Organic & Biomolecular Chemistry

Accepted Manuscript

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/obc

Journal Name

RSCPublishing

ARTICLE

Convenient access to readily soluble symmetrical dialkyl-substituted α-oligofurans†‡

Cite this: DOI: 10.1039/xoxxoooooox

Edward E. Korshin,*[a] Gregory M. Leitus[b] and Michael Bendikov[a]

Received ooth May 2014,
Accepted ooth 2014

DOI: 10.1039/xoxxoooooox

www.rsc.org/

An expedient approach to the synthesis of well soluble symmetrical dialkyl-substituted α-oligofurans containing up to 8 π-conjugated furan heterocycles is reported. An ultimate symmetry and high solubility of these α-oligofurans were guaranteed by using of 3,3′-diheptyl-2,2′-bifuran core and its symmetrical elongation through Suzuki-Miyaura or Stille cross-couplings. 3,3′-Diheptyl-2,2′-bifuran was prepared from 2,2′-bifuran-3,3′-dicarbaldehyde by the Wittig olefination and subsequent Pd/C-catalyzed transfer hydrogenation. The most appropriate access to 2,2′-bifuran-3,3′-dicarbaldehyde was achieved through a regioselective lithiation of 3-furanaldehyde acetal followed by $CuCl_2$-induced homocoupling and deprotection. Single crystal X-ray analysis of 2,2′-bifuran-3,3′-dicarbaldehyde revealed *anti*-arrangement of the furan rings in planar molecules and an unexpected for so small molecules tight herringbone-type packing in crystal.

Introduction

Since the discovery of highly conducting polyacetylene in 1977,[1] π-conjugated organic polymers and oligomers featured with electrons delocalization along the conjugated backbone have attracted an immense attention due to important applications in numerous types of organic electronic devices.[2,3] Advantageous electronic properties and good synthetic availability of variously substituted α-oligothiophenes and α-polythiophenes led these compounds to be the most popular π-conjugated materials.[3] However, unsubstituted α-poly- and α-oligothiophenes starting from α-sexithiophene are practically insoluble and hardly processable.[3,4] Attachment of solubilizing substituents at positions 3 and/or 4 results in twisting of thiophene-thiophene chain from an ideal for π-conjugation coplanar conformation.[5] Thus, an inherent low planar rigidity hampers significant optimization of the thiophene-based electronic materials.

Despite chemical dissimilarity between aromatic thiophene and more cyclic diene-type furan heterocycles, theoretical analysis predicted an essential similarity in the structural and electronic properties of the long α-oligothiophenes and α-oligofurans.[6] In 2001 Curtis *et. al.* reported that head-to-tail regioregular α-poly(3-octylfuran) exhibited conductivity comparable to that of the corresponding polythiophenes.[7] However, a presumption of intrinsic instability of α-oligofurans comprising more than four furan rings[8] survived until the year 2010 when Bendikov *et. al.* disclosed synthesis of unsubstituted α-oligofurans in up to nine furan units length.[9,10] Computational studies predicted elevated planar rigidity of α-oligofuran chain compared to α-oligothiophenes.[9,11] Indeed, unsubstituted α-oligofurans are highly fluorescent and have structured absorption and emission spectra, suggesting coplanar-type conformation in solution.[9,10] Raman spectroscopy evidenced that π-conjugation in α-oligofurans does not reach saturation up to α-octifuran.[12] In the planar ferrocene-capped α-oligofurans an excellent charge delocalization was observed.[13] The first experimental organic field-effect transistors with the active layer fabricated from unsubstituted α-octifuran, hexyl-caped α-sexi- and α-septifurans as well as from styryl-caped α-quaterfurans demonstrated high hole mobilities and on/off ratios akin to the observed in the corresponding oligothiophene-based devices.[14,15]

One of the major practical benefits of π-conjugated furan-based materials consists of enhanced solubility in comparison with the thiophene-based materials. For example, unsubstituted α-sexifuran is 20 times more soluble in chloroform than α-sexithiophene, but solubility of α-septifuran and the higher analogs is still transient.[9] Taking advantage of comparable electronic properties of the thiophene- and furan-based polymers

[a] *Department of Organic Chemistry, Weizmann Institute of Science, Rehovot 76100, Israel. E-mails: edward.korshin@weizmann.ac.il; edward.korshin@gmail.com*

[b] *Department of Chemical Research Support, Weizmann Institute of Science, Rehovot 76100, Israel.*

† In memory of Professor Michael Bendikov (deceased July 2, 2013).

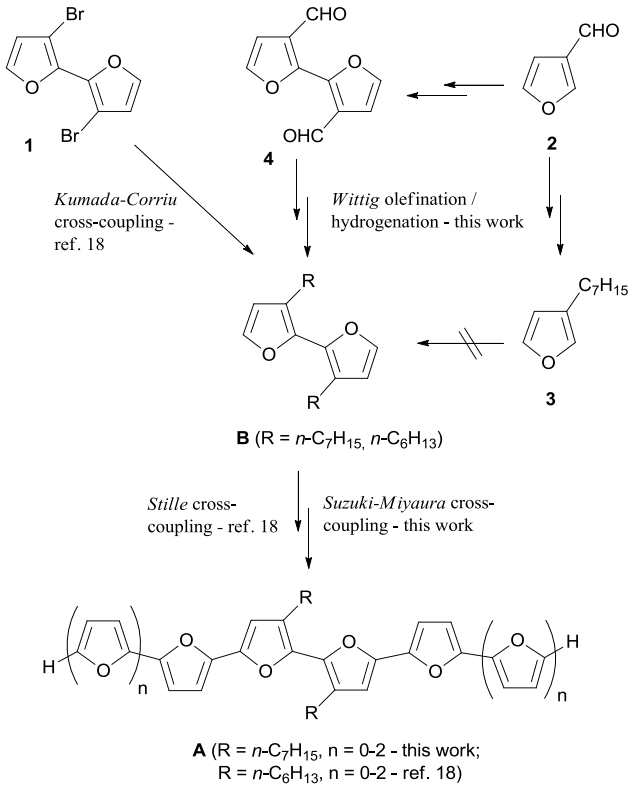
‡ Electronic Supplementary Information (ESI) available: Instrumentation, experimental procedures, details of X-ray measurement and refinement, copies of the NMR spectra. See DOI: 10.1039/b000000x/

with better solubilization of the latter's, Fréchet's[16] and Janssen's groups recently applied oligofuran-diketopyrrole copolymers for fabrication of remarkably efficient bulk heterojunction solar cells with 3-5% power conversion performance.[17]

The valuable optoelectronic properties and a reasonable processability of α-oligo- and α-polyfurans prompt to consider this type of compounds as an emerging alternative to the thiophene-based π-conjugated materials.[9-17] Yet, an assortment of the suitable for organic electronic applications furan-based π-conjugated compounds and convenient methods for their preparation is very limited and should be essentially extended. To address this quest, a study on the synthesis of the well soluble symmetrical disubstituted long α-oligofurans was initiated. This year, the first variant of the synthesis of dihexyl-substituted long α-oligofurans **A**, which was based on the Ni(II)-catalyzed Kumada-Corriu cross-coupling of 3,3′-dibromo-2,2′-bifuran (**1**) with hexylmagnesium bromide followed by bromination and the subsequent Stille cross-coupling, has been published (Scheme 1).[18] Herein, we disclose the details of an expedient complementary approach to the synthesis of similar symmetrical dialkyl-substituted α-oligofurans **A**, for example di-*n*-heptyl-derivatives, starting from furan-3-aldehyde (**2**). We demonstrate a possibility to synthesize these promising well-soluble π-conjugated oligomers by avoiding of highly toxic Ni(II)-complexes and organic tin reagents without essential affecting of the overall synthetic efficiency. A direct comparison of a scarcely exploited for formation of the α,α′-furan-furan junction Pd(II)-catalyzed Suzuki-Miyaura cross-coupling[17,19] and the only applied for assembling of the α-oligofuran chain Stille cross-coupling[8,9,12-16,18,20] revealed a comparable usefulness of both processes with a superior simplicity of the products purification in the first case.

Results and discussion

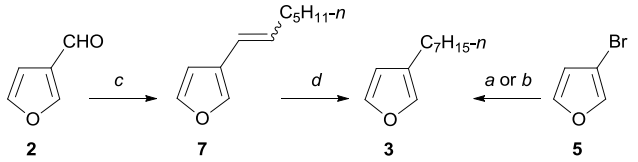
Our study was directed toward elaboration of a general approach to synthesis of symmetrical disubstituted α-oligofurans from simple commercially available furan reagents. In this paper, we describe preparation of the representative di-*n*-heptyl-substituted derivatives, which contain suitable for efficient solubilization of the molecules linear alkyl substituents. From the very beginning, we considered previously unknown 3,3′-dialkyl-2,2′-bifurans of type **B** (Scheme 1) as a valuable central entity, which could be symmetrically elongated to give the soluble long α-oligofurans **A**. However, no reliable methods for preparation of the bifurans **B** have been reported by the beginning of this work. Thus, though dibromide **1** was reported in the year 1978,[21] any reactivity of this compound was unrevealed before the year 2014.[18] As a model, Kumada-Corriu cross-coupling of the parent 3-bromofuran (**5**) with alkylmagnesiums to form the corresponding 3-alkylfurans was documented to be inefficient.[7,22] A complementary bromine-lithium exchange in **5** followed by alkylation with alkyl halides afforded 3-alkylfurans in modest yield.[23]



Scheme 1 General routes to dialkyl-substituted α-oligofurans **A**.

Based on the precedent of a viable CAN-induced head-to-head dimerization of 3-(pyrrol-2-yl)furans to 3,3′-bis(pyrrol-2-yl)-2,2′-bifurans,[24] at the outset of this work we considered an option of the most straightforward access to the bifuran **B** directly from 3-alkylfuran **3**. Following to the reported low-yielded procedures for 3-octyl-[7] and 3-propylfurans,[22] the starting 3-*n*-heptylfuran (**3**) was initially prepared by cross-coupling of 3-bromofuran (**5**) with a freshly generated *n*-heptylmagnesium bromide in the presence of (dppp)$NiCl_2$ or (dppe)$NiCl_2$ in 20% and 24% yield respectively (Scheme 2). Alkylation of **5** through a low-temperature bromine-lithium exchange with *n*-BuLi in THF/HMPA followed by alkylation with alkyl halide[23] failed completely with *n*-heptyl bromide and gave only 27% of **3** with *n*-heptyl iodide. On the other hand, Wittig olefination of the aldehyde **2** with *n*-hexyltriphenylphosphonium bromide (**6**) and LDA with subsequent Pd/C-catalyzed transfer hydrogenation[25,26] of the 3-alkenyl-intermediate **7** provided 3-*n*-heptylfuran (**3**) in reasonable yield (Scheme 2).

However, all our efforts toward preparatively suitable homocoupling of 3-heptylfuran (**3**) to form either head-to-head dimer **8** = **B** (R = *n*-C_7H_{15}) or other possible dimers were unsuccessful. In contrast to the recently reported homocoupling of 3-(pyrrol-2-yl)furans to 3,3′-bis(pyrrol-2-yl)-2,2′-bifurans,[24] similar treatment of **3** with CAN in aqueous acetonitrile as well as in the dry solvent at -20 °C led to complex reaction mixtures containing <5% of the desired bifuran **8**. It is known that 3-alkyl-substituents do not provide a valid differentiation of C-2 and C-5 positions in furans upon direct lithiation.[27] Indeed, lithiation of **3** with *n*-BuLi in THF followed by treatment with anhydrous

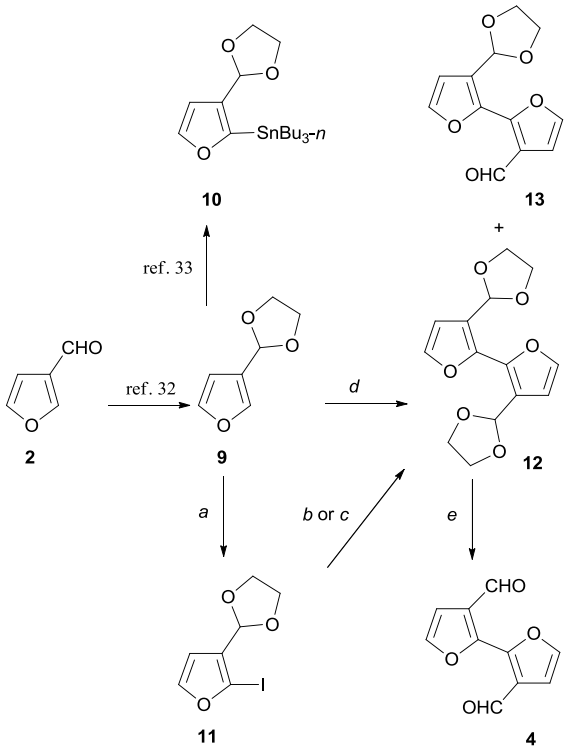


Scheme 2 Synthesis of 3-*n*-heptylfuran (**3**). *Reagents and conditions: a*, *n*-$C_7H_{15}MgBr$ (1.4 equiv.), $LNiCl_2$ (5 mol%), ether, reflux, 16 h, 20% if L = dppp, 24% if L = dppe; *b*, (*i*) *n*-BuLi (1.05 equiv.), THF, -78 °C, 1 h ; (*ii*) *n*-$C_7H_{15}I$ (1.3 equiv.), THF/HMPA, -60 °C, 14 h, 27%; *c*, (*i*) (*n*-C_6H_{13})Ph_3P^+ Br^- (**6**) (1.5 equiv.), LDA (1.5 equiv.), THF, -78 °C to r.t.; (*ii*) r.t., 14 h; d) $HCOO^-$ NH_4^+ (3.2 equiv.), 5% Pd/C (1.5 mol% Pd), MeOH, reflux, 2 h, 66% of **3** in two steps.

$NiCl_2$[28] or $CuCl_2$[29] resulted in regiorandom couplings to give inseparable mixtures of all three possible *bis*-heptyl-bifurans in 18%- and 32% total yields respectively and *ca.* 20% content of the head-to-head bifuran **8** in each mixture. Hence, further attempts on preparation of the bifuran **8** from 3-heptylfuran (**3**) were abandoned.

At this stage, we considered an alternative formation of **B** from 2,2′-bifuran-3,3′-dialdehyde (**4**) using the same olefination/hydrogenation sequence as for the preparation of **3** from aldehyde **2** (Scheme 2). The dialdehyde **4** was assumed to be derived from some acetal of the aldehyde **2** taking advantage from the heteroatom directed *ortho*-lithiation/coupling methodology.[30,31] Indeed, lithiation of the cyclic acetal **9**, which is readily available from aldehyde **2**,[32] in boiling ether followed by stannylation led to 2-tributylstannyl-derivative **10** exclusively.[33] Similarly to that, the supplementary 2-iodofuran-acetal **11** we prepared by lithiation of the acetal **9** in ether followed by the treatment of the corresponding 2-lithiofuran intermediate with molecular iodine. In the next step, a traditional for assembling of α,α′-furan-furan junction $(Ph_3P)_4Pd$-catalyzed Stille cross-coupling[8,9,12-16,18,20]of stannylfuran **10** with iodofuran **11** in boiling toluene afforded the head-to-head dimer **12** in 54% yield (Scheme 3).

An access to the head-to-head dimeric acetal **12** might be additionally simplified if a single precursor could be used. So, we attempted to dimerize the iodide **11** through the conventional Ullmann biaryl synthesis.[34] While all our attempts to accomplish a copper powder promoted reductive homocoupling of the iodoacetal **11** were unsuccessful, 14 h heating of **11** with excess zinc powder and KI in the presence of (dppp)$NiCl_2$ (30 mol%) in HMPA at 100-110 °C led to the diacetal **12** (20%) along with the aldehyde-acetal dimer **13** (6%). Finally, we were delighted to find that the diacetal **12** (63%) along with the minor aldehyde-acetal **13** (4%) could be prepared directly from the acetal **9** through its lithiation in THF followed by $CuCl_2$-promoted oxidative homocoupling (Scheme 3). Surprisingly, no head-to-tail and tail-to-tail dimers related to **12** were detected in the reaction mixture. A recently reported application of $NiCl_2$[28] instead of $CuCl_2$[29] almost arrested the coupling leading to poor yields of **12** (5%) and **13** (1%). When lithiation of **9** and subsequent $CuCl_2$-induced coupling were carried out in ether, poor solubility of $CuCl_2$ and the copper-containing intermediates in this media



Scheme 3 Synthesis of 2,2′-bifuran-3,3′-dicarbaldehyde (**4**). *Reagents and conditions: a*, (*i*) *n*-BuLi (1.1 equiv.), ether, -78 °C to r.t.; (*ii*) I_2 (1.1 equiv.), THF, -78 °C to rt, 57%; *b*, **10** (1.45 equiv.), $(Ph_3P)_4Pd$ (5 mol%), toluene, reflux, 8 h, 54% of **12**; *c*, (dppp)$NiCl_2$ (30 mol%), KI (2 equiv.), Zn powder (4 equiv.), HMPA, 100-110 °C, 14 h; 20% of **12** and 6% of **13**; *d*, (*i*) *n*-BuLi (1.05 equiv.), THF, -78 °C to 0 °C; (*ii*) $CuCl_2$ (1.05 equiv.), -78 °C to rt, 63% of **12** and 4% of **13**; *e*, glyoxalic acid monohydrate (12 equiv.), *p*-TsOH monohydrate (6 mol%), dichloromethane, rt, overnight, 98%.

affected feasibility of the process, resulting in 16% yield of **12** and 2% of **13**. In the next step, diacetal **12** was mildly deprotected with excess glyoxalic acid monohydrate[35] and catalytic amount of *p*-TsOH monohydrate in methylene chloride to give the *bis*-aldehyde **4** in 98% yield (Scheme 3). A similar deprotection of the aldehyde-acetal **13** afforded the dialdehyde **4** quantitatively. Molecular structure of the head-to-head dimeric dialdehyde **5** was determined by ^1H- and ^{13}C NMR, IR-spectra, HRMS, and detailed by single crystal X-ray analysis (Fig. 1).[36]

Unlike the only reported for 3,3′-substituted 2,2′-bifurans X-ray structure of 3,3′-bis(pyrrol-2-yl)-2,2′-bifuran, which is characterized by a highly twisted *syn*-conformation of the furan rings,[24] molecules of dialdehyde **4** in a solid state are C_2-symmetrical with a planar *anti*-conformation of the furan rings (Fig. 1a). A planar *anti*-conformation is typical for all the previously X-ray studied unsubstituted in positions 3 and 4 α-oligofurans[9,13,15]and α-bifurans.[20,37-39] Noteworthy, planarity of the oligofuran backbone is almost unaffected even by the head-to-head junction in 3‴,4‴-dihexyl α-sexifuran.[18] The inter-furan C2–C2′ bond in bifuran-dialdehyde **4** is 1.4370 (11) Å. This bond length is similar to that of longer α-oligofurans (1.431-1.439 Å),[9]

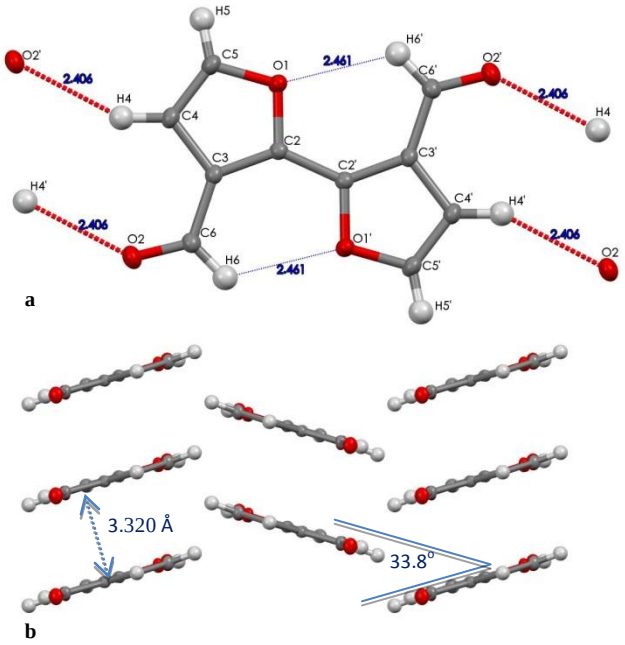


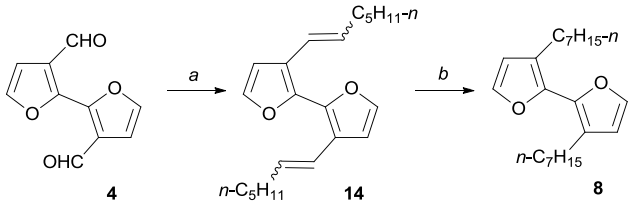
Fig. 1 (*a*) Crystal structure (ellipsoid presentation at 50% of probability) of 2,2′-bifuran-3,3′-dicarbaldehyde (**4**) molecule.[36] Hydrogen bonds are shown: intramolecular O1···H6 bond 2.4612(5) Å and intermolecular O2···H4′ bond 2.4061(5) Å. The O2···H4′ and O2′···H4 intermolecular bonds combine molecules **4** in infinite plane chains lying in planes (111) and (1-11). (*b*) Herringbone-type packing of the molecule **4** chains (view along the [1 0 -1] direction).

5,5′-di(thien-2-yl)-2,2′-bifuran (1.434 Å),[37a] and 2,2′-bithieno[3,2-b]furan (1.432 Å),[38] and slightly shorter compared to C5″–C2‴ bond length in 3‴,4"-dihexyl α-sexifuran (1.449-1.451 Å).[18] In the solid state planar structure of **4** short intramolecular contacts between hydrogen atoms of the aldehyde groups and the oxygen atoms of the neighboring furan rings (H6···O2′ 2.4612 Å) are observed. According to the NMR data, the planar *anti*-conformation of **4** is likely preserved in $CDCl_3$ solution. Indeed, in the ^{1}H NMR spectra of **4** the aldehyde proton is detected as a broadened singlet at δ 10.50 ppm. This proton is considerably deshielded compared to the corresponding aldehyde proton in the additional furan ring lacking 3-formyl- and in 2-methyl-3-formylfuran (δ 9.90-9.95 ppm)[40] as well as in 2-phenyl-3-formylfuran (δ 10.15 ppm).[41] A noticeable low field chemical shift of the aldehyde proton in **4** is probably resulted from a through the space deshielding by a closely positioned electronegative oxygen atom, which could be effective at such a short distance between the atoms as shown in Fig. 1a. A similar strong through the space deshielding of methylene protons by proximal oxygen atoms we earlier observed in the 2,3-dioxabicyclo[3.3.1]nonane series.[42]

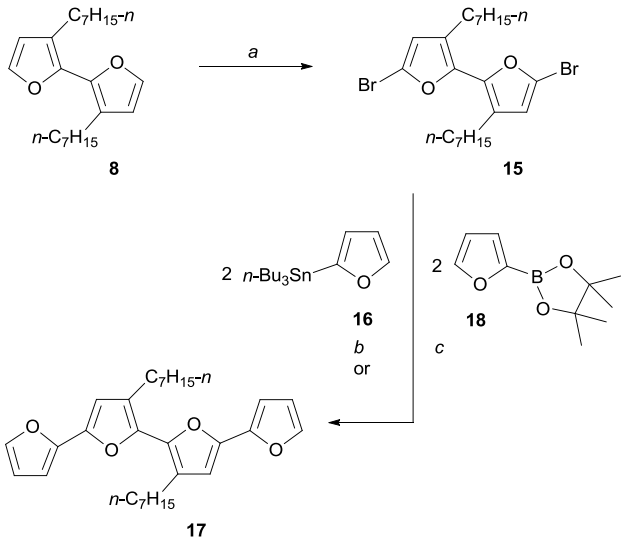
Unexpectedly, the packing of **4** is more similar to the packing of unsubstituted α-sexifuran than to the less regular packing of the more structurally related α-terfuran.[9] The bifuran dialdehyde molecules **4** are combined by two hydrogen O2···H4′ bonds 2.4061(5) Å in planar chains. The chains lie in planes (111) and (1-11), forming a herringbone structural motif (Fig. 1b) with angle 146.22(4)°. The herringbone angle of 33.8° is much more acute than that of α-sexifuran.[9] Two adjacent chains are connected with O2···H5 bonds 2.5396(4) Å. The distance between two parallel chains is 3.320(1) Å. Overall, the molecules of 2,2′-bifuran-3,3′-dicarbaldehyde (**4**) are surprisingly tightly packed in crystals, and such a tight packing is reflected in an unpredictably high melting point (184 °C) and density (D_c = 1.574 g/cm^3).

Having an optimized access to dialdehyde **4**, we processed it further to 3,3′-di-*n*-heptyl-2,2′-bifuran (**8**) (Scheme 4). Thus, Wittig olefination of dialdehyde **4** with excess of the phosphorane, generated *in situ* from the phosphonium salt **6** and LDA, led to the corresponding 3,3′-*bis*-alkenyl-derivative **14** as a mixture of *E*- and *Z*-isomers almost quantitatively. Subsequent Pd/C-catalyzed transfer hydrogenation of **14** with excess ammonium formate as a hydrogen source in boiling methanol afforded 90% of the desired 3,3′-di-*n*-heptylbifuran (**8**) as a colorless mobile oil. Being solidified at -25 °C, bifuran **8** could be stored for years as a stock precursor for longer α-oligofurans. Apparently, application of other reagents to olefination of dialdehyde **4** and the following hydrogenation would enable access to a variety of 3,3′-disubstituted-2,2′-bifurans structurally related to **8**.

Following a traditional approach to the synthesis of α-oligo- and α-polyfurans through the Stille coupling of the corresponding 2-furylstannanes and 2-bromofurans,[8,9,13-16,18,20] we performed a bromination of bifuran **8** with NBS to obtain the corresponding 5,5′-dibromo-2,2′-bifuran **15** in up to 98% yield (Scheme 5). A freshly generated dibromide **15** could be purified by flash chromatography (FC) on silica gel in the dark and isolated in the NMR pure state as yellowish oil solidified at -25 °C. However, inherent instability of the dibromide **15** required its use in the next transformations as soon as possible, without any storage.[43] In the next step, $(Ph_3P)_4Pd$-catalyzed reaction of the freshly prepared dibromide **15** with 2-furylstannane **16** in boiling toluene afforded the diheptyl-substituted quaterfuran **17** in high yield. However, huge amount of hardly removable tin-contaminants are ultimately formed in the Stille cross-coupling, and at least three sequential FC was required for isolation of **17**



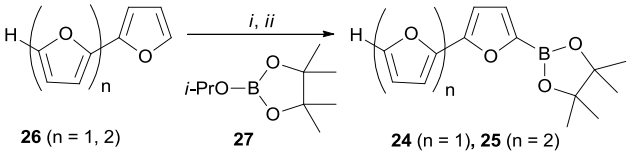
Scheme 4 Synthesis of 3,3′-di-*n*-heptyl-2,2′-bifuran (**8**). *Reagents and conditions: a*, (*i*) (*n*-C_6H_{13})Ph_3P^+ Br^- (**6**) (5.75 equiv.), LDA (5.8 equiv.), THF, -78 °C to rt; (*ii*) 50-60 °C, 4 h, 98% (*E*-/*Z*- *ca.* 1 : 1); *b*, $HCOO^-$ NH_4^+ (10 equiv.), 5% Pd/C (2 mol% Pd), MeOH, reflux, 1 h, 90%.



Scheme 5 Synthesis of 3′,3″-di-*n*-heptyl-2′,2″-quaterfuran (**17**). *Reagents and conditions: a*, NBS (2.03 equiv.), benzene-CH_2Cl_2, rt, 2 h, 98%; *b*, **16** (2.5 equiv.), $(Ph_3P)_4Pd$ (10 mol%), toluene, reflux, 8 h, 90%; *c*, **18** (3 equiv.), $Pd(OAc)_2$ (7 mol%), XPhos (14 mol%), K_3PO_4 (6 equiv.), 1,4-dioxane-H_2O (10 : 1), 55-60 °C, 12 h, 73%.

of ≥95% purity.[44] Since both stability and the yield of α-oligofurans are essentially decreased with elongation of the π-conjugated system,[8,9] it was highly desirable to identify a viable synthetic method which granted an easier purification of these sensitive compounds. We were delighted to find that quaterfuran **17** could be efficiently synthesized through an almost uncharted for the preparation of α-oligofurans Suzuki-Miyaura cross-coupling.[17,19] Indeed, after fruitless experiments with 2-furylboronic acid and potassium 2-furyltrifluoroborate, a mild heating of the dibromide **15** with 2-(2-furyl)-1,3,2-dioxaborolane **18**[45,46] in dioxane-water (10 : 1) in the presence of catalytic amount of $Pd(OAc)_2$ and XPhos afforded pure quaterfuran **17** in 73% yield after one FC only (Scheme 5).

Bromination of the quaterfuran **17** with NBS afforded 5,5‴-dibromoquaterfuran **19**, which was isolated by FC as an unstable yellow solid.[43] Being considerably more labile comparing to dibromobifurane **15**, a purified **19** spontaneously exothermically decomposed over less than an hour at rt. Though dibromoquaterfuran **19** could be used without isolation in the Stille coupling with big excess **16** to give diheptylsexifuran **20** in 12% yield after tedious FC purifications,‡ for more reasonable access to **20** and to diheptyloctifuran **21** we turned to the cross-couplings of more stable dibromobifuran **15**. In fact, all the previously reported syntheses of α-sexifurans and α-octifurans were achieved using Stille coupling of 5,5′-dibromo-2,2′-bifurans with 5-tributyltin-2,2′-bifuran (**22**) and 5-tributyltin-2,2′:5′,2″-terfuran (**23**) respectively.[9,18] For elongation of α-oligofuran chain through Suzuki-Miyaura reaction α-oligofuran pinacolboronates **24** (n = 1) and **25** (n = 2) were prepared by lithiation of bifuran **26** (n = 1) or terfuran **26** (n = 2) followed by borylation with 2-*iso*-propoxy-1,3,2-dioxaborolane **27** (Scheme 6).

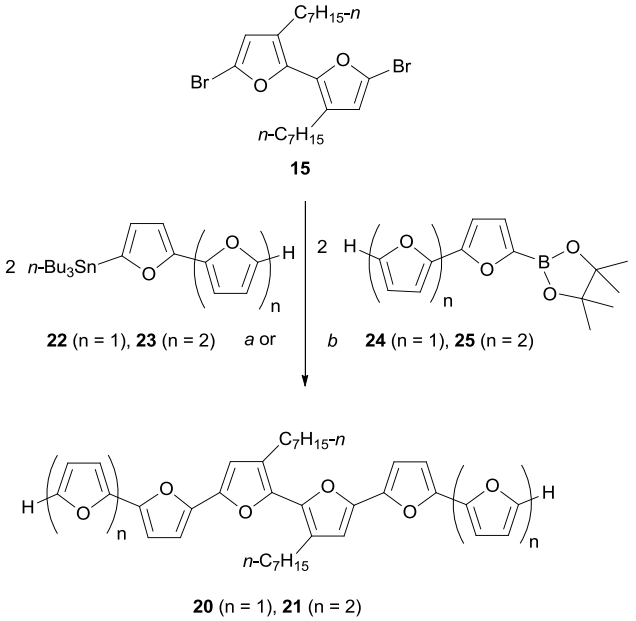


Scheme 6 Preparation of 2-(α-oligofur-5-yl)-1,3,2-dioxaborolanes **24** and **25**. *Reagents and conditions: i*, *n*-BuLi (1.15 equiv.), THF, -78 °C to 0 °C; *ii*, **27** (1.4 equiv.), -78 °C to rt, overnight at rt; 49% of **24** and 33% of **25**.

$(Ph_3P)_4Pd$-Catalyzed Stille cross-coupling of the dibromobifuran **15** with 3 equiv. of 5-stannylbifuran **22** in boiling toluene afforded the diheptyl-substituted α-sexifuran **20**, which was isolated by sequential FC in 41% yield (Scheme 7). Upon using of 5-stannylated terfuran **23** in the Stille coupling with dibromide **15**, diheptyl-substituted α-octifuran **21** was prepared in 23%r yield. The supplementary $Pd(OAc)_2$/XPhos-catalyzed Suzuki-Miyaura cross-coupling of **15** with excess of the bifurane-pinacolboronate **24** gave 35% yield of α-sexifuran **20**. α-Octifuran **21** (19%) was also synthesized through a similar Suzuki-Miyaura cross-coupling of **15** with 5-terfurylboronate **25** (Scheme 7).

All the cross-couplings depicted in Scheme 7 are evidently accompanied with a number of competing processes. Particularly, protodeboronation[47] of the α-oligofurylboronates **24** and **25** resulting in the release of α-bifuran **26** (n = 1) or α-terfuran **26** (n = 2) was detected in the syntheses of long α-oligofurans **20** and **21** by Suzuki-Miyaura reactions. TLC monitoring revealed a premature consumption of the boronates **24** and **25** after 8 h warming at 55-60 °C, while considerable amount of dibromide **15** still remained in the reaction mixture. So, second portions of boronates **24** and **25** were added for completion of the Suzuki-Miyaura cross-couplings, and heating of the reaction mixtures was continued for additional 8 h. In another vein, substantial amounts of α-quaterfuran and α-sexifuran resulted from the Pd-catalyzed deboronative homocoupling[48,49] of α-oligofurylboronates **24** and **25** were also isolated in the studied Suzuki-Miyaura reactions. Similar destannylative homocouplings,[50] albeit at the less extent, were observed in the Stille cross-couplings of the dibromide **15** with 5-stannyl-α-oligofurans **22** and **23**. For the time being, we did not succeed in suppressing of these competing processes without affecting the desired cross-couplings.

Both applied Stille and Suzuki-Miyaura cross-couplings provided very moderate yields of the soluble long α-oligofurans **20** and **21** (Scheme 7). On the other hand, the previously reported hardly soluble unsubstituted α-oligofurans were isolated in even lower yields using a time-consuming vacuum sublimation as a purification technique.[9] The isolated yields of α-oligofurans **20** and **21** were slightly lower in the Suzuki-Miyaura couplings comparing to the Stille alternative. From a practical point of view, faintly lower yields in the developed Suzuki-Miyaura reactions are overcompensated by avoiding of the poisonous organic tin compounds as well as by the less laborious isolation of the products (only 2-3 FC were required for purification in the



Scheme 7 Synthesis of long α-oligofurans **20** and **21**. *Reagents and conditions: a*, **22** or **23** (3 equiv.), $(Ph_3P)_4Pd$ (10 mol%), toluene, reflux, 12 h, 41% yield of **20** or 23% of **21**; *b*, **24** or **25** (3 + 2 equiv.), $Pd(OAc)_2$ (8 mol%), XPhos (16 mol%), K_3PO_4 (6 equiv.), 1,4-dioxane/H_2O (10 : 1), 55-60 °C, 8 + 8 h, 34% yield of **20** or 21% of **21**.

case of boron instead of 5-6 FC in the case of tin).

The long α-oligofurans **20** and **21** are reasonably stable, high melting point deep-yellow and yellow-orange solids respectively, soluble in most organic solvents. For example, a solubility of **20** and **21** in C_6D_6 is more than 10 mg/mL. A similar solubility was observed in 1,4-dioxane and in propylene carbonate, which could be also used for a formulation of relatively stable solutions.

Diheptyl-substituted sexifuran **20** and octifuran **21** were characterized by 1D and 2D (COSY, HSQC and HMBC) NMR, and by the field desorption (FD) HRMS, which gave intensive $[M]^+$-peaks. The UV/Vis and fluorescence spectra of diheptyl-substituted α-sexifuran **20** and α-octifuran **21**, which are essential for characterization of π-conjugated compounds, were found to be very similar to the thoroughly discussed data for dihexyl-substituted analogues.[18] Evaluation of the synthesized α-oligofurans **20** and **21** as potential organic electronic materials will be reported in due course of the study.

Conclusions

In summary, we elaborated a convenient 7-step synthesis of symmetrical and well soluble dialkyl-substituted long α-oligofurans from the commercially available furan-3-aldehyde. In the key step of the synthesis, acetal of furan-3-aldehyde was subjected to regioselective heteroatom-directed lithiation followed by $CuCl_2$-induced homocoupling to give the head-to-head dimer. A mild deprotection of the latter afforded 2,2′-bifuran-3,3′-carbaldehyde. High yielding attachment of the *n*-heptyl substituents to give 3,3′-diheptyl-2,2′-bifuran was accomplished through a Wittig olefination followed by Pd/C-catalyzed transfer hydrogenation. Subsequent bromination led to the corresponding 5,5′-dibromo-2,2′-bifuran. It was converted to the final diheptyl-substituted long α-oligofurans using either rarely applied for assembling of the α-oligofuran junction Suzuki-Miyaura cross-coupling or conventional Stille cross-coupling. Both processes resulted in similar yields of α-oligofurans, but much less laborious purifications of the products were required in the case of Suzuki-Miyaura reactions.

Experimental section‡

Synthesis of 3,3'-di(1,3-dioxolan-2-yl)-2,2'-bifuran (12) and 3'-(1,3-dioxolan-2-yl)-[2,2'-bifuran]-3-carbaldehyde (13) through a one-pot lithiation of 3-(1,3-dioxolan-2-yl)furan (9) followed by $CuCl_2$-induced homocoupling. To a solution of **9** (2.170 g, 15.485 mmol) in dry THF (20 mL) at -78 °C a solution of *n*-BuLi (6.5 mL of 2.5M in hexane, 16.25 mmol, 1.05 equiv) was added. The heterogeneous reaction mixture was allowed to warm to ambient temperature and stirred for 1 h. The reaction mixture was cooled to -78 °C, and solid $CuCl_2$ (2.189 g, 16.28 mmol, 1.05 equiv) was added in 3 portions (with 10 min interval between additions) under overpressure of argon and intensive stirring. The reaction mixture was stirred for 1 h at to -78 °C, for 2 h at -35 °C, for 1 h at 0 °C and for 2 h at r.t. After cooling to 0 °C, the reaction mixture was quenched by addition of solid NH_4Cl (883 mg, 16.5 mmol), stirred for 30 min at 0 °C and 30 min at rt. The mixture was diluted with ether (100 mL) and stirred for 1 h for better sedimentation of inorganic black precipitate. A supernatant solution was filtered via a plug of anhydrous Na_2SO_4, and the remaining black precipitate was thoroughly extracted with ether-EtOAc (3 : 7). All the extracts were filtered; the combined organic solution was washed with 10% aq. solution of glycine (2 x 75 mL), water, satd. $NaHCO_3$ and brine, dried over $MgSO_4$. The solution was filtered, evaporated, the residue was subjected to flash chromatography (FC) on silica gel (gradient elution, from 5% to 40% EtOAc-hexane) to give the acetal-dimer **12** (1.362 g, 63%) and the aldehyde-acetal dimer **13** (78 mg, 4%).

Acetal-dimer 12. Colorless solid; m.p. 120-121 °C; R_f 0.26 (EtOAc-hexane = 2 : 3); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.44 (d, J = 2.0 Hz, 2H), 6.60 (d, J = 2.0 Hz, 2H), 6.20 (s, 2H), 4.18-3.98 (sym m, 8H); ^{13}C NMR ($CDCl_3$, 126 MHz): δ 143.57 (C), 142.58 (CH), 121.12 (C), 110.04 (CH), 97.63 (CH), 65.30 (2 CH_2); HRMS (FD): calcd for $C_{14}H_{14}O_6$ $[M]^+$ 278.0790; found 278.0797.

Aldehyde-acetal dimer 13. Yellowish solid; m.p. 89-91 °C, R_f 0.30 (EtOAc-hexane = 2 : 3); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 10.41 (br s, 1H), 7.54 (br d, J = 1.8 Hz, 1H), 7.44 (dd, J = 2.0, 0.8 Hz, 1H), 6.88 (br d, J = 2.0 Hz, 1H), 6.70 (br d, J = 1.8 Hz, 1H), 6.29 (s, 1H), 4.20-4.02 (sym m, 4H); ^{13}C NMR ($CDCl_3$, 126 MHz): δ 186.13 (CH=O), 151.23 (C), 144.23 (CH), 143.20 (CH), 142.85 (C), 124.58 (C), 124.10 (C), 110.99 (CH), 108.81 (CH), 97.25 (CH), 65.47 (2 CH_2); IR (CH_2Cl_2): ν 3157 (w), 3131 (w), 3060 (w), 2959 (m), 2929 (w), 2891 (m), 1673 (vs) (C=O), 1481 (m, br), 1397 (m), 1172 (s), 1116 (s, br), 1077 (s), 1033 (s), 888 (s) cm^{-1}; HRMS (FD): calcd for $C_{12}H_{10}O_5$ $[M]^+$ 234.0528; found 234.0534.

2,2'-Bifuran-3,3'-dicarbaldehyde (4). A heterogeneous mixture of the acetal-dimer **12** (1.285 g, 4.618 mmol), glyoxalic acid monohydrate (5.10 g, 55.415 mmol, 12.0 equiv.) and *p*-TsOH monohydrate (57 mg, 0.300 mmol, 0.065 equiv.) in CH_2Cl_2 (50 mL) was stirred for 12 h at rt. Water (40 mL) was added, and the

mixture extracted with CH_2Cl_2. The combined organic layer was washed with satd. $NaHCO_3$ and dried over $MgSO_4$. Filtration, evaporation, followed by purification by FC on silica gel (gradient elution, from 25% to 50% EtOAc in hexane) afforded the title dialdehyde **4** (860 mg, 98%) as pale yellow shining crystals; m.p. 184 °C; R_f 0.29 (EtOAc-hexane = 3 : 7). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 10.50 (br s, 2H), 7.57 (dd, J = 2.0, 0.6 Hz, 2H), 6.98 (br d, J = 2.0 Hz, 2H); ^{13}C NMR ($CDCl_3$, 126 MHz): δ 185.38 (CH=O), 149.50 (C), 144.85 (CH), 126.08 (C), 109.69 (CH); IR (CH_2Cl_2): ν 3157 (w), 3133 (w), 3060 (w), 2927 (w), 2890 (w), 2863 (w), 1673 (vs) (C=O), 1540 (m), 1478 (m), 1397 (s), 1172 (s), 1034 (m), 888 (s) cm^{-1}; HRMS (FD): calcd for $C_{10}H_6O_4$ $[M]^+$ 190.0266; found 190.0271.

3,3'-Di-*n*-heptyl-2,2'-bifuran (8).

*(i) Preparation of 3,3'-di-(n-hept-1-en-1-yl)-2,2'-bifuran (**14**).* To a cold (-78 °C) suspension of phosphonium salt **7** (6.656 g, 15.22 mmol, 5.74 equiv.) in dry THF (40 mL) a solution of LDA (7.7 mL of 2 M sol-n in THF-heptane-ethyl benzene, 15.4 mmol) was added dropwise. The deep orange reaction mixture was stirred at rt for 1 h and cooled again to -78 °C. Solid *bis*-aldehyde **4** (504 mg, 2.65 mmol) was added in one portion under overpressure of dry argon. The reaction mixture was stirred at rt overnight and heated at 50-60 °C for 4 h. The reaction was quenched by addition of solid NH_4Cl (1.07g, 20.0 mmol); the mixture was stirred for 30 min at rt and for 1 h at 50-60 °C. The mixture was diluted with ether (100 mL). After sedimentation of precipitate the mixture was filtered through a plug of Na_2SO_4 and evaporated. FC on silica gel (hexane) gave the title *bis*-alkenyl-derivative **14** (851 mg, 98%, a mixture of *E*- and *Z*-isomers *ca.* 45:55) as a yellowish mobile oil; R_f 0.36 (hexane). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.43 (br dd, J = 3.5, 1.9 Hz, 1.1H), 7.31 (br dd, $J \approx$ 2.2, 2.2 Hz, 0.9H), 6.69 (br dd, J = 15.8, 1.2 Hz, 0.9H), 6.62 (dd, J = 3.5, 1.9 Hz, 1.1H), 6.60 (br dd, $J \approx$ 2.2, 2.2 Hz, 0.9H), 6.52 (br d, J = 11.5 Hz, 1.1H), 6.02 (dt, J = 15.8, 7.0 Hz, 0.9 H), 5.61 (dt, J = 11.5, 7.2 Hz, 1.1H), 2.32 (dtd, J = 7.2, 7.2, 1.8 Hz, 2.2 H), 2.17 (br dtdd, $J \approx$ 7.0, 7.0, 1.6, 1.6 Hz, 1.8H), 1.51-1.42 (m, 4H), 1.37-1.30 (m, 8H), 0.92-0.87 (m, 6H); ^{13}C NMR ($CDCl_3$, 126 MHz): δ 143.48, 143.29 and 141.63 (C); 142.44, 142.21, 141.95 and 141.74 (CH); 132.77 and 132.72 (CH); 132.04 and 131.98 (CH); 121.94, 121.52, 120.36 and 119.95 (C); 120.14 and 120.10 (CH); 119.03 and 119.02 (CH); 112.11 and 112.08 (CH); 108.84 and 108.82 (CH); 33.15, 33.12, 31.63, 31.47, 31.45, 29.41, 29.39, 29.20, 29.15, 28.97, 28.95, 22.57 (CH_2); 14.06 (CH_3); MS (ESI): *m/z* (%) 327.2 (100%) $[M + H]^+$, 349.1 (92%) $[M + Na]^+$, 365.2 (53%) $[M + K]^+$.

*(ii) Hydrogenation of 3,3'-di-(n-hept-1-en-1-yl)-2,2'-bifuran (**14**).* A mixture of ***E/Z*-14**, (840 mg, 2.573 mmol), ammonium formate (1.622 g, 25.73 mmol, 10 equiv.) and 5% Pd/C (105 mg; 0.049 mmol Pd, 1.9 mol%) in MeOH (40 mL) was intensively stirred for 1.5 h at rt under overpressure of argon and gently refluxed for 1 h. The reaction mixture was diluted with ether (100 mL), filtered via a cotton wool and concentrated to *ca.* 5 mL volume. The concentrate was diluted with water (60 mL) and extracted with 25% EtOAc-hexane. The combined organic phase was washed with satd. $NaHCO_3$ and brine, dried over $MgSO_4$. Filtration, evaporation followed by FC on silica gel (hexane) afforded bifuran **8** (763 mg, 90%) as a colorless mobile oil; R_f 0.50 (hexane). ^{1}H NMR (C_6D_6, 500 MHz): δ 7.10 (d, J = 1.8 Hz, 2H), 6.16 (d, J = 1.8 Hz, 2H), 2.76 (t, J = 7.7 Hz, 4H), 1.60 (br tt, $J \approx$ 7.5, 7.5 Hz, 4H), 1.35-1.28 (m, 4H), 1.28-1.16 (m, 12H), 0.87 (t, J = 7.0 Hz, 6H); ^{13}C NMR (C_6D_6, 126 MHz): δ 143.05 (C), 141.32 (CH), 123.03 (C), 113.05 (CH), 32.17 (CH_2), 30.79 (CH_2), 29.67 (CH_2), 29.52 (CH_2), 25.37 (CH_2), 23.03 (CH_2), 14.29 (CH_3); HRMS (FD): calcd. for $C_{22}H_{34}O_2$ $[M]^+$ 330.2559; found 330.2564.

5,5'-Dibromo-3,3'-di-*n*-heptyl-2,2'-bifuran (15).[43] To a solution of 3,3'-diheptyl-2,2'-bifuran (**8**) (305 mg, 0.923 mmol) in dry benzene (6 mL) and CH_2Cl_2 (1 mL) solid NBS (334 mg, 1.876 mmol, 2.03 equiv.) was added. The covered with aluminum foil reaction mixture was stirred for 2 h at rt. The reaction mixture was poured into 10% aqueous $Na_2S_2O_3$ (20 mL), and extracted with EtOAc-hexane (1 : 2). The organic extract was washed with satd. $NaHCO_3$ and brine, dried over $MgSO_4$. Filtration, evaporation followed by FC on silica gel (hexane) gave dibromide **15** (442 mg, 98%) as an unstable colorless solid; R_f 0.56 (hexane). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 6.26 (s, 2H,), 2.52 (t, J = 7.6 Hz, 4H), 1.53 (br tt, $J \approx$ 7.5, 7.5 Hz, 4H), 1.38-1.22 (m, 16H), 0.88 (t, J = 6.9 Hz, 6H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 142.76 (C), 126.55 (C), 121.21 (C), 114.18 (CH), 31.78 (CH_2), 29.93 (CH_2), 29.13 (CH_2), 29.01 (CH_2), 24.89 (CH_2), 22.65 (CH_2), 14.09 (CH_3); HRMS (FD): calcd. for $C_{22}H_{32}{}^{79}Br^{81}BrO_2$ $[M]^+$ 488.0749; found 488.0744 (correct isotope pattern).

3'',4'-Di-*n*-heptyl-2,2':5',2'':5'',2'''-quaterfuran (17).

a) Synthesis of 17 through the Stille cross-coupling. A solution of a freshly prepared dibromide **15** (383 mg, 0.784 mmol), 2-tributylstannylfuran (**16**) (700 mg, 1.960 mmol, 2.5 equiv.) and $(Ph_3P)_4Pd$ (91 mg, 0.0784 mmol, 10 mol%) in dry toluene (8.0 mL) was gently refluxed for 8 h. The resulted mixture was evaporated, subjected to two sequential FC on silica gel (hexane) and, finally, on Et_3N-pretreated silica gel[44] to give the title quaterfuran **17** (327 mg, 90%).

b) Synthesis of 17 through the Suzuki-Miyaura cross-coupling. A mixture of a freshly prepared dibromide **15** (251 mg, 0.514 mmol), 2-furylpinacolborolane (**18**) (300 mg, 1.545 mmol, 3 equiv.), $Pd(OAc)_2$ (8.2 mg, 0.036 mmol, 7 mol%), XPhos (34.3 mg, 0.072 mmol, 14 mol%) and K_3PO_4 (658 mg, 3.10 mmol, 6 equiv.) in 1,4-dioxane-water (10 : 1, total 6.6 mL) was stirred at 55-60 °C for 12 h. The resulted mixture was diluted with water (50 mL) and extracted with 10% EtOAc in hexane. The combined organic extract was washed with water and brine, dried over $MgSO_4$. Filtration, evaporation followed by FC on Et_3N-pretreated silica gel[44] (hexane) afforded the quaterfuran **17** (173 mg, 73%).

Diheptyl quaterfuran 17. A colorless oil; R_f 0.22 (hexane); ^{1}H NMR (C_6D_6, 500 MHz): δ 7.04 (dd, J = 1.8, 0.7 Hz, 2H), 6.58 (s, 2H), 6.55 (br d, J = 3.4 Hz, 2H), 6.12 (dd, J = 3.4, 1.8 Hz, 2H), 2.80 (t, J = 7.7 Hz, 4H), 1.64 (br tt, $J \approx$ 7.5, 7.5 Hz, 4H), 1.41-1.35 (sym m, 4H), 1.31-1.18 (m, 12H), 0.88 (t, J = 7.0 Hz, 6H); ^{13}C NMR (C_6D_6, 126 MHz): δ 147.22 (C), 145.43 (C), 142.23 (C), 142.03 (CH), 125.01 (C), 111.69 (CH), 109.18 (CH), 105.33 (CH), 32.26 (CH_2), 30.62 (CH_2), 29.85 (CH_2), 29.71 (CH_2), 25.63 (CH_2), 23.04 (CH_2), 14.32 (CH_3); HRMS (FD): calcd. for $C_{30}H_{38}O_2$ $[M]^+$ 462.2770; found 462.2777.

2-([2,2'-Bifuran]-5-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (24). To a solution of 2,2'-bifuran (**26**, n = 1) (975 mg, 7.274 mmol) in dry THF (12 mL) at -78 °C a solution of *n*-BuLi in hexane (5.2 mL of 1.6 M solution, 8.3 mmol, 1.15 equiv.) was added. The reaction mixture was allowed to warm to rt, stirred for 2 h and cooled again to -78 °C. A solution of 2-isopropoxypinacolborolane (**27**) (1.98 g, 10.20 mmol, 1.4

equiv.) in THF (5 mL) was added over 5 min. The reaction mixture was stirred at -78 °C for 1 h and at rt overnight. After cooling to 0 °C the reaction was quenched by addition of AcOH (0.60 g, 10.0 mmol) in ether (5 mL). The resulted mixture was stirred for 30 min at 0 °C, poured into cold water, and extracted with 50% EtOAc-hexane. The combined organic phase was washed with water and brine, dried over $MgSO_4$. Filtration, evaporation followed by sequential FC on silica gel (gradient elution, from 5% to 30% EtOAc in hexane) gave the title boronate **24** (920 mg, 49%) as a colorless solid; m.p. 68-69 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.41 (dd, J = 1.8, 0.7 Hz, 1H), 7.11 (d, J = 3.5 Hz, 1H), 6.73 (dd, J = 3.4, 0.7 Hz, 1H), 6.59 (d, J = 3.5 Hz, 1H), 6.44 (dd, J = 3.4, 1.8 Hz, 1H), 1.35 (s, 12H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 150.87 (C), 146.39 (C), 142.15 (CH), 125.19 (CH), 111.44 (CH), 106.68 (CH), 105.86 (CH), 84.17 (C), 24.67 (CH_3). The resonance signal of the boron-bound carbon atom was significantly broadened by a quadrupolar boron nucleus and was not observed. HRMS (FD): calcd. for $C_{14}H_{17}BO_4$ $[M]^+$ 260.1220; found 260.1217.

2-([2,2':5',2''-Terfuran]-5-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (25). Prepared following the procedure given for the synthesis of **24**, from terfuran (**26**, n = 2) (1.050 g, 5.243 mmol), 1.6 M solution of *n*-BuLi in hexane (3.8 mL, 6.1 mmol, 1.15 equiv.) and borolane **27** (1.424 g, 7.340 mmol, 1.4 equiv.) to yield **25** (562 mg, 33%) as a crème color solid; m.p. 81-83 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.43 (dd, J = 1.8, 0.7 Hz, 1H), 7.13 (d, J = 3.5 Hz, 1H), 6.80 (d, J = 3.6 Hz, 1H), 6.66 (d, J = 3.5 Hz, 1H), 6.63 (d, J = 3.4 Hz, 1H), 6.61 (d, J = 3.6 Hz, 1H), 6.47 (dd, J = 3.4, 1.8 Hz, 1H), 1.36 (s, 12H); ^{13}C NMR ($CDCl_3$, 126 MHz): δ 150.56 (C), 146.19 (C), 146.13 (C), 145.55 (C), 142.06 (CH), 125.34 (CH), 111.50 (CH), 108.64 (CH), 107.05 (CH), 106.25 (CH), 105.71 (CH), 84.26 (C), 24.73 (CH_3). The resonance signal of the boron-bound carbon atom was not observed since it is significantly broadened by a quadrupolar boron nucleus. HRMS (FD): calcd. for $C_{18}H_{19}BO_5$ $[M]^+$ 326.1326; found 326.1320.

3''',4''-Di-*n*-heptyl-2,2':5',2'':5'',2''':5''',2'''':5'''',2''''-sexifuran (20).

a) Synthesis of 20 through the Stille cross-coupling of dibromobifuran 15. A solution of a freshly prepared dibromobifuran **15** (255 mg, 0.522 mmol), tributylstannylbifuran **22** (666 mg, 1.574 mmol, 3.0 equiv.) and $(Ph_3P)_4Pd$ (61 mg, 0.0527 mmol, 10 mol%) in dry toluene (6 mL) was gently refluxed for 12 h. The reaction mixture was evaporated and subjected to three sequential FC on silica gel (gradient elution, from hexane to 3% EtOAc-hexane) followed by the final FC on Florisil[44] (hexane) to give the sexifuran **20** (126 mg, 41%).

b) Synthesis of 20 through the Suzuki-Miyaura cross-coupling. A mixture of a freshly prepared dibromide **15** (232 mg, 0.475 mmol), bifuryl pinacolboronate **24** (372 mg, 1.430 mmol, 3 equiv.), palladium acetate (8.5 mg, 0.038 mmol, 8 mol%), XPhos (36.2 mg, 0.076 mmol, 16 mol%) and K_3PO_4 (605 mg, 2.85 mmol, 6 equiv.) in 1,4-dioxane-water (10 : 1, total 6.0 mL) was heated at 55-60 °C for 8 h. At that time, the second portion of **24** (247 mg, 0.950 mmol, 2.0 equiv.) was added, and heating at 55-60 °C was continued for additional 8 h. The reaction mixture was diluted with water and extracted with 25% EtOAc in hexane. The combined organic extract was washed with water and brine, dried over $MgSO_4$. Filtration, evaporation, FC on silica gel (gradient elution, from hexane to 3% EtOAc-hexane) followed by FC on Florisil[44] (hexane) gave the sexifuran **20** (95 mg, 34%).

Diheptyl sexifuran 20. A yellow solid; m.p. 109-110 °C; R_f 0.25 (benzene-hexane = 1 : 10); ^{1}H NMR (C_6D_6, 400 MHz): δ 7.02 (dd, J = 1.8, 0.5 Hz, 2H), 6.60 (s, 2H), 6.57 (br d, J = 3.4 Hz, 2H), 6.56 (d, J = 3.5 Hz, 2H), 6.54 (d, J = 3.5 Hz, 2H),6.09 (dd, J = 3.4, 1.8 Hz, 2H), 2.81 (t, J = 7.6 Hz, 4H), 1.66 (br tt, $^3J \approx$ 7.4, 7.4 Hz, 4H), 1.44-1.38 (sym m, 4H), 1.34-1.20 (m, 12H), 0.87 (t, J = 6.9 Hz, 6H; ^{13}C NMR (C_6D_6, 101 MHz): δ 146.84 (C), 146.41 (C), 146.30 (C), 145.02 (C), 142.45 (C), 142.19 (CH), 125.29 (C), 111.72 (CH), 109.65 (CH), 107.56 (CH), 107.27 (CH), 105.77 (CH), 32.21 (CH_2), 30.61 (CH_2), 29.86 (CH_2), 29.58 (CH_2), 25.70 (CH_2), 23.04 (CH_2), 14.28 (CH_3); UV/Vis (1,4-dioxane): λ_{max} 406, 448 (sh) nm; Fluorescence spectrum (1,4-dioxane): λ_{max} 446, 475 nm; HRMS (FD): calcd. for $C_{38}H_{42}O_6$ $[M]^+$ 594.2981; found 594.2971.

3''',4'''-Di-*n*-heptyl-2,2':5',2'':5'',2''':5''',2'''':5'''',2''''':5''''', 2''''':5''''',2''''''-octifuran (21).

a) Synthesis of 21 through the Stille cross-coupling. Octifuran **21** was synthesized following the procedure given for the synthesis **20** from a freshly prepared dibromobifuran **15** (237 mg, 0.485 mmol), tributylstannylterfuran **23** (716 mg, 1.462 mmol, 3.0 equiv.) and $(Ph_3P)_4Pd$ (57 mg, 0.0493 mmol, 10 mol%). Five sequential FC on silica gel (from hexane to 3% EtOAc-hexane) followed by the final FC on Et_3N-pretreated silica gel[44] (0.5% EtOAc-hexane) gave the title product **21** (80 mg, 23%).

b) Synthesis of 21 through the Suzuki-Miyaura cross-coupling. Octifuran **21** was synthesized as described for the synthesis of **20** from a freshly prepared dibromobifuran **15** (161 mg, 0.330 mmol), terfuryl pinacolboronate **25** (total 540 mg, 1.655 mmol, 5 equiv.), $Pd(OAc)_2$ (6.3 mg, 0.028 mmol, 8 mol%), XPhos (26.7 mg, 0.056 mmol, 16 mol%) and K_3PO_4 (425 mg, 2.0 mmol, 6 equiv.). Two sequential FC on silica gel (from 1% to 3% EtOAc-hexane) followed by the final FC on Florisil[44] (0.5% EtOAc-hexane) gave the product **21** (51 mg, 21%).

Diheptyl octifuran 21. A yellow-orange solid; m.p. 140-141 °C; R_f 0.37 (benzene-hexane = 1:5); ^{1}H NMR (C_6D_6, 500 MHz): δ 6.99 (dd, J = 1.8, 0.5 Hz, 2H), 6.62 (s, 2H), 6.58 and 6.57 (AB-q, J = 3.6 Hz, 4H), 6.56 (d, J = 3.5 Hz, 2H), 6.53 (br d, J = 3.4 Hz, 2H), 6.51 (d, J = 3.5 Hz, 2H), 6.06 (dd, J = 3.4, 1.8 Hz, 2H), 2.83 (t, J = 7.6 Hz, 4H), 1.67 (br tt, $J \approx$ 7.5, 7.5 Hz, 4H), 1.42 (br tt, $J \approx$ 7.3, 7.3 Hz, 4H), 1.37-1.18 (m, 12H), 0.88 (t, J = 7.0 Hz, 6H); ^{13}C NMR (C_6D_6, 126 MHz): δ 146.69 (C), 146.57 (C), 146.48 (C), 145.97 (C), 145. 90 (C), 144.98 (C), 142.51 (C), 142.23 (CH), 125.36 (C), 111.73 (CH), 109.81 (CH), 107.95 (CH), 107.79 (CH), 107.55 (CH), 107.42 (CH), 105.96 (CH), 32.22 (CH_2), 30.62 (CH_2), 29.86 (CH_2), 29.59 (CH_2), 25.71 (CH_2), 23.05 (CH_2), 14.31 (CH_3); UV/Vis (1,4-dioxane): λ_{max} 428, 460 (sh) nm; Fluorescence spectrum (1,4-dioxane): λ_{max} 472, 503 nm; HRMS (FD): calcd. for $C_{46}H_{46}O_8$ $[M]^+$ 726.3193; found 726.3204.

Acknowledgements

The authors thank Dr. A. Tishby for recording HRMS, Dr. L. Konstantinovski and Dr. O. Gidron for their help in the measurements of 2D NMR spectra and fluorescence spectra respectively. The authors acknowledge financial support from the MINERVA Foundation (Germany) and from the Helen and Martin Kimmel Center for Molecular Design (Weizmann

Institute). E.E.K. and G.M.L. thank Israel Ministry of Absorption for Kamea Excellence Fellowships. M.B. was a member *ad personam* of the Lise Meitner - Minerva Center for Computational Quantum Chemistry.

Notes and references

1 H. Shirakawa, E. Louis, A. G. MacDiarmid, C. K. Chiang and A. J. Heeger, *J. Chem. Soc., Chem. Commun.*, 1977, 578-580.

2 (*a*) *Organic Field-Effect Transistors*, ed. Z. Bao and J. Locklin, CRC Press, Boca Raton, FL, 2007; (*b*) *Organic Light-Emitting Materials and Devices*, ed. Z. Li and H. Meng, CRC Press, Boca Raton, FL, 2006; (*c*) *Handbook of Conducting Polymers*, ed. J. Reynolds and T. A. Skotheim, CRC Press, Boca Raton, FL, 3rd edn., 2007; (*d*) P. Bäuerle, in *Electronic Materials: The Oligomer Approach*, ed. K. Müllen and G. Wegner, Wiley-VCH, Weinheim, 1998, pp. 105-197; (*e*) C. Wang, H. Dong, W. Hu, Y. Liu and D. Zhu, *Chem. Rev.*, 2012, **112**, 2208-2267; (*f*) Y. Lin, Y. Li and X. Zhan, *Chem. Soc. Rev.*, 2012, **41**, 4245-4272; (*g*) A. Mishra and P. Bäuerle, *Angew. Chem., Int. Ed.*, 2012, **51**, 2020-2067.

3 (*a*) *Handbook of Thiophene-Based Materials: Applications in Organic Electronics and Photonics*, ed. I. F. Perepichka and D. F. Perepichka, Wiley, Chichester, 2009; (*b*) A. Mishra, C.-Q. Ma and P. Bäuerle, *Chem. Rev.*, 2009, **109**, 1141-1276.

4 Y. Miyata, T. Nishinaga and K. Komatsu, *J. Org. Chem.*, 2005, **70**, 1147–1153.

5 (*a*) P. Bäuerle, T. Fischer, B. Bindlingmeier, A. Stabel and J. P. Rabe, *Angew. Chem., Int. Ed.*, 1995, **34**, 303-307; (*b*) S. S. Zade and M. Bendikov, *Chem. Eur. J.*, 2007, **13**, 3688-3700.

6 (*a*) G. R. Hutchison, M. A. Ratner and T. J. Marks, *J. Am. Chem. Soc.*, 2005, **127**, 2339-2350; (*b*) S. S. Zade and M. Bendikov, *Org. Lett.*, 2006, **8**, 5243-5246.

7 J. K. Politis, J. C. Nemes and M. D. Curtis, *J. Am. Chem. Soc.*, 2001, **123**, 2537-2547.

8 G. Distefano, D. Jones, M. Guerra, L. Favaretto, A. Modelli and G. Mengoli, *J. Phys. Chem.*, 1991, **95**, 9746-9753.

9 O. Gidron, Y. Diskin-Posner and M. Bendikov, *J. Am. Chem. Soc.*, 2010, **132**, 2148-2150.

10 For highlights on α-oligofurans, see: (*a*) U. H. F. Bunz, *Angew. Chem., Int. Ed.*, 2010, **49**, 5037-5040; (*b*) O. Gidron and M. Bendikov, *Angew. Chem., Int. Ed.*, 2014, **53**, 2546-2555.

11 S. Sharma and M. Bendikov, *Chem. Eur. J.*, 2013, **19**, 13127-13139.

12 C. C. Ferrón, M. C. R. Delgado, O. Gidron, S. Sharma, D. Sheberla, Y. Sheynin, M. Bendikov, J. T. L. Navarrete and V. Hernández, *Chem. Commun.*, 2012, **48**, 6372-6374.

13 O. Gidron, Y. Diskin-Posner and M. Bendikov, *Chem. Eur. J.*, 2013, **19**, 13140-13150.

14 O. Gidron, A. Dadvand, Y. Sheynin, M. Bendikov and D. F. Perepichka, *Chem. Commun.*, 2011, **47**, 1976-1978.

15 O. Gidron, A. Dadvand, E. W.-H. Sun, I. Chung, L. J. W. Shimon, M. Bendikov and D. F. Perepichka, *J. Mater. Chem. C*, 2013, **1**, 4358-4367.

16 (*a*) C. H. Woo, P. M. Beaujuge, T. W. Holcombe, O. P. Lee and J. M. J. Fréchet, *J. Am. Chem. Soc.*, 2010, **132**, 15547-15549; (*b*) M. S. Chen, O. P. Lee, J. R. Niskala, A. T. Yiu, C. J. Tassone, K. Schmidt, P. M. Beaujuge, S. S. Onishi, M. F. Toney, A. Zettl and J. M. J. Fréchet, *J. Am. Chem. Soc.*, 2013, **135**, 19229-19236.

17 J. C. Bijleveld, B. P. Karsten, S. G. J. Mathijssen, M. M. Wienk, D. M. de Leeuw and R. A. J. Janssen, *J. Mater. Chem.*, 2011, **21**, 1600-1606.

18 X.-H. Jin, D. Sheberla, L. J. W. Shimon and M. Bendikov, *J. Am. Chem. Soc.*, 2014, **136**, 2592-2601.

19 J. Lin, X. Jin, Y. Bu, D. Cao, N. Zhang, S. Li, Q. Sun, C. Tan, C. Gao and Y. Jiang, *Org. Biomol. Chem.*, 2012, **10**, 9734-9746.

20 H. Ishida, K. Yui, Y. Aso, T. Otsubo and F. Ogura, *Bull. Chem. Soc. Jpn.*, 1990, **63**, 2828-2835.

21 T. Kauffmann, B. Greving, R. Kriegesmann, A. Mitschker and A. Woltermann, *Chem. Ber.*, 1978, **111**, 1330-1336.

22 L. N. Pridgen and S. S. Jones, *J. Org. Chem.*, 1982, **47**, 1490-1492.

23 (*a*) M. J. Kurth and C. J. Soares, *Tetrahedron Lett.*, 1987, **28**, 1031-1034; (*b*) I. Bock, H. Bornowski, A. Ranft and R. Theis, *Tetrahedron*, 1990, **46**, 1199-1210.

24 B. Alcaide, P. Almendros, R. Carrascosa and M. R. Torres, *Eur. J. Org. Chem.*, 2010, 823-826.

25 For the only reported example of Pd/C-catalyzed transfer hydrogenation of 3-alkenylfurans, see: M. Kolympadi, M. Liapis and V. Ragoussis, *Tetrahedron*, 2005, **61**, 2003-2010.

26 For general reviews on heterogeneous catalytic transfer hydrogenation, see: (*a*) R. A. W. Johnstone and A. H. Wilby, *Chem. Rev.*, 1985, **85**, 129-170; (*b*) R. M. Kellogg, in *Comprehensive Organic Synthesis*, ed. B. M. Trost and I. Reming, Pergamon Press, Oxford, 1991, vol. 8, pp. 79-106.

27 (*a*) M. Tofi, T. Georgiou, T. Montagnon and G. Vassilikogiannakis, *Org. Lett.*, 2005, **7**, 3347-3350; (*b*) E. S. Wang, Y. M. Choy and H. N. C. Wong, *Tetrahedron*, 1996, **52**, 12137-12158; (*c*) M. R. Kernan and D. J. Faulkner, *J. Org. Chem.*, 1988, **53**, 2773-2776.

28 W. Tochtermann, D. Kuckling, C. Meints, J. Kraus and G. Bringmann, *Tetrahedron*, 2003, **59**, 7791-7801.

29 T. Kauffmann and H. Lexy, *Chem. Ber.*, 1981, **114**, 3667-3673. For a recent synthesis of 5,5′-diaryl-2,2′-bifuran through α-lithiation followed by $CuCl_2$-induced homocoupling, see: K. Oniwa, T. Kanagasekaran, T. Jin, M. Akhtaruzzaman, Y. Yamamoto, H. Tamura, I. Hamada, H. Shimotani, N. Asao, S. Ikeda and K. Tanigaki, *J. Mater. Chem. C*, 2013, **1**, 4163-4170.

30 For a general review on the heteroatom directed *ortho*-lithiation/coupling methodology, see: E. J.-G. Anctil and V. Snieckus, in *Metal-Catalyzed Cross-Coupling Reactions*, ed. A. De Meijere and F. Diederich), Wiley-VCH: Weinheim, 2004, vol. 2, pp. 761-813.

31 For an early comprehensive survey on heteroatom-facilitated *ortho*-lithiation, see: H. W. Gschwend and H. R. Rodriguez, *Org. React.*, 1979, **26**, 1-360.

32 G. D. Hartman, W. Halczenko, J. D. Prugh and T. M. Williams, *J. Heterocycl. Chem.*, 1990, **27**, 679-682.

33 S. Gronowitz and G. Timari, *J. Heterocycl. Chem.*, 1990, **27**, 1159-1160.

34 For selected reviews on the Ullmann reaction, see: (*a*) J. Hassan, M. Sévignon, C. Gozzi, E. Schulz and M. Lemaire, *Chem. Rev.*, 2002, **102**, 1359-1469;(*b*) T. D. Nelson and R. D. Crouch, *Org. React.*, 2004, **63**, 265-555; (*c*) G. Evano, N. Blanchard and M. Toumi, *Chem. Rev.*, 2008, **108**, 3054-3131.

35 A. M. Szpilman, E. E. Korshin, H. Rozenberg and M. D. Bachi, *J. Org. Chem.*, 2005, **70**, 3618-3632.

36 CCDC-970220 for 2,2′-bifuran-3,3′-dicarbaldehyde (**4**) contains 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.

37 (*a*) O. Gidron, N. Varsano, L. J. W. Shimon, G. Leitus and M. Bendikov, *Chem. Commun.*, 2013, **49**, 6256-6258; (*b*) C. Mallet, Y. Didane, T. Watanabe, N. Yoshimoto, M. Allain, C. Videlot-Ackermann and P. Frère, *ChemPlusChem*, 2013, **78**, 459-466.

38 J. T. Henssler and A. J. Matzger, *J. Org. Chem.*, 2012, **77**, 9298-9303.

39 A. S. Ionkin and W. J. Marshall, *Organometallics*, 2004, **23**, 3276-3283.

40 (*a*) R. J. Abraham, D. J. Chadwick and F. A. E. G. Sancassan, *Tetrahedron*, 1982, **38**, 3245-3254; (*b*) D. L. Comins and M. O. Killpack, *J. Org. Chem.*, 1987, **52**, 104-109.

41 A. R. Kelly, M. H. Kerrigan and P. J. Walsh, *J. Am. Chem. Soc.*, 2008, **130**, 4097-4104.

42 E. E. Korshin, R. Hoos, A. M. Szpilman, L. Konstantinovski, G. H. Posner and M. D. Bachi, *Tetrahedron*, 2002, **58**, 2449-2469.

43 *CAUTION!* In our first experiments with 5,5′-dibromo-3,3′-di-*n*-heptyl-2,2′-bifuran (**15**) we attempted a storage of this NMR pure compound. However, initially yellowish solid **15** after one day storage at -25 ^{o}C with protection from light turned colour to greenish one even being cold. Upon warming to rt, it spontaneously exothermically decomposed to give an insoluble in $CDCl_3$ and C_6D_6 dark green stuff. An intensive white acidic fuming was observed during decomposition. Therefore, we suggest using the dibromide **15** in the next step as soon as possible after its isolation by flash chromatography (FC). Although no accidents occurred in our laboratory, it is obligatory to observe appropriate precautions for working with potentially hazardous materials like dibromides **15** and **19**.

44 Since all the α-oligofurans are acid-, light- and oxygen-sensitive, at least the final FC of the quaterfuran **17** and the longer α-oligofurans is recommended to perform on Et_3N-pretreated silica gel or on Frorisil. Upon protection from a direct light, anaerobic conditions are not mandatory for FC purification of α-oligofurans up to α-octifuran **21**.

45 For recent Suzuki-Miyaura (het)arylations and alkenylations of 2-(2-furyl)borolane **18**, see: (*a*) C. Sánchez-Sixto, V. F. V. Prazeres, L. Castedo, S. W. Suh, H. Lamb, A. R. Hawkins, F. J. Cañada, J. Jiménez-Barbero and C. González-Bello, *ChemMedChem*, 2008, **3**, 756-770; (*b*) Q. Tang and R. Gianatassio, *Tetrahedron Lett.*, 2010, **51**, 3473-3476; (*c*) A. El Kadib, K. McEleney, T. Seki, T. K. Wood and C. M. Crudden, *ChemCatChem*, 2011, **3**, 1281-1285; (*d*) H. Sakai, T. Hirano, S. Mori, S. Fujii, H. Masuno, M. Kinoshita, H. Kagechika and A. Tanatani, *J. Med. Chem.*, 2011, **54**, 7055-7065; (*e*) S. Asano, S. Kamioka and Y. Isobe, *Tetrahedron*, 2012, **68**, 272-279; (*f*) T. Muroga, T. Sakaguchi and T. Hashimoto, *Polymer*, 2012, **53**, 4380-4387.

46 D. C. Ebner, J. T. Bagdanoff, E. M. Ferreira, R. M. McFadden, D. D. Caspi, R. M. Trend and B. M. Stoltz, *Chem. Eur. J.*, 2009, **15**, 12978-12992.

47 Protodeboronation of (hetero)arylboronic acids and esters is a well-known side process, which frequently suppress viability of Suzuki-Miyaura cross-coupling. For some recent advancements in heteroaryl Suzuki-Miyaura cross-couplings, see: (*a*) A. J. J. Lennox and G. Lloyd-Jones, *Isr. J. Chem.*, 2010, **50**, 664-674; (*b*) D. M. Knapp, E. P. Gillis and M. D. Burke, *J. Am. Chem. Soc.*, 2009, **131**, 6961-6963; (*c*) G. A. Molander, B. Canturk and L. E. Kennedy, *J. Org. Chem.*, 2009, **74**, 973-980; (*d*) K. Billingsley and S. L. Buchwald, *Angew. Chem., Int. Ed.*, 2008, **47**, 4695-4698; (*e*) M. A. Oberli and S. L. Buchwald, *Org. Lett.*, 2012, **14**, 4606-4609.

48 For recent examples of substantial Pd-catalyzed deboronative homocoupling of 2-furylpinacolboronates, see: J. Bárta, L. Slavětínská, B. Klepetářová and M. Hocek, *Eur. J. Org. Chem.*, 2010, 5432-5443.

49 For selected examples on Pd-catalyzed deboronative homocoupling of 2-benzofurylboronic acids and -boronates, see: (*a*) Y. Yamamoto, *Adv. Synth. Catal.*, 2010, **352**, 478-492; (*b*) Y. Kitamura, S. Sako, A. Tsutsui, Y. Monguchi, T. Maegawa, Y. Kitade and H. Sajiki, *Adv. Synth. Catal.*, 2010, **352**, 718-730. See also reference 39.

50 For some examples of efficient Pd-catalyzed destannylative homocoupling of 2-furylstannanes, see: I. Efremov and L. A. Paquette, *Heterocycles*, 2002, **56**, 35-38.