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Synthesis of Thiophene-fused Helicenes

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The synthesis of three penta- and three hexahelicenes containing two terminal thiophene units is described. The syntheses of pentahelicenes consist of 1,4-bisalkynylation of a benzene precursor and double Suzuki coupling in 2,3-position to introduce thiophene units. The *ortho,ortho'* fusion yielding the final products was achieved with Fürstner's protocol using platinum(II) chloride or JohnPhos-complexed gold(I) as catalysts. A similar approach to hexahelicenes started with a

naphthalene derivative, where 2,7-bisalkynylation and subsequent double Suzuki coupling with thiophene-2-boronic acid at 1,8-position furnished precursors, in which *ortho,ortho'* fusion to the respective hexahelicenes was achieved with platinum(II) chloride or, favourably, with indium(III) chloride. UV/Vis spectra and cyclic voltammograms were recorded for all helicenes and HOMO/LUMO gaps were calculated with DFT methods.

Introduction

The IUPAC defines helicenes^[1] as "ortho-fused polycyclic aromatic or heteroaromatic compounds in which all rings (minimum five) are angularly arranged so as to give helically shaped molecules, which are thus chiral".^[2] Following a more recent definition, at least six fused rings are required in a helicene,^[3] although smaller arrangements are repeatedly named accordingly.^[1b,4] This definition not only allows for the presence of benzene rings (A, B; Figure 1), but also of cyclopentadiene (C)^[5] or heteroaromatic rings.^[6] Thiophene rings can here be present in different positions and (if present in the terminal rings) in various orientations (e.g., D–F). In our previous work, we used *ortho,ortho'* fusions in suitably substituted terphenyls G and synthesized diaza[5]helicenes H

and I, indolo[2,3-*c*]carbazoles J (Scheme 1),^[7] and helicene-shaped cyclopenta-fused polyaromatic hydrocarbons C, where the latter were partly obtained as radical species.^[5] Helicenes bearing thiophene rings^[8] in the terminal positions have occasionally been synthesized. Methods applied for their

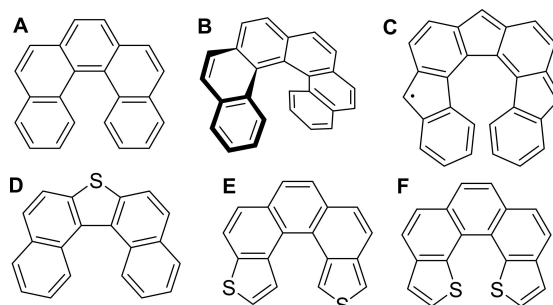
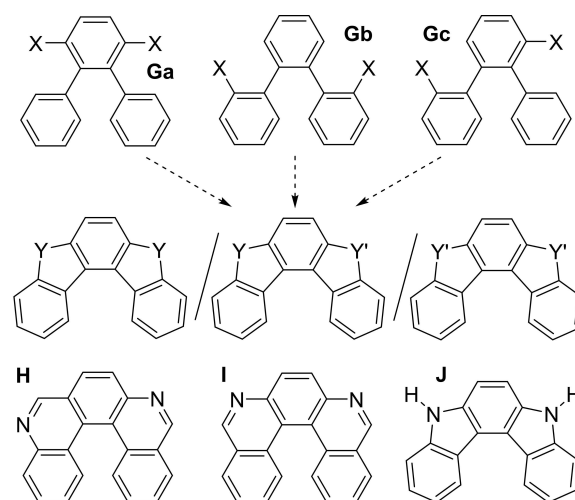


Figure 1. [5]- and [6]helicene, a carbohelicene radical with cyclopentadiene units,^[5] and a selection of pentahelicenes bearing thiophene moieties.



Scheme 1. Top: General scheme for *ortho,ortho'*-fusion in substituted terphenyls (Y, Y': Two orientations of Y are possible if it is a nonsymmetric bridging unit); bottom: structures already achieved in our group.

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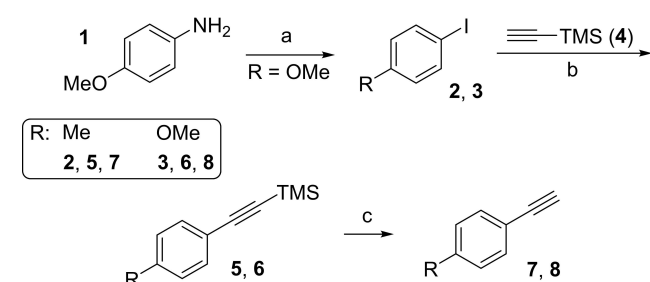
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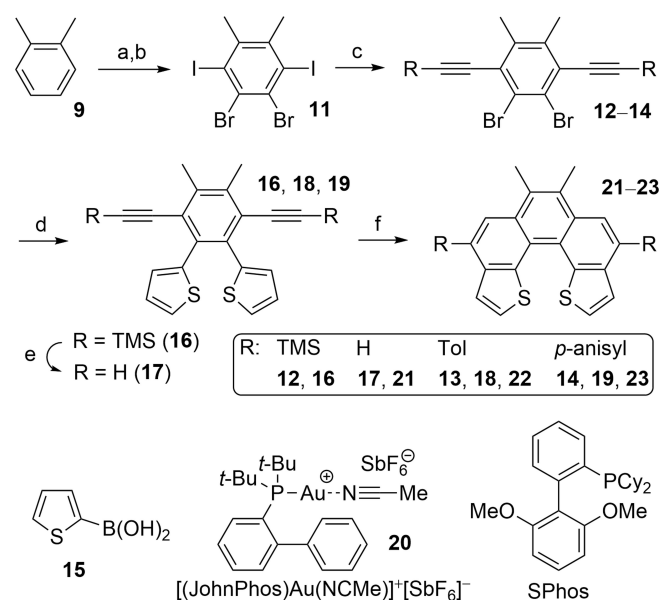
preparation include photocyclizations,^[9] sulfide additions to arylacetylenes,^[10] [2 + 2] cycloadditions,^[11] cyclizations with electrophilic sulfur reagents,^[12] and McMurry olefinations.^[13] These thiahelicenes^[8a,14] and other structurally related helical compounds have interesting electrochemical,^[15] electronic,^[16] optoelectronic,^[17] chiroptic,^[18] supramolecular,^[19] catalytic,^[20] and biological^[21] properties and are used in numerous applications.

Results and Discussion

For the synthesis of thiophene-fused helicenes we planned to adopt a method, which has been developed by Fürstner et al. for the synthesis of phenanthrenes and related compounds from 2-ethynylbiphenyls.^[22] This method has already been



Scheme 2. Synthesis of terminal alkynes **7** and **8**. Conditions: a) *p*-TosOH·H₂O, NaNO₂, MeCN, 10 °C to rt, then KI, quant.; b) **4**, cat. Pd(PPh₃)₂Cl₂, cat. CuI, Et₃N, rt; R = Me, **5**: 21 h, 94%; R = OMe, **6**: 4 h, 85%; c) K₂CO₃; R = Me, **7**: CH₂Cl₂/MeOH (1 : 1), rt, 8 h, 92%; R = Me, **8**: MeOH, rt, 6 h, 99%.



Scheme 3. Synthesis of thiophene-derived dithiapentahelicenes **21–23**. Conditions: a) I₂, Br₂, 0 °C to rt, overnight, 1,2-dibromo-4,5-dimethylbenzene (**10**): 35%; b) H₂O₂, I₂, H₂SO₄, 0 °C to rt, 23 h, 34%; c) alkynes **4**, **7**, **8**, respectively, cat. Pd(PPh₃)₂Cl₂, cat. CuI, toluene/Et₃N (1 : 1); R = TMS, **12**: 65 °C, 66 h, 47%; R = *p*-Tol, **13**: 45 °C, 22 h, 54%; R = *p*-anisyl, **14**: 40 °C, 20 h, 64%; d) **15**, cat. Pd(OAc)₂, SPhos, Cs₂CO₃, 80 °C; R = TMS, **16**: dioxane/H₂O (6 : 1), 20 h, 47%; R = *p*-Tol, **18**: dioxane/H₂O (10 : 1), 21 h, 54%; R = *p*-anisyl, **19**: dioxane/H₂O (10 : 1), 23 h, 64%; e) K₂CO₃, CH₂Cl₂/MeOH (1 : 1), rt, 20 h, 99%; f) see Table 1.

applied to a cyclization of analogous thiophene-derived precursors.^[15b–d] In our adaption of this protocol we intended to cyclize di(thienyl)di(alkynyl)arenes to the respective penta- and hexahelicenes. For the introduction of alkynyl substituents using a Sonogashira coupling we required the respective terminal alkynes: Trimethylsilylacetylene (TMS-acetylene, **4**) was purchased and tolyl- and anisyl-substituted acetylenes were prepared by Sandmeyer iodination,^[23] Sonogashira coupling with TMS-acetylene,^[24] and desilylation (Scheme 2).^[25]

For the synthesis of pentahelicenes we started with *ortho*-xylene (**9**), which was converted into tetrahalogenated xylene **11** by a known two-step procedure (Scheme 3).^[26] Couplings of terminal alkynes with participation of the iodo atoms were achieved by Sonogashira coupling using a standard protocol.^[27] Bisalkynes **12–14** were thus obtained in 47 to 64 % yield. Suzuki coupling at the remaining bromo positions with 2-thienylboronic acid (**15**) furnished *ortho*-teraryls **16**, **18**, and **19**. For this we used a protocol well established in our group with palladium(II) acetate as catalyst, SPhos as ligand, and cesium carbonate as base.^[28] The trimethylsilyl groups in bisalkyne **16** were cleaved with potassium carbonate yielding terminal alkyne groups. Non-substituted bisalkyne **17** was obtained here with virtually quantitative yield.

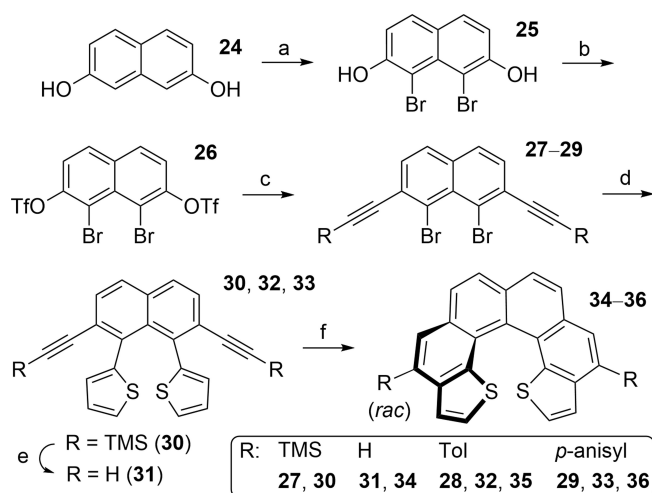
The *ortho,ortho'* cyclizations towards the pentahelicenes were achieved using Fürstner's protocol.^[22] While the parent precursor **17** (R = H) could be cyclized using platinum(II) dichloride (albeit with a poor 39 % yield), no reaction was observed, when this catalyst was used together with diaryl-substituted precursors **18** or **19** (Table 1). Helicenes **22** and **23** were neither obtained with indium(III) chloride,^[29] nor with platinum(II), or gold(III) chloride as catalysts. However, clean reactions were observed with JohnPhos-complexed gold(I) catalyst **20**.^[30] Pentahelicenes **21–23** were here obtained with yields ranging from 70 to 95 %.

A naphthalene-derived building block was considered for the synthesis of the respective hexahelicenes (Scheme 4). We started with 2,7-dihydroxynaphthalene (**24**), which could be

Table 1. Cyclization to Thiophene-derived Dithiahelicenes **21–23** and **34–36**.

| Bisalkyne (R) | Conditions | Product | Yield [%] |
|-------------------------------|---|-----------|------------------|
| 17 (H) | cat. PtCl ₂ , toluene, 110 °C, 66 h | 21 | 39 |
| 17 (H) | cat. 20 , <i>o</i> -C ₆ H ₄ Cl ₂ , 120 °C, 16 h | 21 | 70 |
| 18 (<i>p</i> -Tol) | cat. InCl ₃ , toluene, 100 °C, 45 h | 22 | – ^[a] |
| 18 (<i>p</i> -Tol) | cat. PtCl ₂ , toluene, 100 °C, 23 h | 22 | – |
| 18 (<i>p</i> -Tol) | cat. PtCl ₂ , xylene, 120 °C, 64 h | 22 | – |
| 18 (<i>p</i> -Tol) | cat. AuCl ₃ , <i>o</i> -C ₆ H ₄ Cl ₂ , 130 °C, 64 h | 22 | – |
| 18 (<i>p</i> -Tol) | cat. 20 , <i>o</i> -C ₆ H ₄ Cl ₂ , 160 °C, 4 h | 22 | 95 |
| 19 (<i>p</i> -anisyl) | cat. InCl ₃ , toluene, 100 °C, 47 h | 23 | – ^[b] |
| 19 (<i>p</i> -anisyl) | cat. PtCl ₂ , toluene, 100 °C, 17 h | 23 | – |
| 19 (<i>p</i> -anisyl) | cat. PtCl ₂ , xylene, 120 °C, 64 h | 23 | – |
| 19 (<i>p</i> -anisyl) | cat. AuCl ₃ , <i>o</i> -C ₆ H ₄ Cl ₂ , 130 °C, 64 h | 23 | – |
| 19 (<i>p</i> -anisyl) | cat. 20 , Cl(CH ₂) ₂ Cl, 80 °C, 20 h | 23 | 90 |
| 31 (H) | cat. PtCl ₂ , toluene, 110 °C, 21 h | 34 | 16 |
| 31 (H) | cat. 20 , <i>o</i> -C ₆ H ₄ Cl ₂ , 80 °C, 3 h | 34 | 40 |
| 32 (<i>p</i> -Tol) | cat. InCl ₃ , toluene, 80 °C, 48 h | 35 | 67 |
| 33 (<i>p</i> -anisyl) | cat. InCl ₃ , toluene, 80 °C, 19 h | 36 | 70 |

[a] 74 % of the starting material was recovered; [b] 49 % of the starting material was recovered.



Scheme 4. Synthesis of thiophene-derived dithiahexahelicenes **34–36**. Conditions: a) NBS, CHCl₃, rt, 2 h, 87%; b) Tf₂O, pyridine, CH₂Cl₂, 0 °C to rt, 19 h, 51%; c) alkynes **4**, **7**, or **8**, respectively, cat. Pd(PPh₃)₂Cl₂, cat. CuI, DMF/Et₃N (1 : 1), rt; R = TMS, **27**: 22 h, 38%; R = *p*-Tol, **14**: 3 h, 65%; R = *p*-anisyl, **14**: 22 h, 69%; d) R = *p*-Tol: **15**, cat. Pd₂(dba)₃, SPhos, K₃PO₄, THF, 50 °C, 24 h, 44%; R = TMS or *p*-anisyl: **15**, cat. Pd(PPh₃)₄, K₂CO₃, dioxane/H₂O (10 : 1), 80 °C, 23 h; R = TMS, **30**: 53%; R = *p*-anisyl, **33**: 88%; e) K₂CO₃, CH₂Cl₂/MeOH (1 : 1), rt, 21 h, quant; f) see Table 1.

selectively brominated in 1,8-positions following a published procedure.^[31] Triflate **26** was likewise obtained following a proven protocol.^[32] The known bisalkynes **28** and **29** have already been used for the synthesis of carbohelicenes;^[32] they were again synthesized by Sonogashira couplings and the parent bisalkyne **27** was synthesized using the protocol described above. Coupling of thienyl-2-boronic acid (**15**) was achieved with the proven method, where the terminal alkyne moieties in **31** were again obtained by cleavage of the TMS groups. Thiophene-fused hexahelicenes **34–36** were accessible by *ortho,ortho'* fusion of bisalkynes **30–32**, respectively, using platinum(II) or indium(III) chloride as catalysts (Table 1), where a poor 16% yield of **34** could be increased to 40% with gold catalyst **20**.

Yellow crystals of pentahelicene **21** suitable for X-ray crystallographic analysis were obtained by slow evaporation of a chloroform solution (Figure 2).^[33] **21** crystallizes as conglomerate from the racemic mixture, where a *P* crystal was picked from the mixture and used for analysis (see Supporting

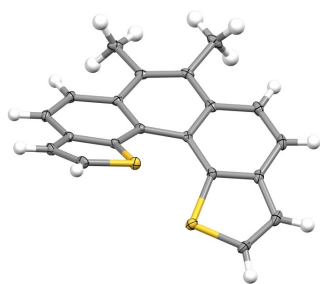


Figure 2. Projection of the molecular structure in the solid state of compound **21**. (Thermal ellipsoids are depicted at the 30% probability level.)

Information, SI). The interplanar angle between the terminal thiophene rings was thus determined to be 51.0°, which is very close to those of comparable carbohelicenes^[1c] (parent [5]helicene: 51.7°^[34]). The mean dihedral angle of the three atom groups (each of four consecutive atoms) in the bay region is 20.1°.

Slow evaporation of a tetrahydrofuran solution of hexahelicene **36** furnished yellow crystals suitable for X-ray crystallographic analysis (Figure 3).^[33] **36** crystallized as racemic crystals; both enantiomers are present in the unit cell, where only one is depicted in the figure (see SI). The interplanar angle of the terminal thiophenes is here 58.7° and the mean dihedral of the four groups of four consecutive atoms in the bay region amounts to 18.9°. Possibly due to packing effects the declinations of the anisyl groups have opposite signs. While the anisyl group on the left (as given in Figure 3) is twisted out of coplanarity by +50.3°, the dihedral angle accounts for –40.6° for the right anisyl group.

The electrochemical properties of **21** and **36** were exemplarily determined by cyclic voltammetry (CV, potentials vs. the ferrocene/ferrocenium couple, Fc/Fc⁺); the voltammograms are given in Figures 4 and 5. Quasi-reversible redox processes were observed in tetrahydrofuran at E_{1/2} = –2.84 V for pentahelicene **21** and at –2.65 V for hexahelicene **36**, which can thus be assigned to reductions of the helicenes. The electrochemical LUMO energy can be estimated from these values^[35] to be E_{LUMO} = –(5.1 eV + E_{1/2}) = –(5.1–2.84) eV = –2.26 eV for pentahe-

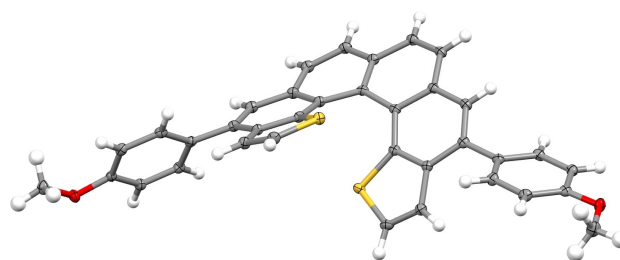


Figure 3. Projection of the molecular structure in the solid state of compound **36**. (Thermal ellipsoids are depicted at the 30% probability level.)

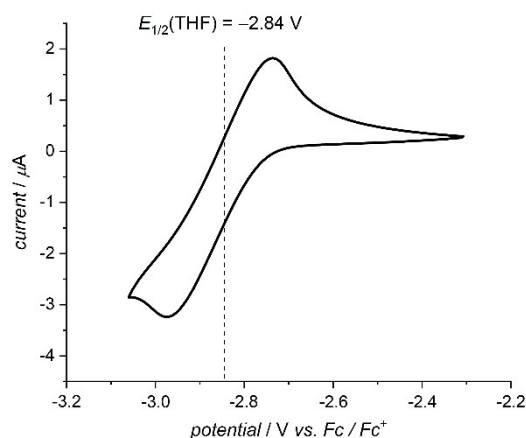


Figure 4. Cyclic voltammogram of **21** in THF measured at room temperature (vs. Fc/Fc⁺; ν = 250 mV · s^{–1}; Pt/[n-Bu₄N][Al(OC(CF₃)₃)₄]/Ag).

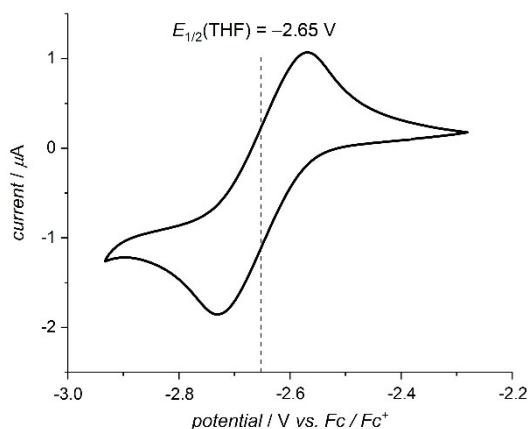


Figure 5. Cyclic voltammogram of **36** in THF measured at room temperature (vs. Fc/Fc⁺; $\nu = 100 \text{ mV} \cdot \text{s}^{-1}$; Pt/[n-Bu₄N][Al(OC(CF₃)₃)₄]/Ag).

licene **21** and accordingly to be $E_{\text{LUMO}} = -2.45 \text{ eV}$ for hexahelicene **36**. Although oxidations might similarly have been expected for thiophene derivatives,^[36] the respective waves were not observed; only stripping of the solvent tetrahydrofuran occurred.

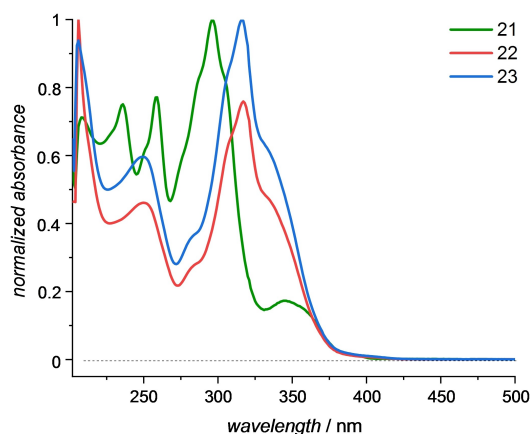


Figure 6. UV/Vis spectra of pentahelicenes **21–23** in THF.

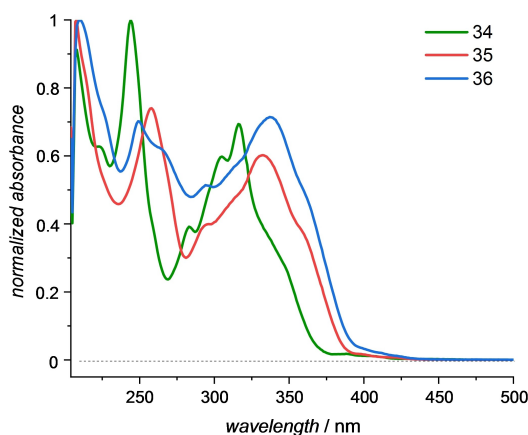


Figure 7. UV/Vis spectra of hexahelicenes **34–36** in THF.

UV/Vis spectra were recorded for all synthesized pentahelicenes (Figure 6) and hexahelicenes (Figure 7). Pentahelicenes **21–23** show long-wavelength absorption bands at about 345 nm, partly as shoulders of the strongest band found between 300 and 320 nm. Similar observations were made for hexahelicenes **34–36**, although the shoulder at around 350–370 nm is much less pronounced, and the strongest bands are observed in the range of 320–340 nm. (Calculated UV/Vis spectra are given in the SI for comparison.)

Electronic circular dichroism (ECD) spectra of the helicenes were not recorded since a separation of the enantiomers was not attempted, not least because a persistent enantiomeric integrity of the enantiomers was quite unlikely at room temperature.^[37] However, ECD spectra were calculated and are given in the SI.

HOMO/LUMO gaps were similarly calculated for all helicenes. Frontier orbitals of pentahelicene **21** and of hexahelicene **34** are depicted in Figure 8 (corresponding pictures of frontier orbitals for all helicenes are given in the SI). HOMO and LUMO energies of -5.84 and -1.46 eV , respectively, were calculated for pentahelicene **21**, resulting in a HOMO/LUMO gap of 4.38 eV . The respective numbers for hexahelicene **34** are -6.05 and -1.65 eV ($E_{\text{gap}} = 4.40 \text{ eV}$). HOMO/LUMO energies for all synthesized helicenes are given in Table 2. Aryl-substituted hexahelicenes show the smallest gaps; E_{gap} is only 3.82 eV for helicene **36**.

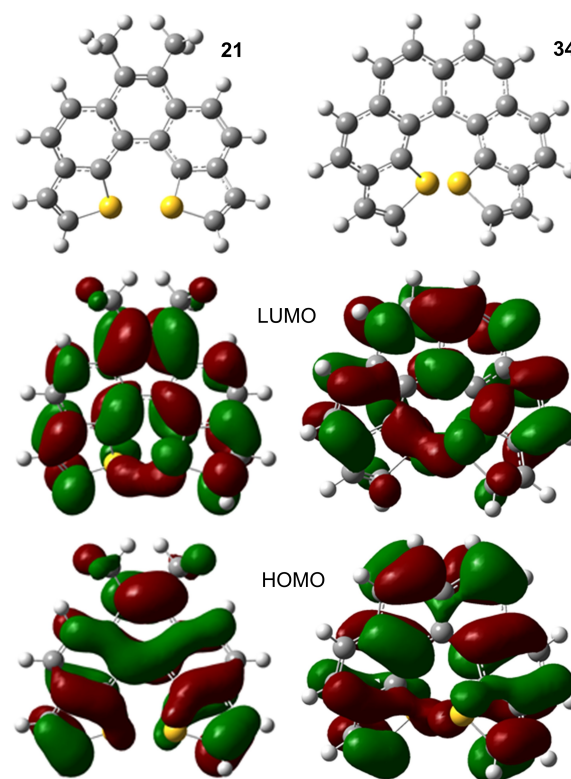


Figure 8. FMOs of pentahelicene **21** (left) and hexahelicene **34** (right). The orientation of the molecules is given in the top row as ball-stick models. Details on the calculations are given in the SI.

Table 2. FMO Energies and HOMO/LUMO Gaps of Helicenes 21–23 and 34–36. [a]

| Compound | R | E_{HOMO} [eV] | E_{LUMO} [eV] | $E_{\text{LUMO}}-E_{\text{HOMO}}$ [eV] |
|----------|------------------|------------------------|------------------------|--|
| 21 | H | -5.84 | -1.46 | 4.38 |
| 22 | <i>p</i> -Tol | -5.81 | -1.46 ^[b] | 4.35 |
| 23 | <i>p</i> -anisyl | -5.72 | -1.44 | 4.28 |
| 34 | H | -6.05 ^[c] | -1.65 | 4.40 |
| 35 | <i>p</i> -Tol | -5.88 ^[d] | -1.66 | 4.22 |
| 36 | <i>p</i> -anisyl | -5.53 | -1.71 | 3.82 |

[a] Calculated at the M06/6-311++g(d,p)//M06/6-311++g(d,p) level; [b] 22 has two very close LUMOs at -1.46 and -1.45 eV; [c] 34 has two very close HOMOs at -6.05 and -6.06 eV; [d] 35 has two very close HOMOs at -5.88 and -5.90 eV.

Conclusions

We showed that alkyne isomerizations are well suited for the preparation of thiophen-containing penta- and hexahelicenes with and without further substituents. It can be assumed that this method can be used for the synthesis of larger scaffolds, when starting with suitably expanded precursors. Work in this direction is ongoing in our laboratories.

Experimental Section

Synthesis of Pentahelicene 22

1,2-Dibromo-4,5-dimethyl-3,6-bis(4-tolylethynyl)benzene (13): Degassed Et_3N (30 mL), $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (68 mg, 97 μmol), and CuI (37 mg, 194 μmol) were added under an argon atmosphere to a degassed suspension of diiodide 11 (1.00 g, 1.94 mmol) and alkyne 7 (676 mg, 5.82 mmol) in toluene (30 mL) and the mixture was stirred for 22 h at 45 °C, cooled to rt, and 1 M HCl (200 mL) was added. The aqueous layer was extracted with CH_2Cl_2 (3 \times 120 mL) and the combined organic layers were dried (Na_2SO_4), concentrated at reduced pressure, and purified by column chromatography (silica gel, pentane/ CH_2Cl_2 50:1 \rightarrow 30:1 \rightarrow 20:1) to yield 13 as a pale green solid (512 mg, 1.04 mmol, 54%). $R_f = 0.36$ (pentane/ CH_2Cl_2 10:1); ^1H NMR (500 MHz, CDCl_3): $\delta = 2.39$ (s, 6 H, 2 \times 4'- CH_3), 2.52 (s, 6 H, 4- CH_3 , 5- CH_3), 7.18 (d, $^3J = 7.9$ Hz, 4 H, 2 \times 3'-H, 2 \times 5'-H), 7.48 ppm (d, $^3J = 8.1$ Hz, 4 H, 2 \times 2'-H, 2 \times 6'-H); ^{13}C NMR (126 MHz, CDCl_3): $\delta = 19.5$ (2 \times CH_3), 21.8 (2 \times CH_3), 88.1 (2 \times C), 99.6 (2 \times C), 119.9 (2 \times C), 125.7 (2 \times C), 126.6 (2 \times C), 129.4 (4 \times CH), 131.7 (4 \times CH), 139.0 (2 \times C), 139.3 ppm (2 \times C); IR (ATR): $\tilde{\nu} = 2916$ (vw), 2851 (w), 2207 (vw), 1508 (w), 1384 (w), 815 (m), 530 cm^{-1} (m); MS (EI, 130 °C): m/z (%): 492 (87) $[\text{M}]^+$, 414 (42), 346 (100), 316 (48), 300 (18), 239 (15), 119 (25); HRMS (EI): m/z calcd for $\text{C}_{26}\text{H}_{20}^{79}\text{Br}_2$: 489.9926; found: 489.9928.

2,2'-[4,5-Dimethyl-3,6-bis(4-tolylethynyl)-1,2-phenylene]dithiophene (18): Boronic acid 15 (117 mg, 0.914 mmol), SPhos (19 mg, 46 μmol), $\text{Pd}(\text{OAc})_2$ (6.9 mg, 31 μmol), and degassed dioxane/ H_2O (10:1; 11 mL) were added under an argon atmosphere to a mixture of dibromide 13 (150 mg, 0.305 mmol) and Cs_2CO_3 (298 mg, 0.915 mmol). The suspension was stirred for 21 h at 80 °C, cooled to rt, filtered over Celite, and rinsed with CH_2Cl_2 . The filtrate was dried (Na_2SO_4), concentrated at reduced pressure, and purified by column chromatography (silica gel, pentane/ CH_2Cl_2 30:1 \rightarrow 20:1) to yield 18 as an orange solid (117 mg, 0.235 mmol, 77%). $R_f = 0.38$ (pentane/ CH_2Cl_2 5:1); ^1H

NMR (400 MHz, CD_2Cl_2): $\delta = 2.33$ (s, 6 H, 4- CH_3 , 5- CH_3), 2.61 (s, 6 H 2 \times 4'- CH_3), 6.94–6.99 (m, 4 H, 2 \times 4'-H, 2 \times 5'-H or 2 \times 3'-H), 7.14–7.02 (m, Hz, 8 H, 2 \times 2'-H, 2 \times 3'-H, 2 \times 5'-H, 2 \times 6'-H), 7.31 ppm (dd, $^3J = 4.9$ Hz, $^4J = 1.4$ Hz, 2 H, 2 \times 3'-H or 2 \times 5'-H); ^{13}C NMR (100 MHz, CD_2Cl_2): $\delta = 19.1$ (2 \times CH_3), 21.8 (2 \times CH_3), 88.2 (2 \times C), 99.5 (2 \times C), 120.7 (2 \times C), 125.2 (2 \times C), 126.4 (2 \times CH), 126.5 (2 \times CH), 129.4 (2 \times CH), 129.6 (4 \times CH), 131.7 (4 \times CH), 135.8 (2 \times C), 139.3 (2 \times C), 139.3 (2 \times C), 141.3 ppm (2 \times C); IR (ATR): $\tilde{\nu} = 2913$ (vw), 2205 (m), 1509 (w), 1400 (w), 1210 (w), 1033 (w), 813 (m), 695 (m), 525 cm^{-1} (m); MS (FAB): m/z (%): 498 (18) $[\text{M}]^+$, 395 (73), 369 (15), 155 (19); HRMS (FAB): m/z calcd for $\text{C}_{34}\text{H}_{26}^{32}\text{S}_2$: 498.1470; found: 498.1468.

6,7-Dimethyl-4,9-di-4-tolylphenanthro[4,3-b:5,6-b']dithiophene

(22): Based on a published procedure,^[38] [(JohnPhos)Au-(NCMe)][SbF₆] (20) (6.2 mg, 8.0 μmol) was added to a solution of dithiophene 18 (40.0 mg, 80.2 μmol) in dichlorobenzene (1.6 mL) placed in a pyrex tube. The mixture was stirred for 4 h at 160 °C, cooled to rt, filtered over Celite, and rinsed with CH_2Cl_2 . Pentane was added and the precipitate was washed with pentane und MeOH to yield 22 as an orange-greenish solid (38.0 mg, 76.2 μmol , 95%). ^1H NMR (600 MHz, CD_2Cl_2): $\delta = 2.50$ (s, 6 H, 6- CH_3 , 7- CH_3), 2.83 (s, 6 H, 2 \times 4'- CH_3), 7.39 (d, $^3J = 7.6$ Hz, 4 H, 2 \times 3'-H, 2 \times 5'-H), 7.42 (d, $^3J = 5.4$ Hz, 2 H, 3-H, 10-H), 7.55 (d, $^3J = 5.5$ Hz, 2 H, 2-H, 11-H), 7.70 (d, $^3J = 7.6$ Hz, 4 H, 2 \times 2'-H, 2 \times 6'-H), 8.12 ppm (s, 2 H, 5-H, 8-H); ^{13}C NMR (151 MHz, CDCl_3): $\delta = 16.7$ (2 \times CH_3), 21.4 (2 \times CH_3), 120.6 (2 \times CH), 123.2 (2 \times C), 123.4 (2 \times CH), 123.8 (2 \times CH), 129.5 (4 \times CH), 129.6 (4 \times CH), 130.0 (2 \times C), 131.5 (2 \times C), 135.9 (2 \times C), 136.9 (2 \times C), 137.5 (2 \times C), 137.8 (2 \times C), 138.4 ppm (2 \times C); IR (ATR): $\tilde{\nu} = 3023$ (vw), 2920 (w), 2860 (vw), 1736 (w), 1510 (w), 1445 (w), 1394 (w), 868 (w), 817 (w), 764 (w), 729 cm^{-1} (w); UV/Vis (THF) $\lambda_{\text{max}} = 250, 317, 332$ nm; MS (MALDI, 300 °C): m/z (%): 499 (41) $[\text{M} + 1]^+$, 498 (99) $[\text{M}]^+$, 374 (34), 333 (25); HRMS (MALDI): m/z calcd for $\text{C}_{34}\text{H}_{26}^{32}\text{S}_2$: 498.1472; found: 498.1471.

Synthesis of Hexahelicene 34

1,8-Dibromo-2,7-bis(trimethylsilylethynyl)naphthalene (27): Degassed Et_3N (7 mL), $\text{Pd}(\text{dppf})\text{Cl}_2\text{-CH}_2\text{Cl}_2$ (70 mg, 86 μmol), and CuI (33 mg, 0.17 mmol) were added under an argon atmosphere to a solution of ditosylate 26 (1.00 g, 1.72 mmol) in DMF (3 mL) which had been degassed by ultrasonication (10 min). TMS-acetylene (degassed by 3 freeze-pump-thaw cycles; 0.952 mL, 675 mg, 6.87 mmol) was added and the mixture was stirred for 23 h at rt. H_2O (10 mL) and 1 M HCl (10 mL) was added, the aqueous layer was extracted with CH_2Cl_2 (2 \times 20 mL) and the combined organic layers were dried (Na_2SO_4), concentrated at reduced pressure, and purified by column chromatography (silica gel, pentane) to yield 27 as a red-orange solid (315 mg, 0.658 mmol, 38%). $R_f = 0.20$ (pentane); ^1H NMR (500 MHz, CDCl_3): $\delta = 0.30$ [s, 18 H, 2 \times Si(CH_3)₃], 7.51 (d, $^3J = 8.3$ Hz, 2 H, 3-H, 6-H), 7.66 ppm (d, $^3J = 8.3$ Hz, 2 H, 4-H, 5-H); ^{13}C NMR (100 MHz, CDCl_3): $\delta = -0.06$ (6 \times CH_3), 102.6 (C), 105.0 (C), 124.0 (C), 128.3 (2 \times CH), 128.4 (C), 130.4 (C), 130.6 (2 \times CH), 135.5 ppm (C); IR (ATR): $\tilde{\nu} = 2957$ (vw), 2151 (w), 1493 (w), 1331 (w), 1244 (w), 834 (m), 758 (m), 634 cm^{-1} (w); MS (FAB): m/z (%): 478 (70) $[\text{M}]^+$, 409 (67), 391 (14), 337 (11), 226 (23), 136 (100); HRMS (FAB): m/z calcd for $\text{C}_{20}\text{H}_{22}^{79}\text{Br}^{81}\text{Br}^{28}\text{Si}_2$: 477.9601; found: 477.9599.

2,2'-[2,7-Bis(trimethylsilylethynyl)naphthalene-1,8-diyl]dithiophene (30): Boronic acid 15 (214 mg, 1.67 mmol), $\text{Pd}(\text{PPh}_3)_4$ (24 mg, 21 μmol), and then degassed dioxane/ H_2O (10:1; 17 mL) were added under an argon atmosphere to dibromide 27 (200 mg, 0.418 mmol) and K_2CO_3 (173 mg, 1.25 mmol). The mixture was stirred for 23 h at 80 °C, cooled to rt, filtered over celite, and rinsed with CH_2Cl_2 . The filtrate was dried (Na_2SO_4), concentrated at reduced pressure, and purified by column chromatography (silica

gel, pentane/CH₂Cl₂ 50:1→30:1) to yield **30** as an orange solid (107 mg, 0.221 mmol, 53%). $R_f = 0.35$ (pentane/CH₂Cl₂ 10:1); ¹H NMR (500 MHz, CDCl₃): $\delta = 0.01$ [s, 18 H, Si(CH₃)₃], 6.48 (dd, ³J = 3.5 Hz, ⁴J = 1.1 Hz, 2 H, 2×5'-H or 2×3'-H), 6.64–6.68 (m, 2 H, 2×4'-H), 7.10 (dd, ³J = 5.1 Hz, ⁴J = 1.1 Hz, 2 H, 2×3'-H or 2×5'-H), 7.56 (d, ³J = 8.4 Hz, 2 H, 3-H, 6-H), 7.79 ppm (d, ³J = 8.4 Hz, 2 H, 4-H, 5-H); ¹³C NMR (126 MHz, CDCl₃): $\delta = -0.24$ (6×CH₃), 100 (C), 104.1 (C), 125.1 (2×CH), 126.3 (2×CH), 129.0 (2×CH), 129.1 (2×CH), 129.2 (2×CH), 133.6 (C), 133.7 (C), 136.6 (C), 141.3 ppm (C); IR (ATR): $\tilde{\nu} = 2957$ (w), 2144 (w), 1498 (w), 1318 (w), 1246 (m), 834 (s), 756 (m), 684 (m), 633 cm⁻¹ (m); MS (FAB): m/z (%): 484 (100) [M]⁺, 397 (14), 217 (10), 154 (15), 136 (15); HRMS (FAB): m/z calcd for C₂₈H₂₈³²S₂Si₂: 484.1166; found: 484.1168.

2,2'-(2,7-Diethynyl)naphthalene-1,8-diyl)dithiophene (31): Based on a published protocol,^[9] K₂CO₃ (145 mg, 1.05 mmol) was added to a solution of silane **30** (254 mg, 0.524 mmol) in CH₂Cl₂/MeOH (1:1; 20 mL) and the mixture was stirred for 21 h at rt. 1 M HCl (15 mL) was added and the aqueous layer was extracted with CH₂Cl₂ (3×20 mL). The combined organic layers were dried (Na₂SO₄) and concentrated at reduced pressure to yield **31** as a brown solid (178 mg, 0.523 mmol, quant.), which was used without further purification. ¹H NMR (400 MHz, CD₂Cl₂): $\delta = 3.05$ (s, 2 H, 2×ethynyl-H), 6.51 (dd, ³J = 3.6 Hz, ⁴J = 1.2 Hz, 2 H, 2×4'-H), 6.69 (dd, ³J = 5.2 Hz, ⁴J = 3.5 Hz, 2×5'-H or 2×3'-H), 7.13 (dd, ³J = 5.1 Hz, ⁴J = 1.2 Hz, 2 H, 2×3'-H or 2×5'-H), 7.63 (d, ³J = 8.4 Hz, 2 H, 3-H, 6-H), 7.84 ppm (d, ³J = 8.4 Hz, 2 H, 4-H, 5-H); ¹³C NMR (100 MHz, CDCl₃): $\delta = 82.7$ (C), 82.8 (2×CH), 125.4 (C), 125.6 (2×CH), 126.7 (2×CH), 129.2 (2×CH), 129.3 (2×CH), 129.9 (2×CH), 133.7 (C), 133.9 (C), 136.4 (C), 141.0 ppm (C); IR (ATR): $\tilde{\nu} = 3275$ (w), 2922 (vw), 2101 (vw), 1500 (vw), 1427 (vw), 1316 (w), 1229 (w), 1040 (w), 840 (m), 691 (m), 629 (m), 594 cm⁻¹ (m); MS (FAB): m/z (%): 341 (29) [M + 1]⁺, 340 (37) [M]⁺, 316 (39), 282 (23), 245 (18), 195 (39); HRMS (FAB): m/z calcd for C₂₂H₁₂³²S₂: 340.0375; found: 340.0373.

Benzo[1',2':3,4]phenanthrene[5,6-b:4',5'-b']dithiophene (34): Based on a published procedure,^[38] [(JohnPhos)Au(NCMe)][SbF₆] (**20**) (11 mg, 14 μmol) was added to a solution of dithiophene **31** (50 mg, 0.15 mmol) in dichlorobenzene (2 mL) placed in a pyrex tube. The mixture was stirred for 3 h at 80 °C and cooled to rt. The mixture was applied to a chromatography column and purified (silica gel, pentane/CH₂Cl₂ 30:1) to yield **34** as a yellow-orange solid (20 mg, 59 μmol, 40%). $R_f = 0.30$ (pentane/CH₂Cl₂ 10:1); ¹H NMR (400 MHz, CD₂Cl₂): $\delta = 7.22$ (d, ³J = 5.5 Hz, 2 H, 3-H, 12-H), 7.37 (d, ³J = 5.4 Hz, 2 H, 2-H, 13-H), 7.86 (d, ³J = 8.4 Hz, 2 H, 6-H, 9-H), 8.00 (d, ³J = 8.5 Hz, 2 H, 7-H, 8-H), 8.03–8.07 ppm (m, 4 H, 4-H, 5-H, 10-H, 11-H); ¹³C NMR (100 MHz, CDCl₃): $\delta = 123.1$ (2×CH), 123.2 (2×CH), 124.0 (C), 125.0 (2×CH), 125.2 (2×CH), 125.4 (C), 126.0 (2×CH), 128.3 (2×CH), 131.1 (C), 132.7 (C), 138.5 (C), 138.7 ppm (C); IR (ATR): $\tilde{\nu} = 3096$ (vw), 2020 (w), 1348 (w), 1299 (w), 1235 (w), 467 (w), 837 (m), 796 (m), 694 (m), 677 (m), 583 cm⁻¹ (m); UV/Vis (THF) $\lambda_{\text{max}} = 224$, 244, 283, 305, 316, 340 nm; MS (FAB): m/z (%): 341 (65) [M + 1]⁺, 340 (100) [M]⁺, 217 (35), 155 (22); HRMS (FAB): m/z calcd for C₂₂H₁₂³²S₂: 340.0375; found: 340.0377.

Supporting Information

Additional references cited within the Supporting Information.^[40–53]

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: Alkynes · Gold catalysis · Helicenes · Sonogashira coupling · Thiophenes

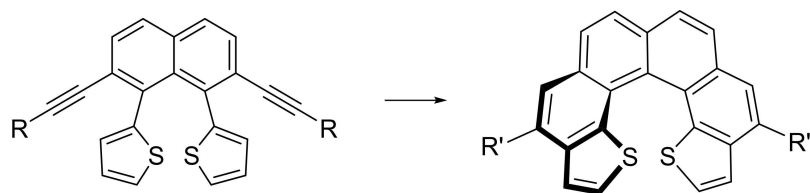
- [1] a) R. H. Martin, *Angew. Chem.* **1974**, *86*, 727–738; *Angew. Chem. Int. Ed. Engl.* **1974**, *13*, 649–660; b) Y. Shen, C.-F. Chen, *Chem. Rev.* **2012**, *112*, 1463–1535; c) C.-F. Chen, Y. Shen, *Helicene Chemistry - From Synthesis to Applications*, Springer-Verlag, Berlin, Heidelberg, **2017**; d) M. Gingras, *Chem. Soc. Rev.* **2013**, *42*, 968–1006; e) M. Gingras, G. Félix, R. Peresutti, *Chem. Soc. Rev.* **2013**, *42*, 1007–1050; f) M. Gingras, *Chem. Soc. Rev.* **2013**, *42*, 1051–1095.
- [2] G. P. Moss, *Pure Appl. Chem.* **1996**, *68*, 2193–2222.
- [3] H. A. Favre, W. H. Powell, *Nomenclature of Organic Chemistry: IUPAC Recommendations and Preferred Names 2013*, The Royal Society of Chemistry, Cambridge (UK), **2013**.
- [4] a) L. Rulišek, O. Exner, L. Cwiklik, P. Jungwirth, I. Starý, L. Pospíšil, Z. Havlas, *J. Phys. Chem. C* **2007**, *111*, 14948–14955; b) Y. Nakai, T. Mori, Y. Inoue, *J. Phys. Chem. A* **2012**, *116*, 7372–7385; c) P. Ravat, R. Hinkelmann, D. Steinebrunner, A. Prescimone, I. Bodoky, M. Juriček, *Org. Lett.* **2017**, *19*, 3707–3710; d) T. Hartung, R. Machleid, M. Simon, C. Golz, M. Alcarazo, *Angew. Chem.* **2020**, *132*, 5709–5713; *Angew. Chem. Int. Ed.* **2020**, *59*, 5660–5664.
- [5] S. Herzog, A. Hinz, F. Breher, J. Podlech, *Org. Biomol. Chem.* **2022**, *20*, 2873–2880.
- [6] K. Dhbaibi, L. Favereau, J. Crassous, *Chem. Rev.* **2019**, *119*, 8846–8953.
- [7] a) A. Weiß, J. Podlech, *Eur. J. Org. Chem.* **2019**, 6697–6701; b) S. Herzog, I. Marten, A. Weiß, J. Podlech, *Synthesis* **2022**, *54*, 4220–4234.
- [8] a) E. Licandro, S. Cauteruccio, D. Dova, in *Adv. Heterocycl. Chem.*, Vol. 118 (Eds.: E. F. V. Scriven, C. A. Ramsden), Academic Press, **2016**, pp. 1–46; b) J. Kaiser, A. Mekić, A. H. Parham, H. Buchholz, B. König, *Eur. J. Org. Chem.* **2020**, 66–69.
- [9] a) J. H. Dopper, D. Oudman, H. Wynberg, *J. Am. Chem. Soc.* **1973**, *95*, 3692–3698; b) D. Miao, M. Daigle, A. Lucotti, J. Boismenu-Lavoie, M. Tommasini, J.-F. Morin, *Angew. Chem.* **2018**, *130*, 3650–3654; *Angew. Chem. Int. Ed.* **2018**, *57*, 3588–3592; c) P. Sarkar, B. K. Das, D. Chakraborty, K. Muthamma, *J. Mol. Struct.* **2019**, *1195*, 309–314.
- [10] S. M. Hoenig, Y. Yan, E. A. Dougherty, R. Hudson, S. Petovic, C. K. Lee, Y. Hu, L. S. Gomez, J. L. Katz, *J. Org. Chem.* **2020**, *85*, 4553–4559.
- [11] O. Palata, A. Andronova, M. Šámal, J. Nejedlý, J. Rybáček, M. Buděšínský, L. Bednářová, L. Pospíšil, I. Císařová, I. Starý, I. G. Stará, *Helv. Chim. Acta* **2022**, *105*, e202100225.
- [12] a) A. Rajca, H. Wang, M. Pink, S. Rajca, *Angew. Chem.* **2000**, *112*, 4655–4657; *Angew. Chem. Int. Ed.* **2000**, *39*, 4481–4483; b) X. Liu, H. Sun, W. Xu, S. Wan, J. Shi, C. Li, H. Wang, *Org. Chem. Front.* **2018**, *5*, 1257–1261; c) J. Wang, G. Wang, C. Li, Y. Dong, Z. Ma, H. Wang, *J. Org. Chem.* **2021**, *86*, 4413–4422.
- [13] Z. Wang, J. Shi, J. Wang, C. Li, X. Tian, Y. Cheng, H. Wang, *Org. Lett.* **2010**, *12*, 456–459.

- [14] V. Pelliccioli, F. Cardano, G. Renno, F. Vasile, C. Graiff, G. Mazzeo, A. Fin, G. Longhi, S. Abbate, A. Rosetti, C. Villani, G. Viscardi, E. Licandro, S. Cauteruccio, *Catalysts* **2022**, *12*, 366.
- [15] a) S. Arnaboldi, S. Cauteruccio, S. Grecchi, T. Benincori, M. Marcaccio, A. Orbelli Biroli, G. Longhi, E. Licandro, P. R. Mussini, *Chem. Sci.* **2019**, *10*, 1539–1548; b) Y. Li, A. Concellón, C.-J. Lin, N. A. Romero, S. Lin, T. M. Swager, *Chem. Sci.* **2020**, *11*, 4695–4701; c) P. Hou, S. Peschtrich, W. Feuerstein, R. Schoch, S. Hohloch, F. Breher, J. Paradies, *ChemistryOpen* **2023**, *12*, e202300003; d) P. Hou, S. Peschtrich, N. Huber, W. Feuerstein, A. Bihlmeier, I. Krummenacher, R. Schoch, W. Klopfer, F. Breher, J. Paradies, *Chem. Eur. J.* **2022**, *28*, e202200478.
- [16] a) E. Botek, J.-M. André, B. Champagne, T. Verbiest, A. Persoons, *J. Chem. Phys.* **2005**, *122*, 234713; b) A. Bossi, E. Licandro, S. Maiorana, C. Rigamonti, S. Righetto, G. R. Stephenson, M. Spassova, E. Botek, B. Champagne, *J. Phys. Chem. C* **2008**, *112*, 7900–7907; c) P. K. Sharma, D. Mallick, H. Sharma, S. Das, *Org. Lett.* **2023**, *25*, 2201–2206.
- [17] a) T. Fukumi, T. Sakaguchi, M. Miya, H. Nakagawa, K.-i. Yamada, H. Kawazura, *Rev. Laser Eng.* **1994**, *22*, 409–414; b) C. A. Daul, I. Ciofini, V. Weber, *Int. J. Quantum Chem.* **2003**, *91*, 297–302; c) B. Champagne, J.-M. André, E. Botek, E. Licandro, S. Maiorana, A. Bossi, K. Clays, A. Persoons, *ChemPhysChem* **2004**, *5*, 1438–1442; d) E. Botek, M. Spassova, B. Champagne, I. Asselberghs, A. Persoons, K. Clays, *Chem. Phys. Lett.* **2005**, *412*, 274–279; e) B. Champagne, S. N. Labidi, *Chem. Phys. Lett.* **2016**, *644*, 195–200.
- [18] W. Wang, X. Li, Z. Qi, B. Ji, Z. Wang, S. Wang, J. Xiao, *Org. Lett.* **2023**, *25*, 1343–1347.
- [19] a) T. Nakamura, H. Kondoh, M. Matsumoto, *Mol. Cryst. Liq. Cryst. Sci. Technol. Sect. A* **1999**, *337*, 273–276; b) S. Chaunchaiyakul, P. Krukowski, T. Tsuzuki, Y. Minagawa, M. Akai-Kasaya, A. Saito, H. Osuga, Y. Kuwahara, *J. Phys. Chem. C* **2015**, *119*, 21434–21442; c) P. Krukowski, S. Chaunchaiyakul, M. Akai-Kasaya, A. Saito, H. Osuga, Y. Kuwahara, *J. Phys. Chem. C* **2021**, *125*, 9419–9427.
- [20] a) M. Monteforte, S. Cauteruccio, S. Maiorana, T. Benincori, A. Forni, L. Raimondi, C. Graiff, A. Tiripicchio, G. R. Stephenson, E. Licandro, *Eur. J. Org. Chem.* **2011**, 5649–5658; b) S. Cauteruccio, A. Loos, A. Bossi, M. C. Blanco Jaimes, D. Dova, F. Rominger, S. Prager, A. Dreuw, E. Licandro, A. S. K. Hashmi, *Inorg. Chem.* **2013**, *52*, 7995–8004; c) S. Cauteruccio, D. Dova, M. Benaglia, A. Genoni, M. Orlandi, E. Licandro, *Eur. J. Org. Chem.* **2014**, 2694–2702; d) D. Dova, L. Viglianti, P. R. Mussini, S. Prager, A. Dreuw, A. Voituriez, E. Licandro, S. Cauteruccio, *Asian J. Org. Chem.* **2016**, *5*, 537–549; N. Otani, K. Higashiyama, H. Sakai, T. Hasobe, D. Takahashi, K. Toshima, *Eur. J. Org. Chem.* **2023**, 26, e202300287.
- [21] a) H. Nakagawa, K. Gomi, K.-i. Yamada, *Chem. Pharm. Bull.* **2001**, *49*, 49–53; b) Y. Xu, Y. X. Zhang, H. Sugiyama, T. Umano, H. Osuga, K. Tanaka, *J. Am. Chem. Soc.* **2004**, *126*, 6566–6567; c) K.-i. Shinohara, Y. Sannohe, S. Kaieda, K.-i. Tanaka, H. Osuga, H. Tahara, Y. Xu, T. Kawase, T. Bando, H. Sugiyama, *J. Am. Chem. Soc.* **2010**, *132*, 3778–3782; d) S. Cauteruccio, C. Bartoli, C. Carrara, D. Dova, C. Errico, G. Ciampi, D. Dinucci, E. Licandro, F. Chiellini, *ChemPlusChem* **2015**, *80*, 490–493; e) T. Taroni, S. Cauteruccio, R. Vago, S. Franchi, N. Barbero, E. Licandro, S. Arzizzone, D. Meroni, *Appl. Surf. Sci.* **2020**, *520*, 146351.
- [22] a) A. Fürstner, V. Mamane, *J. Org. Chem.* **2002**, *67*, 6264–6267; b) V. Mamane, P. Hannen, A. Fürstner, *Chem. Eur. J.* **2004**, *10*, 4556–4575.
- [23] E. A. Krasnokutskaya, N. I. Semenischeva, V. D. Filimonov, P. Knochel, *Synthesis* **2007**, 81–84.
- [24] I. Van Overmeire, S. A. Boldin, K. Venkataraman, R. Zisling, S. De Jonghe, S. Van Calenberg, D. De Keukeleire, A. H. Futerman, P. Herdewijn, *J. Med. Chem.* **2000**, *43*, 4189–4199.
- [25] D. Nishikawa, K. Hirano, M. Miura, *J. Am. Chem. Soc.* **2015**, *137*, 15620–15623.
- [26] a) P. R. Ashton, U. Girreser, D. Giuffrida, F. H. Kohnke, J. P. Mathias, F. M. Raymo, A. M. Z. Slawin, J. F. Stoddart, D. J. Williams, *J. Am. Chem. Soc.* **1993**, *115*, 5422–5429; b) W. Eberhardt, M. Hanack, *Synthesis* **1998**, 1760–1764.
- [27] J. M. Tour, A. M. Rawlett, M. Kozaki, Y. Yao, R. C. Jagessar, S. M. Dirk, D. W. Price, M. A. Reed, C.-W. Zhou, J. Chen, W. Wang, I. Campbell, *Chem. Eur. J.* **2001**, *7*, 5118–5134.
- [28] M. Altemöller, J. Podlech, D. Fenske, *Eur. J. Org. Chem.* **2006**, 1678–1684.
- [29] a) A. Fürstner, V. Mamane, *Chem. Commun.* **2003**, 2112–2113; b) A. Fürstner, V. Mamane, G. Seidel, D. Laurich, *Org. Synth.* **2006**, *83*, 103–110; *Coll.* **2009**, *11*, 826–833.
- [30] a) C. Nieto-Oberhuber, S. López, A. M. Echavarren, *J. Am. Chem. Soc.* **2005**, *127*, 6178–6179; b) C. Nieto-Oberhuber, S. López, M. P. Muñoz, D. J. Cárdenas, E. Buñuel, C. Nevado, A. M. Echavarren, *Angew. Chem.* **2005**, *117*, 6302–6304; *Angew. Chem. Int. Ed.* **2005**, *44*, 6146–6148; c) M. P. Muñoz, J. Adrio, J. C. Carretero, A. M. Echavarren, *Organo-metallics* **2005**, *24*, 1293–1300; d) C. Nieto-Oberhuber, S. López, M. P. Muñoz, E. Jiménez-Núñez, E. Buñuel, D. J. Cárdenas, A. M. Echavarren, *Chem. Eur. J.* **2006**, *12*, 1694–1702; e) C. Nieto-Oberhuber, M. P. Muñoz, S. López, E. Jiménez-Núñez, C. Nevado, E. Herrero-Gómez, M. Raducan, A. M. Echavarren, *Chem. Eur. J.* **2006**, *12*, 1677–1693; *Chem. Eur. J.*; **2008**, *14*, 5096; f) M. Gaydou, A. M. Echavarren, in *Encyclopedia of Reagents for Organic Synthesis*, John Wiley & Sons; for gold catalysis in general, see: g) A. S. K. Hashmi, *Chem. Rev.* **2007**, *107*, 3180–3211; for the first gold-catalyzed hydroarylations, see: h) A. S. K. Hashmi, L. Schwarz, J.-H. Choi, T. M. Frost, *Angew. Chem.* **2000**, *112*, 2382–2385; *Angew. Chem. Int. Ed.* **2000**, *39*, 2285–2288; i) G. Dyker, E. Muth, A. S. K. Hashmi, L. Ding, *Adv. Synth. Catal.* **2003**, *345*, 1247–1252; j) A. S. K. Hashmi, M. C. Blanco, *Eur. J. Org. Chem.* **2006**, *2006*, 4340–4342.
- [31] C. Thirsk, G. E. Hawkes, R. T. Kroemer, K. R. Liedl, T. Loerting, R. Nasser, R. G. Pritchard, M. Steele, J. E. Warren, A. Whiting, *J. Chem. Soc. Perkin Trans. 2* **2002**, 1510–1519.
- [32] L. D. M. Nicholls, M. Marx, T. Hartung, E. González-Fernández, C. Golz, M. Alcarazo, *ACS Catal.* **2018**, *8*, 6079–6085.
- [33] Deposition Numbers 2266698 (for 21) and 2266699 (for 36) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.
- [34] K. Yamamoto, M. Okazumi, H. Suemune, K. Usui, *Org. Lett.* **2013**, *15*, 1806–1809.
- [35] a) J. Pommerehne, H. Vestweber, W. Guss, R. F. Mahrt, H. Bässler, M. Porsch, J. Daub, *Adv. Mater.* **1995**, *7*, 551–554; b) C. M. Cardona, W. Li, A. E. Kaifer, D. Stockdale, G. C. Bazan, *Adv. Mater.* **2011**, *23*, 2367–2371; c) J. Sworakowski, *Synth. Met.* **2018**, *235*, 125–130; d) E. V. Tretyakov, P. V. Petunin, S. I. Zhivetyeva, D. E. Gorbunov, N. P. Gritsan, M. V. Fedin, D. V. Stass, R. I. Samoilova, I. Y. Bagryanskaya, I. K. Shundrina, A. S. Bogomyakov, M. S. Kazantsev, P. S. Postnikov, M. E. Trusova, V. I. Ovcharenko, *J. Am. Chem. Soc.* **2021**, *143*, 8164–8176.
- [36] D. J. Guerrero, X. Ren, J. P. Ferraris, *Chem. Mater.* **1994**, *6*, 1437–1443.
- [37] H. Wynberg, M. B. Groen, *J. Chem. Soc. D* **1969**, 964–965.
- [38] R. Heckershoff, G. May, J. Däumer, L. Eberle, P. Krämer, F. Rominger, M. Rudolph, F. F. Mulks, A. S. K. Hashmi, *Chem. Eur. J.* **2022**, *28*, e202201816.
- [39] K. Kasten, A. M. Z. Slawin, A. D. Smith, *Org. Lett.* **2017**, *19*, 5182–5185.
- [40] W. C. Still, M. Kahn, A. Mitra, *J. Org. Chem.* **1978**, *43*, 2923–2925.
- [41] a) G. M. Sheldrick, *Acta Crystallogr. Sect. A* **2015**, *71*, 3–8; b) G. M. Sheldrick, *Acta Crystallogr. Sect. C* **2015**, *71*, 3–8; c) O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Crystallogr.* **2009**, *42*, 339–341.
- [42] E. Voutyritsa, M. Garreau, M. G. Kokotou, I. Triandafillidi, J. Waser, C. G. Kokotos, *Chem. Eur. J.* **2020**, *26*, 14453–14460.
- [43] W. Liu, X. Yang, Y. Gao, C.-J. Li, *J. Am. Chem. Soc.* **2017**, *139*, 8621–8627.
- [44] G. E. Collis, A. K. Burrell, S. M. Scott, D. L. Officer, *J. Org. Chem.* **2003**, *68*, 8974–8983.
- [45] L. D. Marciasini, J. Richard, B. Cacciuto, G. Sartori, M. Birepinte, L. Chabaud, S. Pinet, M. Pucheault, *Tetrahedron* **2019**, *75*, 164–171.
- [46] Y. Zhao, D. G. Truhlar, *Theor. Chem. Acc.* **2008**, *120*, 215–241.
- [47] a) A. J. H. Wachtors, *J. Chem. Phys.* **1970**, *52*, 1033–1036; b) P. J. Hay, *J. Chem. Phys.* **1977**, *66*, 4377–4384; c) A. D. McLean, G. S. Chandler, *J. Chem. Phys.* **1980**, *72*, 5639–5648; d) R. Krishnan, J. S. Binkley, R. Seeger, J. A. Pople, *J. Chem. Phys.* **1980**, *72*, 650–654; e) T. Clark, J. Chandrasekhar, G. W. Spitznagel, P. von R. Schleyer, *J. Comput. Chem.* **1983**, *4*, 294–301; f) K. Raghavachari, G. W. Trucks, *J. Chem. Phys.* **1989**, *91*, 1062–1065.
- [48] Gaussin 09, Revision A.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B.

- Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian, Inc.: Wallingford CT, 2009.
- [49] a) B. G. Johnson, M. J. Frisch, *Chem. Phys. Lett.* **1993**, *216*, 133–140; b) B. G. Johnson, M. J. Frisch, *J. Chem. Phys.* **1994**, *100*, 7429–7442; c) R. E. Stratmann, J. C. Burant, G. E. Scuseria, M. J. Frisch, *J. Chem. Phys.* **1997**, *106*, 10175–10183.
- [50] a) R. E. Stratmann, G. E. Scuseria, M. J. Frisch, *J. Chem. Phys.* **1998**, *109*, 8218–8224; b) R. Bauernschmitt, R. Ahlrichs, *Chem. Phys. Lett.* **1996**, *256*, 454–464; c) M. E. Casida, C. Jamorski, K. C. Casida, D. R. Salahub, *J. Chem. Phys.* **1998**, *108*, 4439–4449.
- [51] a) A. Klamt, G. Schüürmann, *J. Chem. Soc. Perkin Trans. 2* **1993**, 799–805; b) V. Barone, M. Cossi, *J. Phys. Chem. A* **1998**, *102*, 1995–2001; c) M. Cossi, N. Rega, G. Scalmani, V. Barone, *J. Comput. Chem.* **2003**, *24*, 669–681.
- [52] N. M. O'Boyle, A. L. Tenderholt, K. M. Langner, *J. Comput. Chem.* **2008**, *29*, 839–845.
- [53] Gaussview 3.0, Gaussian Inc.: Pittsburgh, 2003.

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RESEARCH ARTICLE



Synthesis of penta- and hexahelicenes with terminal thiophene rings is achieved by isomerization of *ortho,ortho'*-alkynyl-substituted teraryls using

Fürstner's method. Best results were obtained with JohnPhos-complexed gold(I) as catalyst.

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Synthesis of Thiophene-fused Helicenes

