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Oxahelicene NHC ligands in the asymmetric synthesis of nonracemic helicenes†

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Isabel Gay Sánchez,[a] Michal Šámal,[a] Jindřich Nejedlý,[a] Manfred Karras,[a] Jiří Klívar,[a] Jiří Rybáček,[a] Miloš Buděšínský,[a] Lucie Bednárová,[a] Beata Seidlerová,[a] Irena G. Stará*[a] and Ivo Starý*[a]

A straightforward approach to enantiopure 2*H*-pyran-modified amino[5]helicenes and amino[6]helicene was developed. They were converted to 1,3-disubstituted imidazolium salts and used as NHC ligand precursors in the Ni^0-catalysed enantioselective [2+2+2] cycloisomerisation of aromatic triynes to receive the model helicene derivatives in up to 86% *ee*.

Helicene-derived[1] 1,3-disubstituted imidazolium salts are rare in the chemical literature despite the fact that they represent inherently chiral entities attractive for material science, chiroscience and catalysis. In fact, only a few related papers have so far been published. Teplý *et al*. succeeded in embedding the imidazolium core into the backbone of racemic helicene-like mono- or tricationic compounds.[2] Storch *et al*. synthesised a racemic imidazolium salt bearing a hexahelicen-2-ylmethyl unit and used it for fabrication of a fully reversible thin-layer humidity sensor.[3] Finally, Crassous, Autschbach *et al*. utilised the same hexahelicene motif in the preparation of the first enantiopure helicene–NHC–iridium complexes whose stereochemical, electronic and chiroptical properties were studied both experimentally and computationally.[4]

To the best of our knowledge, helicene-based imidazolium salts as precursors of helical N-heterocyclic carbenes (NHC)[5] have never been employed in enantioselective catalysis.[6] Actually, a reason for that might be the lack of a methodology for the preparation of key enantiopure aminohelicene building blocks through asymmetric synthesis. Racemic aminohelicenes with the amino group attached directly to the helicene backbone were already described but their number is rather limited.[7]

In this communication, we report on a straightforward synthetic approach to enantiopure oxahelicene amines represented by the 2*H*-pyran-modified 2-amino[5]helicene and 2-amino[6]helicene derivatives and their conversion to 1,3-disubstituted imidazolium salts **1**-**3** (Fig. 1). Helically/centrally chiral NHC ligands generated *in situ* from these salts were then used in the Ni^0-catalysed enantioselective [2+2+2] cycloisomerisation of aromatic triynes to receive model helicene derivatives in up to 86% *ee*.

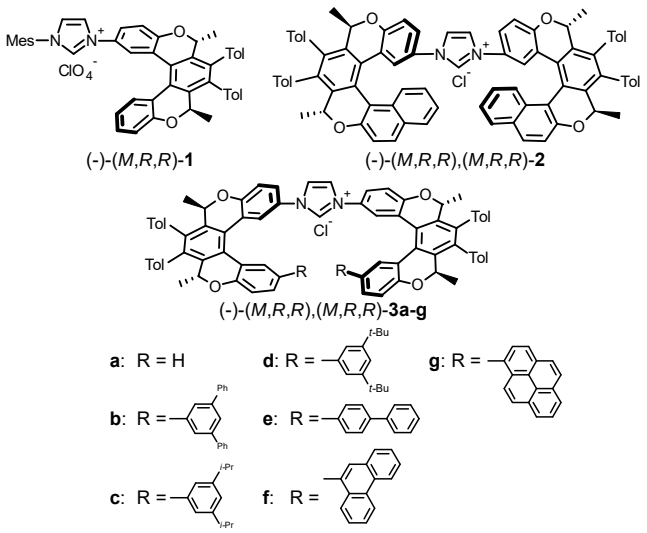
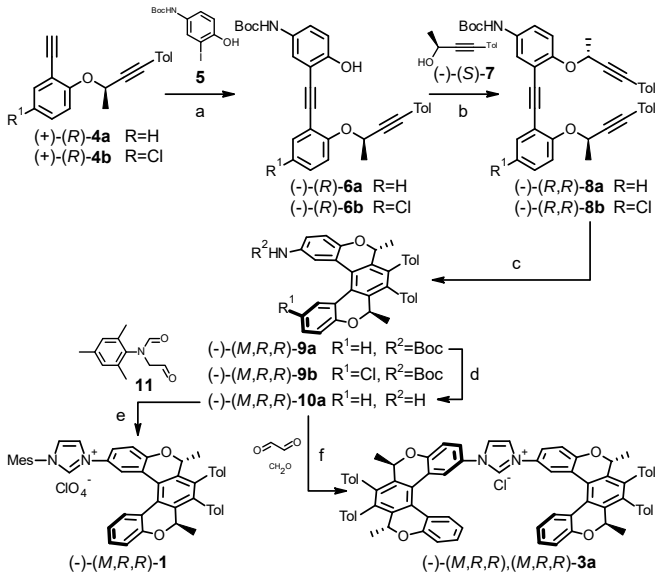


Fig. 1 Enantiopure oxahelicene 1,3-disubstituted imidazolium salts **1**-**3** as precursors to helically/centrally chiral NHC ligands (Mes: mesityl, Tol: 4-tolyl).

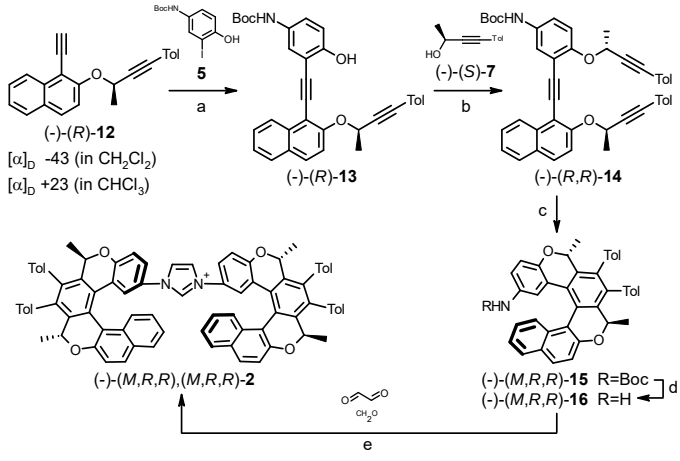
The synthesis of the imidazolium salts **1**-**3** relied on the general methodology for the preparation of 2*H*-pyran-modified helicenes in an enantio- and diastereomerically pure form that we developed recently.[8] The starting enantiopure diyne (+)-(*R*)-**4a**[8] was subjected to Sonogashira coupling with aryl iodide **5** bearing OH and Boc-protected NH_2 groups (Scheme 1). The free phenolic group in (-)-(*R*)-**6a** was propargylated by the enantiopure alcohol (-)-(*S*)-**7** under Mitsunobu reaction conditions (with an inversion of the configuration at the stereogenic centre) to provide triyne

[a] Institute of Organic Chemistry and Biochemistry, Czech Academy of Sciences, Flemingovo nám. 2, 166 10 Prague 6, Czech Republic. E-mail: stara@uochb.cas.cz, stary@uochb.cas.cz

† I. G. Sánchez and M. Šámal contributed equally to this work.
Electronic Supplementary Information (ESI) available: Experimental procedures and spectroscopic data of all new compounds. See DOI: 10.1039/x0xx00000x



Scheme 1 Asymmetric synthesis of the enantiopure 2*H*-pyran-modified 2-amino[5]helicenes **10a** and **9b** and conversion of the former to the corresponding 1,3-disubstituted imidazolium salts **1** and **3a**. (a) **5** (0.8 equiv.), $Pd(PPh_3)_2Cl_2$ (2 mol%), CuI (3 mol%), *i*-Pr_2NH (1.6 equiv. for **4a**, 1.0 equiv. for **4b**), toluene, room temperature, 3 h, 66% for **6a** or 67% for **6b**; (b) **7** (1.2 equiv.), PPh_3 (1.2 equiv.), DIAD (1.2 equiv.), benzene, room temperature, 3-4 h, 90% for **8a** or 77% for **8b**; (c) CpCo(CO)(fum) (30 mol% for **8a**, 50 mol% for **8b**), THF, microwave reactor, $[bdmim]BF_4$ (25 µl/ml of the reaction solution), 140 °C, 15 min, 82% for **9a** or 74% for **9b**; (d) TFA (15 equiv.), CH_2Cl_2, room temperature, overnight, 78%; (e) **11** (1.9 equiv.), acetic anhydride (excess), $HClO_4$ (70% in water, 3.6 equiv.), room temperature, 12 h, then **10a** (1.0 equiv.), room temperature, 4 h, then $HClO_4$ (70% in water, 3.6 equiv.), 80 °C, overnight, 38%; (f) glyoxal (40% in water, 0.5 equiv.), formaldehyde (37% in water, 0.7 equiv.), glacial acetic acid, 40 °C, 25 min, work-up with saturated aq. NaCl, 66%. $[bdmim]BF_4$ = 1-butyl-2,3-dimethylimidazolium tetrafluoroborate; DIAD = diisopropyl azodicarboxylate; fum = dimethyl fumarate; TFA = trifluoroacetic acid.



Scheme 2 Asymmetric synthesis of the enantiopure 2*H*-pyran-modified 2-amino[6]helicene **16** and its conversion to the corresponding 1,3-disubstituted imidazolium salt **2**. (a) **5** (0.8 equiv.), $Pd(PPh_3)_2Cl_2$ (2 mol%), CuI (4 mol%), *i*-Pr_2NH (1.7 equiv.), benzene, 45 °C, 4.5 h, 70%; (b) **7** (1.2 equiv.), PPh_3 (1.2 equiv.), DIAD (1.2 equiv.), benzene, room temperature, 2.5 h, 88%; (c) CpCo(CO)(fum) (40 mol%), THF, microwave reactor, $[bdmim]BF_4$ (25 µl/ml of the reaction solution), 140 °C, 15 min, 63%; (d) TFA (15 equiv.), CH_2Cl_2, room temperature, overnight, 77%; (e) glyoxal (40% in water, 0.5 equiv.), formaldehyde (37% in water, 0.6 equiv.), glacial acetic acid, 55 °C, 35 min, 78%.

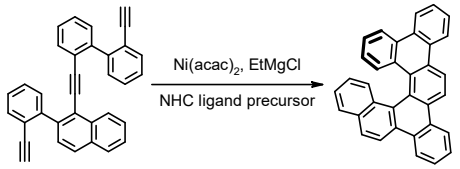
(-)-(*R*,*R*)-**8a**. It underwent microwave-assisted [2+2+2] cyclotrimerisation in the presence of CpCo(CO)(fum)[9] that resulted in the diastereo- and enantiomerically pure oxa[5]helicene (-)-(*M*,*R*,*R*)-**9a** (for the discussion about efficient stereocontrol by the 1,3-allylic-type strain, see refs 8 and 10). After the removal of the Boc protecting group, the free helical amine (-)-(*M*,*R*,*R*)-**10a** was transformed either into the unsymmetrical 1-oxahelicenyl-3-mesityl imidazolium salt (-)-(*M*,*R*,*R*)-**1** (employing the *N*-(2-oxoethyl)formamide derivative **11** according to the stepwise procedure by Fürstner *et al*.)[11] or the symmetrical 1,3-bisoxahelicenyl imidazolium salt (-)-(*M*,*R*,*R*),(*M*,*R*,*R*)-**3a** (on reaction with aqueous glyoxal and formaldehyde according to Baslé, Mauduit *et al*.).[12]

The versatility of this synthetic methodology was further underlined by the preparation of the homologous diastereo- and enantiomerically pure oxa[6]helicene amine (-)-(*M*,*R*,*R*)-**16** starting from the enantiopure naphthalene building block (-)-(*R*)-**12**[8] (Scheme 2). The amine was finally converted to the symmetrical 1,3-bisoxahelicenyl imidazolium chloride (-)-(*M*,*R*,*R*),(*M*,*R*,*R*)-**2** on reaction with aqueous glyoxal and formaldehyde as described above.

NHC ligands are known to form with Ni^0 efficient catalytic systems for a plethora of intra- and intermolecular cycloaddition reactions to construct carbo- and heterocycles.[13] Having the enantiopure oxahelicene imidazolium salts (-)-(*M*,*R*,*R*)-**1**, (-)-(*M*,*R*,*R*),(*M*,*R*,*R*)-**2** and (-)-(*M*,*R*,*R*),(*M*,*R*,*R*)-**3a** in hand, we could explore their efficiency in the benchmark enantioselective Ni^0-catalysed alkyne [2+2+2] cycloisomerisation.[14] Instead of using the capriciously unstable $Ni(cod)_2$ (necessary to handle in a drybox), we generated a Ni^0 species *in situ* by reducing dry $Ni(acac)_2$ with EtMgCl in excess, which mediated also the release of the NHC ligands from the corresponding imidazolium salts. EtMgCl was found superior to other reducing agents such as *n*-BuLi, DIBAH, L-Selectride or Super-Hydride with respect to the yields of the alkyne [2+2+2] cycloisomerisation reaction (on 0.025 mmol scale), stability under dilution and ease of determination of its concentration (by titration with iodine). We focused first on cyclisation of the aromatic triyne **17** to helical dibenzo[6]helicene **18** (Table 1). The Ni^0-catalysed [2+2+2] cycloisomerisation in the presence of the helical NHC ligands generated from (-)-(*M*,*R*,*R*)-**1**, (-)-(*M*,*R*,*R*),(*M*,*R*,*R*)-**2** or (-)-(*M*,*R*,*R*),(*M*,*R*,*R*)-**3a** delivered uniformly (+)-(*P*)-**18** in high yield but with different enantiomeric excesses. Due to the poor performance of **1** (Table 1, entry 1) the unsymmetrical imidazolium salt (and possible analogues) was excluded from further study. Instead, attention was focused on the symmetrical 1,3-bisoxahelicenyl imidazolium salts **2** and **3a** that provided promising enantiomeric excesses (Table 1, entries 2 and 3).

Obviously, the design of the helical NHC ligands required modifications to improve enantioselectivity of the Ni^0-catalysed alkyne [2+2+2] cycloisomerisation. We reasoned that diversifying the structure of the 1,3-bisoxahelicenyl imidazolium salts in the late stage of their synthesis would facilitate the access to a small library of ligands.[15] Accordingly, we turned our attention to the readily accessible enantiopure

Table 1 Enantioselective [2+2+2] cycloisomerisation of triyne **17** to dibenzo[6]helicene **18** in the presence of enantiopure NHC ligands generated from **1**, **2** or **3a**



17 (+)-(*P*)-**18**

Entry	NHC ligand precursor	Conv. (%)[a,b]	*ee* (%)[c] of **18**
1	(-)-(*M*,*R*,*R*)-**1**	>90	17 (+)
2	(-)-(*M*,*R*,*R*),(*M*,*R*,*R*)-**3a**	>90	41 (+)
3	(-)-(*M*,*R*,*R*),(*M*,*R*,*R*)-**2**	>90	59 (+)

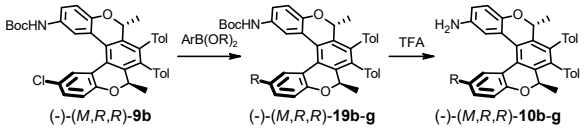
[a] $Ni(acac)_2$ (20 mol%), EtMgCl (0.4 M in THF, 0.9 equiv.), NHC ligand precursor **1**, **2** or **3a** (44 mol%), THF, room temperature, 2 h. [b] Estimated by HPLC. [c] Determined by HPLC on a Chiralpak IA column.

Boc-protected 2-aminooxa[5]helicene (-)-(*M*,*R*,*R*)-**9b** bearing the chlorine atom (Scheme 1). The following Suzuki-Miyaura coupling of (-)-(*M*,*R*,*R*)-**9b** with diverse arylboronic acids or esters proceeded smoothly allowing the variable extension of the oxa[5]helicene backbone in (-)-(*M*,*R*,*R*)-**19b**-**g** (Table 2). After removal of the Boc protecting group, the free amines (-)-(*M*,*R*,*R*)-**10b**-**g** were converted to the desired symmetrical bisoxahelicenyl imidazolium salts (-)-(*M*,*R*,*R*),(*M*,*R*,*R*)-**3b**-**g** on reaction with aqueous glyoxal and formaldehyde (Table 3).

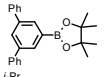
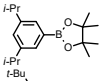
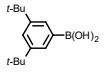
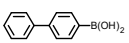
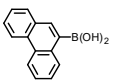
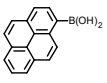
Indeed, the installation of a bulky aryl group at the opposite terminus of the oxa[5]helicene backbone with respect to the position of the imidazolium unit led to a noticeable improvement in enantiomeric excess of (+)-(*P*)-**18**: From 41% *ee* (for nonarylated **3a**; Table 1, entry 2) to 61% *ee* (for 3,5-diphenylphenyl-substituted **3b**), 64% *ee* (for 3,5-diisopropylphenyl-substituted **3c**) or 66% *ee* (for 3,5-di-*tert*-butylphenyl-substituted **3d**) (Table 4, entries 1-3). The presence of a less bulky aryl group such as (1,1'-biphenyl)-4-yl in **3e** or those exhibiting conformational ambiguity such as phenanthren-9-yl in **3f** or pyren-1-yl in **3g** resulted in a small increase in enantiomeric excess of (+)-(*P*)-**18** (Table 4, entries 4-6).

The highest level of chirality transfer from a helical NHC ligand to a helical product was achieved in [2+2+2] cycloisomerisation of the aromatic triyne **20** to dibenzo[7]helicene (+)-(*P*)-**21** (Table 5). Although the reactivity of **20** was slightly lower than that of **17**, employing the oxa[6]helicene imidazolium salt **2** (Table 5, entry 1) or oxa[5]helicene imidazolium salt **3a** (Table 5, entry 2) resulted in (+)-(*P*)-**21** with 74% or 72% *ee*, respectively. Finally, 3,5-diisopropylphenyl-substituted oxa[5]helicene imidazolium salt **3c** outperformed the other NHC ligand precursors by providing (+)-(*P*)-**21** with 86% *ee* (Table 5, entry 3).

Table 2 Suzuki-Miyaura coupling of the chloro derivative **9b** with arylboronic acids or esters followed by the Boc removal to provide the 2-aminooxa[5]helicenes **10b**-**g**

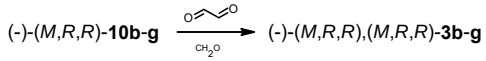


(-)-(*M*,*R*,*R*)-**9b** (-)-(*M*,*R*,*R*)-**19b**-**g** (-)-(*M*,*R*,*R*)-**10b**-**g**

Entry	$ArB(OR)_2$	**19b**-**g** (%)[a,b]	**10b**-**g** (%)[b,c]
1		**19b** (79)	**10b** (97)
2		**19c** (89)	**10c** (98)
3		**19d** (82)	**10d** (85)
4		**19e** (87)	**10e** (78)
5		**19f** (89)	**10f** (76)
6		**19g** (82)	**10g** (86)

[a] Arylboronic acid or ester (2.1-3.3 equiv.), XPhos Pd G2 (5-8 mol%), K_3PO_4 (0.5M in water, 1.1-2.5 equiv.), THF, 100 °C, 1-6 h. [b] Preparative yield. [c] TFA (15-33 equiv.), CH_2Cl_2, room temperature, 3-16 h.

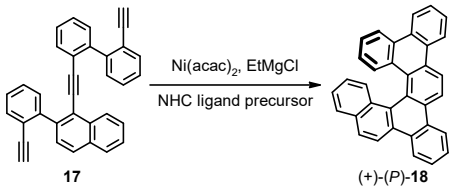
Table 3 The conversion of the 2-aminooxa[5]helicenes **10b**-**g** to the symmetrical 1,3-disubstituted imidazolium salts **3b**-**g**



Entry	Educt	Product[a]	Yield (%)[b]
1	**10b**	**3b**	57
2	**10c**	**3c**	64
3	**10d**	**3d**	82
4	**10e**	**3e**	83
5	**10f**	**3f**	82
6	**10g**	**3g**	61

[a] Glyoxal (40% in water, 0.5-0.6 equiv.), formaldehyde (37% in water, 0.6-0.8 equiv.), glacial acetic acid, 45-55 °C, 0.7-3.7 h, work-up with saturated aq. NaCl. [b] Preparative yield.

Table 4 Enantioselective [2+2+2] cycloisomerisation of triyne **17** to dibenzo[6]helicene **18** in the presence of enantiopure NHC ligands generated from **3b**-**g**

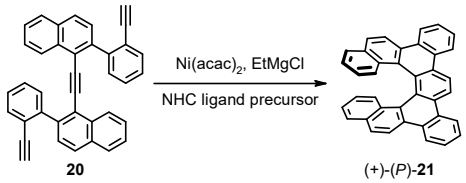


17 (+)-(*P*)-**18**

Entry	NHC ligand precursor	Conv. (%)[a,b]	*ee* (%)[c] of **18**
1	(-)-(*M*,*R*,*R*),(*M*,*R*,*R*)-**3b**	90	61 (+)
2	(-)-(*M*,*R*,*R*),(*M*,*R*,*R*)-**3c**	90	64 (+)
3	(-)-(*M*,*R*,*R*),(*M*,*R*,*R*)-**3d**	81	66 (+)
4	(-)-(*M*,*R*,*R*),(*M*,*R*,*R*)-**3e**	89	44 (+)
5	(-)-(*M*,*R*,*R*),(*M*,*R*,*R*)-**3f**	73	56 (+)
6	(-)-(*M*,*R*,*R*),(*M*,*R*,*R*)-**3g**	90	47 (+)

[a] $Ni(acac)_2$ (20 mol%), EtMgCl (0.4 M in THF, 0.9 equiv.), NHC ligand precursor **3b**-**g** (44 mol%), THF, room temperature, 2 h. [b] Estimated by HPLC. [c] Determined by HPLC on a Chiralpak IA column.

Table 5 Enantioselective [2+2+2] cycloisomerisation of triyne **20** to dibenzo[7]helicene **21** in the presence of enantiopure NHC ligands generated from **2**, **3a** or **3c**



20 (+)-(*P*)-**21**

Entry	NHC ligand precursor	Conv. (%)[a,b]	*ee* (%)[c] of **18**
1	(-)-(*M*,*R*,*R*),(*M*,*R*,*R*)-**2**	76	74 (+)
2	(-)-(*M*,*R*,*R*),(*M*,*R*,*R*)-**3a**	64	72 (+)
3	(-)-(*M*,*R*,*R*),(*M*,*R*,*R*)-**3c**	86	86 (+)

[a] $Ni(acac)_2$ (20 mol%), EtMgCl (0.4 M in THF, 0.9 equiv.), NHC ligand precursor **2**, **3a** or **3c** (44 mol%), THF, room temperature, 2 h. [b] Estimated by HPLC. [c] Determined by HPLC on a Chiralpak IA column.

In summary, we developed a straightforward access to optically pure 2-aminooxa[5]helicenes (-)-(*M*,*R*,*R*)-**10a**-**g** and 2-aminooxa[6]helicene (-)-(*M*,*R*,*R*)-**16** employing the key [2+2+2] cycloisomerisation of chiral functionalised triynes (-)-(*R*,*R*)-**8a**,**b** and (-)-(*R*,*R*)-**14** featuring ultimate stereocontrol. We showed that the structure of the chloro-substituted helical Boc-protected amine (-)-(*M*,*R*,*R*)-**9b** could further be diversified by attaching aryl substituents through Suzuki-Miyaura coupling with arylboronic acids or esters. The 2-aminooxa[5]helicenes (-)-(*M*,*R*,*R*)-**10a**-**g** and 2-aminooxa[6]helicene (-)-(*M*,*R*,*R*)-**16** were converted to the corresponding 1,3-disubstituted imidazolium salts (-)-(*M*,*R*,*R*)-**1**, (-)-(*M*,*R*,*R*),(*M*,*R*,*R*)-**2** and (-)-(*M*,*R*,*R*),(*M*,*R*,*R*)-**3a**-**g** (symmetrical or unsymmetrical). These enantiopure precursors to helical NHC ligands were employed in the enantioselective Ni^0-catalysed triyne [2+2+2] cycloisomerisation to provide dibenzo[6]helicene (+)-(*P*)-**17** or dibenzo[7]helicene (+)-(*P*)-**21** with up to 66% *ee* or 86% *ee*, respectively. It reveals the potential of the oxahelicene NHC ligands in enantioselective transition metal catalysis. The study on the conformational flexibility of the oxahelicene NHC ligands and the mechanism of chirality transfer is in progress.

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