Helical Structures

DOI: 10.1002/anie.201301739

Rapid Access to Dibenzohelicenes and their Functionalized Derivatives**

Andrej Jančařík, Jiří Rybáček, Kevin Cocq, Jana Vacek Chocholoušová, Jaroslav Vacek, Radek Pohl, Lucie Bednárová, Pavel Fiedler, Ivana Císařová, Irena G. Stará, and Ivo Starý**

Dedicated to E. Peter Kündig

Visions of applying unique helically chiral π-electron systems in diverse areas of chemistry and physics have fueled the intensifying research aimed at the development of a practical and general methodology for the preparation of functionalized helicenes and their heteroanalogues.[1] Despite the fact that significant progress has recently been achieved in this regard,[1a–e] there is plenty of opportunity to substantially shorten, simplify, and generalize the synthesis of helicenes. If such an endeavor meets with success, then an on-demand preparation of tailormade helicenes would ultimately not be a limiting step for their wider exploitation.

Herein, we report on the development of a simple and versatile synthesis of a series of dibenzo[5]-, dibenzo[6]-, and dibenzo[7]helicenes (**1**–**3**; Figure 1)[2] and their functionalized derivatives, including heteroanalogues. Construction of dibenzohelicenes relies on the pivotal Sonogashira and Suzuki–Miyaura couplings to assemble the key aromatic triynes, with a subsequent [2+2+2] alkyne cycloisomerization[3] to form the helical backbones. The structures of the dibenzohelicenes **1**–**3** represent, in fact, a formal fusion of picene (i.e., [5]phenacene) with the corresponding parent carbohelicenes. Recently, Tanaka et al. developed the synthesis of complementary 1,1′-bitriphenylenes by a rhodium-catalyzed double [2+2+2] cycloaddition of biaryl-linked tetraynes with 1,4-diynes,[4a] thus providing other dibenzo analogues of parent helicenes. Durola et al. synthesized *tert*-butylated dibenzo[5]helicene and its triply helical analogue by a Scholl cyclization featuring an intriguing regioselectivity,[4b] and Siegel and Ernst et al. reported the new dibenzo[5]-helicene **1** as prepared from difluoroquinquephenyl by an intramolecular Friedel–Crafts-type arylation through silylium ion promoted C–F bond activation.[4c]

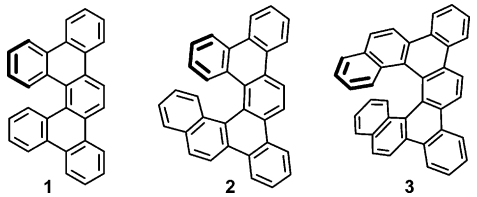


Figure 1. Dibenzo[5]-, dibenzo[6]-, and dibenzo[7]helicene (**1**–**3**).

There are good reasons for paying attention to dibenzohelicenes: 1) The presence of two extra annulated benzene rings simplifies the synthesis and makes it more efficient (see below), 2) the methodology allows the preparation of fully aromatic, helically chiral systems, which are known to exhibit remarkable chiroptical properties,[5] and 3) the lateral extension of the aromatic helix by additional benzene ring(s) can be advantageous for efficient chirality transfer in enantioselective reactions mediated by helicene-based catalysts.[6] Extending the aromatic scaffold raises a practical question about its solubility, which could be substantially lowered owing to an extensive intermolecular π–π stacking. However, the twist of dibenzohelicenes (i.e., nonplanarity) should minimize such an interaction (see below).

Nowadays, the intra/intermolecular [2+2+2] cycloisomerization of alkynes has been established as a standard method for the synthesis of helical (hetero)aromatics as reported by our group,[7] Vollhardt et al.,[8] Teplý et al.,[9] Tanaka et al.,[4a] Shibata et al.,[10] Carbery et al.,[11] and Diederich et al.[12] By utilizing this methodology, we previously carried out the direct cycloisomerization of aromatic *Z*,*Z* dienetriynes into helicenes (**4**→**5**; Scheme 1).[7d] As this method of helicene synthesis has limits in the chemical stability (and accessibility) of the starting *Z*,*Z* dienetriynes, we propose herein their stabilized analogues as exemplified by **4** where the (*Z*)-1,2-vinylene fragments are embedded in the *ortho*-phenylene moieties. Provided cycloisomerization is feasible, the formation of **1** from **4** should be highly exergonic as the calculated value of ΔG at 25 °C in THF is −124.7 kcal mol^{-1} (comparable to $\Delta G = -135.1$ kcal mol^{-1} for **4**→**5**).[13]

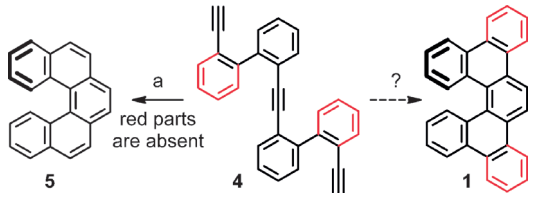
Indeed, the incorporation of the *ortho*-phenylene tethers into the aromatic triynes like **4** substantially simplified their synthesis whether they were symmetrical or not. Based purely on the powerful coupling methodologies (except for the

[*] A. Jančařík, Dr. J. Rybáček, K. Cocq, Dr. J. Vacek Chocholoušová, Dr. J. Vacek, Dr. R. Pohl, Dr. L. Bednárová, Dr. P. Fiedler, Dr. I. G. Stará, Dr. I. Starý
Institute of Organic Chemistry and Biochemistry
Academy of Sciences of the Czech Republic
Flemingovo nám. 2, 166 10 Prague 6 (Czech Republic)
E-mail: stara@uochb.cas.cz
stary@uochb.cas.cz

Dr. I. Císařová
Department of Inorganic Chemistry, Faculty of Science
Charles University in Prague, Prague 2 (Czech Republic)

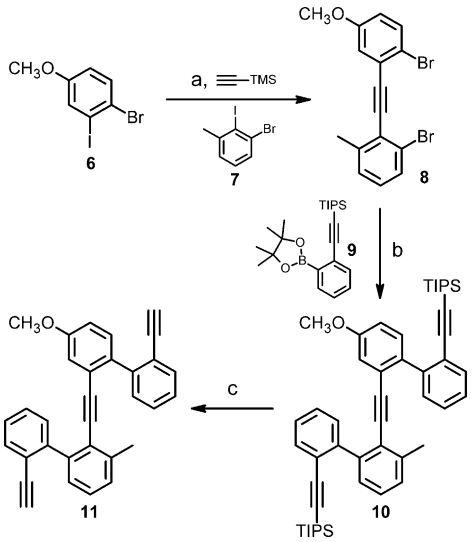
[**] This work was supported by the Czech Science Foundation (P207/10/2207), the Ministry of Education, Youth and Sports of the Czech Republic (MSM0021620857), and the Institute of Organic Chemistry and Biochemistry, Academy of Sciences of the Czech Republic (RVO: 61388963). Reinhard Kaiser is acknowledged for his contribution to the synthesis development.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201301739.



Scheme 1. [2+2+2] Alkyne cycloisomerization in the formation of a helicene scaffold; a) $[Ni(cod)_2]$, PPh_3, 64%.[7d] cod = cyclo-1,5-octadiene.

desilylation step(s); see below), we developed complementary step-economic, high-yielding, synthetic protocols, which we have generally used in the preparation of the desired aromatic triynes as illustrated in Scheme 2. To obtain unsymmetrical triynes such as the prototypal **11**, the diaryl acetylene **8** was prepared from the aryliodides **6** and **7** and trimethylsilylacetylene by a chemoselective Sonogashira coupling/in situ desilylation/chemoselective Sonogashira coupling sequence as a one-pot operation (for details, see the Supporting Information).[14] Alternatively, such a multistep protocol was modified if a product of the first Sonogashira coupling (i.e., trimethylsilylethynyl aromatics) was commercially available or the stepwise approach to diarylacetylene resulted in its higher overall yield. The *ortho*-phenylene-tethered alkyne units were attached by the treatment of **8** with the arylboronic acid pinacol ester **9** (or with the corresponding arylboronic acid)[15] under the Suzuki–Miyaura coupling conditions to receive the protected triyne **10**, which upon smooth desilylation provided the key aromatic triyne **11**. In the case of the synthesis of symmetrical triynes, trimethylsilylacetylene in the first Sonogashira coupling was replaced by gaseous acetylene.[16]



Scheme 2. The general synthetic route to the unsymmetrical aromatic triynes such as **11**: a) TMS-C≡CH (1.0 equiv), $[Pd(PPh_3)_2Cl_2]$ (6 mol%), CuI (10 mol%), diisopropylamine (6.0 equiv), benzene, room temperature, 2.5 h, then **7** (1.0 equiv), DBU (excess), water (40 mol%), 45 °C, 18 h, 75%; b) **9** (2.5 equiv), $[Pd(PPh_3)_2Cl_2]$ (8 mol%), K_2CO_3 (2.0 equiv), toluene/ethanol/water (4:4:1), 90 °C, 2 h, 75%; c) nBu_4NF (2.2 equiv), THF, room temperature, 15 min, 97%. DBU = 1,8-diazabicyclo[5.4.0] undec-7-ene, THF = tetrahydrofuran, TIPS = triisopropylsilyl.

Thus having a representative series of triynes **4**, **11**–**18** and **27**–**31** including functionalized ones, which were stable (in contrast to the *Z*,*Z* dienetriynes mentioned above) and prepared basically within three to five synthetic operations, we embarked on studying their intramolecular [2+2+2] cycloisomerization to dibenzohelicenes (Table 1 and Table 2). Gratifyingly, the test model triyne **4** underwent a smooth and clean cyclization reaction under Ni^0/PPh_3 catalysis, thus affording a fully aromatic corresponding dibenzo[5]helicene **1** in nearly quantitative yield (Table 1, entry 1). Encouraged by this result, we screened a collection of related triynes (**11**–**18**) and found that they gave rise to new functionalized dibenzo[5]helicenes (**19**–**26**) in good to high yields (Table 1, entries 2–9). To our delight, the nickel(0)-catalyzed cyclization exhibited a broad tolerance to substituents and functional groups such as Ph (entry 2), CH_3 (entries 3, 4, 6, and 7), CH_3O (entries 4 and 5), Cl (entry 6), NO_2 (entry 7), and the incorporated pyridine unit(s) placed at the termini of the helicene scaffold (entries 8 and 9). Note that the presence of the CH_3 group in position 1 of **20**, **21**, **23**, and **24** significantly increases the racemization barrier of the dibenzo[5]helicene scaffold.

However, the versatility of any methodology for the helicene synthesis is judged by the fact of whether it is suitable for the preparation of higher homologues of [5]helicene. We therefore attempted the preparation of dibenzo[6]- and dibenzo[7]helicenes (Table 2). The triynes **27**–**31** were assembled from dihalogenated benzene/naphthalene building blocks using the straightforward Sonogashira and Suzuki–Miyaura coupling methodology (for details, see the Supporting Information).

For the sake of pursuing intramolecular [2+2+2] cycloisomerization and thus forming the helicene backbone, the triynes **27**–**31** were treated with a catalytic amount of the in situ generated Ni^0/PPh_3 complex. To our delight, the triynes **27**–**29** and **31** provided the corresponding dibenzo[6]-, azadibenzo[6]-, or dibenzo[7]helicenes in good to high yields regardless of whether the tethered alkyne units were terminal or substituted by *p*-tolyl groups (Table 2, entries 1–3 and 5). However, to our disappointment, we failed to cyclize the triyne **30** into the dibenzo[7]helicene **3** because the starting material polymerized (Table 2, entry 4, reaction conditions A). We were therefore obliged to screen other reaction conditions. Indeed, the use of PCy_3 instead of PPh_3 in the nickel catalysis suppressed polymerization and promoted cyclization to deliver the desired dibenzo[7]helicene **3** in good yield (Table 2, entry 4, reaction conditions B). Additionally, the conversion of **30** into **3** could also be enforced by using the [CpCo(CO)(fum)] catalyst[17] under microwave irradiation (Table 2, entry 4, reaction conditions C). The single-crystal analyses of racemic **2** and **25**, which formed racemic compounds in the solid state, were performed to confirm the structures (for details, see the Supporting Information).

Analytical samples of the racemic dibenzohelicenes **2**, **3**, and **20** were resolved to optically pure enantiomers by HPLC on a Chiralpak IA column (*n*-heptane/chloroform 70:30; for

Table 1: [2+2+2] Cycloisomerization of the aromatic triynes **4** and **11**–**18** into the corresponding dibenzo[5]helicenes.

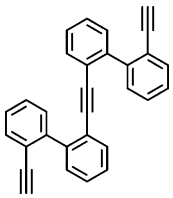
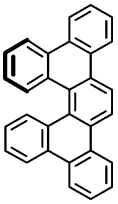
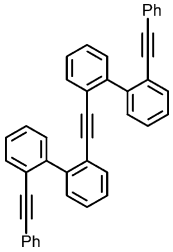
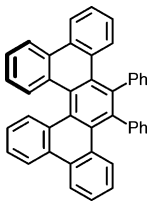
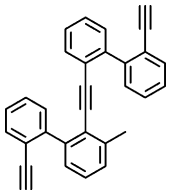
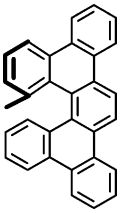
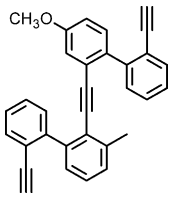
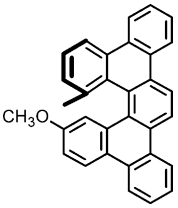
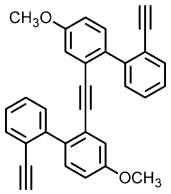
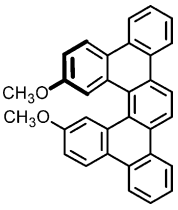
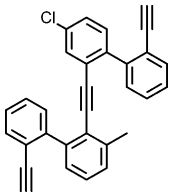
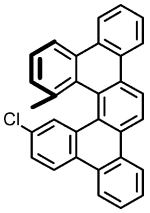
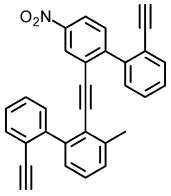
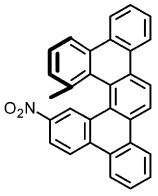
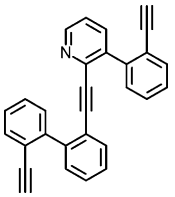
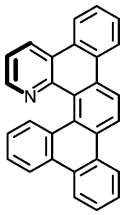
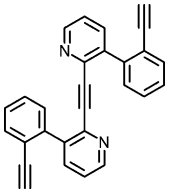
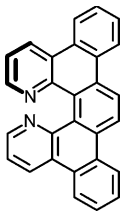
Entry	Triyne	Cond.[a]	Helicene[b]	Yield [%][c,d]
1	 **4**	A	 **1**	96 (67%, 4)
2	 **12**	A	 **19**	88 (58%, 5)
3	 **13**	A	 **20**	86 (24%, 5)
4	 **11**	A	 **21**	91 (50%, 4)
5	 **14**	A	 **22**	98 (54%, 4)
6	 **15**	A	 **23**	84 (55%, 4)
7	 **16**	A	 **24**	63 (53%, 4)

Table 1: (Continued)

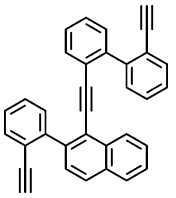
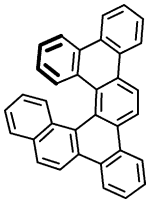
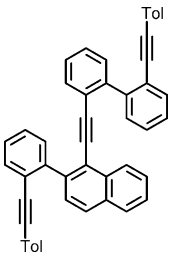
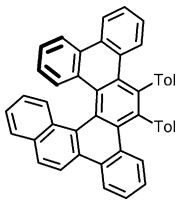
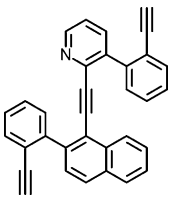
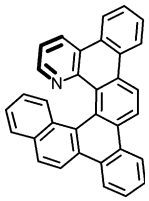
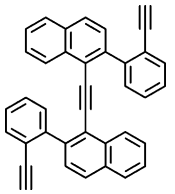
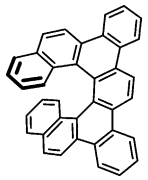
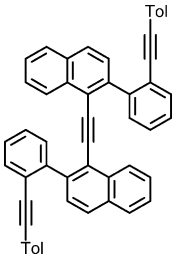
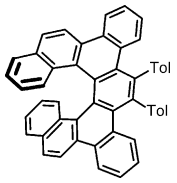
Entry	Triyne	Cond.[a]	Helicene[b]	Yield [%][c,d]
8	 **17**	A	 **25**	85 (60%, 4)
9	 **18**	A	 **26**	80 (31%, 4)

[a] Reaction conditions A: $[Ni(cod)_2]$ (20 mol%), PPh_3 (40 mol%), THF, room temperature, 10–40 min. [b] Racemates; only *P* enantiomers are shown for clarity. [c] Yield of isolated product. [d] The overall yield of the synthetic sequence starting from commercial chemicals and the number of steps (one-pot operations) are given within parentheses.

details, see the Supporting Information). We could see that the formal annulation of two benzene rings to the backbone of the parent 1-methyl[5]-, [6]-, and [7]helicene significantly diminished the specific optical rotatory power of **2**, **3**, and **20**, respectively (Table 3, entries 3 versus 4 and 5 versus 6), but the barriers to racemization were affected only slightly (Table 3, entries 1 versus 2, 3 versus 4, and 5 versus 6). To assign the helicity of the individual enantiomers of the representative dibenzohelicenes **2**, **3**, **20**, and **32** we correlated their experimental ECD spectra with those of parent [5]-, [6]- and [7]helicenes or, as given for (−)-(*M*)-**20**, with the calculated ECD spectrum (for details, see the Supporting Information). Given the results, the rule of thumb for helicene chemistry, that is, fully aromatic systems are of *P* helicity (or *M* helicity) if they are dextrorotatory (or laevorotatory), was obeyed in the case of dibenzohelicenes.

From a practical and economic point of view, an asymmetric synthesis of nonracemic dibenzohelicenes by enantioselective [2+2+2] alkyne cycloisomerization would be the most advantageous. Thus, based on our previous experience,[24] we focused on the challenging enantioselective nickel(0) catalysis employing axially chiral monophosphines (Table 4). Indeed, the cyclization of the the model triyne **27** provided the dibenzo[6]helicene **2** with moderate *ee* values if BOP,[25] or *N*- and *O*-PINAP[26] ligands were used (Table 4, entries 1–3). The best ligand we identified was QUINAP,[27] which allowed achievement of up to 80% *ee* when conducting the cyclization at −20°C (Table 4, entries 4 and 5). A further decrease in temperature resulted, however, in unreactive **27** (Table 4, entry 6). To make the transition state of cyclization more sterically congested and, perhaps, to achieve higher enantiocontrol, we attached *p*-tolyl groups to the pendant alkyne units as in the triyne **28**. Then, by using QUINAP, we obtained **32** in 85% *ee* when performing the cyclization at room temperature and 87% *ee* when lowering the temper-

Table 2: [2+2+2] Cycloisomerization of aromatic the triynes **27**–**31** into the corresponding dibenzo[6]- and dibenzo[7]helicenes.

Entry	Triyne	Cond.[a]	Helicene[b]	Yield [%][c,d]
1	 **27**	A	 **2**	92 (53%, 5)
2	 **28**	A	 **32**	90 (43%, 6)
3	 **29**	A	 **33**	68 (39%, 5)
4	 **30**	A B C	 **3**	0 75 (34%, 5) 80 (36%, 5)
5	 **31**	A	 **34**	80 (30%, 6)

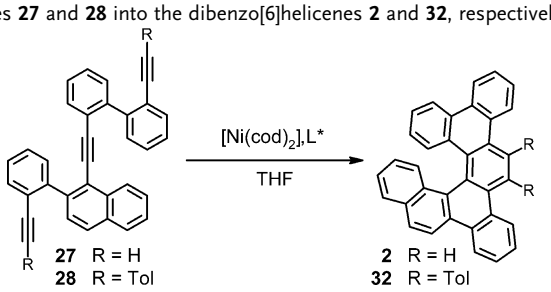
[a] Reaction conditions A: $[Ni(cod)_2]$ (20 mol%), PPh_3 (40 mol%), THF, room temperature, 10 min. Reaction conditions B: $[Ni(cod)_2]$ (20 mol%), PCy_3 (40 mol%), THF, room temperature, 10 min. Reaction conditions C: [CpCo(CO)(fum)] (1.0 equiv), 1-butyl-2,3-dimethylimidazolium tetrafluoroborate (25 µL/1 mL), THF, microwave reactor, 180°C, 10 min. [b] Racemates. Only *P* enantiomers are shown for clarity. [c] Yield of isolated product. [d] The overall yield of the synthetic sequence starting from commercial chemicals and the number of steps (one-pot operations) are given within parentheses. Cp = cyclopentadienyl, fum = dimethyl fumarate, Tol = *p*-tolyl.

Table 3: Optical rotations and barriers to racemization of representative dibenzohelicenes (**2**, **3**, and **20**) compared to the properties of the parent helicenes.

Entry	Dibenzohelicene or helicene	$[\alpha]_D^{25}$[a]	$\Delta\Delta G^{\neq}$ [kcal mol^{-1}]
1	1-methyldibenzo[5]helicene (**20**)	+529[b]	37.5[c]
2	1,3,6-trimethyl[5]helicene		38.7[d]
3	dibenzo[6]helicene (**2**)	+1470[e]	35.8[f]
4	[6]helicene	+3750[g]	36.2[h]
5	dibenzo[7]helicene (**3**)	+1773[i]	40.9[c]
6	[7]helicene	+5900[j]	42.5[k]

[a] Optical rotations of (+)-enantiomers given; measured at $\lambda = 589$ nm in $CHCl_3$ (unless stated otherwise). [b] Measured in CH_2Cl_2, 98% *ee*. [c] Determined in hexadecane at 230°C. [d] Determined in $(n\text{BuOCH}_2\text{CH}_2)_2\text{O}$ at 200°C (Ref. [19]). [e] 95% *ee*. [f] Determined in hexadecane at 200°C. [g] Ref. [20]. [h] Determined in naphthalene at 188°C.[21] [i] > 99% *ee*. [j] Determined at $\lambda = 579$ nm.[22] [k] Determined in naphthalene at 239°C.[23]

Table 4: Enantioselective [2+2+2] cycloisomerization of the aromatic triynes **27** and **28** into the dibenzo[6]helicenes **2** and **32**, respectively.

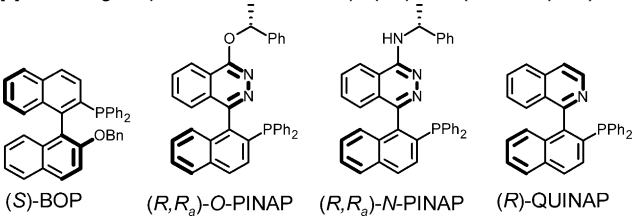


27 R = H
28 R = Tol

2 R = H
32 R = Tol

Entry	Triyne	Ligand	Reaction conditions	Product	*ee* [%][a]	Yield [%][b]
1	**27**	(*S*)-BOP[c]	RT, 10 min	(−)-**2**	31	> 90
2	**27**	(*R*)-*N*-PINAP[c]	RT, 10 min	(+)-**2**	33	> 90
3	**27**	(*R*)-*O*-PINAP[c]	RT, 10 min	(+)-**2**	40	> 90
4	**27**	(*R*)-QUINAP[d]	RT, 10 min	(+)-**2**	72 (95)[e]	> 90
5	**27**	(*R*)-QUINAP[c]	−20°C, 16 h	(+)-**2**	80	> 90
6	**27**	(*R*)-QUINAP[c]	−40°C, 24 h	–	–	–
7	**28**	(*R*)-QUINAP[c]	RT, 5 h	(+)-**32**	85 (> 99)[e]	80
8	**28**	(*R*)-QUINAP[c]	0°C, 16 h	(+)-**32**	87	30

[a] Determined by HPLC on a Chiralpak IA column (250 × 4.6 mm, 5 µm, *n*-heptane–chloroform 85:15, 1.0 mL min^{-1}). [b] Yields determined by ^{1}H NMR spectroscopy using an internal standard (*p*-methoxyacetophenone). [c] Ni: 20 mol%, L*: 40 mol%). [d] Ni: 3 mol%, L*: 6 mol%. [e] After single crystallization from THF/2-propanol (ca. 60% yield).



(*S*)-BOP (*R*,*R*$_a$)-*O*-PINAP (*R*,*R*$_a$)-*N*-PINAP (*R*)-QUINAP

ature to 0°C, thus identifying the reactivity limit of **28** (Table 4, entries 7 and 8). Finally, a single crystallization of the enantioenriched samples of **2** and **32** from THF/2-propanol allowed further increase in their *ee* values to 95% and 99%, respectively, with approximately 60% yield from the crystallization (Table 4, entries 4 and 7).

In summary, we have developed a general approach to dibenzo[5]-, dibenzo[6]-, and dibenzo[7]helicenes as well as their functionalized derivatives. These helically chiral aromatics can usually be synthesized within four to six operations in overall yields ranging from 24% to 67% by employing a short sequence of reliable processes such as Sonogashira coupling, Suzuki–Miyaura coupling, desilylation, and [2+2+2] alkyne cycloisomerization. With a few exceptions,[4] there are only scattered examples of dibenzohelicenes

described in the literature[2] and this study on their preparation and properties is so far the most comprehensive. Dibenzohelicenes have an advantage over the parent helicenes because of the simplicity of their non-photochemical preparation and, therefore, they have the potential to mimic or even substitute parent helicenes in envisaged applications. Moreover, we have demonstrated one of the highest degrees of enantiocontrol (see Ref. [4a], [10], and [28]) in the asymmetric synthesis of helicenes by transition-metal-catalyzed [2+2+2] alkyne cycloisomerization, and developed a straightforward approach to the optically pure paradigmatic dibenzo[6]helicene.

Received: February 28, 2013
Revised: June 13, 2013
Published online: August 9, 2013

Keywords: alkynes · aromaticity · asymmetric synthesis · chirality · helical structures

[1] For recent and early reviews, see: a) M. Gingras, *Chem. Soc. Rev.* **2013**, *42*, 968 – 1006; b) M. Gingras, G. Félix, R. Peresutti, *Chem. Soc. Rev.* **2013**, *42*, 1007 – 1050; c) M. Gingras, *Chem. Soc. Rev.* **2013**, *42*, 1051 – 1095; d) A. Urbano, M. C. Carreño, *Org. Biomol. Chem.* **2013**, *11*, 699 – 708; e) Y. Shen, C.-F. Chen, *Chem. Rev.* **2012**, *112*, 1463 – 1535; f) I. G. Stará, I. Starý in *Science of Synthesis, Vol. 45b* (Eds.: J. S. Siegel, Y. Tobe), Thieme, Stuttgart, **2010**, pp. 885 – 953; g) F. Dumitrascu, D. G. Dumitrescu, I. Aron, *Arkivoc* **2010**, *i*, 1 – 32; h) I. Starý, I. G. Stará in *Strained Hydrocarbons* (Ed.: H. Dodziuk), Wiley-VCH, Weinheim, **2009**, pp. 166 – 176; i) A. Rajca, M. Miyasaka in *Functional Organic Materials* (Eds.: T. J. J. Müller, U. H. F. Bunz), Wiley-VCH, Weinheim, **2007**, pp. 547 – 581; j) S. K. Collins, M. P. Vachon, *Org. Biomol. Chem.* **2006**, *4*, 2518 – 2524; k) A. Urbano, *Angew. Chem.* **2003**, *115*, 4116 – 4119; *Angew. Chem. Int. Ed.* **2003**, *42*, 3986 – 3989; l) K. Sato, S. Arai in *Cyclophane Chemistry for the 21st Century* (Ed.: H. Takemura), Research Signpost, Trivandrum, **2002**, pp. 173 – 197; m) H. Hopf in *Classics in Hydrocarbon Chemistry: Syntheses, Concepts, Perspectives*, Wiley-VCH, Weinheim, **2000**, pp. 323 – 330; n) T. J. Katz, *Angew. Chem.* **2000**, *112*, 1997 – 1999; *Angew. Chem. Int. Ed.* **2000**, *39*, 1921 – 1923; o) F. Vögtle in *Fascinating Molecules in Organic Chemistry*, Wiley, New York, **1992**, pp. 156 – 180; p) G. Oremek, U. Seiffert, A. Janecka, *Chem.-Ztg.* **1987**, *111*, 69 – 75; q) K. P. Meurer, F. Vögtle, *Top. Curr. Chem.* **1985**, *127*, 1 – 76; r) W. H. Laarhoven, W. J. C. Prinsen, *Top. Curr. Chem.* **1984**, *125*, 63 – 130; s) R. H. Martin, *Angew. Chem.* **1974**, *86*, 727 – 738; *Angew. Chem. Int. Ed. Engl.* **1974**, *13*, 649 – 660; t) H. Wynberg, *Acc. Chem. Res.* **1971**, *4*, 65 – 73.

[2] For the dibenzo[5]helicene **1**, see: a) W. H. Laarhoven, P. G. F. Boumans, *Recl. Trav. Chim. Pays-Bas* **1975**, *94*, 114 – 118; b) W. H. Laarhoven, T. J. H. M. Cuppen, R. J. F. Nivard, *Recl. Trav. Chim. Pays-Bas* **1968**, *87*, 687 – 698; c) A. Jenard-De Koninck, N. Defay, R. De Ridder, *Bull. Soc. Chim. Belg.* **1960**, *69*, 558 – 562; for the dibenzo[7]helicene **3**, see: d) W. H. Laarhoven, R. J. F. Nivard, *Tetrahedron* **1976**, *32*, 2445 – 2450; the dibenzo[6]helicene **2** is not known.

[3] G. Domínguez, J. Pérez-Castells, *Chem. Soc. Rev.* **2011**, *40*, 3430 – 3444.

[4] a) Y. Sawada, S. Furumi, A. Takai, M. Takeuchi, K. Noguchi, K. Tanaka, *J. Am. Chem. Soc.* **2012**, *134*, 4080 – 4083, and references therein; b) A. Pradhan, P. Dechambenoit, H. Bock, F. Durola, *Angew. Chem.* **2011**, *123*, 12790 – 12793; *Angew. Chem. Int. Ed.* **2011**, *50*, 12582 – 12585; c) J. Seibel, O. Allemann, J. S. Siegel, K.-H. Ernst, *J. Am. Chem. Soc.* **2013**, *135*, 7434 – 7437.

[5] E. Anger, M. Rudolph, C. Shen, N. Vanthuyne, L. Toupet, C. Roussel, J. Autschbach, J. Crassous, R. Réau, *J. Am. Chem. Soc.* **2011**, *133*, 3800 – 3803, and references therein.

[6] Takenaka et al. introduced azahelicene-derived organocatalysts with an additional annulated benzene ring, and they were superior to the parent catalysts in the desymmetrization of *meso* epoxides: a) N. Takenaka, R. S. Sarangthem, B. Captain, *Angew. Chem.* **2008**, *120*, 9854 – 9856; *Angew. Chem. Int. Ed.* **2008**, *47*, 9708 – 9710; in enantioselective propargylation of aldehydes: b) J. Chen, B. Captain, N. Takenaka, *Org. Lett.* **2011**, *13*, 1654 – 1657; in acid-catalyzed asymmetric Friedel – Crafts reaction: c) N. Takenaka, J. Chen, B. Captain, R. S. Sarangthem, A. Chandrakumar, *J. Am. Chem. Soc.* **2010**, *132*, 4536 – 4537.

[7] For leading references, see: a) P. Sehnal, I. G. Stará, D. Šaman, M. Tichý, J. Míšek, J. Cvačka, L. Rulíšek, J. Chocholoušová, J. Vacek, G. Goryl, M. Szymonski, I. Císařová, I. Starý, *Proc. Natl. Acad. Sci. USA* **2009**, *106*, 13169 – 13174; b) J. Míšek, F. Teplý, I. G. Stará, M. Tichý, D. Šaman, I. Císařová, P. Vojtíšek, I. Starý, *Angew. Chem.* **2008**, *120*, 3232 – 3235; *Angew. Chem. Int. Ed.* **2008**, *47*, 3188 – 3191; c) F. Teplý, I. G. Stará, I. Starý, A. Kollárovič, D. Šaman, P. Fiedler, Š. Vyskočil, *J. Org. Chem.* **2003**, *68*, 5193 – 5197; d) F. Teplý, I. G. Stará, I. Starý, A. Kollárovič, D. Šaman, L. Rulíšek, P. Fiedler, *J. Am. Chem. Soc.* **2002**, *124*, 9175 – 9180.

[8] 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.* **2002**, *114*, 3361 – 3364; *Angew. Chem. Int. Ed.* **2002**, *41*, 3227 – 3230.

[9] L. Adriaenssens, L. Severa, D. Koval, I. Císařová, M. Martínez Belmonte, E. C. Escudero-Adán, P. Novotná, P. Sázelová, J. Vávra, R. Pohl, D. Šaman, M. Urbanová, V. Kašička, F. Teplý, *Chem. Sci.* **2011**, *2*, 2314 – 2320, and references therein.

[10] T. Shibata, T. Uchiyama, Y. Yoshinami, S. Takayasu, K. Tsuchikama, K. Endo, *Chem. Commun.* **2012**, *48*, 1311 – 1313.

[11] M. R. Crittall, H. S. Rzepa, D. R. Carbery, *Org. Lett.* **2011**, *13*, 1250 – 1253.

[12] J. Roose, S. Achermann, O. Dumele, F. Diederich, *Eur. J. Org. Chem.* **2013**, 3223 – 3231.

[13] Calculated by DFT (B3LYP/cc-pVTZ), solvent (THF) described by the CPCM model (for details, see the Supporting Information).

[14] M. J. Mio, L. C. Kopel, J. B. Braun, T. L. Gadzikwa, K. Hull, R. G. Brisbois, C. J. Markworth, P. A. Grieco, *Org. Lett.* **2002**, *4*, 3199 – 3202.

[15] Although the Suzuki – Miyaura reaction with the arylboronic acid pinacol ester **9** is possible, the respective free arylboronic acid is more practical to prepare and purify owing to its better stability (see the Supporting Information). For the synthesis of **9**, see: B. Felber, F. Diederich, *Helv. Chim. Acta* **2005**, *88*, 120 – 153.

[16] It is worth noting that a higher yield as well as cleaner diarylacetylenes were obtained if the reaction was performed in the presence of a controlled amount of gaseous acetylene (1.2–1.3 equiv of acetylene, volumetrically dosed, per two aryl iodides to be coupled).

[17] A. Geny, N. Agenet, L. Iannazzo, M. Malacria, C. Aubert, V. Gandon, *Angew. Chem.* **2009**, *121*, 1842 – 1845; *Angew. Chem. Int. Ed.* **2009**, *48*, 1810 – 1813.

[18] CCDC 920132 (*rac*-**2**) and 920131 (*rac*-**25**) 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.

[19] H. Scherübl, U. Fritzsche, A. Mannschreck, *Chem. Ber.* **1984**, *117*, 336 – 343.

[20] M. S. Newman, R. S. Darlak, L. Tsai, *J. Am. Chem. Soc.* **1967**, *89*, 6191 – 6193.
[21] a) R. H. Martin, M. J. Marchant, *Tetrahedron Lett.* **1972**, *13*, 3707 – 3708; b) H. H. Wassermann, P. M. Keehn, *J. Am. Chem. Soc.* **1967**, *89*, 2770 – 2772.
[22] R. H. Martin, M. J. Marchant, *Tetrahedron* **1974**, *30*, 343 – 345.
[23] R. H. Martin, M. J. Marchant, *Tetrahedron* **1974**, *30*, 347 – 349.
[24] a) B. Heller, M. Hapke, C. Fischer, A. Andronova, I. Starý, I. G. Stará, *J. Organomet. Chem.* **2013**, *723*, 98 – 102; b) I. G. Stará, A. Andronova, A. Kollárovič, Š. Vyskočil, S. Jugé, G. C. Lloyd-Jones, P. J. Guiry, I. Starý, *Collect. Czech. Chem. Commun.* **2011**, *76*, 2005 – 2022.
[25] Y. Uozumi, A. Tanahashi, S.-Y. Lee, T. Hayashi, *J. Org. Chem.* **1993**, *58*, 1945 – 1948.
[26] a) T. F. Knöpfel, P. Aschwanden, T. Ichikawa, T. Watanabe, E. M. Carreira, *Angew. Chem.* **2004**, *116*, 6097 – 6099; *Angew. Chem. Int. Ed.* **2004**, *43*, 5971 – 5973; b) T. F. Knöpfel, P. Zarotti, T. Ichikawa, E. M. Carreira, *J. Am. Chem. Soc.* **2005**, *127*, 9682 – 9683.
[27] a) T. Thaler, F. Geittner, P. Knochel, *Synlett* **2007**, 2655 – 2658; b) N. W. Alcock, J. M. Brown, D. L. Hulmes, *Tetrahedron: Asymmetry* **1993**, *4*, 743 – 756.
[28] J. Žádný, A. Jančařík, A. Andronova, M. Šámal, J. Vacek Chocholoušová, J. Vacek, R. Pohl, D. Šaman, I. Císařová, I. G. Stará, I. Starý, *Angew. Chem.* **2012**, *124*, 5959 – 5963; *Angew. Chem. Int. Ed.* **2012**, *51*, 5857 – 5861.

