH_3$), 16.6 [2C($CH_3$)], 20.0 ($CH_2CH_3$), 20.6 ($CH_2CH_3$), 29.1 ($CH_2$), 31.5 ($CH_2$), 54.8 [$C$($CH_3$)], 55.2 [$C$($CH_3$)], 63.4 ($OCH_3$), 90.1 (O$C$C=O), 117.0, 118.7, 119.9 (ArCH), 123.6 (ArCH), 124.4, 125.6 (ArCH), 126.1, 126.8 (ArCH), 127.1 (ArCH), 127.2 (4×PhCH), 127.6, 127.7 (4×PhCH), 127.9 (ArCH), 128.0, 128.2 (ArCH), 128.3 (ArCH), 128.4 (ArCH), 128.7 (ArCH), 129.0, 129.7 (ArCH), 130.4, 131.3, 133.4, 134.5, 140.8, 141.2, 142.1, 149.8, 150.3, 152.0, 167.2 (OC=O), 178.3 (OC=O) ppm. MS (FAB): *m*/*z* (%) = 862 (100) [M$^+$], 783 (10) [M$^+$ – Br], 681 (13) [M$^+$ – $C_{10}H_{13}O_3$].

**Monocamphanate (*P*)-14:** $R_f$ = 0.12 ($CH_2Cl_2$/PE, 1:1). Yield: 0.25 g (0.29 mmol, 38% based on one diastereomer). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 0.26 (t, $^3J_{H,H}$ = 7.5 Hz, 3 H, $CH_2CH_3$), 0.69 (s, 3 H, $CH_3$), 0.74 (s, 3 H, $CH_3$), 1.09 (t, $^3J_{H,H}$ = 7.5 Hz, 3 H, $CH_2CH_3$), 1.10 (s, 3 H, $CH_3$), 1.65 (ddd, $^2J_{H,H}$ = 13.3, $^3J_{H,H}$ = 8.3, $^3J_{H,H}$ = 4.4 Hz, 1 H, $CH_2$), 1.71 (dq, $^2J_{H,H}$ = 13.6, $^3J_{H,H}$ = 7.4 Hz, 1 H, $CH_2CH_3$), 1.77 (ddd, $^2J_{H,H}$ = 13.3, $^3J_{H,H}$ = 8.3, $^3J_{H,H}$ = 4.4 Hz, 1 H, $CH_2$), 1.97 (ddd, $^2J_{H,H}$ = 13.2, $^3J_{H,H}$ = 8.3, $^3J_{H,H}$ = 4.9 Hz, 1 H, $CH_2$), 2.01 (ddd, $^2J_{H,H}$ = 13.2, $^3J_{H,H}$ = 8.3, $^3J_{H,H}$ = 4.9 Hz, 1 H, $CH_2$), 2.16 (dq, $^2J_{H,H}$ = 14.3, $^3J_{H,H}$ = 7.3 Hz, 1 H, $CH_2CH_3$), 2.54 (dq, $^2J_{H,H}$ = 13.6, $^3J_{H,H}$ = 7.5 Hz, 1 H, $CH_2CH_3$), 2.85 (dq, $^2J_{H,H}$ = 13.7, $^3J_{H,H}$ = 7.4 Hz, 1 H, $CH_2CH_3$), 4.02 (s, 3 H, $OCH_3$), 6.39 (d, $^4J_{H,H}$ = 1.8 Hz, 1 H, 14-H), 7.07 (dd, $^3J_{H,H}$ = 8.7, $^4J_{H,H}$ = 1.8 Hz, 1 H, 16-H), 7.16 (d, $^3J_{H,H}$ = 8.7 Hz, 1 H), 7.17 (d, $^3J_{H,H}$ = 8.2 Hz, 1 H), 7.20–7.14 (m, 3 H), 7.29–7.25 (m, 1 H), 7.33 (d, $^3J_{H,H}$ = 8.4 Hz, 1 H), 7.34 (dd, $^3J_{H,H}$ = 6.9, $^4J_{H,H}$ = 1.4 Hz, 1 H), 7.41

(d, $^3J_{H,H}$ = 8.7 Hz, 1 H), 7.47 (d, $^3J_{H,H}$ = 8.7 Hz, 1 H), 7.54–7.50 (m, 2 H), 7.60 (d, $^3J_{H,H}$ = 8.7 Hz, 1 H), 7.69 (d, $^3J_{H,H}$ = 8.4 Hz, 1 H), 7.87 (d, $^3J_{H,H}$ = 8.7 Hz, 1 H), 7.89–7.84 (m, 2 H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 9.7 [C(*C*H$_3$)], 13.7 (CH$_2$*C*H$_3$), 15.3 (CH$_2$*C*H$_3$), 16.7 [C(*C*H$_3$)], 16.8 [C(*C*H$_3$)], 19.9 (*C*H$_2$CH$_3$), 20.4 (*C*H$_2$CH$_3$), 29.1 (CH$_2$), 30.7 (CH$_2$), 54.1 [2 × *C*(CH$_3$)], 63.4 (OCH$_3$), 90.0 (O*C*C=O), 117.2, 118.7, 119.6 (ArCH), 123.7 (ArCH), 124.6, 125.9 (ArCH), 126.2, 126.9 (ArCH), 127.0 (ArCH), 127.2 (2 × Ph*C*H), 127.4, 127.5 (2 × Ph*C*H), 127.6 (2 × Ph*C*H), 127.7 (2 × Ph*C*H), 127.8 (ArCH), 127.9 (ArCH), 128.0 (ArCH), 128.1 (ArCH), 128.2, 128.5 (ArCH), 129.0, 129.5 (ArCH), 129.5 (ArCH), 130.2, 130.6, 131.2, 132.7, 134.3, 141.1, 141.3, 142.3, 150.6, 150.8, 152.0, 166.7 (OC=O), 178.3 (OC=O) ppm. MS (FAB): *m*/*z* (%) = 862 (36) [M$^+$], 783 (3) [M$^+$ – Br], 681 (9) [M$^+$ – $C_{10}H_{13}O_3$].

**Preparation of Non-Racemic Monoquinone 9 from Monocamphanates 14:** KOH powder (0.43 g, 7.6 mmol) was added to a solution of diastereomerically pure (*M*)-**14** or (*P*)-**14** (0.16 g, 0.19 mmol) in methanol (20 mL) and the mixture was stirred at room temp. for 1 h. It was then quenched with 5 M HCl (2 mL) and diluted with water (20 mL). Extraction with EtOAc (3 × 20 mL) and solvent exchange to $CH_2Cl_2$ (20 mL) resulted in a yellow solution, which was poured into a mixture of CAN (0.52 g, 0.95 mmol) in water (20 mL) at 0 °C. After stirring for 1 h in an ice bath the organic layer was separated, and the aqueous layer was extracted with $CH_2Cl_2$ (3 × 10 mL). The combined organic layers were washed with brine (3 × 25 mL) and dried ($MgSO_4$). The solvent was stripped off, and the orange solid was chromatographed ($CH_2Cl_2$/PE, 1:1, $R_f$ = 0.52) to give (*M*)-**9** or (*P*)-**9** (0.10 g, 0.16 mmol). The $^1$H and $^{13}$C NMR spectra were identical to those of racemic **9**.

**General Procedure C. Synthesis of Carbene Complexes 16–19:** *n*BuLi (1.6 M in hexane, 3.8 mL, 6.05 mmol) was slowly syringed into a solution of 2.88 mmol of 2,2′-bridged dibromo-1,1′-binaphthyl **2** (1.68 g) or **3** (1.75 g) in THF (50 mL) at –88 °C. Stirring for 90 min and warming to –78 °C led to a brownish mixture, to which hexacarbonyl chromium (1.9 g, 8.64 mmol) was added. After stirring for 2.5 h the reaction mixture was allowed to reach room temp., and was subsequently concentrated in vacuo. The reddish brown residue was dissolved in $CH_2Cl_2$ (50 mL) and treated with $Me_3O^+BF_4^-$ (0.93 g, 6.34 mmol). After stirring for 2 h at room temp. the solvent was removed, and the deep-red residue was subjected to column chromatography (*t*BuOMe/PE, 1:3), with the red biscarbene complex **16** or **18** eluting first followed by the monocarbene complex **17** or **19** as a red by-product.

**(*R*,*S*)-10,13-[4,4-Di-*tert*-butyldinaphtho[2,1-*d*:1′,2′-*f*][1,3,2]-dioxasilepindiyl]bis(methoxycarbene)bis[(pentacarbonyl)chromium] (16):** $R_f$ = 0.64. Yield: 1.23 g (1.38 mmol, 48%). IR (petroleum ether): ν(CO) = 2062 (m), 1992 (w), 1961 (vs), 1936 (sh) cm$^{-1}$. $^1$H NMR (300 MHz, $CD_2Cl_2$): $\delta$ = 0.99 [s, 18 H, C(C*H*$_3$)$_3$], 4.58 (s, 6 H, OC*H*$_3$), 7.09 (s, 2 H, 11/12-H), 7.16 (dd, $^3J_{H,H}$ = 8.5, $^4J_{H,H}$ = 1.7 Hz, 2 H, 9/14-H), 7.52 (d, $^3J_{H,H}$ = 8.9 Hz, 2 H), 7.84 (d, $^3J_{H,H}$ = 8.5 Hz, 2 H, 8/15-H), 7.90 (d, $^3J_{H,H}$ = 8.9 Hz, 2 H) ppm. $^{13}$C NMR (75 MHz, $CD_2Cl_2$): $\delta$ = 21.3 [Si*C*(CH$_3$)$_3$], 27.4 [SiC(*C*H$_3$)$_3$], 67.5 (OCH$_3$), 118.2, 121.0, 123.1, 124.2, 128.4, 129.9, 131.0, 133.3, 152.3, 153.3, 216.0 (*cis*-CO), 224.8 (*trans*-CO), 350.8 (C=Cr) ppm. MS (FAB): *m*/*z* (%) = 894 (6) [M$^+$], 838 (4) [M$^+$ – 2CO], 754 (88) [M$^+$ – 5CO], 670 (46) [M$^+$ – 8CO], 642 (70) [M$^+$ – 9CO], 614 (78) [M$^+$ – 10CO].

**(*R*,*S*)-10-[4,4-Di-*tert*-butyldinaphtho[2,1-*d*:1′,2′-*f*][1,3,2]-dioxasilepinyl](methoxycarbene)(pentacarbonyl)chromium (17):** $R_f$ = 0.46. Yield: 0.63 g (0.95 mmol, 33%). IR (petroleum ether): ν(CO) = 2063 (m), 1988 (w), 1956 (vs), 1940 (sh) cm$^{-1}$ – $^1$H NMR (300 MHz, $CD_2Cl_2$): $\delta$ = 0.98 [s, 9 H, C(C*H*$_3$)$_3$], 0.99 [s, 9 H, C(C*H*$_3$)$_3$], 4.40 (s, 3 H, OC*H*$_3$), 6.82 (s, 1 H, 11-H), 7.00 (d, $^3J_{H,H}$ = 8.5 Hz, 1 H), 7.16 (ddd, $^3J_{H,H}$ = 6.9, $^3J_{H,H}$ = 8.4, $^4J_{H,H}$ = 1.6 Hz, 1 H, 13/14-H), 7.25 (dd, $^3J_{H,H}$ = 8.5, $^4J_{H,H}$ = 1.6 Hz, 1 H), 7.33 (ddd, $^3J_{H,H}$ = 6.9, $^3J_{H,H}$ = 8.2, $^4J_{H,H}$ = 1.2 Hz, 1 H, 13/14-H), 7.44 (d, $^3J_{H,H}$ = 8.9 Hz, 1 H), 7.50 (d, $^3J_{H,H}$ = 8.9 Hz, 1 H), 7.84 (d, $^3J_{H,H}$ = 8.1 Hz, 1 H), 7.90 (d, $^3J_{H,H}$ = 8.9 Hz, 1 H), 7.91 (2d, $^3J_{H,H}$ = 8.5 Hz, 2 H) ppm. $^{13}$C NMR (75 MHz, $CD_2Cl_2$): $\delta$ = 21.3 [Si*C*(CH$_3$)$_3$], 27.5 [SiC(*C*H$_3$)$_3$], 67.2 (OCH$_3$), 118.7, 119.4, 120.8, 122.3, 122.9, 124.1, 124.2, 126.5, 127.5, 128.3, 128.3, 128.5, 129.6, 130.3, 130.5, 133.3, 133.9, 151.7, 152.3, 153.3, 216.0 (*cis*-CO), 224.8 (*trans*-CO), 351.1 (C=Cr) ppm. MS (FAB): *m*/*z* (%) = 660 (1) [M$^+$], 520 (100) [M$^+$ – 5CO].

**(*R*,*S*)-10,13-[4,4-Diphenyldinaphtho[2,1-*d*:1′,2′-*f*][1,3]-dioxepindiyl]-bis(methoxycarbene)bis[(pentacarbonyl)chromium] (18):** $R_f$ = 0.48. Yield: 1.29 g (1.41 mmol, 49%). IR (petroleum ether): ν(CO) = 2063 (m), 1992 (w), 1961 (vs), 1936 (sh) cm$^{-1}$. $^1$H NMR (400 MHz, $CD_2Cl_2$): $\delta$ = 4.66 (s, OC*H*$_3$, 6 H), 7.03 (d, $^3J_{H,H}$ = 8.7 Hz, 2 H), 7.35–7.28 (m, 8 H), 7.60–7.50 (m, 6 H), 7.71 (d, $^3J_{H,H}$ = 8.7 Hz, 2 H), 7.86 (d, $^3J_{H,H}$ = 8.5 Hz, 2 H) ppm. $^{13}$C NMR (100 MHz, $CD_2Cl_2$): $\delta$ = 67.7 (O*C*H$_3$), 117.7, 119.9, 122.5, 124.8 (Ar*C*H), 127.2 (Ph*C*H), 127.2, 127.5, 128.0 (Ph*C*H), 128.6 (3Ar*C*H), 128.6, 129.1, 131.5, 132.2, 141.1, 151.2, 152.2, 216.1 (*cis*-CO), 224.6 (*trans*-CO), 350.4 (C=Cr) ppm. MS (FAB): *m*/*z* (%) = 919 (8) [M$^+$], 779 (46) [M$^+$ – 5CO], 695 (34) [M$^+$ – 8CO], 667 (100) [M$^+$ – 9CO], 639 (54) [M$^+$ – 10CO].

**(*R*,*S*)-10-[4,4-Diphenyldinaphtho[2,1-*d*:1′,2′-*f*][1,3]-dioxepinyl](methoxycarbene)(pentacarbonyl)chromium (19):** $R_f$ = 0.32. Yield: 0.59 g (0.86 mmol, 30%). IR (petroleum ether): ν(CO) = 2063 (m), 1988 (w), 1954 (vs), 1942 (sh) cm$^{-1}$. $^1$H NMR (300 MHz, $CD_2Cl_2$): $\delta$ = 4.49 (s, OC*H*$_3$, 3 H), 6.94 (d, $^3J_{H,H}$ = 8.7 Hz, 1 H), 7.02 (d, $^3J_{H,H}$ = 8.9 Hz, 1 H), 7.34–7.24 (m, 8 H), 7.36 (ddd, $^3J_{H,H}$ = 7.1, $^3J_{H,H}$ = 8.2, $^4J_{H,H}$ = 1.2 Hz, 1 H, 13/14-H), 7.45 (ddd, $^3J_{H,H}$ = 6.8, $^3J_{H,H}$ = 8.2, $^4J_{H,H}$ = 1.4 Hz, 1 H, 13/14-H), 7.61–7.52 (m, 5 H), 7.71 (d, $^3J_{H,H}$ = 8.7 Hz, 1 H), 7.72 (d, $^3J_{H,H}$ = 8.6 Hz, 1 H), 7.86 (d, $^3J_{H,H}$ = 7.5 Hz, 1 H), 7.91 (d, $^3J_{H,H}$ = 8.5 Hz, 1 H) ppm. $^{13}$C NMR (100 MHz, $CD_2Cl_2$): $\delta$ = 67.4 (O*C*H$_3$), 117.6, 120.0, 120.4, 123.0 (Ar*C*H), 124.9 (Ar*C*H), 125.3 (Ar*C*H), 125.8, 126.6 (2 × Ar*C*H), 127.2 (2 × Ph*C*H), 127.3 (Ar*C*H), 128.0 (2 × Ph*C*H), 128.0 (Ar*C*H), 128.5 (3Ar*C*H), 128.7(Ar*C*H), 129.0 (Ar*C*H), 129.5 (Ar*C*H), 131.3, 131.9, 132.2, 141.2 (×2), 150.4, 151.3, 216.1 (*cis*-CO), 224.7 (*trans*-CO), 350.8 (C=Cr) ppm. MS (FAB): *m*/*z* (%) = 684 (5) [M$^+$], 600 (10) [M$^+$ – 3CO], 572 (8) [M$^+$ – 4CO], 544 (65) [M$^+$ – 5CO], 529 (19) [M$^+$ – 5CO – CH$_3$].

**(*R*,*S*)-4,4-Di-*tert*-butyl-11,12-diethylnaphtho[1,2-*f*]phenanthro[2,1-*d*][1,3,2]-dioxasilepin-10,13-dione (20):** Procedure B. Benzannulation of carbene complex **17** (0.66 g) with 3-hexyne (0.45 mL). $R_f$ = 0.85 (*t*BuOMe/PE, 1:2). Yield: 0.30 g (0.54 mmol, 54%). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 0.55 (t, $^3J_{H,H}$ = 7.6 Hz, 3 H, CH$_3$), 0.86 (t, $^3J_{H,H}$ = 7.5 Hz, 3 H, CH$_3$), 1.05 [s, 9 H, C(CH$_3$)$_3$], 1.10 [s, 9 H, C(CH$_3$)$_3$], 1.38 (dq, $^2J_{H,H}$ = 12.9, $^3J_{H,H}$ = 7.5 Hz, 2 H, CH$_2$), 1.76 (dq, $^2J_{H,H}$ = 12.9, $^3J_{H,H}$ = 7.6 Hz, 1 H, CH$_2$), 2.12 (dq, $^2J_{H,H}$ = 12.9, $^3J_{H,H}$ = 7.6 Hz, 1 H, CH$_2$), 2.42 (dq, $^2J_{H,H}$ = 12.9, $^3J_{H,H}$ = 7.5 Hz, 1 H, CH$_2$), 6.29 (d, $^3J_{H,H}$ = 8.6 Hz, 1 H), 6.84 (ddd, $^3J_{H,H}$ = 6.9, $^3J_{H,H}$ = 8.6, $^4J_{H,H}$ = 1.4 Hz, 1 H), 7.12 (ddd, $^3J_{H,H}$ = 6.9, $^3J_{H,H}$ = 8.1, $^4J_{H,H}$ = 1.2 Hz, 1 H), 7.49 (d, $^3J_{H,H}$ = 9.1 Hz, 1 H), 7.51 (d, $^3J_{H,H}$ = 9.1 Hz, 1 H), 7.66 (d, $^3J_{H,H}$ = 8.1 Hz, 1 H), 7.75 (d, $^3J_{H,H}$ = 8.7 Hz, 1 H), 7.89 (d, $^3J_{H,H}$ = 8.7 Hz, 1 H), 7.99 (d, $^3J_{H,H}$ = 8.4 Hz, 1 H), 8.01 (d, $^3J_{H,H}$ = 8.4 Hz, 1 H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 13.6 (2*C*H$_2$CH$_3$), 19.1 (CH$_2$*C*H$_3$), 19.8 (CH$_2$*C*H$_3$), 21.4 [Si*C*(CH$_3$)$_3$], 21.6 [Si*C*(CH$_3$)$_3$], 27.7 [SiC(*C*H$_3$)$_3$], 27.8 [SiC(*C*H$_3$)$_3$], 120.1 (ArCH), 122.0, 122.7 (ArCH), 123.4 (ArCH), 123.7, 124.8 (ArCH), 125.4 (ArCH), 126.6 (ArCH), 128.0 (ArCH),

129.3 (ArCH), 130.0 (ArCH), 131.0, 131.1, 131.4, 132.0, 132.4 (ArCH), 132.7, 136.0, 143.8, 148.5, 151.8, 155.1, 185.1 (C=O), 185.9 (C=O) ppm. MS (70 eV, EI): *m*/*z* (%) = 562 (100) [$M^+$], 506 (17) [$M^+ - C_4H_8$]. HR-MS ($C_{36}H_{38}O_4Si$): calcd. 562.2539; found 562.2537.

**(*R*,*S*)-4,4-Di-*tert*-butyl-12-phenylnaphtho[1,2-*f*]phenanthro-[2,1-*d*][1,3,2]-dioxasilepin-10,13-dione (21):** Procedure B. Benzannulation of carbene complex **17** (0.66 g) with phenylacetylene (0.44 mL), product 1. $R_f$ = 0.57 ($CH_2Cl_2$). Yield: 0.14 g (0.24 mmol, 24%). $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 1.04 [s, 9 H, $C(CH_3)_3$], 1.07 [s, 9 H, $C(CH_3)_3$], 6.35 (d, $^3J_{H,H}$ = 8.7 Hz, 1 H), 6.53 (s, 1 H, 11-H), 6.68 (dd, $^3J_{H,H}$ = 8.4, $^4J_{H,H}$ = 1.0 Hz, 1 H), 6.69 (dd, $^3J_{H,H}$ = 8.3, $^4J_{H,H}$ = 2.1 Hz, 1 H), 6.88 (ddd, $^3J_{H,H}$ = 6.9, $^3J_{H,H}$ = 8.7, $^4J_{H,H}$ = 1.5 Hz, 1 H), 7.04 (ddd, $^3J_{H,H}$ = 6.9, $^3J_{H,H}$ = 8.1, $^4J_{H,H}$ = 1.2 Hz, 1 H), 7.24–7.17 (m, 2 H), 7.32 (dddd, $^3J_{H,H}$ = 6.8, $^3J_{H,H}$ = 8.1, $^4J_{H,H}$ = 1.2 Hz, 1 H), 7.43 (d, $^3J_{H,H}$ = 8.7 Hz, 1 H), 7.47–7.37 (m, 1 H), 7.54 (d, $^3J_{H,H}$ = 8.7 Hz, 1 H), 7.58 (d, $^3J_{H,H}$ = 8.9 Hz, 1 H), 7.94 (d, $^3J_{H,H}$ = 8.9 Hz, 1 H), 8.04 (d, $^3J_{H,H}$ = 8.5 Hz, 1 H), 8.10 (d, $^3J_{H,H}$ = 8.5 Hz, 1 H) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 21.4 [Si*C*($CH_3$)], 21.7 [Si*C*($CH_3$)], 27.7 [SiC(*C*$H_3$)], 27.8 [SiC(*C*$H_3$)], 119.8 (ArCH), 122.2, 122.8 (ArCH), 123.6 (ArCH), 125.2 (ArCH), 125.8 (ArCH), 126.1, 126.3 (ArCH), 127.7 (ArCH), 128.3 (ArCH), 128.8 (ArCH), 129.6 (ArCH), 129.8 (ArCH), 130.2 (ArCH), 130.8, 131.1, 131.8, 132.1, 132.7, 133.1, 133.1 (ArCH), 136.2, 149.5, 151.8, 155.5, 162.3, 185.1 (C=O), 185.2 (C=O) ppm. MS (70 eV, EI): *m*/*z* (%) = 582 (100) [$M^+$], 526 (11) [$M^+ - C_4H_8$], 483 (14) [$M^+ - C_4H_8 - C_3H_7$]. HR-MS ($C_{38}H_{34}O_4Si$): calcd. 582.2226; found 582.2231.

**(*R*,*S*)-4,4-Di-*tert*-butyl-10-phenylanthra[2,1-*d*]naphtho[1,2-*f*][1,3,2]-dioxasilepin-9,12-dione (22):** Procedure B. Benzannulation of carbene complex **17** (0.66 g) with phenylacetylene (0.44 mL), product 2. $R_f$ = 0.32 ($CH_2Cl_2$). Yield: 0.13 g (0.22 mmol, 22%). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 0.97 [s, 9 H, $C(CH_3)_3$], 0.98 [s, 9 H, $C(CH_3)_3$], 6.88 (d, $^3J_{H,H}$ = 8.5 Hz, 1 H), 6.96 (s, 1 H), 7.09 (ddd, $^3J_{H,H}$ = 6.9, $^3J_{H,H}$ = 8.5, $^4J_{H,H}$ = 1.4 Hz, 1 H), 7.31 (ddd, $^3J_{H,H}$ = 6.9, $^3J_{H,H}$ = 8.0, $^4J_{H,H}$ = 1.1 Hz, 1 H), 7.42 (d, $^3J_{H,H}$ = 8.8 Hz, 1 H), 7.47–7.42 (m, 3 H), 7.59–7.52 (m, 2 H), 7.59 (d, $^3J_{H,H}$ = 8.8 Hz, 1 H), 7.80 (s, 1 H), 7.86 (d, $^3J_{H,H}$ = 8.0 Hz, 1 H), 7.93 (d, $^3J_{H,H}$ = 8.8 Hz, 1 H), 8.10 (d, $^3J_{H,H}$ = 8.8 Hz, 1 H), 8.71 (s, 1 H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 21.3 [Si*C*($CH_3$)], 21.4 [Si*C*($CH_3$)], 27.6 (2SiC(*C*$H_3$)], 118.7, 122.2 (ArCH), 123.2, 124.2 (ArCH), 125.9 (ArCH), 126.1 (ArCH), 126.3 (ArCH), 127.3 (ArCH), 127.4, 128.4, 128.4 (Ph*C*H), 128.5 (ArCH), 129.4 (Ph*C*H), 129.4, 129.7 (ArCH), 129.9 (ArCH), 130.2, 130.8 (ArCH), 131.6, 131.7 (ArCH), 133.9, 136.2, 136.8 (ArCH), 149.1, 152.2, 155.3, 183.9 (C=O), 184.5 (C=O) ppm. MS (70 eV, EI): *m*/*z* (%) = 582 (100) [$M^+$], 526 (16) [$M^+ - C_4H_8$], 483 (56) [$M^+ - C_4H_8 - C_3H_7$]. HR-MS ($C_{38}H_{34}O_4Si$): calcd. 582.2226; found 582.2234.

**(*R*,*S*)-11,12-Diethyl-4,4-diphenylnaphtho[1,2-*f*]phenanthro[2,1-*d*]-[1,3]dioxepin-10,13-dione (23):** Procedure B. Benzannulation of carbene complex **19** (0.68 g) with 3-hexyne (0.45 mL). $R_f$ = 0.33 ($CH_2Cl_2$/PE, 1:1). Yield: 0.30 g (0.51 mmol, 51%). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 0.23 (t, $^3J_{H,H}$ = 7.5 Hz, 3 H, $CH_2CH_3$), 0.89 (t, $^3J_{H,H}$ = 7.5 Hz, 3 H, $CH_2CH_3$), 1.22 (dq, $^2J_{H,H}$ = 13.0, $^3J_{H,H}$ = 7.5 Hz, 1 H, $CH_2CH_3$), 1.73 (dq, $^2J_{H,H}$ = 12.9, $^3J_{H,H}$ = 7.5 Hz, 1 H, $CH_2CH_3$), 2.17 (dq, $^2J_{H,H}$ = 13.0, $^3J_{H,H}$ = 7.5 Hz, 1 H, $CH_2CH_3$), 2.41 (dq, $^2J_{H,H}$ = 12.9, $^3J_{H,H}$ = 7.5 Hz, 1 H, $CH_2CH_3$), 6.86 (d, $^3J_{H,H}$ = 8.6 Hz, 1 H), 6.90 (d, $^3J_{H,H}$ = 8.7 Hz, 1 H), 6.95 (ddd, $^3J_{H,H}$ = 6.9, $^3J_{H,H}$ = 8.6, $^4J_{H,H}$ = 1.4 Hz, 1 H), 6.96 (d, $^3J_{H,H}$ = 8.6 Hz, 1 H), 7.16 (ddd, $^3J_{H,H}$ = 6.9, $^3J_{H,H}$ = 8.1, $^4J_{H,H}$ = 1.1 Hz, 1 H), 7.25–7.17 (m, 6 H), 7.50 (d, $^3J_{H,H}$ = 8.7 Hz, 1 H), 7.55–7.48 (m, 2 H), 7.61 (d, $^3J_{H,H}$ = 8.7 Hz, 1 H), 7.67–7.59 (m, 3 H), 7.93 (d, $^3J_{H,H}$ = 8.6 Hz, 1 H), 8.03 (d, $^3J_{H,H}$ = 8.6 Hz, 1 H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 12.9 ($CH_2CH_3$), 13.5 ($CH_2CH_3$), 19.2 ($CH_2CH_3$), 19.7 ($CH_2CH_3$), 116.3 (C4), 120.9 (ArCH), 123.3 (ArCH), 124.4 (ArCH), 125.0 (ArCH), 125.9 (ArCH), 126.0 (ArCH), 127.3 (2×Ph*C*H), 127.5 (2×Ph*C*H), 127.7 (2×Ph*C*H), 127.8 (2×Ph*C*H), 128.1, 128.3 (2×ArCH), 128.4 (ArCH), 128.8 (ArCH), 129.6 (ArCH), 129.7, 130.4, 131.8, 131.9, 133.1 (ArCH), 134.1, 134.1, 135.3, 140.9, 141.2, 143.6, 148.9, 149.2, 152.5, 185.2 (C=O), 186.1 (C=O) ppm. MS (70 eV, EI): *m*/*z* (%) = 586 (100) [$M^+$], 404 (60) [$M^+ - OC(C_6H_5)_2$]. HR-MS ($C_{41}H_{30}O_4$): calcd. 586.2144; found 586.2152.

**(*R*,*S*)-4,4-Diphenyl-11,12-dipropylnaphtho[1,2-*f*]phenanthro-[2,1-*d*]-[1,3]dioxepin-10,13-dione (24):** Procedure B. Benzannulation of carbene complex **19** (0.68 g) with 4-octyne (0.59 mL), product 1. $R_f$ = 0.55 ($CH_2Cl_2$/PE, 1:1). Yield: 0.19 g (0.31 mmol, 31%). $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 0.41–0.25 (m, 1 H, $CH_2CH_2CH_3$), 0.57 (t, $^3J_{H,H}$ = 7.4 Hz, 3 H, $CH_2CH_2CH_3$), 0.87 (t, $^3J_{H,H}$ = 7.4 Hz, 3 H, $CH_2CH_2CH_3$), 1.45–1.20 (m, 4 H, $CH_2CH_2CH_3$), 1.90–1.76 (m, 1 H, $CH_2CH_2CH_3$), 2.19 (ddd, $^2J_{H,H}$ = 12.7, $^3J_{H,H}$ = 8.3, $^3J_{H,H}$ = 7.2 Hz, 1 H, $CH_2CH_2CH_3$), 2.47 (ddd, $^2J_{H,H}$ = 12.7, $^3J_{H,H}$ = 8.5, $^3J_{H,H}$ = 6.8 Hz, 1 H, $CH_2CH_2CH_3$), 6.91 (dd, $^3J_{H,H}$ = 8.7, $^4J_{H,H}$ = 0.8 Hz, 1 H), 6.96 (d, $^3J_{H,H}$ = 8.7 Hz, 1 H), 7.02 (ddd, $^3J_{H,H}$ = 6.7, $^3J_{H,H}$ = 8.4, $^4J_{H,H}$ = 1.7 Hz, 1 H), 7.03 (d, $^3J_{H,H}$ = 8.7 Hz, 1 H), 7.23 (ddd, $^3J_{H,H}$ = 6.8, $^3J_{H,H}$ = 8.1, $^4J_{H,H}$ = 1.3 Hz, 1 H), 7.37–7.24 (m, 6 H), 7.63–7.55 (m, 3 H), 7.70 (d, $^3J_{H,H}$ = 8.5 Hz, 1 H), 7.72 (d, $^3J_{H,H}$ = 8.7 Hz, 1 H), 7.76–7.66 (m, 2 H), 8.02 (d, $^3J_{H,H}$ = 8.5 Hz, 1 H), 8.10 (d, $^3J_{H,H}$ = 8.5 Hz, 1 H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 14.2 ($CH_2CH_2CH_3$), 14.3 ($CH_2CH_2CH_3$), 21.7 ($CH_2CH_2CH_3$), 22.4 ($CH_2CH_2CH_3$), 28.0 ($CH_2CH_2CH_3$), 28.7 ($CH_2CH_2CH_3$), 116.3 (C4), 121.0 (ArCH), 123.3 (ArCH), 124.5 (ArCH), 125.0 (ArCH), 125.9 (ArCH), 126.0 (ArCH), 127.3 (2×Ph*C*H), 127.5 (2×Ph*C*H), 127.8 (4×Ph*C*H), 128.2, 128.2 (ArCH), 128.3 (2×ArCH), 128.4, 128.7 (ArCH), 129.6 (ArCH), 129.8, 130.4, 131.9, 132.0, 133.1 (ArCH), 134.2, 135.3, 140.9, 141.2, 142.5, 148.6, 148.9, 152.5, 185.3 (C=O), 186.0 (C=O) ppm. MS (70 eV, EI): *m*/*z* (%) = 614 (100) [$M^+$], 432 (82) [$M^+ - OC(C_6H_5)_2$]. HR-MS ($C_{43}H_{34}O_4$): calcd. 614.2457; found 614.2456.

**(*R*,*S*)-1-Nitro-4,4-diphenyl-11,12-dipropylnaphtho[1,2-*f*]phenanthro-[2,1-*d*][1,3]-dioxepin-10,13-dione (25):** Procedure B. Benzannulation of carbene complex **19** (0.68 g) with 4-octyne (0.59 mL), product 2. $R_f$ = 0.45 ($CH_2Cl_2$/PE, 1:1). Yield: 60 mg (90 μmol, 9%). $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 0.40–0.25 (m, 1 H, $CH_2CH_2CH_3$), 0.61 (t, $^3J_{H,H}$ = 7.9 Hz, 3 H, $CH_2CH_2CH_3$), 0.86 (t, $^3J_{H,H}$ = 7.3 Hz, 3 H, $CH_2CH_2CH_3$), 1.43–1.21 (m, 4 H, $CH_2CH_2CH_3$), 1.90 (ddd, $^2J_{H,H}$ = 12.9, $^3J_{H,H}$ = 7.7, $^3J_{H,H}$ = 7.2 Hz, 1 H, $CH_2CH_2CH_3$), 2.23 (ddd, $^2J_{H,H}$ = 12.9, $^3J_{H,H}$ = 7.8, $^3J_{H,H}$ = 7.8 Hz, 1 H, $CH_2CH_2CH_3$), 2.46 (ddd, $^2J_{H,H}$ = 12.8, $^3J_{H,H}$ = 6.9, $^3J_{H,H}$ = 8.2 Hz, 1 H, $CH_2CH_2CH_3$), 7.01 (d, $^3J_{H,H}$ = 8.3 Hz, 1 H), 7.03 (d, $^3J_{H,H}$ = 8.7 Hz, 1 H), 7.05 (d, $^3J_{H,H}$ = 8.7 Hz, 1 H), 7.14 (ddd, $^3J_{H,H}$ = 7.0, $^3J_{H,H}$ = 8.5, $^4J_{H,H}$ = 1.2 Hz, 1 H), 7.38–7.32 (m, 3 H), 7.31–7.25 (m, 3 H), 7.46 (ddd, $^3J_{H,H}$ = 7.1, $^3J_{H,H}$ = 8.6, $^4J_{H,H}$ = 1.4 Hz, 1 H), 7.60–7.54 (m, 2 H), 7.68–7.62 (m, 2 H), 7.72 (s, 1 H, 6-H), 7.78 (d, $^3J_{H,H}$ = 8.7 Hz, 1 H), 8.06 (d, $^3J_{H,H}$ = 8.5 Hz, 1 H), 8.14 (d, $^3J_{H,H}$ = 8.5 Hz, 1 H), 8.46 (d, $^3J_{H,H}$ = 8.7 Hz, 1 H) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 14.1 ($CH_2CH_2CH_3$), 14.3 ($CH_2CH_2CH_3$), 22.0 ($CH_2CH_2CH_3$), 22.4 ($CH_2CH_2CH_3$), 28.1 ($CH_2CH_2CH_3$), 28.9 ($CH_2CH_2CH_3$), 116.9 (4-C), 121.5 (ArCH), 121.6 (ArCH), 123.6, 123.9 (ArCH), 125.8 (2×ArCH), 126.5, 127.0 (2×Ph*C*H), 127.1 (ArCH), 127.4 (2×Ph*C*H), 127.7 (ArCH), 128.0 (2×Ph*C*H), 128.2 (2×Ph*C*H), 128.3, 128.7 (ArCH), 129.0 (ArCH), 131.0, 131.0 (ArCH), 132.5, 133.6 (ArCH), 134.0, 134.2, 137.4, 140.0, 140.1, 143.2, 145.4, 146.8, 148.3, 152.9, 185.0 (C=O), 186.2 (C=O) ppm. MS (70 eV, EI): *m*/*z* (%) = 659 (100) [$M^+$], 477 (41) [$M^+$ –

$OC(C_6H_5)_2$]. HR-MS ($C_{43}H_{33}NO_6$): calcd. 659.2308; found 659.2311.

**(*R*,*S*)-12-*tert*-Butyl-4,4-diphenylnaphtho[1,2-*f*]phenanthro[2,1-*d*]-[1,3]dioxepin-10,13-dione (26):** Procedure B. Benzannulation of carbene complex **19** (0.68 g) with 3,3-dimethyl-1-butyne (0.47 mL). $R_f$ = 0.71 (*t*BuOMe/PE, 1:2). Yield: 0.28 g (0.47 mmol, 47%). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 0.54 [s, 9 H, $C(CH_3)_3$], 6.45 (s, 1 H, 11-H), 6.86 (d, $^3J_{H,H}$ = 8.0 Hz, 1 H), 6.88 (d, $^3J_{H,H}$ = 8.7 Hz, 1 H), 7.00 (d, $^3J_{H,H}$ = 8.6 Hz, 1 H), 7.05 (ddd, $^3J_{H,H}$ = 7.0, $^3J_{H,H}$ = 8.6, $^4J_{H,H}$ = 1.4 Hz, 1 H), 7.23 (ddd, $^3J_{H,H}$ = 7.0, $^3J_{H,H}$ = 8.1, $^4J_{H,H}$ = 1.1 Hz, 1 H), 7.35–7.23 (m, 6 H), 7.50 (d, $^3J_{H,H}$ = 8.7 Hz, 1 H), 7.60–7.55 (m, 2 H), 7.69 (d, $^3J_{H,H}$ = 8.7 Hz, 1 H), 7.72–7.64 (m, 3 H), 8.03 (d, $^3J_{H,H}$ = 8.5 Hz, 1 H), 8.07 (d, $^3J_{H,H}$ = 8.5 Hz, 1 H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 28.9 [$C(CH_3)$], 35.1 [$C(CH_3)$], 116.2 (4-C), 120.5 (ArCH), 123.2 (ArCH), 124.4 (ArCH), 125.0 (ArCH), 126.0 (ArCH), 126.0, 127.4 (2×Ph*C*H), 127.6 (2×Ph*C*H), 127.7 (2×Ph*C*H), 127.8 (2×Ph*C*H), 128.4 (3ArCH), 128.5, 128.9 (ArCH), 129.0, 129.7, 129.7 (ArCH), 130.1, 130.3 (ArCH), 131.5, 132.5, 133.4 (ArCH), 134.6, 136.2, 140.7, 141.1, 149.0 (2a/5a-C), 152.5 (2a/5a-C), 160.3 (11-C), 184.8 (C=O), 186.1 (C=O) ppm. MS (70 eV, EI): *m*/*z* (%) = 586 (100) [M$^+$], 404 (42) [M$^+$ – $OC(C_6H_5)_2$]. HR-MS ($C_{41}H_{30}O_4$): calcd. 586.2144; found 586.2146.

**(*R*,*S*)-4,4-Diphenyl-12-propylnaphtho[1,2-*f*]phenanthro[2,1-*d*][1,3]dioxepin-10,13-dione (27):** Procedure B. Benzannulation of carbene complex **19** (0.68 g) with 1-pentyne (0.39 mL). $R_f$ = 0.41 ($CH_2Cl_2$/PE, 1:1). Yield: 0.22 g (0.39 mmol, 39%). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 0.55 (t, $^3J_{H,H}$ = 7.3 Hz, 3 H, $CH_2CH_2CH_3$), 0.86–0.68 (m, 2 H, $CH_2CH_2CH_3$), 1.05 (dddd, $^2J_{H,H}$ = 16.5, $^3J_{H,H}$ = 8.3, $^3J_{H,H}$ = 6.6, $^4J_{H,H}$ = 1.6 Hz, 1 H, $CH_2CH_2CH_3$), 1.53 (dddd, $^2J_{H,H}$ = 16.5, $^3J_{H,H}$ = 8.6, $^3J_{H,H}$ = 6.8, $^4J_{H,H}$ = 1.6 Hz, 1 H, $CH_2CH_2CH_3$), 6.19 (t, $^4J_{H,H}$ = 1.6 Hz, 2 H, 11-H), 6.87 (d, $^3J_{H,H}$ = 8.5 Hz, 1 H), 6.90 (d, $^3J_{H,H}$ = 8.7 Hz, 1 H), 6.99 (ddd, $^3J_{H,H}$ = 6.9, $^3J_{H,H}$ = 8.4, $^4J_{H,H}$ = 1.3 Hz, 1 H), 6.99 (d, $^3J_{H,H}$ = 8.7 Hz, 1 H), 7.26–7.15 (m, 7 H), 7.52 (d, $^3J_{H,H}$ = 8.0 Hz, 1 H), 7.55–7.48 (m, 2 H), 7.63 (d, $^3J_{H,H}$ = 8.7 Hz, 1 H), 7.64–7.58 (m, 2 H), 7.67 (d, $^3J_{H,H}$ = 8.9 Hz, 1 H), 7.96 (d, $^3J_{H,H}$ = 8.7 Hz, 1 H), 8.00 (d, $^3J_{H,H}$ = 8.5 Hz, 1 H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 13.4 ($CH_2CH_2CH_3$), 19.5 ($CH_2CH_2CH_3$), 30.1 ($CH_2CH_2CH_3$), 116.3 (C4), 120.7 (ArCH), 123.4 (ArCH), 124.6 (ArCH), 125.0 (ArCH), 126.1 (ArCH), 126.2 (ArCH), 127.3 (2×Ph*C*H), 127.4 (2×Ph*C*H), 127.8 (4×Ph*C*H), 128.0, 128.3 (ArCH), 128.4 (ArCH), 128.4, 128.5 (ArCH), 128.7 (ArCH), 129.5, 129.7 (ArCH), 130.4, 131.8 (×2), 133.4 (ArCH), 134.3, 135.6, 140.8, 141.1, 149.1, 152.7, 154.5, 185.2 (C=O), 186.2 (C=O) ppm. MS (70 eV, EI): *m*/*z* (%) = 572 (72) [M$^+$], 390 (75) [M$^+$ – $OC(C_6H_5)_2$]. HR-MS ($C_{40}H_{28}O_4$): calcd. 572.1988; found 572.1995.

**(*R*,*S*)-4,4,12-Triphenylnaphtho[1,2-*f*]phenanthro[2,1-*d*][1,3]dioxepin-10,13-dione (28):** Procedure B. Benzannulation of carbene complex **19** (0.68 g) with phenylacetylene (0.44 mL), product 1. $R_f$ = 0.56 ($CH_2Cl_2$). Yield: 0.11 g (0.18 mmol, 18%). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 6.40 (dd, $^3J_{H,H}$ = 8.4, $^4J_{H,H}$ = 1.2 Hz, 2 H), 6.70 (s, 1 H, 11-H), 6.96 (d, $^3J_{H,H}$ = 8.7 Hz, 1 H), 7.10 (d, $^3J_{H,H}$ = 8.5 Hz, 1 H), 7.05 (ddd, $^3J_{H,H}$ = 6.7, $^3J_{H,H}$ = 8.4, $^4J_{H,H}$ = 1.5 Hz, 1 H), 7.07 (d, $^3J_{H,H}$ = 8.6 Hz, 1 H), 7.13–7.05 (m, 2 H), 7.12 (ddd, $^3J_{H,H}$ = 6.7, $^3J_{H,H}$ = 8.1, $^4J_{H,H}$ = 1.5 Hz, 1 H), 7.28–7.22 (m, 4 H), 7.32–7.28 (m, 3 H), 7.57 (d, $^3J_{H,H}$ = 8.1 Hz, 1 H), 7.60–7.54 (m, 3 H), 7.69–7.64 (m, 2 H), 7.75 (d, $^3J_{H,H}$ = 8.6 Hz, 1 H), 8.10 (d, $^3J_{H,H}$ = 8.5 Hz, 1 H), 8.14 (d, $^3J_{H,H}$ = 8.5 Hz, 1 H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 116.4 (4-C), 120.7 (ArCH), 123.7 (ArCH), 124.9, 124.9 (ArCH), 126.2 (ArCH), 127.3 (2×Ph*C*H), 127.5 (2×Ph*C*H), 127.7 (2×Ph*C*H), 127.8 (4×Ph*C*H), 128.2, 128.3 (ArCH), 128.4 (2×ArCH), 128.6 (ArCH), 128.6 (2×Ph*C*H), 128.8, 129.5, 129.5 (ArCH), 129.8 (ArCH), 129.9 (ArCH), 130.0, 131.9, 132.2, 132.3, 133.7 (ArCH), 134.5, 135.9, 140.8, 141.1, 149.2, 150.0, 152.8, 185.2 (C=O), 185.5 (C=O) ppm. MS (70 eV, EI): *m*/*z* (%) = 606 (100) [M$^+$], 424 (57) [M$^+$ – $OC(C_6H_5)_2$]. HR-MS ($C_{43}H_{26}O_4$): calcd. 606.1831; found 606.1830.

**(*R*,*S*)-4,4,10-Triphenylanthra[2,1-*d*]naphtho[1,2-*f*][1,3]-dioxepin-9,12-dione (29):** Procedure B. Benzannulation of carbene complex **19** (0.68 g) with phenylacetylene (0.44 mL), product 2. $R_f$ = 0.32 ($CH_2Cl_2$). Yield: 91 mg (0.15 mmol, 15%). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 6.86 (d, $^3J_{H,H}$ = 8.6 Hz, 1 H), 7.04 (d, $^3J_{H,H}$ = 8.7 Hz, 1 H), 7.05 (s, 1 H), 7.31–7.24 (m, 6 H), 7.42 (d, $^3J_{H,H}$ = 8.2 Hz, 1 H), 7.42 (ddd, $^3J_{H,H}$ = 6.9, $^3J_{H,H}$ = 8.2, $^4J_{H,H}$ = 1.2 Hz, 1 H), 7.53–7.45 (m, 8 H), 7.61–7.56 (m, 2 H), 7.72 (d, $^3J_{H,H}$ = 8.7 Hz, 1 H), 7.87 (dd, $^3J_{H,H}$ = 8.8, $^4J_{H,H}$ = 1.3 Hz, 1 H), 7.90 (d, $^3J_{H,H}$ = 8.6 Hz, 1 H), 8.71 (s, 1 H), 8.34 (s, 1 H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 118.0 (C4–C), 122.9, 125.3, 125.7, 126.4, 126.9, 127.3 (2×Ph*C*H), 127.4, 127.4 (2×Ph*C*H), 127.7, 127.8 (4×Ph*C*H), 128.1, 128.3, 128.4 (2×Ph*C*H), 128.5, 128.6, 128.7, 128.9, 129.4 (2×Ph*C*H), 130.0 (×2), 130.1, 131.2, 131.8, 132.0, 133.1, 133.7, 134.1, 136.9, 140.5, 140.6, 149.3, 150.4, 153.3, 183.9 (C=O), 184.5 (C=O) ppm. MS (70 eV, EI): *m*/*z* (%) = 606 (61) [M$^+$], 424 (100) [M$^+$ – $OC(C_6H_5)_2$]. HR-MS ($C_{43}H_{26}O_4$): calcd. 606.1831; found 606.1843.

**General Procedure D. Bidirectional Benzannulation of Biscarbene Complexes 16 and 18 With Oxidative Work-up to Give Helical Bisquinones 30–36:** A Schlenk tube fitted with a condenser jacket and containing 1 mmol of biscarbene complex **16** (0.89g) or **18** (0.92 g) and 8 mmol of alkyne dissolved in $CH_2Cl_2$ (15 mL) was warmed in an oil bath at 55 °C for 4 h. The reaction mixture was cooled to 0 °C, and a solution of CAN (7.67 g, 14 mmol) in water (40 mL) was added. Stirring was continued for 2 h at this temperature, the organic layer was separated and the aqueous layer was extracted with $CH_2Cl_2$ (3×15 mL). The combined organic layers were washed with brine (3×50 mL) and dried ($MgSO_4$). Filtration, evaporation of the solvent and column chromatography afforded the respective helical bisquinone as a red solid.

**(*R*,*S*)-4,4-Di-*tert*-butyl-11,12,15,16-tetraethyldiphenanthro-[3,4-*d*:4′,3′-*f*][1,3,2]-dioxasilepin-10,13,14,17-tetraone (30):** Benzannulation of carbene complex **16** (0.89 g) with 3-hexyne (0.90 mL). $R_f$ = 0.51 ($CH_2Cl_2$/PE, 2:1). Yield: 0.27 g (0.39 mmol, 39%). $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 0.75 (t, $^3J_{H,H}$ = 7.5 Hz, 6 H, $CH_3$), 0.89 (t, $^3J_{H,H}$ = 7.5 Hz, 6 H, $CH_3$), 1.15 [s, 18 H, $C(CH_3)_3$], 1.31 (dq, $^2J_{H,H}$ = 12.7, $^3J_{H,H}$ = 7.5 Hz, 2 H, $CH_2$), 1.66 (dq, $^2J_{H,H}$ = 12.7, $^3J_{H,H}$ = 7.5 Hz, 2 H, $CH_2$), 1.99 (dq, $^2J_{H,H}$ = 12.7, $^3J_{H,H}$ = 7.5 Hz, 2 H, $CH_2$), 2.49 (dq, $^2J_{H,H}$ = 12.7, $^3J_{H,H}$ = 7.5 Hz, 2 H, $CH_2$), 7.61 (d, $^3J_{H,H}$ = 8.7 Hz, 2 H), 7.78 (d, $^3J_{H,H}$ = 8.4 Hz, 2 H), 7.81 (d, $^3J_{H,H}$ = 8.7 Hz, 2 H), 7.82 (d, $^3J_{H,H}$ = 8.4 Hz, 2 H) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 13.5 ($CH_2CH_3$), 14.4 ($CH_2CH_3$), 19.1 ($CH_2CH_3$), 20.6 ($CH_2CH_3$), 21.7 [$SiC(CH_3)$], 27.8 [$SiC(CH_3)$], 119.7 (ArCH), 125.5 (ArCH), 125.6, 129.0, 129.7 (ArCH), 131.5, 132.1 (ArCH), 133.7, 136.0, 144.8, 147.1, 155.3 (2a/5a-C), 184.0 (C=O), 185.1 (C=O) ppm. MS (70 eV, EI): *m*/*z* (%) = 698 (100) [M$^+$]. HR-MS ($C_{44}H_{46}O_6Si$): calcd. 698.3064; found 698.3037.

**(*R*,*S*)-4,4,12,17-Tetra-*tert*-butylanthra[2,1-*f*]phenanthro[4,3-*d*]-[1,3,2]-dioxasilepin-10,13,15,18-tetraone (31):** Benzannulation of carbene complex **16** (0.89 g) with 3,3-dimethyl-1-butyne (0.97 mL). $R_f$ = 0.66 (*t*BuOMe/PE, 1:3). Yield: 0.22 g (0.31 mmol, 31%). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 0.69 [s, 9 H, $C(CH_3)_3$], 1.04 [s, 9 H, $C(CH_3)_3$], 1.11 [s, 9 H, $C(CH_3)_3$], 1.31 [s, 9 H, $C(CH_3)_3$], 6.32 (s, 1 H), 6.64 (s, 1 H), 6.93 (s, 1 H), 7.50 (d, $^3J_{H,H}$ = 8.8 Hz, 1 H), 7.60 (d, $^3J_{H,H}$ = 8.8 Hz, 1 H), 7.88 (d, $^3J_{H,H}$ = 8.8 Hz, 1 H), 7.98 (d,

$^3J_{H,H}$ = 8.8 Hz, 1 H), 8.03 (d, $^3J_{H,H}$ = 8.3 Hz, 1 H), 8.15 (d, $^3J_{H,H}$ = 8.3 Hz, 1 H), 8.39 (s, 1 H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 21.4 [Si*C*($CH_3$)], 21.7 [Si*C*($CH_3$)], 27.6 [C(*C*$H_3$)], 27.9 [C(*C*$H_3$)], 29.2 [C(*C*$H_3$)], 29.3 [C(*C*$H_3$)], 35.2 [*C*($CH_3$)], 35.7 [*C*($CH_3$)], 120.3 (ArCH), 121.2, 124.7 (ArCH), 126.1 (ArCH), 126.3 (ArCH), 126.7, 127.7 (2×), 129.2 (ArCH), 130.4 (ArCH), 131.2 (ArCH), 131.7 (ArCH), 132.1, 132.5, 132.6, 132.9, 133.3, 133.7 (ArCH), 134.5, 135.3 (ArCH), 154.5 (2a/5a-C), 155.4 (2a/5a-C), 159.1 (C-*t*Bu), 159.2 (C-*t*Bu), 184.4 (2 C=O), 184.7 (C=O), 186.0 (C=O) ppm. MS (70 eV, EI): *m*/*z* (%) = 698 (100) [M$^+$]. HR-MS ($C_{44}H_{46}O_6Si$): calcd. 698.3064; found 698.3058.

**(*R*,*S*)-4,4-Di-*tert*-butyl-12,17-dipropylanthra[2,1-*f*]phenanthro-[4,3-*d*][1,3,2]dioxasilepin-10,13,15,18-tetraone (32):** Benzannulation of carbene complex **16** (0.89 g) with 1-pentyne (0.79 mL). $R_f$ = 0.73 (*t*BuOMe/PE, 1:2). Yield: 0.17 g (0.26 mmol, 26%). $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 0.63 (t, $^3J_{H,H}$ = 7.3 Hz, 3 H, $CH_2CH_2CH_3$), 0.96 (t, $^3J_{H,H}$ = 7.4 Hz, 3 H, $CH_2CH_2CH_3$), 1.04 [s, C($CH_3$)$_3$, 9 H), 1.10 [s, C($CH_3$)$_3$, 9 H), 1.38 (dddd, $^2J_{H,H}$ = 16.2, $^3J_{H,H}$ = 8.1, $^3J_{H,H}$ = 6.7, $^4J_{H,H}$ = 1.4 Hz, 1 H, $CH_2CH_2CH_3$), 1.52 (t, $^3J_{H,H}$ = 7.3 Hz, 2 H, $CH_2CH_2CH_3$), 1.56 (tq, $^3J_{H,H}$ = 7.3 Hz, 2 H, $CH_2CH_2CH_3$), 1.73 (dddd, $^2J_{H,H}$ = 16.0, $^3J_{H,H}$ = 8.6, $^3J_{H,H}$ = 7.1, $^4J_{H,H}$ = 1.4 Hz, 1 H, $CH_2CH_2CH_3$), 2.46 (dddd, $^2J_{H,H}$ = 15.1, $^3J_{H,H}$ = 7.6, $^4J_{H,H}$ = 1.2 Hz, 1 H, $CH_2CH_2CH_3$), 2.52 (dddd, $^2J_{H,H}$ = 15.1, $^3J_{H,H}$ = 7.9, $^3J_{H,H}$ = 7.4, $^4J_{H,H}$ = 1.2 Hz, 1 H, $CH_2CH_2CH_3$), 6.12 (t, $^4J_{H,H}$ = 1.2 Hz, 1 H), 6.59 (t, $^4J_{H,H}$ = 1.2 Hz, 1 H), 7.04 (s, 1 H), 7.54 (d, $^3J_{H,H}$ = 8.7 Hz, 1 H), 7.65 (d, $^3J_{H,H}$ = 8.7 Hz, 1 H), 7.97 (d, $^3J_{H,H}$ = 8.7 Hz, 1 H), 8.00 (d, $^3J_{H,H}$ = 8.7 Hz, 1 H), 8.01 (d, $^3J_{H,H}$ = 8.5 Hz, 1 H), 8.15 (d, $^3J_{H,H}$ = 8.5 Hz, 1 H), 8.45 (s, 1 H) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 13.5 ($CH_2CH_2CH_3$), 13.9 ($CH_2CH_2CH_3$), 19.9 ($CH_2CH_2CH_3$), 21.2 ($CH_2CH_2CH_3$), 21.5 [Si*C*($CH_3$)], 21.7 [Si*C*($CH_3$)], 27.6 [C(*C*$H_3$)], 27.7 [C(*C*$H_3$)], 30.5 ($CH_2CH_2CH_3$), 31.6 ($CH_2CH_2CH_3$), 120.5 (ArCH), 120.6, 124.9 (ArCH), 126.4 (ArCH), 126.7 (2×), 126.9 (ArCH), 128.0, 128.8 (ArCH), 130.5 (ArCH), 131.2 (ArCH), 131.3 (ArCH), 131.6, 132.1, 132.7, 133.0, 133.1, 133.6 (ArCH), 134.2, 136.1 (ArCH), 152.7, 152.8, 154.8, 155.5, 183.9 (C=O), 184.5 (C=O), 184.7 (C=O), 185.8 (C=O) ppm. MS (70 eV, EI): *m*/*z* (%) = 670 (100) [M$^+$], 614 (11) [M$^+$ – $C_4H_8$]. HR-MS ($C_{42}H_{42}O_6Si$): calcd. 670.2751; found 670.2727.

**(*R*,*S*)-11,12,15,16-Tetraethyl-4,4-diphenyldiphenanthro-[3,4-*d*:4′,3′-*f*][1,3]dioxepin-10,13,14,17-tetraone (33):** Benzannulation of carbene complex **18** (0.92 g) with 3-hexyne (0.90 mL). $R_f$ = 0.14 ($CH_2Cl_2$/PE, 1:1). Yield: 0.25 g (0.35 mmol, 35%). $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 0.70 (t, $^3J_{H,H}$ = 7.5 Hz, 6 H, $CH_3$), 0.91 (t, $^3J_{H,H}$ = 7.5 Hz, 6 H, $CH_3$), 1.12 (dq, $^2J_{H,H}$ = 12.6, $^3J_{H,H}$ = 7.5 Hz, 2 H, $CH_2$), 1.61 (dq, $^2J_{H,H}$ = 12.6, $^3J_{H,H}$ = 7.5 Hz, 2 H, $CH_2$), 2.05 (dq, $^2J_{H,H}$ = 12.9, $^3J_{H,H}$ = 7.5 Hz, 2 H, $CH_2$), 2.47 (dq, $^2J_{H,H}$ = 12.9, $^3J_{H,H}$ = 7.5 Hz, 2 H, $CH_2$), 7.21 (d, $^3J_{H,H}$ = 8.5 Hz, 2 H), 7.34–7.28 (m, 6 H), 7.68 (d, $^3J_{H,H}$ = 8.5 Hz, 2 H), 7.78–7.72 (m, 4 H), 7.88 (d, $^3J_{H,H}$ = 8.5 Hz, 2 H), 7.92 (d, $^3J_{H,H}$ = 8.5 Hz, 2 H) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 13.7 ($CH_2CH_3$), 14.2 ($CH_2CH_3$), 19.2 ($CH_2CH_3$), 20.5 ($CH_2CH_3$), 115.7, 120.2, 126.3, 126.8, 127.3 (2×PhCH), 127.9 (2×PhCH), 128.4, 129.1, 131.7, 131.9, 133.4, 134.0, 134.8 (ArCH), 141.0 (ArCH), 144.6 (ArCH), 147.9, 151.8, 184.3 (C=O), 185.9 (C=O) ppm. MS (70 eV, EI): *m*/*z* (%) = 722 (100) [M$^+$], 694 (3) [M$^+$ – CO]. HR-MS ($C_{49}H_{38}O_6$): calcd. 722.2668; found 722.2652.

**(*R*,*S*)-12,17-Di-*tert*-butyl-4,4-diphenylanthra[2,1-*f*]phenanthro-[4,3-*d*][1,3]-dioxepin-10,13,15,18-tetraone (34):** Benzannulation of carbene complex **18** (0.92 g) with 3,3-dimethyl-1-butyne (0.97 mL). $R_f$ = 0.50 (*t*BuOMe/PE, 1:2). Yield: 0.19 g (0.26 mmol, 26%). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 0.54 [s, 9 H, C($CH_3$)$_3$], 1.33 [s, 9 H, C($CH_3$)$_3$], 6.42 (s, 1 H, 11/16-H), 6.71 (s, 1 H, 11/16-H), 7.02 (d, $^3J_{H,H}$ = 8.7 Hz, 1 H), 7.06 (d, $^3J_{H,H}$ = 8.7 Hz, 1 H), 7.33–7.25 (m, 6 H), 7.58–7.53 (m, 2 H), 7.59 (s, 1 H), 7.70–7.64 (m, 2 H), 7.72 (d, $^3J_{H,H}$ = 8.5 Hz, 1 H), 7.77 (d, $^3J_{H,H}$ = 8.5 Hz, 1 H), 8.11 (d, $^3J_{H,H}$ = 8.5 Hz, 1 H), 8.14 (d, $^3J_{H,H}$ = 8.5 Hz, 1 H), 8.44 (s, 1 H) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 29.0 [C(*C*$H_3$)], 29.3 [C(*C*$H_3$)], 35.1 [*C*($CH_3$)], 35.8 [*C*($CH_3$)], 117.0, 121.1 (ArCH), 124.9 (ArCH), 125.8 (ArCH), 126.9 (ArCH), 127.2, 127.2 (2×PhCH), 127.5 (2×PhCH), 127.8, 127.9 (4×PhCH), 128.5, 128.7 (2×ArCH), 129.0, 129.9 (ArCH), 130.4 (ArCH), 130.7 (2×ArCH), 131.6, 132.2, 132.9, 134.0, 134.0 (ArCH), 134.7 (2×), 134.8, 135.3 (ArCH), 140.2, 140.7, 151.8 (2a/5a-C), 152.5 (2a/5a-C), 159.3 (C-*t*Bu), 159.4 (C-*t*Bu), 184.3 (C=O), 184.6 (C=O), 185.0 (C=O), 185.6 (C=O) ppm. MS (70 eV, EI): *m*/*z* (%) = 722 (100) [M$^+$], 540 (40) [M$^+$ – OC($C_6H_5$)$_2$]. HR-MS ($C_{49}H_{38}O_6$): calcd. 722.2668; found 722.2671.

**(*R*,*S*)-12,15-Dipropyl-4,4-diphenyldiphenanthro[3,4-*d*:4′,3′-*f*][1,3]dioxepin-10,13,14,17-tetraone (35):** Benzannulation of carbene complex **18** (0.92 g) with 1-pentyne (0.79 mL). $R_f$ = 0.61 (*t*BuOMe/PE, 1:2). Yield: 0.14 g (0.20 mmol, 20%). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 0.78 (t, $^3J_{H,H}$ = 7.3 Hz, 3 H, $CH_2CH_2CH_3$), 0.94 (dddd, $^2J_{H,H}$ = 17.0, $^3J_{H,H}$ = 10.0, $^3J_{H,H}$ = 5.5, $^4J_{H,H}$ = 1.5 Hz, 2 H, $CH_2CH_2CH_3$), 1.15–1.03 (m, 2 H, $CH_2CH_2CH_3$), 1.28–1.18 (m, 2 H, $CH_2CH_2CH_3$), 1.58 (dddd, $^2J_{H,H}$ = 17.0, $^3J_{H,H}$ = 9.7, $^3J_{H,H}$ = 5.7, $^4J_{H,H}$ = 1.7 Hz, 2 H, $CH_2CH_2CH_3$), 6.59 (t, $^4J_{H,H}$ = 1.6 Hz, 2 H, 11/16-H), 7.20 (d, $^3J_{H,H}$ = 8.7 Hz, 2 H), 7.34–7.29 (m, 6 H), 7.71 (d, $^3J_{H,H}$ = 8.7 Hz, 2 H), 7.74–7.68 (m, 4 H), 7.92 (d, $^3J_{H,H}$ = 8.3 Hz, 2 H), 7.99 (d, $^3J_{H,H}$ = 8.3 Hz, 2 H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 13.6 ($CH_2CH_2CH_3$), 19.9 ($CH_2CH_2CH_3$), 29.8 ($CH_2CH_2CH_3$), 115.5 (4-C), 120.3 (ArCH), 126.7 (ArCH), 127.0, 127.4 (2×PhCH), 127.9 (2×PhCH), 128.5 (ArCH), 129.5 (ArCH), 130.1 (ArCH), 131.2, 132.1, 133.7, 134.0 (ArCH), 135.0, 140.7, 152.0, 153.0, 184.4 (C=O), 185.7 (C=O) ppm. MS (70 eV, EI): *m*/*z* (%) = 694 (39) [M$^+$], 512 (13) [M$^+$ – OC($C_6H_5$)$_2$], 91 (100) [$C_7H_7^+$]. HR-MS ($C_{47}H_{34}O_6$): calcd. 694.2355; found 694.2353.

**(*R*,*S*)-12,15-Dioctyl-4,4-diphenyldiphenanthro[3,4-*d*:4′,3′-*f*][1,3]dioxepin-10,13,14,17-tetraone (36):** Benzannulation of carbene complex **18** (0.92 g) with 1-decyne (1.44 mL). $R_f$ = 0.61 ($CH_2Cl_2$/PE, 1:2). Yield: 0.11 g (0.13 mmol, 13%). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 0.78 (t, $^3J_{H,H}$ = 7.1 Hz, 6 H, $CH_3$), 1.09–0.92 (m, 2 H, $CH_2$), 1.34–1.09 (m, 24 H, $CH_2$), 1.58 (dddd, $^2J_{H,H}$ = 16.6, $^3J_{H,H}$ = 9.8, $^3J_{H,H}$ = 5.0, $^4J_{H,H}$ = 1.6 Hz, 2 H, ArC$H_2$), 6.20 (t, $^4J_{H,H}$ = 1.5 Hz, 2 H, 11/16-H), 7.19 (d, $^3J_{H,H}$ = 8.7 Hz, 2 H), 7.35–7.28 (m, 6 H), 7.70 (d, $^3J_{H,H}$ = 8.7 Hz, 2 H), 7.74–7.70 (m, 4 H), 7.91 (d, $^3J_{H,H}$ = 8.3 Hz, 2 H), 7.97 (d, $^3J_{H,H}$ = 8.3 Hz, 2 H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 14.1 ($CH_3$), 22.6 (7$CH_2$), 26.6, 27.9, 29.1, 29.2, 29.3, 31.8, 115.5 (C4), 120.2 (ArCH), 126.7 (ArCH), 127.0, 127.4 (2×PhCH), 127.9 (2×PhCH), 128.5 (ArCH), 129.4 (ArCH), 130.0 (ArCH), 131.2, 132.1, 133.7, 134.1 (ArCH), 135.0, 140.8, 152.0, 153.3, 184.4 (C=O), 185.8 (C=O) ppm. MS (FAB): *m*/*z* (%) = 836 (53) [M$^+$].

**X-ray Crystallographic Study:** Orange to bright-red crystals of **20**, **23**, **25**, **30**, **31** and **33** were obtained by slow evaporation of concentrated solutions of each compound in dichloromethane/*n*-hexane or of **32**, **34**, **35** and **36** in dichloromethane/*n*-heptane at 10 °C. Pale-yellow crystals of **2** and **3** were collected from solvent mixtures of dichloromethane with a small amount of methanol or from chloroform/THF at the same temperature. Recrystallisation of the camphanate (*R*)-**14** from THF yielded a yellow clathrate with THF of host-guest stoichiometry 1:1.

Crystallographic data were collected with a Nonius–Kappa CCD diffractometer at 123 K. The molecular structures were solved by

Table 1. Crystal data and details of the structure determination.[a]

| | (*rac*)-**2** (X = Si*t*Bu$_2$) | (*rac*)-**3** (X = CPh$_2$) |
|---|---|---|
| Formula | $C_{28}H_{28}Br_2O_2Si$ | $C_{33}H_{20}Br_2O_2$ |
| Formula mass | 584.41 | 608.31 |
| Crystal system | triclinic | triclinic |
| Space group | $P\bar{1}$ (no.2) | $P\bar{1}$ (no.2) |
| *a* [Å] | 9.4278(1) | 8.3580(1) |
| *b* [Å] | 11.7999(2) | 11.9878(2) |
| *c* [Å] | 23.8838(4) | 13.8015(3) |
| *α* [°] | 85.199(1) | 98.550(1) |
| *β* [°] | 80.045(1) | 98.321(1) |
| *γ* [°] | 89.719(1) | 106.089(1) |
| Volume [Å$^3$] | 2607.69(7) | 1288.50(4) |
| *Z* | 4 | 2 |
| $D_{calcd.}$ [g cm$^{-3}$] | 1.489 | 1.568 |
| *μ* [mm$^{-1}$] | 3.177 | 3.175 |
| *F*(000) | 1184 | 608 |
| Cryst. size [mm] | 0.50 × 0.25 × 0.10 | 0.20 × 0.15 × 0.08 |
| *θ* limits [°] | 1.87–25.00 | 2.99–25.00 |
| Index ranges | $-11 \le h \le 11$ | $-9 \le h \le 9$ |
| | $-12 \le k \le 14$ | $-14 \le k \le 14$ |
| | $-28 \le l \le 28$ | $-16 \le l \le 16$ |
| Total data | 34176 | 24306 |
| Unique data | 9046 | 4520 |
| Parameters/restr. | 595/0 | 334/0 |
| *R* (*F*) [$I > 2\sigma(I)$] | 0.0371 | 0.0245 |
| *wR*2 $F^2$ (all data) | 0.1001 | 0.0660 |
| GOF on $F^2$ | 1.022 | 1.048 |
| CCDC no. | 250963 | 250964 |

[a] All measurements were performed at 123(2) K with a Nonius Kappa-CCD diffractometer using Mo-$K_\alpha$ graphite-monochromated radiation ($\lambda$ = 0.71073 Å).

direct methods (SHELXS-97) and Patterson methods (**3**), respectively.[54] The non-hydrogen atoms were refined anisotropically on $F^2$ (SHELXL-97);[55] hydrogen atoms were refined isotropically using a riding model. An empirical absorption correction was applied for **2** and **3**. The absolute configuration of **14** was determined by refinement of Flack's *x*-parameter [$x$ = 0.007(5)].[56] Details are presented in Table 1, Table 2 and Table 3 along with the respective CCDC numbers. CCDC-250963 to -250975 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.

## Acknowledgments

Financial support from the Deutsche Forschungsgemeinschaft (SFB 624) is gratefully acknowledged. We also thank Prof. Dr. H. Baltruschat and Prof. Dr. F. Vögtle for helpful discussions, S. Müller and Dr. G. Pawlitzki for assistance in recording the CD spectra, and A. Schneider for HPLC separations. Dr. K. Nättinen thanks the Finnish Academy and Dr. M. Nieger the DAAD for financial support.

[1] H. C. Jahr, M. Nieger, K. H. Dötz, *Chem. Eur. J.* accepted for publication.
[2] R. H. Martin, *Angew. Chem.* **1974**, *86*, 727–738; *Angew. Chem. Int. Ed. Engl.* **1974**, *13*, 649–660.
[3] M. S. Newman, D. Lednicer, *J. Am. Chem. Soc.* **1955**, *77*, 3420–3421.
[4] For overviews on helicenes and related compounds, see: a) C. Schmuck, *Angew. Chem.* **2003**, *115*, 2552–2556; *Angew. Chem. Int. Ed.* **2003**, *42*, 2448–2452; b) H. Hopf, *Classics in Hydro-*

Table 2. Crystal data and details of the structure determination.[a]

| | (*R*)-**14** (X = CPh$_2$) | (*rac*)-**20** (X = Si*t*Bu$_2$) | (*rac*)-**23** (X = CPh$_2$) | (*rac*)-**25** (X = CPh$_2$) | (*rac*)-**30** (X = Si*t*Bu$_2$) |
|---|---|---|---|---|---|
| Formula | $C_{52}H_{45}BrO_7 \cdot C_4H_8O$ | $C_{36}H_{38}O_4Si$ | $C_{41}H_{30}O_4$ | $C_{43}H_{33}NO_6$ | $C_{44}H_{46}O_6Si$ |
| Formula mass | 933.89 | 562.75 | 586.65 | 659.70 | 698.90 |
| Crystal system | orthorhombic | monoclinic | monoclinic | orthorhombic | orthorhombic |
| Space group | $P2_12_12_1$ (no.19) | $P2_1/c$ (no.14) | $P2_1/c$ (no.14) | *Pbcn* (no.60) | *Pnna* (no.52) |
| *a* [Å] | 12.6180(2) | 17.7980(3) | 12.5661(2) | 32.1074(10) | 15.4273(2) |
| *b* [Å] | 14.1703(2) | 13.1553(2) | 30.9857(4) | 7.8587(2) | 32.4780(5) |
| *c* [Å] | 25.3307(5) | 39.1913(7) | 7.9474(1) | 25.7312(6) | 14.7764(2) |
| *α* [°] | 90 | 90 | 90 | 90 | 90 |
| *β* [°] | 90 | 100.548(2) | 102.271(1) | 90 | 90 |
| *γ* [°] | 90 | 90 | 90 | 90 | 90 |
| Volume [Å$^3$] | 4529.15(13) | 9021.1(3) | 3023.78(7) | 6492.6(3) | 7403.68(18) |
| *Z* | 4 | 12 | 4 | 8 | 8 |
| $D_{calcd.}$ [g cm$^{-3}$] | 1.370 | 1.243 | 1.289 | 1.350 | 1.254 |
| *μ* [mm$^{-1}$] | 0.966 | 0.117 | 0.082 | 0.090 | 0.112 |
| *F*(000) | 1952 | 3600 | 1232 | 2768 | 2976 |
| Cryst. size [mm] | 0.35 × 0.25 × 0.10 | 0.60 × 0.20 × 0.20 | 0.30 × 0.25 × 0.20 | 0.40 × 0.20 × 0.02 | 0.50 × 0.30 × 0.20 |
| *θ* limits [°] | 2.87–25.32 | 2.92–27.48 | 2.70–25.01 | 2.99–25.00 | 2.76–25.00 |
| Index ranges | $-15 \le h \le 15$ | $-23 \le h \le 20$ | $-13 \le h \le 14$ | $-37 \le h \le 35$ | $-16 \le h \le 18$ |
| | $-17 \le k \le 17$ | $-17 \le k \le 15$ | $-36 \le k \le 36$ | $-8 \le k \le 6$ | $-38 \le k \le 38$ |
| | $-30 \le l \le 30$ | $-50 \le l \le 42$ | $-9 \le l \le 8$ | $-16 \le l \le 30$ | $-17 \le l \le 17$ |
| Total data | 33589 | 41837 | 21864 | 23027 | 44756 |
| Unique data | 8219 | 19800 | 5221 | 5062 | 6509 |
| Parameters/restr. | 586/6 | 1108/0 | 406/0 | 449/27 | 461/0 |
| *R* (*F*) [$I > 2\sigma(I)$] | 0.0343 | 0.0453 | 0.0584 | 0.0453 | 0.0517 |
| *wR*2 $F^2$ (all data) | 0.0770 | 0.0877 | 0.1602 | 0.0923 | 0.1521 |
| GOF on $F^2$ | 0.961 | 0.813 | 1.081 | 0.821 | 1.061 |
| CCDC no. | 250965 | 250966 | 250967 | 250968 | 250969 |

[a] All measurements were performed at 123(2) K with a Nonius Kappa-CCD diffractometer using Mo-$K_\alpha$ graphite-monochromated radiation ($\lambda$ = 0.71073 Å).

Table 3. Crystal data and details of the structure determination.[a]

| | (*rac*)-**31** (X = Si*t*Bu$_2$) | (*rac*)-**32** (X = Si*t*Bu$_2$) | (*rac*)-**33** (X = CPh$_2$) | (*rac*)-**34** (X = CPh$_2$) | (*rac*)-**35** (X = CPh$_2$) | (*rac*)-**36** (X = CPh$_2$) |
|---|---|---|---|---|---|---|
| Formula | $C_{44}H_{46}O_6Si\cdot C_6H_{14}$ | $C_{42}H_{42}O_6Si\cdot \frac{1}{2}C_7H_{16}$ | $C_{49}H_{38}O_6\cdot CH_2Cl_2\cdot \frac{1}{2}C_6H_{14}$ | $C_{49}H_{38}O_6\cdot \frac{1}{2}C_7H_{16}$ | $C_{47}H_{34}O_6$ | $C_{57}H_{54}O_6\cdot \frac{1}{2}C_7H_{16}$ |
| Formula mass | 785.07 | 720.95 | 850.81 | 772.89 | 694.74 | 885.10 |
| Crystal system | triclinic | triclinic | triclinic | triclinic | monoclinic | triclinic |
| Space group | $P\bar{1}$ (no.2) | $P\bar{1}$ (no.2) | $P\bar{1}$ (no.2) | $P\bar{1}$ (no.2) | $P2_1/c$ (no.14) | $P\bar{1}$ (no.2) |
| *a* [Å] | 12.3246(5) | 13.0956(2) | 10.9344(1) | 13.7489(2) | 9.8045(2) | 16.8101(4) |
| *b* [Å] | 12.6060(6) | 17.8666(3) | 13.7182(1) | 14.1560(2) | 34.8693(5) | 17.8691(6) |
| *c* [Å] | 15.0743(8) | 18.2785(3) | 15.7120(2) | 21.4580(3) | 10.4006(2) | 19.7898(6) |
| $\alpha$ [°] | 78.910(2) | 73.375(1) | 70.379(1) | 85.794(1) | 90 | 63.165(2) |
| $\beta$ [°] | 77.094(2) | 73.557(1) | 86.829(1) | 79.653(1) | 100.994(1) | 67.271(2) |
| $\gamma$ [°] | 83.199(2) | 76.310(1) | 75.365(1) | 87.517(1) | 90 | 82.381(2) |
| Volume [Å$^3$] | 2233.23(18) | 3873.51(11) | 2146.80(4) | 4095.44(10) | 3490.46(11) | 4886.1(2) |
| *Z* | 2 | 4 | 2 | 4 | 4 | 4 |
| $D_{calcd.}$ [g cm$^{-3}$] | 1.167 | 1.236 | 1.316 | 1.254 | 1.322 | 1.203 |
| $\mu$ [mm$^{-1}$] | 0.100 | 0.109 | 0.204 | 0.081 | 0.087 | 0.076 |
| *F*(000) | 844 | 1540 | 894 | 1636 | 1456 | 1892 |
| Cryst. size [mm] | 0.25 × 0.15 × 0.08 | 0.50 × 0.40 × 0.30 | 0.25 × 0.20 × 0.15 | 0.60 × 0.30 × 0.10 | 0.40 × 0.16 × 0.08 | 0.50 × 0.30 × 0.10 |
| $\theta$ limits [°] | 2.80–25.00 | 2.92–25.03 | 3.08–25.00 | 2.98–25.03 | 3.07–25.02 | 2.94–25.01 |
| Index ranges | $-12 \le h \le 14$<br>$-14 \le k \le 11$<br>$-17 \le l \le 14$ | $-15 \le h \le 15$<br>$-21 \le k \le 21$<br>$-21 \le l \le 19$ | $-13 \le h \le 13$<br>$-16 \le k \le 16$<br>$-18 \le l \le 18$ | $-16 \le h \le 16$<br>$-16 \le k \le 16$<br>$-25 \le l \le 25$ | $-11 \le h \le 11$<br>$-41 \le k \le 41$<br>$-12 \le l \le 12$ | $-19 \le h \le 19$<br>$-18 \le k \le 21$<br>$-23 \le l \le 22$ |
| Total data | 22039 | 35242 | 48983 | 32483 | 27027 | 42469 |
| Unique data | 7508 | 13631 | 7537 | 14419 | 6163 | 16168 |
| Parameters/ restr. | 484/0 | 939/95 | 547/15 | 1054/0 | 478/0 | 1163/1737 |
| $R$ ($F$) [$I > 2\sigma(I)$] | 0.0579 | 0.0509 | 0.0534 | 0.0401 | 0.0360 | 0.1268 |
| $wR2$ $F^2$ (all data) | 0.1468 | 0.1540 | 0.1707 | 0.0969 | 0.0855 | 0.4310 |
| GOF on $F^2$ | 0.853 | 1.014 | 1.039 | 0.931 | 0.938 | 0.943 |
| CCDC no. | 250970 | 250971 | 250972 | 250973 | 250974 | 250975 |

[a] All measurements were performed at 123(2) K with a Nonius Kappa-CCD diffractometer using Mo-$K_\alpha$ graphite-monochromated radiation ($\lambda$ = 0.71073 Å).

*carbon Chemistry*, Wiley-VCH, Weinheim, **2000**, 321–330; c) T. J. Katz, *Angew. Chem. Int. Ed.* **2000**, *39*, 1921–1923; *Angew. Chem.* **2000**, *112*, 1997–1999; d) F. Vögtle, *Fascinating molecules in Organic Chemistry*, John Wiley & Sons, New York, **1992**, 156–180; e) K. P. Meurer, F. Vögtle, *Top. Curr. Chem.* **1985**, *127*, 1–76; f) W. H. Laarhoven, W. J. Prinsen, *Top. Curr. Chem.* **1984**, *125*, 63–120; g) H. Wynberg, *Acc. Chem. Res.* **1971**, *4*, 65–73.

[5] a) B. Kiupel, C. Niederalt, M. Nieger, S. Grimme, F. Vögtle, *Angew. Chem. Int. Ed.* **1998**, *37*, 3031–3034; *Angew. Chem.* **1998**, *110*, 3206–3209; b) I. G. Stará, I. Starý, A. Kollárovič, F. Teplý, D. Šaman, M. Tichý, *J. Org. Chem.* **1998**, *63*, 4046–4050; c) I. G. Stará, I. Starý, M. Tichý, J. Závada, P. Fiedler, *J. Org. Chem.* **1994**, *59*, 1326–1332.

[6] P. Lustenberger, E. Martinborough, T. Mordasini Denti, F. Diederich, *J. Chem. Soc., Perkin Trans. 2* **1998**, 747–761.

[7] a) M. McCarthy, P. J. Guiry, *Tetrahedron* **2001**, *57*, 3809–3844; b) R. Noyori, *Asymmetric Catalysis in Organic Synthesis*, John Wiley & Sons, New York, **1994**; c) H. Brunner, W. Zettelmeier, *Handbook of Enantioselective Catalysis with Transition Metal Compounds*, Wiley-VCH, Weinheim, **1993**, vols. 1 and 2.

[8] a) N. Ruiz, A. Aaliti, J. Forniés-Cámer, A. Ruiz, C. Claver, C. J. Cardin, D. Fabbri, S. Gladiali, *J. Organomet. Chem.* **1997**, *545–546*, 79–87; b) K. Yamamoto, K. Noda, Y. Okamoto, *J. Chem. Soc., Chem. Commun.* **1985**, 1065–1066; c) A. E. Sollewijn Gelpke, H. Kooijman, A. L. Spek, H. Hiemstra, *Chem. Eur. J.* **1999**, *5*, 2472–2482.

[9] a) L. Owens, C. Thilgen, F. Diederich, C. B. Knobler, *Helv. Chim. Acta* **1993**, *76*, 2757–2774; b) K. Yamamoto, T. Ikeda, T. Kitsuki, Y. Okamoto, H. Chikamatsu, M. Nakazaki, *J. Chem. Soc., Perkin Trans. 1* **1990**, 271–276; c) I. Sato, R. Yamashima, K. Kadowaki, J. Yamamoto, T. Shibata, K. Soai, *Angew. Chem.* **2001**, *113*, 1130–1132; *Angew. Chem. Int. Ed.* **2001**, *40*, 1096–1098; d) M. T. Reetz, S. Sostmann, *J. Organomet. Chem.* **2000**, *603*, 105–109; e) M. T. Reetz, E. W. Beutemüller, R. Goddard, *Tetrahedron Lett.* **1997**, *38*, 3211–3214.

[10] S. Grimme, J. Harren, A. Sobanski, F. Vögtle, *Eur. J. Org. Chem.* **1998**, 1491–1509.

[11] L. Vycklický, S. H. Eichhorn, T. J. Katz, *Chem. Mater.* **2003**, *15*, 3594–3601.

[12] F. B. Mallory, C. W. Mallory, *Organic Reactions*, John Wiley & Sons, New York **1984**, *30*, 1–456.

[13] For a recent summary, see: A. Urbano, *Angew. Chem.* **2003**, *115*, 4116–4119; *Angew. Chem. Int. Ed.* **2003**, *42*, 3986–3989.

[14] a) L. Liu, T. J. Katz, *Tetrahedron Lett.* **1990**, *31*, 3983–3986; b) N. D. Willmore, L. Liu, T. J. Katz, *Angew. Chem.* **1992**, *104*, 1081–1082; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1093–1095; c) K. Paruch, L. Vycklický, D. Z. Wang, T. J. Katz, C. Incarvito, L. Zakharov, L. A. Rheingold, *J. Org. Chem.* **2003**, *68*, 8539–8544.

[15] a) M. C. Carreño, S. García-Cerrada, A. Urbano, *J. Am. Chem. Soc.* **2001**, *123*, 7929–7930; b) M. C. Carreño, S. García-Cerrada, A. Urbano, *Chem. Eur. J.* **2003**, *9*, 4118–4131.

[16] a) S. Han, D. R. Anderson, A. D. Bond, H. V. Chu, R. L. Disch, D. Holmes, J. M. Schulman, S. J. Teat, K. P. C. Vollhardt, G. D. Whitener, *Angew. Chem. Int. Ed.* **2002**, *41*, 3223–3230; *Angew. Chem.* **2002**, *114*, 3361–3364; b) D. Peña, A. Cobas, D. Pérez, E. Guitián, L. Castedo, *Org. Lett.* **2003**,

*5*, 1863–1866; c) I. G. Stará, I. Starý, A. Kollárovič, F. Teplý, D. Šaman, P. Fiedler, *Collect. Czech. Chem. Commun.* **2003**, *68*, 917–930.
[17] a) K. H. Dötz, J. Stendel Jr., in *Modern Arene Chemistry* (Ed.: D. Astruc), Wiley-VCH, Weinheim, **2002**, 250–296; b) K. H. Dötz, P. Tomuschat, *Chem. Soc. Rev.* **1999**, *28*, 187–198.
[18] For a summary of applications, see: A. de Meijere, H. Schirmer, M. Duetsch, *Angew. Chem.* **2000**, *112*, 4124–4162; *Angew. Chem. Int. Ed.* **2000**, *39*, 3964–4002.
[19] A. V. Vorogushin, W. D. Wulff, H.-J. Hansen, *Org. Lett.* **2001**, *3*, 2641–2644.
[20] a) H. C. Jahr, M. Nieger, K. H. Dötz, *J. Organomet. Chem.* **2002**, *641*, 185–194; b) H. C. Jahr, M. Nieger, K. H. Dötz, *in preparation*; c) J. Stendel Jr., M. Nieger, S. Müller, S. Ketrat, M. Dolg, K. H. Dötz, *in preparation.*
[21] a) P. Lustenberger, F. Diederich, *Helv. Chim. Acta* **2000**, *83*, 2865–2883; b) M. Bandin, S. Casolari, P. G. Cozzi, G. Proni, E. Schmohel, G. P. Spada, E. Tagliavini, A. Umani-Ronchi, *Eur. J. Org. Chem.* **2000**, 491–497.
[22] a) W. Dilthey, F. Quint, J. Heinen, *J. Prakt. Chem.* **1939**, *152*, 66–68; b) B. M. Trost, C. G. Caldwell, *Tetrahedron Lett.* **1981**, *22*, 4999–5002; c) R. H. Cragg, R. D. Lane, *J. Organomet. Chem.* **1984**, *267*, 1–71; d) T. Takada, M. Arisawa, M. Gyoten, R. Hamada, H. Tohma, Y. Kita, *J. Org. Chem.* **1998**, *63*, 7698–7706.
[23] K. H. Dötz, P. Tomuschat, M. Nieger, *Chem. Ber./Recueil* **1997**, *130*, 1605–1609.
[24] a) J. P. Mitchel, S. Hajela, S. K. Brookhart, K. I. Hardcastle, L. M. Henling, J. E. Bercaw, *J. Am. Chem. Soc.* **1996**, *118*, 1045–1053; b) L. L. Schafer, T. D. Tilley, *J. Am. Chem. Soc.* **2001**, *123*, 2683–2684.
[25] a) C. Stammel, R. Fröhlich, C. Wolff, H. Wenck, A. de Meijere, J. Mattay, *Eur. J. Org. Chem.* **1999**, 1709–1718; b) A. Terfort, H. Görls, H. Brunner, *Synthesis* **1997**, 79–86.
[26] K. H. Dötz, N. Szesni, M. Nieger, K. Nättinen, *J. Organomet. Chem.* **2003**, *671*, 58–74.
[27] a) S. D. Dreher, T. J. Katz, K.-C. Lam, A. L. Rheingold, *J. Org. Chem.* **2000**, *65*, 815–822; b) K. Paruch, T. J. Katz, C. Incarvito, K.-C. Lam, B. Rhatigan, A. L. Rheingold, *J. Org. Chem.* **2000**, *65*, 7602–7608.
[28] G. Höfle, W. Steglich, H. Vorbrüggen, *Angew. Chem.* **1978**, *90*, 602–615; *Angew. Chem. Int. Ed.* **1978**, *17*, 569–583.
[29] a) D. B. Grotjahn, F. E. K. Kroll, T. Schäfer, K. H. Dötz, *Organometallics* **1992**, *11*, 298–310; b) J. M. Vernier, L. S. Hegedus, D. B. Miller, *J. Org. Chem.* **1992**, *57*, 6914–6920; c) W. D. Wulff, V. Dragisich, J. C. Huffman, R. W. Kaesler, D. C. Yang, *Organometallics* **1989**, *8*, 2196–2207.
[30] T. Thongpanchang, K. Paruch, T. J. Katz, A. L. Rheingold, C.-L. Lam, L. Liable-Sands, *J. Org. Chem.* **2000**, *65*, 1850–1856.
[31] See ref. [23] and: a) M. Landman, H. Görls, S. Lotz, *Eur. J. Inorg. Chem.* **2001**, 233–238; b) E. O. Fischer, W. Röll, N. H. T. Huy, K. Ackermann, *Chem. Ber.* **1982**, *115*, 2951–3212; c) R. Neidlein, S. Gürtler, C. Krieger, *Helv. Chim. Acta* **1994**, *77*, 2303–2322.
[32] A. Minatti, Diploma Thesis, University of Bonn, Germany, **2001**.
[33] For further linear benzannulations, see ref. [20a] and: a) M. F. Semmelhack, S. Ho, D. Cohen, M. Steigerwald, M. C. Lee, G. Lee, A. M. Gilbert, W. D. Wulff, R. G. Ball, *J. Am. Chem. Soc.* **1994**, *116*, 7108–7122; b) K. H. Dötz, M. Popall, *Tetrahedron* **1985**, *41*, 5797–5802.
[34] See reference ref. [20c] and K. H. Dötz, R. Dietz, *Chem. Ber.* **1978**, *111*, 2517–2526.
[35] a) R. El Abed, B. Ben Hassine, J.-P. Genêt, M. Gorsane, A. Marinetti, *Eur. J. Org. Chem.* **2004**, 1517–1522; b) M. L. Tedjamulia, Y. Tominaga, R. N. Castle, M. L. Lee, *J. Heterocycl. Chem.* **1983**, *20*, 861; c) F. Dietz, M. Scholz, *Tetrahedron* **1968**, *24*, 6845.
[36] S. Koo, L. S. Liebeskind, *J. Am. Chem. Soc.* **1995**, *117*, 3389–3404.
[37] For further examples of aromatic nitration with CAN, see: a) R. Sathunuru, U. N. Rao, E. Biehl, *ARKIVOC* **2003**, *15*, 124–133; b) J.-L. Grenier, J. P. Catteau, P. Cotelle, *Synth. Commun.* **1999**, *29*, 1201–1208; c) E. Gräff, PhD. Thesis, University of Bonn, Germany, **2004**.
[38] J. J. G. S. van Es, H. A. M. Biemans, E. W. Meijer, *Tetrahedron: Asymmetry* **1997**, *8*, 1825–1831.
[39] a) N. H. T. Huy, P. Lefloch, *J. Organomet. Chem.* **1988**, *344*, 303–311; b) P. Tomuschat, L. Kröner, E. Steckhan, M. Nieger, K. H. Dötz, *Chem. Eur. J.* **1999**, *5*, 700–707; c) L. Quast, M. Nieger, K. H. Dötz, *Organometallics* **2000**, *19*, 2179–2183.
[40] W. H. Laarhoven, T. J. H. M. Cuppen, R. J. F. Nivard, *Tetrahedron* **1970**, *26*, 4865–4881.
[41] a) R. H. Martin, M. J. Marchant, M. Baes, *Helv. Chim. Acta* **1971**, *54*, 358; b) D. C. Harrowven, M. I. T. Nunn, D. R. Fenwick, *Tetrahedron Lett.* **2002**, *43*, 7345–7347; c) S. D. Dreher, D. J. Weix, T. J. Katz, *J. Org. Chem.* **1999**, *64*, 3671–3678.
[42] C. Wachsmann, E. Weber, M. Czugler, W. Seichter, *Eur. J. Org. Chem.* **2003**, 2863–2876.
[43] P. Hobza, Z. Havlas, *Chem. Rev.* **2000**, *100*, 4253–4264.
[44] G. R. Desiraju, R. Parthasarathy, *J. Am. Chem. Soc.* **1989**, *111*, 8725–8726.
[45] See ref.[42] and: I. Pischel, S. Grimme, S. Kotila, M. Nieger, F. Vögtle, *Tetrahedron: Asymmetry* **1996**, *7*, 109–116.
[46] See ref.[21b] and: C. Rosini, I. Rosati, G. P. Spada, *Chirality* **1995**, *7*, 353–358.
[47] C. Rosini, S. Superchi, H. W. I. Peerlings, E. W. Meijer, *Eur. J. Org. Chem.* **2000**, 61–71.
[48] S. Imajo, K. Shingu, H. Kuritani, A. Kato, *Tetrahedron Lett.* **1981**, *22*, 107–110.
[49] a) K. Yamamura, S. Ono, H. Ogoshi, H, Masuda, Y. Kuroda, *Synlett* **1989**, 18–19; b) G. Gottarelli, G. Proni, G. P. Spada, D. Fabbri, S. Gladiali, C. Rosini, *J. Org. Chem.* **1996**, *61*, 2013–2019.
[50] A. R. Wartini, J. Valenzuela, H. A. Staab, F. A. Neugebauer, *Eur. J. Org. Chem.* **1998**, 221–227.
[51] See ref.[39b] and: J. Daub, J. Salbeck, I. Aurbach, *Angew. Chem.* **1988**, *100*, 278–280; *Angew. Chem. Int. Ed.* **1988**, *27*, 291–293.
[52] a) B. Yang, L. Liu, T. J. Katz, C. A. Liberko, L. L. Miller, *J. Am. Chem. Soc.* **1991**, *113*, 8993–8994; b) C. A. Liberko, L. L. Miller, T. J. Katz, L. Liu, *J. Am. Chem. Soc.* **1993**, *115*, 2478–2482.
[53] S. R. Rak, L. L. Miller, *J. Am. Chem. Soc.* **1992**, *114*, 1388–1395.
[54] SHELXS-97: G. M. Sheldrick, *Acta Crystallogr., Sect. A* **1990**, *46*, 467–473.
[55] G. M. Sheldrick, *SHELXL-97: Program for Crystal Structure Refinement*, University of Göttingen, Germany, **1997**.
[56] H. D. Flack, *Acta Crystallogr., Sect. A* **1983**, *39*, 876–881.

Received: November 08, 2004