Chemical Science

EDGE ARTICLE

View Article Online
View Journal | View Issue

Check for updates

Cite this: *Chem. Sci.*, 2020, **11**, 403

All publication charges for this article have been paid for by the Royal Society of Chemistry

Received 30th August 2019
Accepted 11th November 2019

DOI: 10.1039/c9sc04378k

rsc.li/chemical-science

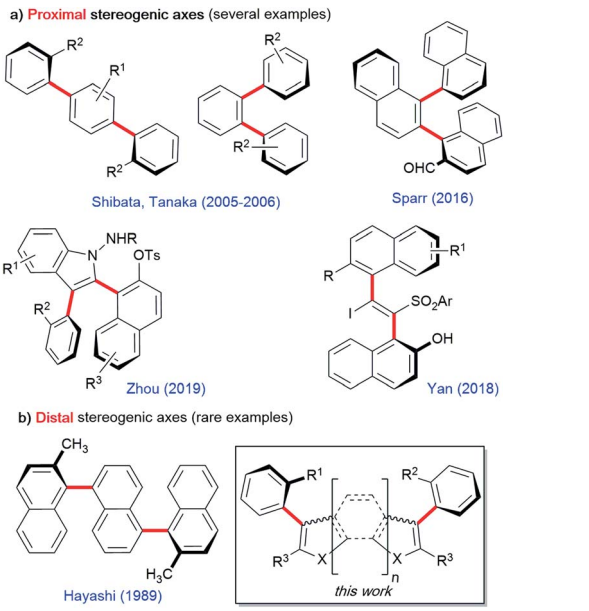
Bidirectional enantioselective synthesis of bis-benzofuran atropisomeric oligoarenes featuring two distal C–C stereogenic axes†

Xiaoze Bao,[a] Jean Rodriguez*[b] and Damien Bonne *[b]

We report the bidirectional enantioselective synthesis of bis-benzofuran atropisomeric oligoarenes featuring two distal C–C stereogenic axes obtained by a two-fold central-to-axial chirality conversion upon oxidative aromatization. The key enantioenriched centrally chiral bis-dihydrobenzofuran precursors were synthesized *via* a bidirectional diastereo- and enantio-selective organocatalyzed domino reaction between simple achiral and easily accessible dihydroxylated aromatics and chloronitroalkenes. Moreover, the stereodivergent nature of the methodology was established by synthesizing both diastereomers of a non-symmetrically functionalized bis-axially chiral oligoarene.

Introduction

Oligoarenes are long pi-conjugated systems commonly used in a wide range of functional materials such as organic photovoltaics, dendrimers, and self-assembling polymers.[1] They are also useful as precursors of more complex poly-aromatic hydrocarbons and graphene nanoribbons.[2] Over the past few decades, tremendous progress has been made in the development of protocols for the synthesis of oligoarenes and polyphenylenes.[3] In this field, functionalized chiral oligoarenes bearing multiple stereogenic axes are particularly attractive for materials sciences, but their efficient enantioselective synthetic access remains a challenging task.[4] In the few reported methods, proximal stereogenic axes are positioned on the same central aromatic core either on a 1,2- or on a 1,4-relationship as in teraryl or bis-styryl derivatives, respectively, or on a carbon–carbon double bond in a vicinal fashion (Scheme 1a). This is the case in the pioneering contributions of the groups of Tanaka and Shibata exploiting metal-catalyzed enantioselective [2 + 2 + 2] cycloadditions of achiral alkynes.[5] More recently, Sparr's[6] and Zhou's[7] groups astutely combined enantioselective organocatalytic activation with chirality conversion[8,9] to control oligo-1,2-naphthylenes or 2,3-diarylbenzoindoles, respectively. Complementarily, Yan[10] and co-workers developed an enantioselective organocatalyzed addition of arylsulfinates to an *in situ* generated vinylidene *o*-quinone methide[11] for the synthesis of vicinal atropisomeric styrenes. Quite surprisingly, very little attention has been paid to the enantioselective synthesis of oligoarenes featuring two C–C stereogenic axes positioned on two distal aromatic rings also found in naturally occurring michellamines (Scheme 1b).[12] In this field, Hayashi's seminal contribution employed an enantioselective double Kumada



Scheme 1 Enantioselective synthesis of bis-atropisomeric oligoarenes featuring either proximal (a) or distal (b) stereogenic axes.

[a]College of Pharmaceutical Science & Collaborative Innovation Center of Yangtze River Delta Region Green Pharmaceuticals, Zhejiang University of Technology, Hangzhou 310014, China

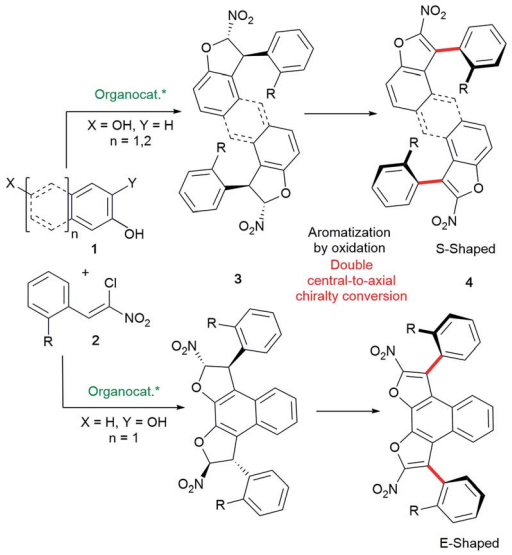
[b]Aix Marseille Université, CNRS, Centrale Marseille, iSm2, Marseille, France. E-mail: jean.rodriguez@univ-amu.fr; damien.bonne@univ-amu.fr

† Electronic supplementary information (ESI) available. CCDC 1922303 and 1921425. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c9sc04378k

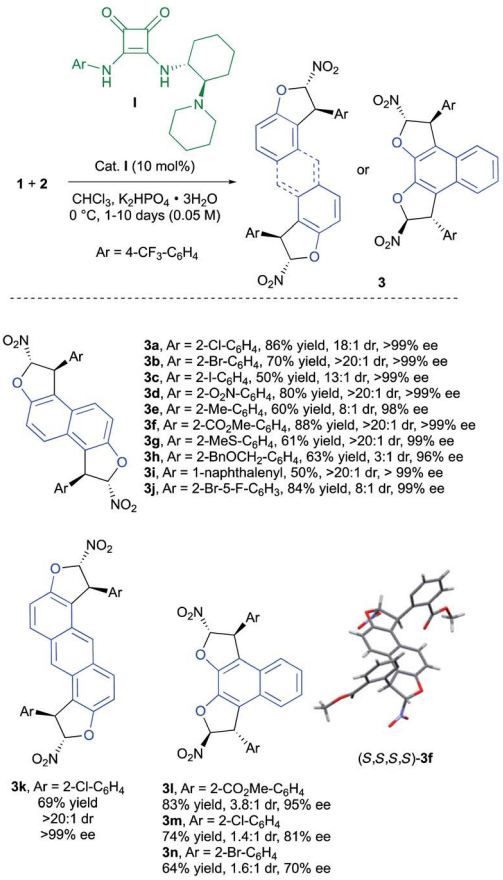
cross-coupling leading to symmetrically substituted ternaphthalene derivatives.[13,14] This lack of methodologies for the enantioselective synthesis of diversely functionalized chiral oligoarenes, especially in the heteroaromatic series, leaves space for a huge untapped potential. To fill this gap, we report a new bidirectional enantioselective synthesis of bis-benzofuran atropisomeric oligoarenes featuring two distal C–C stereogenic axes.

Results and discussion

Our complementary bidirectional strategy starts from simple achiral and easily accessible distal dihydroxy arene derivatives **1** and chloronitroalkenes **2** (Scheme 2). Upon oxidative aromatization of bis-dihydrobenzofurans **3**, a double central-to-axial chirality conversion would deliver the expected optically active S-shaped or E-shaped challenging atropisomeric bis-benzofurans **4** featuring two distal stereogenic axes. Moreover, the relatively large distance between both chiral axes of these new functional polyaromatic scaffolds will forge an interesting helically shaped molecular structure. The success of this approach lies in the combination of a two-fold diastereo- and enantio-selective organocatalyzed domino heterocyclization with double oxidative aromatization resulting in central-to-axial chirality conversion developed by our group.[15] Moreover, it is expected that these two successive catalyst-controlled domino heterocyclizations would benefit a chiral amplification based on the Horeau principle,[16] ensuring very high optical purities. Atropisomeric species built on a five-membered ring are quite difficult to construct in a stereoselective manner because of their lower configurational stability.[17] Consequently, the synthesis of molecules displaying two fused benzofuran atropisomers would be even more rewarding.



Scheme 2 Bidirectional central-to-axial chirality conversion for the synthesis of S- and E-shaped bis-benzofuran atropisomeric oligoarenes **4**.



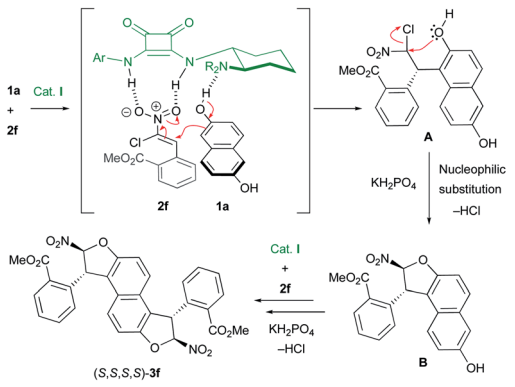
Scheme 3 Control of the central chirality in bis-dihydrobenzofurans **3**.[19]

To validate these assumptions, we targeted first the synthesis of bis-dihydrobenzofurans **3** based on the enantioselective domino Friedel–Crafts-O-alkylation reaction between commercially available 2,6-dihydroxynaphthalene (**1a**) and various *ortho*-substituted (*Z*)-(2-chloro-2-nitroethenyl)benzenes (**2**).[18] The use of the chiral bifunctional squaramide-tertiary amine organocatalyst (*R*,*R*)-**I** in combination with a weak inorganic base (K_2HPO_4) allowed the synthesis of the desired products **3a–k**, with good to excellent diastereoselectivity and an exceptional level of enantiodiscrimination (96 to >99% ee), clearly indicating the beneficial role of the Horeau chiral amplification principle.

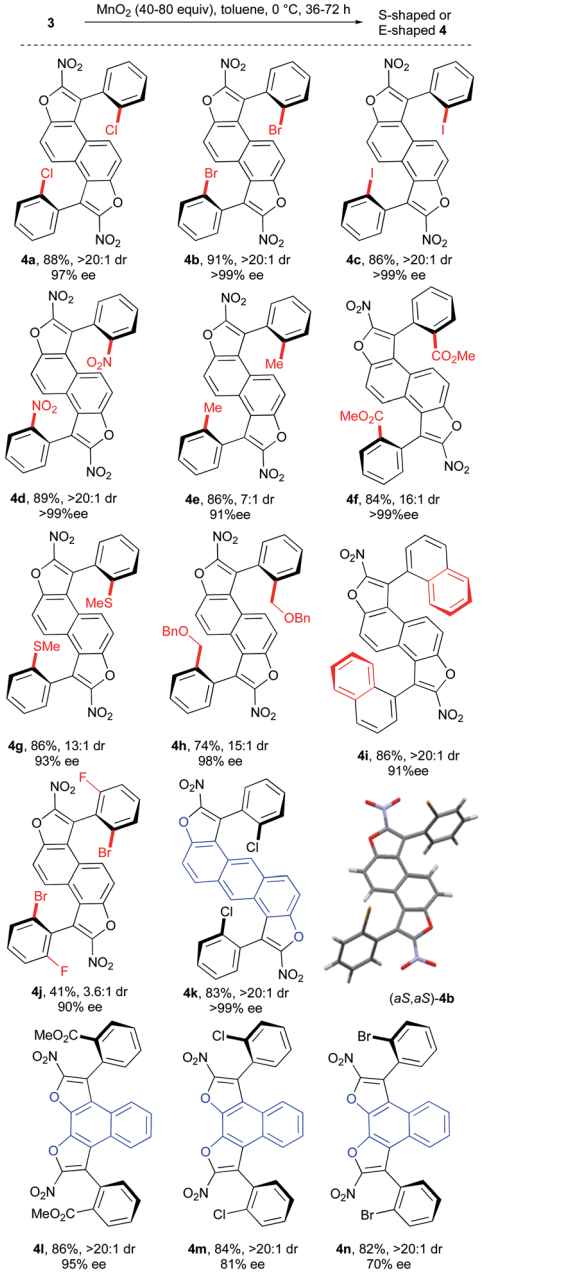
Importantly, the bidirectional domino bis-heterocyclization proceeds smoothly twice under catalyst control delivering mainly chiral diastereomers. However, in some cases, we observed the formation of minor *meso* diastereomers (**3c**, **3e**, **3h** and **3i**) as a result of a competitive substrate-controlled reaction due to the bulkiness of the aryl substituent.[20] Many different functional groups are well tolerated in this reaction such as electron-withdrawing substituents (**3a–d**, **3f**, and **3j**) and electron-donating ones (**3e**, **3g**, and **3h**). The introduction of a 1-naphthalenyl group in **3i** was possible with excellent levels of diastereo- and enantio-selectivities, albeit in lower yield (50%). The use of anthracene-2,6-diol (**1b**) as the starting material gave the

desired fused bis-dihydrobenzofuran **3k** in good yield as virtually a single enantiomer (>20 : 1, >99% ee). To further investigate the scope of the reaction, 2,3-dihydroxynaphthalene (**1c**) was used as the tetra-nucleophilic partner, leading to products **3l–n**. In these cases, the closer proximity of the reactive sites results in a deeper impact of the aryl moiety in **2** toward the steric control of the reaction. A rather small methyl ester function gave very good enantioselectivity (95% ee) but a lower diastereoselectivity (3.8 : 1 dr) arguing for a mismatch situation between catalyst **I** and the mono-dihydrobenzofuran intermediate during the second hetero-cyclization to **3l**. A decrease of the enantioselectivity was observed when the size of the aryl substituent increased (81% ee and 70% ee for products **3m** and **3n** with 2-Cl-C_6H_4 and 2-Br-C_6H_4, respectively). In these two cases, the enantiodiscrimination of the first step is not as efficient, possibly due to the proximity of the two OH functions, which could disturb the hydrogen-bond network in the transition state. Despite the poor diastereoselectivity in these last few cases, both diastereomers could be easily separated by chromatography on silica gel to be engaged in the following oxidative chirality conversion step. The absolute configuration of **3f** was determined to be (*S*,*S*,*S*,*S*) by single crystal X-ray crystallographic analysis.[21] On this basis and with the literature precedent,[22] a plausible transition state is depicted in Scheme 4. The Michael acceptor **2f** is activated by the squaramide moiety of cat. **I** while a hydrogen bond is established between the tertiary amine of cat. **I** and the hydroxy function of **1a**. In this rigid hydrogen bond network, a Michael addition of **1a** on the *Si* face of nitroalkene **2f** would afford the adduct **A**. Then, a base promoted O-cyclization would give the *trans*-dihydrobenzofuran **B**. A second organocatalyzed domino Michael/O-cyclization sequence from **B** delivered the observed (*S*,*S*,*S*,*S*)-**3f**.

Next the investigation of the double central-to-axial chirality conversion was carried out. The use of manganese dioxide in toluene at 0 °C allowed the clean formation of the desired S-shaped bis-benzofuran atropisomers in the naphthalene series with very good yields and good to excellent enantiomeric excesses (Scheme 5, **4a–i**: 91 to >99% ee). Bis-benzofuran **4j** featuring a sterically congested *o*,*o*′-disubstituted aryl moiety is nevertheless obtained albeit with reduced yield (41%) and diastereoselectivity (3.6 : 1 dr) but still an acceptable 90% ee. In contrast, the oxidation of **3k** with an anthracenyl central core gave the desired bis-benzofuran **4k** in good yield and almost perfect diastereo- and enantioselectivities, positioning both stereogenic axes further away from each other. Finally, E-shaped bis-benzofuran atropisomers **4l–n** with 2,3-dihydroxynaphthalene cores were obtained with similar efficiency and no erosion of the enantiomeric excess during the double conversion of chirality. The absolute configuration of product **4b** was unambiguously determined to be (*aS*,*aS*) by X-ray diffraction techniques,[23]



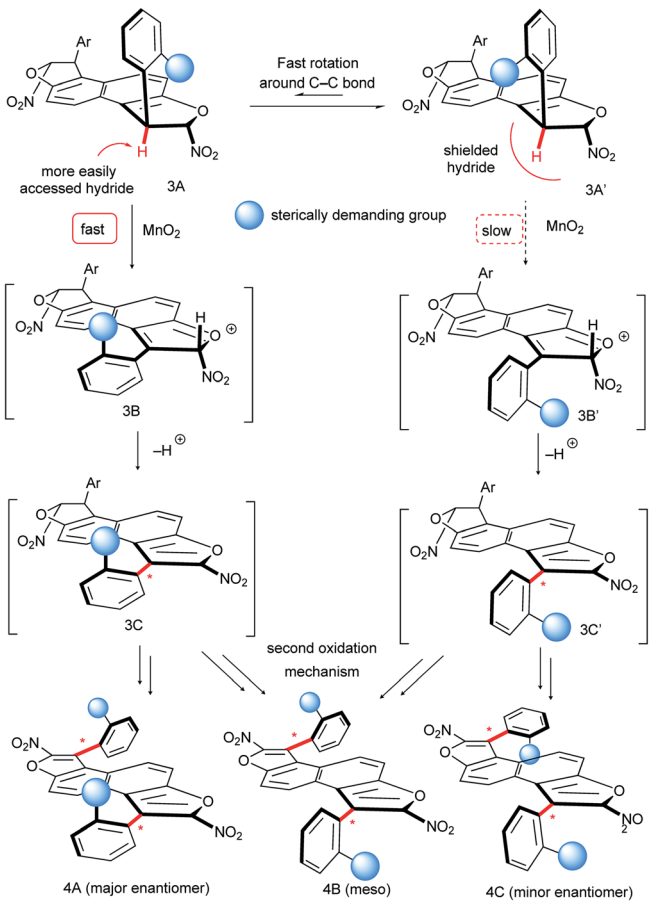
Scheme 4 Proposed mechanism and transition state for the enantioselective synthesis of bis-dihydrobenzofurans **3**.



Scheme 5 Scope of the double central-to-axial chirality conversion.[19]

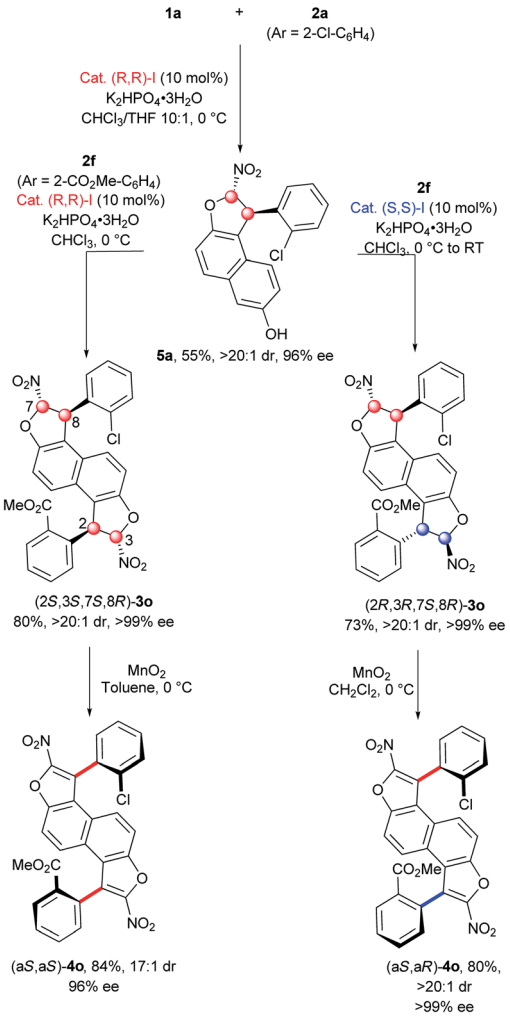
accounting for a similar oxidation mechanism proposed in our previous work,[15b] following the Curtin–Hammett principle (Scheme 6). Hence, the two conformers **3A** and **3A′** are in equilibrium with a preference for **3A′** where the sterically demanding group (blue ball) points outside from the furan subunit (see the X-ray result of **3f**, Scheme 3). This most stable conformation **3A′** is apparently the least reactive under the oxidation conditions, because the hydride is shielded rendering the approach of the hydride acceptor (MnO_2) unfavorable. The result is the fast generation of the oxocarbenium ion intermediate **3B**. Subsequent deprotonation of the acidic hydrogen atom in **3B** gives the enantioenriched **3C** with efficient central-to-axial chirality conversion. Finally, iteration of this oxidative pathway from **3C** gives the expected bis-furan atropisomer **4A**. The *meso* compound **4B** could come from unfavorable stereoselection in either the first or the second oxidation step, while the minor enantiomer **4C** could be obtained by two successive unfavorable stereoselections.

Based on the unique double catalyst-controlled bidirectionality of the process, we next target a stereodivergent approach leading to non-symmetrically functionalized S-shaped bis-atropisomeric oligoarenes (Scheme 7).[24] This important feature has been addressed only once concerning molecules with multiple stereogenic axes.[6b]

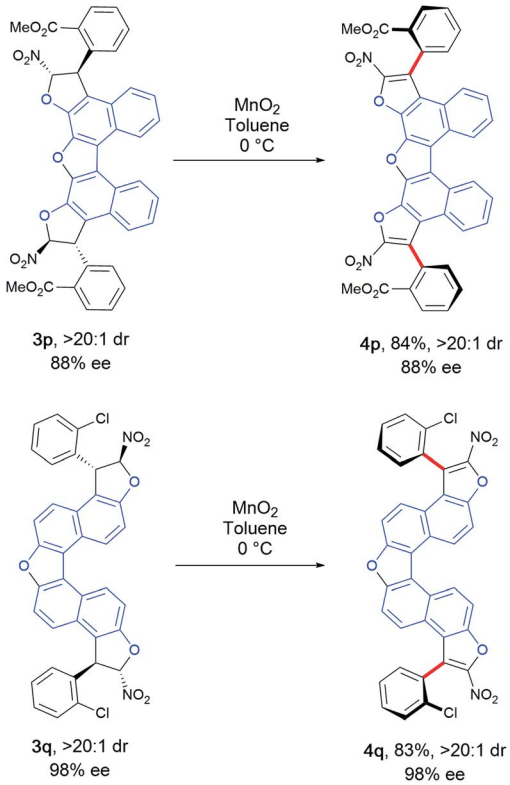


Scheme 6 Mechanism of oxidation.

Accordingly, we investigated the possibility of incorporating two different aryl groups and access to both diastereomers. First, the mono-functionalization of 2,6-dihydroxynaphthalene (**1a**) with 1 equiv. of chloronitroolefin **2a** (Ar = 2-Cl-C_6H_4) and catalyst (*R*,*R*)-**I** in a mixture of $CHCl_3$/THF (10 : 1) allowed the formation of the expected monodihydrobenzofuran **5a** bearing a 2-chlorophenyl group in 55% yield and with excellent diastereo- and enantioselectivities (>20 : 1 dr, 96% ee). The second dihydrobenzofuran motif was constructed using the analogue **2f** (Ar = 2-CO_2Me-C_6H_4). The same catalyst gave the (2*S*,3*S*,7*S*,8*R*)-**3o** product in good yield (80%) and excellent stereoselectivity, while its enantiomer (*S*,*S*)-**I** produced the diastereomer (2*R*,3*R*,7*S*,8*R*)-**3o** in equally good yield (78%) and with perfect stereocontrol indicating absolutely no mismatch effect between **5a** and the (*S*,*S*)-**I** catalyst. Then the oxidation step was accomplished on both diastereomers of **3o**. Gratifyingly, the corresponding bis-benzofuran atropisomers (*aS*,*aS*)-**4o** and (*aS*,*aR*)-**4o** were obtained in good yields and excellent stereocontrol, with only a slight erosion of the diastereomeric ratio for (*aS*,*aS*)-**4o** (17 : 1 dr).



Scheme 7 Stereodivergent synthesis of S-shaped bis-atropisomeric oligoarenes.[19]



Scheme 8 Synthesis of more complex bis-benzofuran atropisomeric oligoarenes **4p** and **4q**.[19]

Moreover, this non-symmetric synthesis shows the possibility of constructing original functionalized π-conjugated push–pull systems, with high potential in materials science.[25]

Finally, a step forward was taken by synthesizing more complex oligoarenes bearing two stereogenic axes even more distant form each other. This was possible starting from bis-naphthobenzofurandiols **1d** and **1e**. Compounds **3p** and **3q** were obtained in low yields (26% and 35%, see the ESI†) and still good to excellent enantioselectivity for the chiral diastereomer (88% and 98% ee) but with an unusual amount of the *meso* one (1 : 1.4 and 3 : 1 dr). Nevertheless, the chiral diastereomers could be separated by chromatography and engaged in the oxidative aromatization step (Scheme 8). Thus, the extended bis-benzofuran atropisomeric oligoarenes **4p** and **4q** were obtained in very good yields without erosion of the enantiomeric excess, accounting for a perfect double central-to-axial chirality conversion.

Conclusions

We have developed a unique bidirectional catalyst-controlled methodology allowing highly enantioselective access to hitherto unknown S- and E-shaped bis-benzofuran atropisomeric oligoarenes featuring two distal C–C stereogenic axes. The key feature lies in a successful double central-to-axial chirality conversion after organocatalyzed activation of simple and easily accessible achiral fused dihydroxyarenes and functionalized nitroolefins. This makes possible an unusual stereodivergent approach to these valuable new molecules featuring two different distal axes of chirality.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

Financial support from the Centre National de la Recherche Scientifique (CNRS), Aix-Marseille Université and Centrale Marseille is gratefully acknowledged. We thank Dr Daniel Dauzonne (Institut Curie) for the synthesis and generous gift of some initial chloronitroalkenes in multigram quantities and also for the know-how in the preparation of these species. We thank Dr Vivek S. Raut for preliminary studies on bidirectional dihydrobenzofuran synthesis. We also thank Dr Nicolas Vanthuyne and Ms Marion Jean (Aix-Marseille Université) for HPLC methods and Dr Michel Giorgi (Aix-Marseille Université) for the X-ray structural analysis.

Notes and references

1 For reviews, see: (*a*) C. Li, M. Liu, N. G. Pschirer, M. Baumgarten and K. Müllen, *Chem. Rev.*, 2010, **110**, 6817–6855; (*b*) Y. Lin, Y. Lia and X. Zhan, *Chem. Soc. Rev.*, 2012, **41**, 4245–4272; (*c*) G. Franc and A. K. Kakkar, *Chem. Soc. Rev.*, 2010, **39**, 1536–1544; (*d*) X. Zhang, T. Higashihara, M. Ueda and L. Wang, *Polym. Chem.*, 2014, **5**, 6121–6141.

2 (*a*) A. Narita, X.-Y. Wang, X. Feng and K. Müllen, *Chem. Soc. Rev.*, 2015, **44**, 6616–6643; (*b*) A. Bohnen, K.-H. Koch, W. Lüttke and K. Müllen, *Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 525–527.

3 (*a*) S. J. Hein, D. Lehnherr, H. Arslan, F. J. Uribe-Romo and W. R. Dichtel, *Acc. Chem. Res.*, 2017, **50**, 2776–2788; (*b*) M. Arseneault, C. Wafer and J.-F. Morin, *Molecules*, 2015, **20**, 9263–9294; (*c*) Q. Fan, J. M. Gottfried and J. Zhu, *Acc. Chem. Res.*, 2015, **48**, 2484–2494.

4 For diastereoselective strategies to optically active derivatives, see: (*a*) N.-X. Hu, S. Xie, Z. Popovic, B. Ong and A.-M. Hor, *J. Am. Chem. Soc.*, 1999, **121**, 5097–5098; (*b*) K. Takaishi, M. Kawamoto and K. Tsubaki, *Org. Lett.*, 2010, **12**, 1832–1835; (*c*) Q. Dherbassy, J.-P. Djukic, J. Wencel-Delord and F. Colobert, *Angew. Chem., Int. Ed.*, 2018, **57**, 4668–4672; (*d*) G. Beutner, R. Carrasquillo, P. Geng, Y. Hsiao, E. C. Huang, J. Janey, K. Katipally, S. Kolotuchin, T. La Porte, A. Lee, P. Lobben, F. Lora-Gonzalez, B. Mack, B. Mudryk, Y. Qiu, X. Qian, A. Ramirez, T. M. Razler, T. Rosner, Z. Shi, E. Simmons, J. Stevens, J. Wang, C. Wei, S. R. Wisniewski and Y. Zhu, *Org. Lett.*, 2018, **20**, 3736–3740; (*e*) T. Yanagi, K. Nogi and H. Yorimitsu, *Synlett*, 2019, DOI: 10.1055/S-0037-1611767.

5 (*a*) T. Shibata, T. Fujimoto, K. Yokota and K. Takagi, *J. Am. Chem. Soc.*, 2004, **126**, 8382–8383; (*b*) T. Shibata and K. Tsuchikama, *Chem. Commun.*, 2005, 6017–6019; (*c*)

T. Shibata, K. Tsuchikama and M. Otsuka, *Tetrahedron: Asymmetry*, 2006, **17**, 614–619; (*d*) K. Tanaka, T. Suda, K. Noguchi and M. Hirano, *J. Org. Chem.*, 2007, **72**, 2243–2246. For related molecules exhibiting both C–C and C–N vicinal axial chiralities, see: (*e*) J. Oppenheimer, R. P. Hsung, R. Figueroa and W. L. Johnson, *Org. Lett.*, 2007, **9**, 3969–3972.

6 (*a*) D. Lotter, M. Neuburger, M. Rickhaus, D. Häussinger and C. Sparr, *Angew. Chem., Int. Ed.*, 2016, **55**, 2920–2923; (*b*) D. Lotter, A. Castrogiovanni, M. Neuburger and C. Sparr, *ACS Cent. Sci.*, 2018, **4**, 656–660.

7 Y.-L. Hu, Z. Wang, H. Yang, J. Chen, Z.-B. Wu, Y. Lei and L. Zhou, *Chem. Sci.*, 2019, **10**, 6777–6784.

8 For seminal studies, see: (*a*) J. A. Berson and E. Brown, *J. Am. Chem. Soc.*, 1955, **77**, 450–453; (*b*) T. R. Hollands, P. de Mayo, M. Nisbet and P. Crabbé, *Can. J. Chem.*, 1965, **43**, 3008–3017; (*c*) E. W. Warnhoff and S. V. Lopez, *Tetrahedron Lett.*, 1967, **28**, 2723–2727; (*d*) A. I. Meyers and D. G. Wettlaufer, *J. Am. Chem. Soc.*, 1984, **106**, 1135–1136.

9 For other recent examples of central-to-axial chirality conversion, see: (*a*) F. Guo, L. C. Konkol and R. J. Thomson, *J. Am. Chem. Soc.*, 2011, **133**, 18–20; (*b*) L. C. Konkol, F. Guo, A. A. Sarjeant and R. J. Thomson, *Angew. Chem., Int. Ed.*, 2011, **50**, 9931–9934; (*c*) G.-Q. Li, H. Gao, C. Keene, M. Devonas, D. H. Ess and L. Kürti, *J. Am. Chem. Soc.*, 2013, **135**, 7414–7417; (*d*) Y.-H. Chen, D.-J. Cheng, J. Zhang, Y. Wang, X.-Y. Liu and B. Tan, *J. Am. Chem. Soc.*, 2015, **137**, 15062–15065; (*e*) J.-Z. Wang, J. Zhou, C. Xu, H. Sun, L. Kürti and Q.-L. Xu, *J. Am. Chem. Soc.*, 2016, **138**, 5202–5205; (*f*) M. Moliterno, R. Cari, A. Puglisi, A. Antenucci, C. Esperandio, E. Moretti, A. Di Sabato, R. Salvio and M. Bella, *Angew. Chem., Int. Ed.*, 2016, **55**, 6525–6529; (*g*) Y.-H. Chen, L.-W. Qi, F. Fang and B. Tan, *Angew. Chem., Int. Ed.*, 2017, **56**, 16308–16312; (*h*) H.-H. Zhang, C.-S. Wang, C. Li, G.-J. Mei, Y. Li and F. Shi, *Angew. Chem., Int. Ed.*, 2017, **56**, 116–121; (*i*) S. Maddox, G. A. Dawson, N. C. Rochester, A. B. Ayonon, C. E. Moore, A. L. Rheingold and J. L. Gustafson, *ACS Catal.*, 2018, **8**, 5443–5447; (*j*) L. W. Qi, J.-H. Mao, J. Zhang and B. Tan, *Nat. Chem.*, 2018, **10**, 58–64.

10 (*a*) Y. Tan, S. Jia, F. Hu, Y. Liu, L. Peng, D. Li and H. Yan, *J. Am. Chem. Soc.*, 2018, **140**, 16893–16898; (*b*) During the proof reading of this article, Yan and co-workers reported the enantioselective synthesis of compounds bearing both helical and axial stereogenic elements: S. Jia, S. Li, Y. Liu, W. Qin and H. Yan, *Angew. Chem., Int. Ed.*, 2019, DOI: 10.1002/anie.201909214.

11 J. Rodriguez and D. Bonne, *Chem. Commun.*, 2019, **55**, 11168–11170.

12 G. Bringmann, R. Götz, S. Harmsen, J. Holenz and R. Walter, *Liebigs Ann.*, 1996, 2045–2058.

13 T. Hayashi, K. Hayashizaki and Y. Ito, *Tetrahedron Lett.*, 1989, **30**, 215–218.

14 A non-stereoselective double Suzuki reaction has also been employed for the total synthesis of naturally occurring racemic michellamines: (*a*) G. Bringmann, R. Götz, P. A. Keller, R. Walter, M. R. Boyd, F. Lang, A. Garcia, J. J. Walsh, I. Tellitu, K. V. Bhaskar and T. R. Kelly, *J. Org. Chem.*, 1998, **63**, 1090–1097; (*b*) P. D. Hobbs, V. U. Upender and M. I. Dawson, *Synlett*, 1997, 965–967.

15 (*a*) O. Quinonero, M. Jean, N. Vanthuyne, C. Roussel, D. Bonne, T. Constantieux, C. Bressy, X. Bugaut and J. Rodriguez, *Angew. Chem., Int. Ed.*, 2016, **55**, 1401–1405; (*b*) V. S. Raut, M. Jean, N. Vanthuyne, C. Roussel, T. Constantieux, C. Bressy, X. Bugaut, D. Bonne and J. Rodriguez, *J. Am. Chem. Soc.*, 2017, **139**, 2140–2143.

16 J. P. Vigneron, M. Dhaenens and A. Horeau, *Tetrahedron*, 1973, **29**, 1055–1059. For a recent review, see: A. M. Harned, *Tetrahedron*, 2018, **74**, 3797–3841.

17 (*a*) D. Bonne and J. Rodriguez, *Chem. Commun.*, 2017, **53**, 12385–12393; (*b*) D. Bonne and J. Rodriguez, *Eur. J. Org. Chem.*, 2018, 2417–2431. For recent contributions, see: (*c*) S.-C. Zheng, Q. Wang and J. Zhu, *Angew. Chem., Int. Ed.*, 2019, **58**, 1494–1498; (*d*) Y. Kwon, J. Li, J. P. Reid, J. M. Crawford, R. Jacob, M. S. Sigman, F. D. Toste and S. J. Miller, *J. Am. Chem. Soc.*, 2019, **141**, 6698–6705; (*e*) H. Li, X. Yan, J. Zhang, W. Guo, J. Jiang and J. Wang, *Angew. Chem., Int. Ed.*, 2019, **58**, 6732–6736; (*f*) X.-L. He, H.-R. Zhao, X. Song, B. Jiang, W. Du and Y.-C. Chen, *ACS Catal.*, 2019, **9**, 4374–4381.

18 (*a*) C. Jarava-Barrera, F. Esteban, C. Navarro-Ranninger, A. Parra and J. Alemán, *Chem. Commun.*, 2013, **49**, 2001–2003; (*b*) M. Rueping, A. Parra, U. Uria, F. Besselièvre and E. Merino, *Org. Lett.*, 2010, **12**, 5680–5683; (*c*) D. Becerra, W. Raimondi, D. Dauzonne, T. Constantieux, D. Bonne and J. Rodriguez, *Synthesis*, 2017, **49**, 195–201; (*d*) For the synthesis of achiral furans from (*Z*)-(2-halo-2-nitroethenyl) benzenes, see: W. Raimondi, D. Dauzonne, T. Constantieux, D. Bonne and J. Rodriguez, *Eur. J. Org. Chem.*, 2012, 6119–6123.

19 Yield of the isolated product. The diastereoselectivity was determined by ^{1}H NMR spectroscopy of the crude reaction mixture. The enantiomeric excess was determined by HPLC analysis on a chiral stationary phase.

20 See the ESI.†

21 (*a*) X.-L. Zhang, K.-X. Feng, A.-B. Xia, Y.-Y. Zheng, C. Li, X.-H. Du and D.-Q. Xu, *Eur. J. Org. Chem.*, 2018, 2918–2925; (*b*) J. Feng, L. Lin, K. Yu, X. Liu and X. Feng, *Adv. Synth. Catal.*, 2015, **357**, 1305–1310.

22 CCDC 1922303 (**3f**) contains the supplementary crystallographic data for this paper.†

23 CCDC 1921425 (**4b**) contains the supplementary crystallographic data for this paper.†

24 S. Krautwald and E. M. Carreira, *J. Am. Chem. Soc.*, 2017, **139**, 5627–5639.

25 (*a*) F. Bures, *RSC Adv.*, 2014, **4**, 58826–58851; (*b*) M. Kivala and F. Diederich, *Acc. Chem. Res.*, 2009, **42**, 235–248.

